Structural, optical and electronic properties in transition metal dichalcogenides

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

SINGAPORE

**STRUCTURAL, OPTICAL AND ELECTRONIC
PROPERTIES IN TRANSITION METAL
DICALCOGENIDES**

STRUCTURAL, OPTICAL AND ELECTRONIC PROPERTIES IN
TRANSITION METAL DICALCOGENIDES

XIA JUAN

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SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

2018

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**STRUCTURAL, OPTICAL AND ELECTRONIC
PROPERTIES IN TRANSITION METAL
DICALCOGENIDES**

XIA JUAN

School of Physical and Mathematical Sciences

A thesis submitted to Nanyang Technological University
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Table of Contents

Acknowledgements	3
List of abbreviations	7
Executive summary	9
Publication list	12
Chapter 1 Background.....	14
1.1 Motivation and highlight.....	14
1.2 Introduction of 2D materials.....	18
1.3 Atomic structure of TMDs	21
Chapter 2 Experimental and theoretical foundations	
24	
2.1 Raman Scattering.....	24
2.1.1 Raman theory	24
2.1.2 Raman modes in TMDs	28
2.2 Confocal Raman and PL system.....	30
2.3 Scanning transmission electron microscopy	32
2.4 First-principles calculations	33
2.5 Fabrication of TMD crystals	34
Chapter 3 A new degree of freedom beyond thickness	
in TMDs—stacking.....	39
3.1 The polytypes of 2L and 3L MoS ₂	39
3.2 Stacking identification of few-layer MoS ₂ by ULF Raman.....	42
3.3 Electronic band structure for few-layer MoS ₂	49
Chapter 4 Thickness and stacking-dependent	
property in TMDs	55
4.1 Spin-valley polarization.....	55
4.2 Second harmonic generation.....	65

Chapter 5	Physical property tuning in TMDs	71
5.1	Strain and fragmentation effect in TMDs	71
5.2	Pressure-induced phase transition in semimetallic WTe ₂	78
5.3	Lithium intercalation induced phase transition in MoS ₂	88
5.4	Experimental details	98
Chapter 6	2D homo- and hetero-junctions based on TMDs	102
6.1	Current rectification in thickness- and stacking-induced TMD homojunctions	102
6.2	Interlayer exciton study in strong-coupled WSe ₂ -MoSe ₂ heterobilayers by pressure engineering	114
6.3	Experimental details	125
Chapter 7	Conclusion and future work	127
7.1	Conclusion of this thesis	127
7.2	Future work	127
References		132

List of abbreviations

2D	Two-dimensional
TMD	Transition metal dichalcogenide
vdWs	van der Waals
ULF	Ultra-low-frequency
PL	Photoluminescence
CP-PL	Circularly-polarized photoluminescence
STEM	Scanning transmission electron microscopy
CVD	Chemical vapor deposition
PVD	Physical vapor deposition
SHG	Second harmonic generation
HR-TEM	High-resolution transmission electron microscopy
SOC	Spin-orbit coupling
SM	Shear mode
BM	Breathing mode
HSs	Heterostructures
MBE	Molecular beam epitaxy
ME	Mechanical exfoliation
LPE	Liquid-phase exfoliation
ALD	Atomic layer deposition
LED	Light emitting diode
FET	Field effect transistor
VBM	Valence band maximum
CBM	Conduction band maximum
EPC	Electron-phonon coupling
DOS	Density of states
LA	Longitudinal acoustic
TA	Transverse acoustic
ZA	Out-of-plane acoustic
CCD	Charge coupled device
BNF	BragGrate Notch Filters
PMMA	Poly (methyl methacrylate)

DFPT	Density-functional perturbation theory
LDA	Local-density approximation
GGA	Generalized gradient approximation
PBE	Perdew, Burke and Ernzerhof
AFM	Atomic force microscopy
QY	Quantum yield
CD	Circular dichroism
EDCs	Energy distribution curves
SARPES	Spin- and angle-resolved photoemission spectroscopy
HE	High energy
LE	Low energy
HER	Hydrogen evolution reaction
RHE	Reversible hydrogen electrode
PC	Polycarbonate
LMR	Large magnetoresistance
MD	Molecular dynamics
BZ	Brillouin zone
NEB	Nudged elastic band
HAADF	High-angle annular dark field
V_{oc}	Open-circuit voltage
I_{ds}	Source-drain current
V_{ds}	Source-drain voltage
V_{gs}	Source-gate voltage

Executive summary

Two-dimensional (2D) transition metal dichalcogenides (TMDs) have attracted intense interests owing to their fascinating physical properties and potential applications. In addition, the physical and chemical properties of few-layer TMD materials can be tuned by their thickness as well as the stacking sequence. For instance, $\text{MoS}_2/\text{WS}_2/\text{MoSe}_2/\text{WSe}_2$ undergoes a transition from the indirect-band-gap to direct-band-gap semiconductors with their thickness reduced to monolayer; the weak van der Waals (vdWs) interaction between layers in TMDs endows various stacking sequences that can be facily obtained by different methods. Hence, thickness and stacking sequence can be used to modulate the electronic band structures, valley polarization and nonlinear optical properties, providing additional useful and convenient ways to manipulate the materials and fabricate devices with novel functionalities. This thesis focuses on thickness and stacking engineering for TMD materials (especially MoS_2) in structural, optical and electronic properties. A systematic investigation is performed on the physical properties of these 2D TMD crystals and their heterostructures through ultra-low-frequency (ULF) Raman spectroscopy, circularly-polarized photoluminescence (CP-PL) measurement, scanning transmission electron microscopy (STEM) and first-principles calculations.

Chapter 1 gives a brief introduction on the concept and diverse categories of two-dimensional (2D) materials, as well as transition metal dichalcogenides (TMDs). The atomic structures of MoS_2 crystals, including 1T, 2H and 3R, are discussed, where the point groups are given as D_{3d} for 1T monolayer MoS_2 and D_{3h} for 1H monolayer MoS_2 . The symmetrical space groups for bulk 2H- and 3R- MoS_2 are different: $P6_3/mmc$ for 2H bulk, $R3m$ for 3R bulk. Besides thickness and stacking, the space group also depends on the parity of layer number, that is, $P3m1$ for even-number layers, $P6m2$ for odd-number layers. Generally, in monolayer and odd-layer TMDs, inversion symmetry is broken for all stacking configurations, which could be potentially used for spintronics and valleytronics.

In Chapter 2, the background and theory of Raman scattering are elaborated, where the classic and quantum models are used to theoretically explain the Stokes/anti-Stokes Raman shift and Raman modes intensity. Based on the symmetry group of TMDs, the irreducible representation of Raman vibrations could be

expressed as $\Gamma = 2A_{2u} + 2E_{1u} + 2B_{2g} + 2E_{2g} + A_{1g} + E_{1g} + B_{1u} + E_{2u}$ for bulk MoS₂ (6 atoms per unit cell), which includes 18 modes in total. When the thickness is reduced to monolayer, it only contains 3 atoms in the primitive cell and hence the representation of 9 vibrational modes is $\Gamma = 2A_2' + A_1' + 2E' + E'$. The confocal Raman microscopy, scanning transmission electron microscopy (STEM), first-principles calculations, fabrication of TMDs are also introduced in detail.

In Chapter 3, AB- and AA-stacking bilayer and ABA-, AAB-/ABB-, AAA-stacking trilayer MoS₂ are fabricated physical vapor deposition (PVD) technique. Based on these stacking configurations, for the first time, we establish the one-to-one correspondence between the macroscopic stacking patterns and the atomic stacking orders, by means of ultra-low-frequency (ULF) Raman spectroscopy and STEM. Our experimental and theoretical results reveal that distinct interlayer coupling behaviors emerge in different structural symmetries, as well as the spin-polarized states. Such findings afford new insight in few-layer 2D systems and provide new possibilities for future spintronics based on various stacking of MoS₂ blocks.

In Chapter 4, thickness- and stacking-dependent spin-valley polarizations in MoS₂ are revealed by circularly-polarized photoluminescence (CP-PL) measurements. The degree of circular dichroic polarization for 2H-stacking MoS₂ becomes smaller with increasing layer number, due to the prominent intralayer-intervalley and interlayer-intervalley hopping effects. As for 3R MoS₂, both interlayer and intralayer hopping are negligible, leading to a larger polarization and independence on thickness. For the CP-PL study of trilayer MoS₂ samples with ABB-, AAB-, AAA-, and ABA-stacking, they exhibit different polarization degrees contributed by their electronic bandstructure and different carrier hopping strength. The second harmonic generation (SHG) in TMDs is reported to be highly sensitive to thickness, crystalline orientation and stacking orders, where the odd-number layers and 3R-stacking TMDs show the strongest SHG intensity, due to the absence of inversion symmetry.

In Chapter 5, three external methods (strain and fragmentation, hydrostatic pressure, lithium intercalation) are involved to tune the structural, optical, electrochemical and electrical properties of TMDs. A facile and versatile method is reported to control the fragmentation of atomically thin TMD materials and

fabricate an ordered array of TMD nanoribbons by harnessing the polymer-based mechanical instabilities. This method is reported to work for a very broad spectrum of semiconducting TMDs (WS_2 , MoS_2 , MoSe_2 , and WSe_2) with thicknesses ranging from monolayers to bulk crystals. Moreover, enhanced electrochemical performance of as-fabricated MoS_2 nanoribbons for hydrogen evolution reaction is discovered. In high-pressure study of TMDs, the Raman peaks at $\sim 120 \text{ cm}^{-1}$ of plane-vertical aligned WTe_2 crystals gradually soften upon increasing pressure and are totally suppressed above 10 GPa, indicating the phase transition from dT to T' phase. This may provide a potential way to switch on/off the Weyl states in one material through high pressure. Through electrochemical lithium intercalation, the phase transition mechanism of MoS_2 as 2H-1T-dT is firstly proposed and explained by ULF Raman, HR-TEM and *ab initio* calculations.

In Chapter 6, the novel concept of MoS_2 homojunctions induced by alternate 2L AA- and AB-stacking domains is defined, where all the homojunctions (2L-1L and 2L AA-2L AB) are found with excellent rectification behaviors and fast photocurrent responses, due to stacking-induced type-I band alignments. Our CVD-grown 2L WSe_2 - MoSe_2 heterostructures show a strong interlayer coupling where both direct and indirect interlayer excitons are discovered with prominent peak intensity. Through experimental and theoretical high-pressure study, the self-competition of electronic bands and changeover of interlayer excitons from K (A, B) to Γ point (C, D) are observed. This may provide a means to reversibly tune interlayer interaction and electron-phonon coupling in TMD HSs via high pressure and may also guide the design of their future applications in pressure sensing and actuating systems.

Overall, our results in this thesis reveal that both the intrinsic factors (thickness and stacking) and extrinsic parameters (mechanical fragmentation, hydrostatic pressure, electrochemical intercalation *etc.*) play key roles in determining the physical/chemical properties in layered TMD materials.

Publication list

First-author Publications

1. **Jiaxu Yan#**, **Juan Xia#**, Xingli Wang, Lei Liu, Jer-Lai Kuo, Beng Kang Tay, Shoushun Chen, Wu Zhou, Zheng Liu and Ze Xiang Shen* (# Contribute equally). 'Stacking-dependent interlayer coupling in trilayer MoS₂ with broken inversion symmetry'. **Nano Letters**, **2015 Nov**.
2. **Juan Xia**, Xingli Wang, Jer-Lai Kuo, Beng Kang Tay, Shoushun Chen, Zheng Liu, Jiaxu Yan*, and Ze Xiang Shen*. 'Valley polarization in stacked MoS₂ by circularly polarized light'. **Nano Research**, **2016 Dec**.
3. **Juan Xia**, Jin Wang, Dongliang Chao, Zhen Chen, Zheng Liu, Jer-Lai Kuo, Jiaxu Yan* and Ze Xiang Shen*. 'Phase evolution of lithium intercalation dynamics in 2H-MoS₂'. **Nanoscale**, **2017 May**.
4. **Juan Xia**, Qingsheng Zeng, Jiadong Zhou, Wu Zhou, Qing Zhang, Jiaxu Yan*, Zheng Liu* and Ze Xiang Shen*. 'Current rectification and asymmetric photoresponse in MoS₂ stacking-induced homojunctions'. **2D Materials**, **2017 June**.
5. **Ming Chen#**, **Juan Xia#**, Jiadong Zhou, Wei Fu, Kaiwei Li, Kazunori Fujisawa, Ting Zhang, Zhe Wang, Xiaoting Jia, Mauricio Terrones, Zexiang Shen, Zheng Liu* & Lei Wei* (# Contribute equally). 'Ordered and atomically perfect fragmentation of layered transition metal dichalcogenides via mechanical instabilities'. **ACS Nano**, **2017 Aug**.
6. **Juan Xia**, Dong-Fei Li, Jia-Dong Zhou, Peng Yu, Jun-Hao Lin, Jer-Lai Kuo, Hai-Bo Li, Zheng Liu, Jia-Xu Yan *, and Ze-Xiang Shen*. 'Pressure-induced phase transition in Weyl semimetallic WTe₂'. **Small**, **2017 Aug**.
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Co-author Publications

1. Jiadong Zhou, Fucai Liu, Junhao Lin, Xiangwei Huang, **Juan Xia**, Bowei Zhang, Qingsheng Zeng, Hong Wang, Chao Zhu, Lin Niu, Xuewen Wang, Wei Fu, Peng Yu, Tay-Rong Chang, Chuang-Han Hsu, Di Wu, Horng-Tay Jeng, Yizhong Huang, Hsin Lin, Zexiang Shen, Changli Yang, Li Lu, Kazu Suenaga, Wu Zhou, Sokrates T. Pantelides, Guangtong Liu and Zheng Liu. 'Large-Area and High-Quality 2D Transition Metal Telluride'. **Advanced Materials**, 2016 Nov.
2. Wai Leong Chow, Peng Yu, Fucai Liu, Jinhua Hong, Xingli Wang, Qingsheng Zeng, Chuang-Han Hsu, Chao Zhu, Jiadong Zhou, Xiaowei Wang, **Juan Xia**, Jiaxu Yan, Yu Chen, Di Wu, Ting Yu, Zexiang Shen, Hsin Lin, Chuanhong Jin, Beng Kang Tay, and Zheng Liu. 'High Mobility 2D Palladium Diselenide Field-effect Transistors with Tunable Ambipolar Characteristics'. **Advanced Materials**, 2017 Apr.
3. Qundong Fu, Xiaowei Wang, Jiadong Zhou, **Juan Xia**, Qingsheng Zeng, Danhui Lv, Chao Zhu, Fucai Liu*, Zexiang Shen, Chuanhong Jin*, Zheng Liu*. 'Synthesis of Atom-thin Metal/Semiconductor Van de Waals Heterostructure NbS₂/MoS₂'. **Advanced Functional Materials (under review)**, 2017 Oct.
4. Jiadong Zhou, Junhao Lin, Xiangwei Huang, Yao Zhou, Yu Chen, **Juan Xia**, Hong Wang, Yu Xie, Huimei Yu, Jincheng Lei, Di Wu, Fucai Liu, Qundong Fu, Qingsheng Zeng, Chuang-Han Hsu, Changli Yang, Li Lu, Ting Yu, Zexiang Shen, Hsin Lin, Boris I. Yakobson, Qian Liu, Kazu Suenaga, Guangtong Liu and Zheng Liu. 'Universal Synthesis of Atom-thin Metal Chalcogenide Libraries'. **Nature (under revision)**, 2017 Nov.

Chapter 1 Background

1.1 Motivation and highlight

Layered transition metal dichalcogenides (TMDs) have been extensively studied among the two-dimensional (2D) materials family, which stems from their intriguing physical properties that have great potential for many applications, such as optical, electronic and optoelectronic devices¹⁻³. Moreover, these physical properties of layered TMDs are strongly correlated to thickness⁴, strain⁵, pressure⁶, stacking sequence⁷ and electromagnetic field⁸. For instance, it is already known that MoS₂/WS₂/MoSe₂/WSe₂ undergoes a transition from the indirect-band-gap to direct-band-gap transition when the thickness is reduced to monolayer^{1, 4}. This thickness-dependent bandgap in TMDs can be explored to the next-generation electronic and optoelectronic devices. Beyond this, the weak van der Waals (vdWs) force between the layers allows TMD materials to be grown with different stacking sequences that governs the crystal symmetry and in turn significantly influence the electronic band structures, magnetism, superconductivity, valley polarization, nonlinear optical effects, and other physical properties⁹⁻¹¹.

Hence stacking is introduced to be a novel degree of freedom beyond thickness, providing another convenient method to manipulate functionalities in 2D materials. Attractive as it would be, the related research remains at its early stage due to numerous stacking orders in few-layer TMDs, deriving from their unique microstructure including diatomic molecules and one-molecule-thickness instead of one-atom-thickness. Unlike monolayer MoS₂, the properties of bilayer and trilayer MoS₂ are stacking-dependent, which arise from the competition between spin-orbit-coupling (SOC) and interlayer coupling effects in different structural symmetries. As far as we know, only bilayer MoS₂ with 2H- and 3R-stacking are reported. Beyond bilayer, the stacking orientation cannot be precisely controlled and direct growth of various stacking multilayers has not been achieved either. **In this thesis, for the first time we grow few-layer MoS₂ samples by chemical vapour deposition (CVD) with different stacking configurations (AA, AB for bilayer; AAB, ABB, ABA, AAA for trilayer) and establish the one-to-one**

correspondence between the macroscopic stacking patterns and the atomic stacking orders, by means of ultra-low-frequency (ULF) Raman spectroscopy and STEM. We demonstrate that the evolution of interlayer interaction with various stacking configurations correlates strongly with layer-breathing mode (LBM) vibrations. Our ab initio calculations reveal that the layer-dependent properties arise from both the SOC and interlayer coupling in different structural symmetries. Such detailed understanding provides useful guidance for future spintronics fabrication using various stacked few-layer MoS₂ blocks.

Another intriguing character related to spin-valley polarization in TMDs is also mediated by stacking configurations¹²⁻¹⁴. Specific to 1L MoS₂ (WS₂), the SOC splits the valence bands by 160 meV (500 meV) with opposite spin signs near the K/K' valley. Together with the time-reversal symmetry, the spin and valley are inherently coupled, leading to valley-contrasting optical dichroism. Consequently, one can selectively excite the carriers using circularly polarized light, making monolayer TMDs the ideal material for valleytronics¹⁵. Bilayer TMDs offers another degree of freedom named as layer pseudospin¹⁶⁻²¹, which refers to the carriers' location, either upper, middle or lower layer and so on. The interplay among spin, valley pseudospins and layer pseudospins opens an unprecedented platform for the control of quantum states, where both spin and valley possess magnetic moments and can be manipulated by magnetic and optical means²²⁻²⁵, while the layer pseudospin can be tuned by an electric field^{21, 26}. Along with the layer number, stacking configuration also has a significant influence on the properties^{9, 11, 27}. For instance, 2H bilayer MoS₂ is inversion symmetric without SOC, and hence the valley-contrasting optical selection rule becomes invalid¹³. Recently, pioneering experiments have demonstrated that valley-dependent spin polarization can be realized in non-centrosymmetric phases including 3R phase, folded bilayer^{16, 28}, and bilayer systems under perpendicular electric fields^{17, 18}. Such manipulation of intrinsic symmetry and spin in even-layer or bulk TMDs has greatly enriched the scope of valley physics and plays a crucial role towards spintronics and valleytronics^{29, 30}. **Without an external electrical or magnetic field, here we will propose a new degree of freedom - stacking and demonstrate new phenomena between this stacking freedom with spin-valley coupling. We investigated all possible stacking configurations of CVD grown trilayer MoS₂ (AAA, ABB, AAB,**

ABA and 3R). While the stackings AAA, ABA, 3R possess a sole peak with lower degree of valley polarization than that in monolayer samples, the AAB (ABB) stackings show two distinct peaks, one similar to that found in monolayer MoS₂, and an additional unpolarized peak at lower energy. Our findings provide a more complete understanding in valley quantum control for future valleytronics.

Besides the structural, electronic, and linear optical properties of TMDs, their nonlinear optical properties, especially second harmonic generations (SHG) have been studied, where the lack of inversion symmetry in monolayer TMDs leads to a strong optical SH response. Bulk 2H-MoS₂ crystal belongs to point group D_{6h}, which possesses inversion symmetry different from monolayer. Consequently, the second-order nonlinear response for 2H-MoS₂ bulk should vanish³⁰. It has been reported that the second-order nonlinear susceptibility for MoS₂ bulk is around 10⁻¹⁴ m/V, much smaller than that of monolayer (10⁻⁷ m/V). This SHG effect proves to be highly sensitive to the thickness, crystalline orientation, as well as stacking configuration^{31, 32}. So far, thickness-dependent optical SHG in odd-layer TMDs have been found³³⁻³⁶, attributed to the non-trivial second-order nonlinearity due to the broken inversion symmetry. *Hsu et al.* have studied the SHG of artificially stacked bilayer MoS₂ with various twist angles. The SHG signals can be described as the coherent superposition of SH signal from individual layer involving a phase difference relying on the twist angle. Therefore, the stacking-dependent polarization of SHG intensity can be served as one accurate and powerful characterization tool to identify their atomic stacking orders³⁷.

Beyond the mediating of intrinsic physical properties in TMD materials, stacking also correlates closely to the electronic and optoelectronic properties. Based on the nature of TMDs, such as the appropriate bandgap, high carrier mobility and high current on/off ratios, they have been acting as the ideal semiconductor material for the field-effect transistors, photovoltaics, photodetectors, and nonvolatile memories¹⁶⁻²⁰. However, most of these devices are based on p-n junctions by heavy doping, Schottky junctions between metal and semiconductor, van der Waals heterojunctions by mechanical transfer, or other homojunctions associated with the strain, phase and layer number modulation. For example, the diode-like rectification effect and valuable drain-source current have been demonstrated in TMDs-based materials, such as layer-dependent MoX₂ homojunctions²¹⁻²³, phase-modified 1T'-2H MoX₂ Schottky junctions²⁴, WS₂-WSe₂²⁵,

WX₂-MoX₂²⁶⁻³⁰, graphene/BP-MoS₂^{31,32} heterojunctions. So far, the homojunctions based on stacking have not been reported yet, even the comparison of the electronic and optoelectronic properties in these stackings. **In this thesis, we firstly report a new type of homojunctions, stacking-dependent junctions formed by the interface of AA-AB stacked bilayer MoS₂ samples, together with AA bilayer-single layer (AA-1L) and AB bilayer-single layer (AB-1L) junctions by one-step chemical vapor deposition (CVD) method. The atomic stacking identification of AA- and AB-MoS₂ domains are accomplished by ULF Raman, PL spectroscopy and STEM. The explicit rectification effect and asymmetric bias-dependent photoresponse in all AA-1L, AB-1L and the unique AA-AB junctions are discovered for the first time. Our finding demonstrates the possibility of using the stacking-modulated 2D materials for future electronics and optoelectronics.**

Recently, 2D vdWs heterostructures (HSs) can be vertically constructed with different 2D TMD crystals, providing increasingly attractive properties and unique functionalities, which originate from different types of band alignment and their interlayer interaction³⁸⁻⁴². Specifically, interlayer excitons, raising from interlayer excitonic states between most of TMD vdWs HSs, possess longer electron-hole recombination lifetimes than intralayer excitons⁴³⁻⁴⁵. As a result, it plays a prominent role in the charge separation process and efficient photoabsorption in solar cells or photodetectors⁴⁶⁻⁴⁸. Exploring the interlayer interaction 2D vdWs HSs, specifically for interlayer excitons, is important not only fundamentally but also practically for photoelectric devices. So far, many investigations on interlayer exciton dynamics have been reported, tuned by material variety, thickness, stacking sequence, electromagnetic field, and strain. However, these explorations have been usually hindered by as-fabricated vdWs HSs by mechanical-stacking methods, with weak or even no interlayer interaction due to unintentional contaminants, as well as the weak external tuning methods which induce limited change in lattice parameters⁴⁹. For example, by strain engineering, one can introduce up to 2% change in lattice parameters and corresponding physical properties in 2D TMD materials⁵⁰. **To solve these problems, in our work, we first grow strong-coupled WSe₂-MoSe₂ HSs by CVD epitaxial growth method, which has two strong interlayer excitons (direct and indirect exciton), which originate from direct and indirect interlayer interband transitions respectively. This phenomenon is always missed in the currently reported mechanically-stacked**

TMD heterostructures, due to their uncontrollable stacking order and induced contaminants at the layer interfaces. Secondly, we employ high pressure to induce extreme changes in lattice parameters, leading to prominent volume changes during compression (e.g. ~10% at 10 GPa for TMDs) and hence many exciting phenomena.

1.2 Introduction of 2D materials

Since Novoselov and Geim were rewarded the Nobel Prize in physics in 2004, graphene and other derivative two-dimensional (2D) materials with atomic thicknesses has become one of the most fast-growing research areas in science and engineering, which represent a perfect playground for investigating the novel physics and applications in low dimensions. Fundamentally, once materials are constructed by strong covalent bonds within each layer and weak van der Waals (vdWs) interaction between adjacent layers, they belong to typical 2D crystals showing single-layer-like properties. Therefore, these layered materials are often referred to as vdWs materials since they can be considered as stacking of 2D monolayers bonded through vdWs interactions. In general, 2D materials cover three types of material family - graphene family (graphene, h-BN, BCN, fluorographene, graphene oxide, etc.), 2D chalcogenides family (MoS₂, WSe₂, ZrS₂, NbSe₂, Bi₂Se₃, etc.), and 2D oxides family (MoO₃, MnO₂, V₂O₃, perovskite-type, hydroxides, etc.), ranging from insulators (BN), semiconductors (MoS₂), semimetals (WTe₂), metals (VSe₂) to superconductor (NbSe₂). Compared with other dimensional materials, 2D crystals show superior properties such as large specific surface area, high electrical mobility, high sensitivity, easily stacked and tuned properties. Based on these, 2D materials have been developed with broad applications in high-speed transistor, flexible display device, solar cells, supercapacitors, printed electronics, chemical sensors and so on.

Graphene family	Graphene	hBN 'white graphene'	BCN	Fluorographene	Graphene oxide
2D chalcogenides	MoS ₂ , WS ₂ , MoSe ₂ , WSe ₂		Semiconducting dichalcogenides: MoTe ₂ , WTe ₂ , ZrS ₂ , ZrSe ₂ and so on	Metallic dichalcogenides: NbSe ₂ , NbS ₂ , TaS ₂ , TiS ₂ , NiSe ₂ and so on	
				Layered semiconductors: GaSe, GaTe, InSe, Bi ₂ Se ₃ and so on	
2D oxides	Micas, BSCCO	MoO ₃ , WO ₃	Perovskite-type: LaNb ₂ O ₇ , (Ca,Sr) ₂ Nb ₃ O ₁₀ , Bi ₄ Ti ₃ O ₁₂ , Ca ₂ Ta ₂ TiO ₁₀ and so on		Hydroxides: Ni(OH) ₂ , Eu(OH) ₂ and so on
	Layered Cu oxides	TiO ₂ , MnO ₂ , V ₂ O ₅ , TaO ₃ , RuO ₂ and so on			Others

Figure 1-1. The diverse categories of two-dimensional (2D) materials⁵¹. Reproduced with permission from ref. [51]. Copyright 2013, Nature Publishing Group.

Just as graphene can be easily exfoliated from graphite, 2D atomic crystals in general could be productively exfoliated from their corresponding bulk layered materials due to the weak vdWs interactions between the unit layers. Routinely, the exfoliated 2D layers should keep the same crystallographic structure as their pristine bulk crystals without any external perturbations. Some of the 2D materials have been widely used for decades and traditionally well-known as dry lubricants, like MoS₂ for example⁵². Few-layer 2D materials could be achieved using top-down methods like mechanical or chemical exfoliation as demonstrated above⁵³ and bottom-up methods, such as molecular beam epitaxy (MBE)⁵⁴, physical vapor deposition (PVD), chemical vapor deposition (CVD), wet chemistry synthesis *etc.* All the above methods have their own advantages and limitations, where the choice of exact method depends on the material categories, as well as the purposes of research. In recent two-dimensional research field, the TMDs have been gradually captured centralized attention among the whole two-dimensional families, which lead to an apparent research trend from graphene to TMDs. Different from graphene, TMDs possess sizable bandgaps and more complex properties resulting from more than one atom element. Furthermore, the optical and electronic properties of few-layered TMDs not only rely on its layer number, but also intimately depend on its stacking order among layers. It is already known that the MoS₂ will become a direct bandgap material when reduced to monolayer and this work aims to study the altering effect of stacking configurations to both phonon and photon behaviors of MoS₂.

H																	He
Li	Be	MX ₂ M = Transition metal X = Chalcogen										B	C	N	O	F	Ne
Na	Mg	3	4	5	6	7	8	9	10	11	12	Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La - Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac - Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Fl	Uup	Lv	Uus	Uuo

Figure 1-2. The details of constituents in transition metal dichalcogenides⁵⁵. Reproduced with permission from ref. [55]. Copyright 2013, Nature Publishing Group.

Different from single-atom-layered graphene, transition metal atoms (typically Mo, W) are sandwiched between two layers of chalcogen atoms (typically S, Se, or Te) to form a TMDs unit layer. Due to the plenty varieties of transition metal and chalcogen atoms, more than 40 different categories of TMDs could be achieved through different combinations of these elements and hence many intriguing physics have been discovered thereupon⁵⁶. MoS₂ is a typical member of TMDs group and has been well studied both theoretically and experimentally, originating from its exotic mechanical, optical and electronic properties⁵⁷. A monolayer MoS₂ is a direct bandgap semiconductor with strong photoluminescence, which makes it potential to be widely investigated in light-emitting diode (LED), field-effect transistors (FET)⁵⁸, solar cells, photovoltaic⁵⁹, microelectronic circuits, as well as sensors⁶⁰, Li ion batteries⁶¹, hydrogen production⁶², and dry lubricant etc. The reported on/off current ratio of single-layer MoS₂ FET reaches up to 10⁸ at room temperature⁵⁷, which is much higher than that of graphene based transistors, and almost comparable with that of the silicon based transistors. Moreover, another special interesting feature of MoS₂ is its promising applications in spintronics and valleytronics⁶³. The factor making MoS₂ unique is the strong spin-orbit coupling (SOC), due to the lack of inversion symmetry in odd-MoS₂, which leads to the scope of valley physics and plays a crucial role towards spintronics and valleytronics.

1.3 Atomic structure of TMDs

As demonstrated above, the TMDs family includes more than 40 layered compounds, which could be expressed as MX_2 thereafter with M representing transition metal atoms (Mo, W, Ti, Hf, Zr, Pd, *etc.*) and X for the chalcogen atoms (S, Se, Te)⁵⁵. So far, the most extensively studied TMD materials are Mo and W chalcogenide 2D crystals for their novel optical and electronic properties. In this case, the most typical 2H- MX_2 (M=Mo, W; X=S, Se) crystals share the same hexagonal crystalline structure, as shown in Figure 1-3a. Each layer is composed of three atomic layers, where one M layer is sandwiched between two X layers, with M and X atoms occupying different trigonal sites. Using MoS_2 for example, which represents a typically layered material with weak vdWs force to stack the adjacent layers, consists of S-Mo-S layers with Mo atom sandwiched between two S atoms by covalent bond⁶⁴. MoS_2 is known as an excellent lubricating candidate similar with graphite which has been widely used in decades. In each sandwich layer, hexagonally arranged Mo atoms are bonded to six S atoms in trigonal prismatic coordination. The S-Mo-S sandwich layers are stacked together by weak vdWs interactions, which contributing to its low friction coefficient and hence excellent lubricating property.

Within each S-Mo-S layer, it has two different symmetries, hexagonal (D_{3h}) and octahedral (D_{3d}) phase, corresponding to 1H (semiconductor) and 1T (metallic) monolayer MoS_2 respectively. The thickness of single-layer MoS_2 is about 0.65 nm while the unit cell of MoS_2 includes two layers with the lattice constant c value ~ 1.23 nm⁶⁵. While stacking the hexagonal (1H) and octahedral (1T) layers in different ways, 2H, 3R and 1T phases could be achieved in multi-layer/bulk MoS_2 . As shown in Figure 1-3b, the 1T- MoS_2 has octahedral coordination of the molybdenum center with one Mo atom in each unit cell⁶⁶, which is proved to be metallic; 2H- MoS_2 has trigonal prismatic coordination and two S-Mo-S units per unit cell⁶⁷; 3R- MoS_2 also has the same coordination as 2H phase with S-Mo-S unit per unit cell⁶⁸. Both the 2H and 3R polytypes have the same lattice parameter a (b=a) with value ~ 3.16 Å and both are semiconductive phases. For 1T- MoS_2 phase, the Mo centers are displaced from their ideal positions, which could be obtained by phase transition of 2H and 3R stacking through temperature modification and lithium intercalation methods.

Figure 1-3. Atomic structure of TMD crystals. (a) Schematics of few-layer MX₂ (M=Mo, W and X=S, Se) consisting of sandwiched M-X-M layers. (b) Top and side view of few-layer MX₂ with 1T (b), 2H (c) and 3R (d) stacking respectively.

It is obvious that for monolayer 1T- or 1H-MoS₂, the inversion symmetry is broken. However, for bulk or even-layer MoS₂ with 2H stacking, such an inversion symmetry in spatial is kept, as shown in Figure 1-4a⁶⁹. The thickness-dependent features in TMDs give the distinct structural symmetry and physical properties of monolayer and bulk MoS₂ for example. In detail, as for monolayer 1H-(1T-) MoS₂, it belongs to D_{3h} (D_{3d}) point group without inversion symmetry. The symmetrical space groups for bulk 2H- and bulk 3R-MoS₂ are different: $P6_3/mmc$ for 2H bulk (with inversion symmetry), $R3m$ for 3R bulk (without inversion symmetry). The most intrinsic difference should be their electronic band structures. The MoS₂ bulk belongs to indirect band gap with gap energy at 1.2 eV, When the thickness is gradually reduced to monolayer, it becomes direct bandgap with gap energy at 1.9 eV which shows a strong PL enhancement. Therefore, monolayer MoS₂ has been used to fabricate various devices due to its strong PL emission as well as spin-valley polarization property as shown in Figure 1-4b.

Besides thickness and stacking, the space group also depends on the parity of layer number, that is, $P3m1$ for even-number layers (with inversion symmetry), and $P6m2$ for odd-number layers (without inversion symmetry). Generally, in the case of monolayer and odd-layer 2H-TMDs, inversion symmetry is broken for all stacking configurations, which could be potentially used for spintronics and

valleytronics. However, the unit cell of 3R structure is composed of a trilayer stacked in such a way, which belongs to a $R3m$ space group and thus the inversion symmetry is kept broken in its bulk form. Different from graphene, the presence of transition-metal (Mo) d orbitals in monolayer MoS₂ gives rise to a trivial SOC⁷⁰. Both the valence band maximum (VBM) and the conduction band minimum (CBM) are contributed primarily from the Mo d-orbitals. As a result, the strong SOC in monolayer MoS₂ due to the absence of inversion symmetry splits the VBM at the K points by around 150 meV⁷¹ with the signs of split spins in K and K' valleys reversed due to the time-reversal symmetry. The reversed sign in different valleys lead to an essential relation of the spins and the valley degrees of freedom. The splitting at the VBM induced by SOC give rise to two low-energy exciton peaks (A and B excitons) in the absorption spectra, which we will discuss the details in Chapter 2.

Figure 1-4. Crystallographic symmetry (a) and electronic band structure (b) for bulk and monolayer MoS₂⁶⁹. Reproduced with permission from ref. [69]. Copyright 2011, American Physical Society.

Chapter 2 Experimental and theoretical foundations

2.1 Raman Scattering

Since the Raman spectroscopic technique was observed in 1927 for the first time, it has been employed as one of the main spectroscopic techniques to probe vibrations of atoms or molecules, which could provide information on chemical structures and physical forms to identify the properties of substances from the "fingerprinting" spectrum⁷². In 1930, Sir C.V. Raman received the Nobel Prize in Physics for the discovering of Raman scattering, which describes how matter interacts with the incident laser light and it scatters photons with wavelength different from that of the incident photons. Moreover, the inelastic scattering of light actually had been theoretically predicted in 1923 by A. Smekal, therefore, sometimes Raman scattering process is also referred as Smekal-Raman effect.

Therefore, Raman spectroscopy is a greatly potent and efficient approach to investigate the morphology variation and phase transition behaviors of 2D materials, especially the ultra-low-frequency (ULF) Raman spectroscopy, which is highly sensitive to interlayer interactions and can reflect even the minute changes and discrepancies of structure. Collocated by polarization components, ULF Raman spectroscopy is an extremely powerful technique to investigate the various interlayer interactions involving rigid motion of atoms in adjacent layers. Perturbed by different layer numbers and layer stacking ways, both shear modes (SM) and layer breathing modes (BM) have been observed but exhibit strikingly different features with different configurations, which can be well explained as the force constant between layers varying along with layer arrangements modeled by linear chain simulation, which we will demonstrate in Chapter 3. Thus, we can easily figure out the layer stacking difference among different samples and even in one particular sample using polarized ULF Raman technique, which nearly cannot be observed in high frequency Raman region.

2.1.1 Raman theory

When a sample is illuminated by light, a fraction of the incident light is reflected and

the rest is transmitted at the surface of the sample. While inside the sample some of the light could be absorbed or scattered, as shown in Figure 2-1. For the absorbed light, some of them may reemit a light with a different frequency, known as photoluminescence (PL), which is defined as the light emission from an actual excited state to ground state. Besides PL, other transmitted light inside the medium are scattered and the scattering process includes two different cases: elastic scattering process and inelastic scattering process. The elastic scattering process means that the frequency of scattered electromagnetic wave is the same as that of the incident photon, which is named as Rayleigh scattering. In the latter case, the frequency of the scattered light is larger (anti-Stokes scattering) or smaller (Stokes scattering) than that of the incident light, which is called Raman scattering phenomenon.

Figure 2-1. (a) Light-matter interaction when a Raman scattering medium is illuminated by an electromagnetic field. The arrows with different colours representing different emitting signals, e.g. PL, Rayleigh scattering, Raman scattering etc. (b) Absorption and emission schematics in a typical Raman scattering process.

Raman scattering is an inelastic scattering process of a photon after interacting with material, in which the scattered photons own frequencies different from that of incident photons⁷³. Basically, there are two scattering types, non-resonant Raman scattering and resonant Raman scattering. In non-resonant scattering, the incident photon energy is not close to the band gap and only one phonon (Γ point) participates in one Raman process, so the spectra are dominated by the Γ point phonons. Contrastively, the energy of incident or outgoing photon matches the bandgap between conduction band (CB) and

valence band (VB) of target materials, and hence the peak intensity of Raman modes will be significantly enhanced. Besides, the electrons excited by the laser excitation can emit or absorb more than one phonons. If we take the first-order or non-resonant Raman spectroscopy for example, there are three general steps in a typical Raman process: 1) the incident photon excites electron from VBs to an intermediate state which can be real electronic or virtual state, 2) the electron emits (Stokes) or absorb (anti-Stokes) a phonon through electron-phonon coupling (EPC), 3) the corresponding electron after 2) recombines with the hole in VB by emitting an outgoing photon. Basically, the intensity of Stokes line is much stronger than anti-Stokes due to the much larger population of electrons at vibrational ground state $v=g$ than the first excited vibrational state $v=n$ by Maxwell-Boltzmann distribution law

$$N_n \propto \exp(-\hbar\omega_{ng} / kT) \quad (2-1).$$

When light (an electromagnetic field) interacts with a molecule, the charges of the molecule (electrons and nuclei) move in the opposite directions in response to the driving potential. Thus, the molecule becomes itself an emitter of electromagnetic radiation. The magnitude of such an effect must be proportional to the induced dipole of the molecule. The relationship between the electrical field and the induced dipole moment can be expressed as follows,

$$P = \alpha \cdot E + (1/2) \cdot \beta \cdot E^2 + (1/6) \cdot \gamma \cdot E^3 + \dots \quad (2-2),$$

where tensors α ($\sim 10^{-40} \text{ C} \cdot \text{V}^{-1} \cdot \text{m}^2$), β ($\sim 10^{-50} \text{ C} \cdot \text{V}^{-1} \cdot \text{m}^2$) and γ ($\sim 10^{-60} \text{ C} \cdot \text{V}^{-1} \cdot \text{m}^2$) are called as polarizability, hyper-polarizability and 2nd hyper-polarizability, respectively. They show big magnitude differences in value and hence the influence of the latter two factors can be neglected in many cases. By only considering the 1st term, the equation above could be re-written as

$$P = \alpha \cdot E \quad (2-3),$$

where E represents a monochromatic electromagnetic field (incident frequency ν_0) with description as

$$E = E_0 \cdot \cos(2\pi \cdot \nu_0 \cdot t) \quad (2-4).$$

The polarizability α usually depends on the normal coordinate of the vibrating molecule, with expression as

$$\alpha = \alpha_0 + \sum_k \left(\frac{\partial \alpha}{\partial Q_k} \right) \cdot Q_k + \frac{1}{2} \sum_{k,l} \left(\frac{\partial^2 \alpha}{\partial Q_k \partial Q_l} \right)_0 \cdot Q_k \cdot Q_l + \dots \quad (2-5).$$

Using first approximation, the different vibrations in target molecule are considered as totally independent and no cross terms are included. Therefore, the equation (2-5) could be simplified as

$$\alpha_v = \alpha_0 + \alpha'_v \cdot Q_v \quad (2-6)$$

$$Q_v = Q_{v0} \cdot \cos(2\pi \cdot \nu_v \cdot t + \varphi_v) \quad (2-7),$$

where ν_v describes the vibrational frequency of target molecules. By substituting equations (2-4), (2-6) and (2-7) into the expression of induced dipole moment (2-3), we could obtain

$$P = \alpha_0 \cdot E_0 \cdot \cos(2\pi\nu_0 t) + \alpha'_v \cdot E_0 \cdot Q_{v0} \cdot \cos(2\pi\nu_0 t) \cdot \cos(2\pi\nu_0 t + \varphi_v) \quad (2-8).$$

Using the trigonometrical formula, we could re-write equation (2-8) as

$$\begin{aligned} P &= \alpha_0 \cdot E_0 \cdot \cos(2\pi \cdot \nu_0 \cdot t) \\ &+ \frac{1}{2} \cdot \alpha'_v \cdot E_0 \cdot Q_{v0} \cdot \cos[2\pi \cdot (\nu_0 + \nu_v) \cdot t + \varphi_v] \quad (2-9). \\ &+ \frac{1}{2} \cdot \alpha'_v \cdot E_0 \cdot Q_{v0} \cdot \cos[2\pi \cdot (\nu_0 - \nu_v) \cdot t - \varphi_v] \end{aligned}$$

Therefore, the induced dipole moment could be considered as a function of the vibrational frequencies of the molecules (ν_v) and the incident radiation (ν_0), with simplified expression as

$$P = P(\nu_0) + P(\nu_0 + \nu_v) + P(\nu_0 - \nu_v) \quad (2-10),$$

where the first term is for Rayleigh scattering, the second term for anti-Stokes scattering, and the third for Stokes scattering.

However, this classical theory of Raman scattering could not be used to explain the higher intensity of Stokes Raman scattering than anti-Stokes Raman scattering from experimental results. In this case, we need to engage quantum mechanics theory to consider the intensity of scattering, where the molecular state could be express by the wave function and its energies are several discrete energy levels. In detail, the intensity of scattering is determined by the Boltzmann distribution, thus depending on the occupation of the initial state. Recalling equation (2-1), we can get the intensity ratio between Stokes and anti-Stokes scattering as

$$\frac{I(Stokes)}{I(anti - Stokes)} = \frac{(\nu_m - \nu_n)^4}{(\nu_m + \nu_n)^4} e^{h\nu_n / kT} \quad (2-11),$$

where ν_m and ν_n represent two vibrational quantum states with small (ν_m) and large (ν_n) quantum number respectively. From equation (2-11), we can find that this intensity ratio sensitively depends on the temperature factor T and thus in turn it could be used to determine the temperature of the sample.

Last but most importantly, from equation (2-9), if a vibration in molecule is Raman active, the $\alpha_\nu' \left(\frac{\partial \alpha}{\partial Q_\nu} \right)$ must be nonzero term. That is, there must be a nonzero change in the polarizability α with the normal coordinate at the equilibrium configuration. Using a tensor format, we have the dipole moment expression as follow

$$\begin{bmatrix} P_x \\ P_y \\ P_z \end{bmatrix} = \begin{bmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{bmatrix} \begin{bmatrix} E_x \\ E_y \\ E_z \end{bmatrix} \quad (2-12),$$

where $\alpha_{ij} = \alpha_{ji}$, and if any one of $\frac{\partial \alpha_{ij}}{\partial Q_\nu} \neq 0$, this mode will be Raman active⁷³.

2.1.2 Raman modes in TMDs

The lattice vibrations could be classified by the irreducible representation of the symmetry group of the TMD crystals. Compared with bulk MoS₂ which possesses D_{6h} point group symmetry, the symmetry in few-layer MoS₂ is reduced due to the translational asymmetry along the z axis with decreasing layer thickness⁷⁴. Figure 2-2 shows the phonon dispersions and density of states (DOS) for monolayer (a) and bulk MoS₂ (b) with experimental data plotted in black dots⁷⁵. Different from monolayer MoS₂, the bulk phonon dispersion has three acoustic modes, the in-plane longitudinal acoustic (LA) mode, transverse acoustic (TA) mode and out-of-plane acoustic (ZA) mode, whereas, the low-frequency optical modes are found at 35.2 and 57.7 cm⁻¹, corresponding to the rigid-layer lateral and vertical motion, respectively.

Figure 2-2. Phonon dispersion curves and density of states for single-layer (a) and bulk (b) MoS₂.

Based on group theory⁷⁶, the phonon modes at Γ -point for bulk MoS₂ can be decomposed into the irreducible representation: $\Gamma = 2A_{2u} + 2E_{1u} + 2B_{2g} + 2E_{2g} + A_{1g} + E_{1g} + B_{1u} + E_{2u}$. These 12 irreducible representations in bulk MoS₂ can be divided into six conjugate pairs (E^1_{1u} and E^2_{2g} , E_{1g} and E_{2u} , E^2_{1u} and E^1_{2g} , A^1_{2u} and B^2_{2g} , A_{1g} and B_{1u} , A^2_{2u} and B^1_{2g}), as shown in Figure 2-3. In each conjugate pair, there is an inversion centre between the two layers, and one phonon mode differs from the other by an interlayer phase shift of 180°. Figure 2-3 shows all the displacement representations for the Γ -point vibrational modes in bulk MoS₂ with frequencies shown below, where R and I represent Raman active and inactive vibrations respectively. All these calculated phonon frequencies are consistent with previous experimental results⁷⁷.

Figure 2-3. Displacement representations for the Gamma-point phonon vibrational modes in bulk MoS₂ with vibrational frequencies shown below. R and I represent Raman active and inactive respectively⁷⁸.

Generally, with considering Raman active and inactive vibration states, the irreducible representations of the phonon modes in bulk 2H-MX₂ crystals (D_{6h} ($/P36/mmc$)) are shown as

$$\Gamma = A_{1g}(R) + 2A_{2u}(IR) + 2B_{2g}(IN) + B_{1u}(IN) + E_{1g}(R) + 2E_{1u}(IR) + 2E_{2g}(R) + E_{2u}(IN) \quad (2-13),$$

where the two-fold degenerate E modes represent in-plane vibrations, and the non-degenerate A and B modes vibrate out-of-plane along the z axis. R , IR , IN represent Raman active, infrared active, and inactive modes, respectively. For 2L TMDs, they belong to the point group D_{3h} , with the irreducible representation of the Γ phonon normal modes obtained as

$$\Gamma = 3A_{1g}(R) + 3A_{2u}(IR) + 3E_g(R) + 3E_u(IR) \quad (2-14).$$

When the thickness of TMD crystals is reduced to monolayer (D_{3h}), the primitive cell of 1L MX_2 contains 3 atoms and hence it has 9 vibrational modes instead of 18 modes in few-layer MX_2 . The derivation of the irreducible representations of the Γ phonon normal modes in 1L MX_2 should be

$$\Gamma = 2A_2''(IR) + A_1'(R) + 2E'(R + IR) + E''(R) \quad (2-15).$$

Note that the phonon normal modes for 2TL and bulk are the same in terms of quantity and vibrational displacements, since they share the same primitive unit cell. In general, 9N normal vibration modes for NL- MX_2 at Γ point can be expressed as

$$\Gamma_{ol} = \frac{3N-1}{2}[A_1'(R) + E''(R)] + \frac{3N+1}{2}[A_2''(IR) + E'(R + IR)], \text{ for odd-layer TMDs } (D_{3h})$$

$$\Gamma_{el} = \frac{3N}{2}[A_{1g}(R) + E_g(R) + A_{2u}(IR) + E_u(IR)], \text{ for even-layer TMDs } (D_{3d}) \quad (2-16).$$

Therefore, for odd-layer TMDs with D_{3h} symmetry, the A_1' and E'' modes are Raman-active, A_2'' mode is IR-active, E' mode is both Raman-active and IR-active. For the even-layer TMDs with D_{3d} space group, due to the existence of inversion symmetry, the phonon modes are exclusively Raman-active (A_{1g} and E_{1g}) or IR-active (A_{2u} and E_u).

2.2 Confocal Raman and PL system

For all the optical contrast images and Raman single spectra/intensity mappings, as well as PL spectra/mapping at room temperature, low temperature and high pressure, we use a Witec CRM200 backscattering Raman system equipped with five lasers with different emission wavelength (325 nm, 457 nm, 532 nm, 633 nm, and 785 nm). Among them, a solid-state YAG laser at 2.33 eV (532 nm) is mostly used in our Raman and PL

experiments, with a proper power avoiding sample heating (usually below 1 mW). The photograph of our Witec CRM200 Raman system containing main components such as the monitor, mechanical stage, microscope, lasers, spectrometer, and other external optics is shown in Figure 2-4a. The size of the laser beam is around 250 nm, which was focused on the sample using an objective (Olympus, 100 $\times$ /NA0.95). For the detailed irradiation and collection mechanism, we usually describe the process as follows. Firstly, a 532 nm (457 nm, 633 nm *etc.*) laser is coupled into a single mode fiber and then is half-reflected and half-transmitted by a holographic beam splitter (50:50), where the reflected laser is focused by an objective lens with a large numerical aperture (NA) and then illuminate the target sample. The sample is placed on the mechanical stage which could be moved along X, Y and Z axes manually, or it could also be moved precisely with a piezoelectronic-control along three axes while doing Raman/PL mapping. The maximum moving distance of this piezo stage is around 200 μ m along x and y directions and $\sim$ 20 μ m along the z -direction. The PL signal, Raman scattering light and Rayleigh scattering light are collected under backscattering mode. While doing regular PL and Raman (high-frequency range) measurements, an edge filter is used to block the Rayleigh light. Then the PL/Raman signals and a small fraction of Rayleigh signals go to the grating (1800/600/150 grooves/mm) and detected by a TE-cooled charge coupled device (CCD). Differently, we always use 600/150 grooves/mm grating for PL signal collection to get a wide wavelength range of spectra, while 1800 grooves/mm grating for Raman scattering collection to obtain good peak resolutions.

The schematic illustration of the light excitation and emission paths in our Witec CRM200 backscattering Raman system is shown in Figure 2-4b. However, one common issue for Raman spectroscopy using conventional edge/notch filter is the low frequency measurements, due to the strong Rayleigh scattering at the position of laser line. Typically, one cannot get the Raman signals below 50 cm^{-1} , which essentially reflect the information of layer shear and breathing vibrations. However, the shear and breathing vibrations are crucial for the study of vdWs interaction and related properties in 2D materials. Therefore, for ultra-low-frequency Raman spectra, we use two BraggGrate Notch Filters (BNF) centered at 532 nm with bandwidths as narrow as 5 cm^{-1} and a large OD (> 4) to achieve low frequency region. Meanwhile, a linear polarizer with different collection angles was used to realize the parallel ($\bar{z}(xx)z$) and perpendicular ($\bar{z}(xy)z$) backscattering configurations respectively.

Figure 2-4. (a) Photograph for Witec CRM200 backscattering Raman system. (b) Schematic illustration of the light excitation and emission paths.

2.3 Scanning transmission electron microscopy

As a direct and powerful tool to examine the crystal atomic structures, aberration-corrected scanning transmission electron microscopy (STEM) can provide real space images at the atomic scale with single atom resolution. Such technology has been successfully employed to characterize a large variety of 2D materials including graphene⁷⁹, BN⁸⁰ and TMDs⁸¹, especially for defect analysis. For example, the STEM images for few-layer MoS₂ clearly show the atomically sharp boundary between monolayer and bilayer, as well as the distinct arrangements between AA and AB stacking bilayers (Figure 2-7 and Figure 3-4). It is because the intensity sensitively relies on the atomic weight and the number of layer. In general, the high intensity sites correspond to the heavy atoms (transition metal atoms in our TMDs case) and thicker samples, leading a contrast step edge. The alternant bright and dark columns within the hexagonal lattice represent the 2H stacking, in which the bright columns are the Mo (S) atoms of the top layer with the overlaid S (Mo) atoms of the bottom layer. In the AA stacking (3R-like) regions, the brightest are the Mo atoms of the top layer with the overlaid S atoms of the bottom layer, the less bright are the Mo atoms of the bottom layer and the least bright in the hollow sites are the S atoms of the top layer. Therefore, the STEM images can unambiguously provide an identification of the stacking orders in for few-layer 2D materials. Technically, the STEM samples were prepared with a poly (methyl methacrylate) (PMMA) assisted method. A layer of PMMA of about 1 μm thick

was spin-coated on the wafer with WTe₂ samples deposited, and then baked at 180 °C for 3 min. Afterwards, the wafer was immersed in NaOH solution (1M) to etch the SiO₂ layer over night. After lift-off, the PMMA/WTe₂ film was transferred into DI water for several cycles to wash away the residual contaminants, and then it was fished by a TEM grid (Quantifoil Mo grid). The transferred specimen was dried naturally in ambient environment, and then dropped into acetone overnight to wash away the PMMA coating layers. The STEM imaging was performed on an aberration-corrected Nion UltraSTEM-100 operating at 100 kV.

2.4 First-principles calculations

To have a quantitative description of experimental observations in Raman spectra, in terms of phonon normal mode assignment and phonon frequencies, first-principles calculations are conducted for the zone center phonon modes in diverse 2D TMD crystals. The first-principles⁸² calculations including geometry optimization, vibrational properties, and molecule dynamics were all carried out using the projector-augmented wave⁸³ method as implemented in the Vienna *ab initio* simulation package (VASP) code⁸⁴ including the spin-orbit coupling effects. To compute the electronic structures are performed with the plane wave basis set as implemented in the QUANTUM ESPRESSO program package⁸⁵. The norm-conserving pseudopotentials⁸⁶, including spin-orbit coupling effects were adopted and a cutoff energy for the basis set was 140 Ry. The exchange correlation potential was described using the local-density approximation in the parametrization of Perdew and Zunger⁸⁷. The Brillouin zone was sampled by a 15×15×1 k-point mesh. The energy convergence for the relaxation was chosen to be less than 10⁻⁵ eV/A.

To account for the interlayer van der Waals interactions, all the simulations were performed using the nonlocal vdW-DF-optB86b functional⁸². We added a vacuum layer of 20 Å along the z-axis to avoid the mirror interactions between neighboring images. The phonon spectrum and Raman intensities are calculated within density-functional perturbation theory (DFPT) as introduced by Lazzeri and Mauri⁸⁸. For the DFPT self-consistent iteration, we used a mixing factor of 0.2 and a high convergence threshold of 10⁻¹⁸ eV. In detail, we calculated the interlayer binding energies using three approaches for treating the vdWs interaction: LDA, GGA-PBE, and van der Waals density

functionals (vdWs-DF) to evaluate the accuracy of our results. As shown in Figure 3-1a in Chapter 3, the LDA and vdWs-DF exhibit similar tendency in describing the interlayer binding, whereas the GGA-PBE predicts much less binding. Moreover, apart from the GGA-PBE data, both LDA and vdWs-DF results are in excellent agreement with the experimental cell parameters. We also compared the relative ground-state total energies with respect to the most stable stacking order in Figure 3-1b obtained by using LDA and vdWs-DF. Obviously, the two methods correctly predict the AB stacking (2H phase) as the most favorable phase and deliver the same stability sequence. Therefore, our results indicate that the LDA yields comparable results with the vdWs-DF for MoS₂ and the LDA can provide a reasonable description for the van der Waals interaction. To do the spin projection calculations, we computed the Wannier functions by the maximally localized algorithm⁸⁹, implemented in the package WANNIER90⁹⁰ using Mo *d* orbitals and S *p* orbitals.

2.5 Fabrication of TMD crystals

In general, there are two mainstream strategies to fabricate few-layer 2D TMDs: top-down and bottom-up. The top-down strategy consists of mechanical exfoliation (ME)⁹¹ and liquid-phase exfoliation (LPE)⁹². Figure 2-5 shows the typical ME process to obtain few-layer MoS₂ from pristine crystals, where the screw dislocations observed in the optical micrographs (Figure 2-5a) from the 2H (left) and 3R (right) single crystals present their hexagonal and trigonal structures respectively¹³. The detailed exfoliation processes and optical/AFM morphology for obtaining few-layer MoS₂ samples are shown in Figure 2-5b and 2-5c^{28, 91}. Due to the low productivity of few-layer TMD sheets in top-down approach, bottom-up strategy becomes more and more popular, which can be extensively realized by CVD⁹³, physical vapor deposition (PVD)⁹⁴, atomic layer deposition (ALD)⁹⁵, as well as epitaxy growth. Compared with ME, the sample growth processes by these methods can be controlled more easily with much higher yield of few-layer samples, where large amount of one to four layered TMD flakes with various stacking configurations have been obtained, while ME method yields predominately 2H stacking sequence only.

Figure 2-5. Mechanical exfoliation of MoS₂. (a) Optical micrograph images of the surface of MoS₂ crystals with 2H (left) and 3R (right) stacking¹¹. Reproduced with permission from ref. [11]. Copyright 2014, Nature Publishing Group. (b) Micromechanical exfoliation processes of MoS₂ crystal⁹⁶. Reproduced with permission from ref. [96]. Copyright 2012, IOP Publishing Group. (c) Optical morphology (left) and AFM image (right) of few-layer MoS₂ by micromechanical exfoliation²⁸. Reproduced with permission from ref. [28]. Copyright 2010, American Chemical Society.

We used both CVD and PVD to grow MoS₂ samples (Figure 2-6). We obtained a large amount of multilayer MoS₂, especially 2L and 3L MoS₂ with various stacking configurations by PVD. The typical growth process and morphologies of 1L-4L samples using the PVD method are shown in Figure 2-6a. We acquired mostly 1L MoS₂ flakes with various shapes by the CVD method (Figure 2-6b). Figure 2-6c compares the structural and electronic properties of graphene and MoS₂ prepared by different methods⁹⁷. The red and blue curves show the mobility of graphene and MoS₂ samples on SiO₂. On one hand, both graphene and MoS₂ samples from the mechanically cleaved method show the best structural and electronic quality, due to fewer defects. On the other hand, CVD/PVD grown samples provide more stacking variations to investigate interlayer coupling effect on optical, electronic, electrical and other intriguing physical properties.

Figure 2-6. Vapor deposition of MoS₂ nanoflakes. The temperature ramping diagram of the growth process and morphologies of as grown MoS₂ flakes by CVD (a) and PVD (b) respectively. (c) Mobility comparison of graphene and MoS₂ grown by various methods. The red curve shows the mobility of graphene on SiO₂, and the blue curve is for MoS₂ on SiO₂⁹⁷. Reproduced with permission from ref. [97]. Copyright 2014, Nature Publishing Group.

From the first-principles calculations, there are five high-symmetry stacking configurations for bilayer MoS₂ as shown in Figure 2-7a, which can be classified into two groups depending on whether the S (Mo) atoms in the top layer are directly situated above the Mo (S) atoms of the bottom layer. The optical image (Figure 2-7a center) shows that PVD grown bilayer MoS₂ sheets exhibit two typical configurations: two triangles in the same orientation (marked as AA) and in reverse orientation (marked as AB). Our previous results indicate that AA and AB stackings are the most favorable among all configurations while other three are energetically unstable. The two natural polytypes of MoS₂ are known as 2H (space group: *P6₃/mmc*) and 3R (space group: *R3m*) respectively, both of which have trigonal prismatic coordination of the Mo

atoms but with distinct stacking orders^{11, 94}. Figure 2-7b shows the optical and Z-contrast scanning transmission electron microscopy (STEM) images of the 1L (left), AA- (middle) and AB- (right) stacked 2L MoS₂. The STEM images clearly show the distinct arrangements between AA and AB stacked bilayer samples. In STEM, the intensity sensitively relies on the atomic weight and the number of layer, where the high intensity sites correspond to the heavy atoms (Mo) and thicker samples, leading a contrast difference. In the 3L MoS₂ samples, there are four typical stacking patterns: ABA, AAA, AAB and ABB following the nomenclature of bilayer system, which lead to three distinct stacking configurations as the ABB and AAB configurations are completely equivalent. The top and side views of atomic structures for ABA-, AAA- and AAB-stacked 3L MoS₂ are shown in Figure 2-8, where the layer number is determined by both optical images and Raman intensity mapping^{29, 94}.

Figure 2-7. Atomic structures of bilayer and trilayer MoS₂ grown by CVD method. (a) All five classic atomic structures of bilayer MoS₂. (b) Optical and Z-contrast STEM images of the monolayer (left), AA- (middle) and AB- (right) stacking MoS₂ bilayer.

Figure 2-8. Top and side views of trilayer MoS₂ with four typical stackings, ABA, AAA, AAB (ABB). Insets are the optical images and Raman mappings of these 3L MoS₂ samples.

Chapter 3 A new degree of freedom beyond thickness in TMDs—stacking

3.1 The polytypes of 2L and 3L MoS₂

As for the sample preparation, we used the physical vapor deposition (PVD) technique to grow few-layer MoS₂ samples, by which we obtain a large amount of multilayer MoS₂ with various stacking configurations on the same SiO₂/Si substrate. The morphology, stacking sequence and the number of layers of our samples cannot be controlled (Figure 3-3). The samples used were randomly selected. According to our first-principle calculations, we have calculated the total energies and phonon dispersions of all five configurations, as shown in Figure 3-1a. Our results show that AB' and AA' are energetically unfavorable among all configurations because the S atoms of one layer are placed directly above the S atoms of the other layer. Due to the strong repulsion between the S atoms, these two stacking configurations are dynamically unstable with imaginary frequencies in the Gamma point. The other three configurations have lower energy and are dynamically stable with distinct frequencies of Raman modes, especially in the ULF region (Figure 3-1b). The A'B configuration has two ULF peaks at ~16.6 and ~32.0 cm⁻¹ belonging to the in-plane shear mode and out-plane breathing mode respectively. These two modes are found at ~25.6 (~26.0), ~40.3 cm⁻¹ (~38.3) in the AB (AA) configuration. Well coincided with all our experimental results, the AB and AA stackings are verified as the most stable configurations of bilayer MoS₂, which should be allocated as 2H and 3R phases correspondingly.

Figure 3-1. (a) Calculated binding energies as a function of cell parameter c in 2H-MoS₂, while fixing the in-plane cell parameter a at the bulk value. The experimental value of c axis is indicated by the vertical line. (b) Relative ground-state total energies with respect to the most stable stacking order of bilayer MoS₂ (2H phase) with five possible stackings obtained by LDA and vdWs-DF, as well as the corresponding ULF Raman shift.

Figure 3-2a and 3-2b show the two natural polytypes of MoS₂, 2H (space group: $P63/mmc$) and 3R (space group: $R3m$) respectively, both of which have trigonal prismatic coordination of the Mo atoms but with distinct stacking orders. In the 2H polytype, the S (Mo) atoms of one layer reside directly above the Mo (S) atoms of the other layer and the bottom layer is fully eclipsed. The 3R polytype consists of three staggered layers, where the S atoms of the middle layer are situated above the Mo atoms of the bottom layer and below the hollow sites of the top layer; the Mo atoms of the middle layer are located above the hollow sites of the bottom layer and below the S atoms of the top layer. In practice, few-layer MoS₂ grown via the bottom-up approach, e.g., by chemical vapor deposition (CVD), may exhibit various stacking orders with interlayer rotations (see Figure 3-2c for bilayers and Figure 3-7a for trilayers). As shown in Figure 3-2d, we consider all five high-symmetry stacking configurations for bilayer MoS₂, which can be classified into two groups depending on whether the S (Mo) atoms in the top layer are directly situated above the Mo (S) atoms of the bottom layer. As a direct and powerful tool to examine the crystal atomic structures, STEM can provide real space images at the atomic scale with single atom resolution, especially for defect analysis. The optical images show that CVD grown bilayer MoS₂ sheets typically exhibit two configurations: two triangles in the same orientation (marked as AA) and in reverse orientation (marked as AB). In the trilayer samples, there are four typical stacking patterns: ABA, AAA, AAB and ABB that we will discuss in detail later. Note that the nomenclature we used here is based on the macroscopic geometries based on the optical images directly, which are not necessarily reflection of the atomic stacking configuration. On the other hand, it is imperative to establish direct correlation between the optical images and the atomic structures.

In order to understand the growth behaviors of MoS₂, we calculated the adhesion energies of few-layer MoS₂. Starting with a monolayer MoS₂, we added one more layer

Figure 3-2. (a, b) Stick-and-ball lattice structure (side view) of layered MoS₂ with typical 2H phase (a) and 3R phase (b). S atoms are shown as red spheres, while Mo atoms sandwiched by two S atomic layers in each unit cell are presented by blue spheres. c, The optical reflection image of measured AA- and AB bilayer MoS₂. d, All five classical atomic structures of bilayer MoS₂.

each time and explored all the possible configurations. As shown in Figure 3-3a, we can make the following remarks: At the initial stage of MoS₂ CVD growth, MoS₂ can adopt various stacking configurations due to the comparable adhesion energies. This is the reason we obtain a large amount of few-layer MoS₂ with various stacking patterns on the same SiO₂/Si substrate. Based on the most-stable configurations of 2L MoS₂ with AB and AA stacking, as well as the selection rules demonstrated above, we could have trilayer MoS₂ systems with four different stackings, ABA, ABB, AAB and AAA following the nomenclature of bilayer system. The atomic structure models for trilayer system are simulated in Figure 3-3b below, in which the ABB and AAB atomic configurations are completely equivalent.

Figure 3-3. (a) Calculated adhesion energies for few layer MoS₂ growth in a successive manner. The adhesion energy for the n th layer MoS₂ is estimated by subtracting the energy of $n-1$ layer and the single layer MoS₂, as illustrated in the inset. (b) Top view and side view of the atomic structures of trilayer MoS₂ with ABA-, AAA- and AAB-(ABB-) stacking respectively.

3.2 Stacking identification of few-layer MoS₂ by ULF Raman

The STEM images clearly show the distinct arrangements between AA and AB stacking bilayers (Figure 3-4(b-e)). It is because the intensity sensitively relies on the atomic weight and the number of layer. In general, the high intensity sites correspond to the heavy atoms (Mo) and thicker samples, leading a contrast step edge. As shown in Figure 3-4b and Figure 3-4d, there is an obvious contrast step across the monolayer and bilayer regions. Figure 3-4c and Figure 3-4e show the Z-contrast images of bilayer regions with AB and AA stacking. The alternative bright and dark columns in the hexagonal lattice indicates the 2H stacking, where the bright (dark) columns are Mo (S) atoms in the top layer with overlaid S (Mo) atoms in the bottom layer, respectively. In the AA stacking (3R-like) regions, the brightest columns are Mo atoms in the top layer with overlaid S atoms in the bottom layer, the less bright columns are Mo atoms in the bottom layer and the least bright columns are S atoms in the top layer located in the hollow sites. The possibility of the metastable A'B stacking here can be ruled out: although the hollow sites are filled from the top view similar to AA stacking, the images should possess the alternative bright and dark columns (two Mo and two S atoms from each layer), rather than three decreasing image intensity in Figure 3-4e. Therefore, the STEM images unambiguously provide an identification of the stacking orders in bilayer MoS₂.

From our first-principles calculations, all the five configurations have distinct frequencies of Raman modes, especially in the ULF region (Figure 3-1b). For example, the A'B configuration has two ULF peaks at ~ 16.6 and ~ 32.0 cm⁻¹ belonging to the in-plane shear mode (SM) and out-plane breathing mode (BM) respectively. Vibrational schematics of SM (left panel) and BM (right panel) in bilayer MoS₂ are shown in Figure 3-5c. The numerical values inserted below are taken from experiments (black) and calculations (red) separately which shows great matching. These two modes are found at

~ 25.6 (~ 26.0), ~ 40.3 cm^{-1} (~ 38.3) in the AB (AA) configuration. Well coincided with all our experimental results, the AB and AA stackings are verified as the most stable configurations of bilayer MoS_2 , which should be allocated as 2H and 3R phases correspondingly.

Figure 3-4. (a) Optical image of typical bilayer MoS_2 samples with AA and AB stacking. (b-e) Z-contrast images of the step edge of AA-stacking MoS_2 bilayer and monolayer (b, c), the step edge of AA-stacking MoS_2 bilayer and monolayer (d, e). The two triangles indicate the orientation of the top and bottom MoS_2 layer.

Compared to our experimental Raman spectra shown in Figure 3-5a, the frequency values and the relative peak position changes are at ~ 22.6 (~ 22.8), ~ 41.6 (~ 38.7) cm^{-1} , in excellent agreement with the calculated results of two most stable configurations (AB and AA stacking). Thus, another dynamically stable metastable A'B configuration is excluded. More importantly, the intensity ratio between the breathing mode and shear mode is very distinct: ~ 1.2 for AB and ~ 4.1 for AA stacking, calculated using the integrated areas of the Stokes Raman peaks. We also performed the polarized Raman measurements in backscattering configurations with parallel and crossed polarization geometry. As shown in Figure 3-5b, in the crossed geometry, all breathing modes are forbidden⁹⁸. The relative intensity ratio of shear modes to breathing modes is consistent with unpolarized measurements.

Figure 3-5. (a-c) Stokes and anti-Stokes low wavenumber Raman spectra of AA and AB bilayer MoS₂ taken without polarization (a), and under the $\bar{z}(xx)z$ and $\bar{z}(xy)z$ polarized backscattering configurations of AB-stacking bilayer MoS₂ and AA-stacking bilayer MoS₂ (b). (d) Vibrational schematics of shear modes (left panel) and interlayer breathing modes (right panel) in bilayer MoS₂. The numerical values inserted below are taken from experiments (black) and calculations (red) separately.

The Raman spectra for AA and AB configurations within the high-frequency range (around 400 cm⁻¹) as well as the PL spectra are also shown in Figure 3-6. There is no prominent stacking-dependence in the high-frequency range. Therefore, the ratio of shear modes to breathing modes in the ULF range (<50 cm⁻¹) can conveniently identify the stacking orders of bilayer MoS₂ and also confirm our previous STEM results and first-principles calculations: macroscopic AA and AB stacking patterns correspond to 3R-like and 2H atomic stacking orders, respectively.

Figure 3-6. Raman spectra and Photoluminescence spectra of bilayer MoS₂ with AA- (a) and AB- (b) stacking respectively.

The layer number of 3L MoS₂ is precisely determined using Raman intensity mappings of corresponding samples as shown in Figure 3-7. The corresponding Photoluminescence and Raman profiles with intensity changes are also plotted in Figure 3-8

Figure 3-7. Optical micrograph (a) and Raman intensity mapping (b) of trilayer MoS₂ with four different stackings ABA, ABB, AAB, AAA.

Figure 3-8. PL (a) and Raman spectra (b) of trilayer MoS₂ from the first layer to third layer with prominent two peaks from A and B excitons respectively.

Before identification of the stacking configurations for trilayer systems, we first examine the bottom two layers in the trilayer MoS₂ samples. As mentioned above, we can identify the stacking orders of bilayer region using the relative intensity of breathing

modes and shear modes by integrating the peak areas. Indeed, as shown in Figure 3-9a, the ratio of the intensity of the breathing mode (I_b) to that of shear mode (I_s) can be used to classify the bilayer regions of the four trilayer samples (ABA, ABB, AAB, AAA stacking) into two groups: the first two stackings (ABA and ABB) with $I_b/I_s \approx 1$ could be classified as AB stacking for the bilayer while the last two stackings (AAB and AAA) with $I_b/I_s \approx 4$ should be considered as AA stacking respectively, which are in perfect agreement with previous bilayer results.

Figure 3-9. The low wavenumber Raman spectra of the second layer (a) and third layer (b) of trilayer MoS_2 . The measurement region corresponds to the second layer in Figure 3-7.

As shown in Figure 3-9b, we find the shear modes and the breathing modes in ULF range are almost merged into one peak, where the ratio of the intensity between the breathing mode (I_b) to that of shear mode (I_s) cannot be used directly to identify the stacking configurations. In order to quantify the difference between the two modes, we use the polarization measurements to identify the different features between the shear mode and breathing $I_{\parallel}/I_{\perp}$ mode. Here, $I_{\parallel}$ is the summation of the parallel components of both shear mode and breathing mode, while $I_{\perp}$ contains only the perpendicular component of shear mode, as the breathing mode is entirely suppressed under perpendicular collection configuration. Thus, I_b/I_s in bilayer systems changes to $I_{\parallel}/I_{\perp}$ for the trilayer systems. As shown in Figure 3-9b, by changing the stacking orders we find the intensity ratio $I_{\parallel}/I_{\perp}$ for AAA stacking is most dramatically reduced, followed by AAB (ABB) stacking, with ABA stacking changes the least.

To more quantitatively explain this stacking-dependent ULF Raman intensity in bilayer

and trilayer MoS₂, we apply the interlayer bond polarizability mode, as although the van der Waals interlayer interactions also have some covalent character⁹⁹. As the stacking shows less effect on the intensity of breathing mode, we consider the shear mode intensity difference to cause the different I_b/I_s values in our trilayer system. In detail, the Raman intensity of the shear mode could be estimated as $I \propto (1+n) |\Delta\alpha|^2$, where n is the phonon population given by the Boltzmann distribution function as $n = [\exp(\hbar\omega / k_B T) - 1]^{-1}$, and $\Delta\alpha$ is the total change of bilayer or trilayer polarizability¹⁰⁰. In our case, we discuss the intensity difference of shear mode with same frequency for different stackings in bilayer and trilayer samples at room temperature, therefore the n is a constant and $I \propto |\Delta\alpha|^2$. Based on $\Delta\alpha = \alpha'(q_1 - q_2)$ in bilayer MoS₂, where α' is the differential bond polarizability and q₁ and q₂ are the layer displacement from the equilibrium position. The normalized layer displacements (q₁ and q₂) in bilayer AA and AB are $\frac{1}{\sqrt{2}}(1, -1)$, which gives the change in dipole moment for AA and AB as $\Delta\alpha_{AA} = \sqrt{2}\alpha'_{AA}$, $\Delta\alpha_{AB} = \sqrt{2}\alpha'_{AB}$. The differential bond polarizability α'_{AA} and α'_{AB} are intrinsic parameters strongly affected by relative layer-layer atomic alignments and hence the stacking sequences¹⁰¹. One possible explanation is that, the bonds in two individual layers of AB stacking are pointing in opposite directions, while the bonds are pointing in the same direction for AA stacking. Therefore, AB stacking has a larger change in dipole moment with adjacent layers moving completely out-of-phase⁹⁹. As a result, in our bilayer system, we have experimental I_{AB}/I_{AA}=3.34 and thus $\Delta\alpha_{AB} / \Delta\alpha_{AA} = 1.83$ or $\alpha'_{AB} / \alpha'_{AA} = 1.83$.

In trilayer system, the total change of trilayer polarizability is a sum of the changes in the two interlayer bonds with normalized (q₁ q₂, q₃) as $\frac{1}{\sqrt{6}}(1, -2, 1)$, so approximately we have the following polarizability change in trilayer MoS₂ with ABA, ABB (AAB) and AAA stackings.

$$\begin{aligned}\Delta\alpha_{ABA} &= \Delta\alpha_{12(AB)} + \Delta\alpha_{32(AB)} = \alpha'_{AB}(q_1 - q_2) + \alpha'_{AB}(q_3 - q_2) = \sqrt{6}\alpha'_{AB} \\ \Delta\alpha_{ABB} &= \Delta\alpha_{12(AB)} + \Delta\alpha_{32(AA)} = \alpha'_{AB}(q_1 - q_2) + \alpha'_{AA}(q_3 - q_2) = \frac{\sqrt{6}}{2}(\alpha'_{AB} + \alpha'_{AA}) \\ \Delta\alpha_{AAA} &= \Delta\alpha_{12(AA)} + \Delta\alpha_{32(AA)} = \alpha'_{AA}(q_1 - q_2) + \alpha'_{AA}(q_3 - q_2) \approx \sqrt{6}\alpha'_{AA}\end{aligned}$$

With the results of bilayer system ($\alpha'_{AB}/\alpha'_{AA} = 1.83$), we are able to calculate the value of polarizability change as $\Delta\alpha_{ABA} \approx 1.8$, $\Delta\alpha_{ABB} \approx 1.4$, $\Delta\alpha_{AAA} \approx 1.0$, and thus with intensity ratio of shear modes as $I_{ABA} : I_{ABB} : I_{AAA} \approx 3.2 : 1.9 : 1.0$, which is consistent with our experimental results ($I_{ABA}' : I_{ABB}' : I_{AAA}' \approx 3.3 : 1.5 : 1.0$). However, for interlayer breathing mode, $I(B)_{AB} \approx I(B)_{AA}$ and hence $\alpha'(B)_{AB} \approx \alpha'(B)_{AA}$ in bilayer MoS₂ contribute to the less influence on trilayer MoS₂ by stacking sequence. Therefore, the intensity difference for different stackings in trilayer MoS₂ is attributed to different change of total polarizability while performing shear vibration. Besides, we also calculated Gamma-point phonon frequencies of ABA-, AAA- and ABB-stacking trilayer MoS₂ respectively displayed in Figure 3-10.

Stacking	ABA	AAA	ABB
E'' [R]	12.13	13.56	11.96
A' ₁ [R]	28.47	25.78	26.73
E' [I+R]	28.58	30.49	28.32
E' [I+R]	283.77	286.41	285.56
E' [I+R]	380.86	382.44	381.89
E'' [R]	382.86	383.88	383.11
E' [I+R]	382.93	384.14	383.86
A' ₁ [R]	403.72	404.86	403.87
A' ₁ [R]	463.63	466.47	466.30

Figure 3-10. Calculated Gamma-point phonon frequencies of ABA-, AAA- and ABB-stacking trilayer MoS₂ respectively.

Based on the previous experimental and theoretical results, we summarize the intensity ratios of the interlayer breathing modes to shear modes for bilayer (~1 for AB stacking and ~4 for AA stacking) and trilayer MoS₂ (~3 for ABA stacking, ~6 for AAB and ABB stacking, ~8 for AAA stacking) in Figure 3-11. Obviously, the intensity ratio is

stacking-dependent for both bilayer and trilayer MoS₂, which can be used to identify the stacking orders in few-layer MoS₂.

Figure 3-11. The intensity ratio of the interlayer breathing mode and shear mode (blue dot) for bilayer MoS₂ in Figure 3-5, and the $\bar{z}(xx)z$ (//) and $\bar{z}(xy)z$ ($\perp$) collection (red) for trilayer MoS₂ in Figure 3-9 with error bars of experimental standard deviation for several samples.

3.3 Electronic band structure for few-layer MoS₂

It has been reported that MoS₂/WS₂/MoSe₂/WSe₂ undergoes a transition from the indirect-band-gap to direct-band-gap semiconductor with their thickness reduced to monolayer. Correspondingly, the PL quantum yield (QY) shows an obvious enhancement while the TMD crystal undergoing from the indirect-gap bulk to the direct-gap monolayer¹⁰². Systematic studies of the evolution of the optical properties and electronic structures in layered TMD crystals as a function of layer number (N) have been reported. With the reduction of thickness, the confinement-induced band gap varies from the bulk value of 1.29 eV to over 1.90 eV in monolayer. Moreover, the change in the energy of indirect band gap at Γ point is about 0.7 eV, much larger than that of the band gap at K point of about 0.1 eV (Figure 3-12a). The corresponding PL spectra obtained from samples of different layer thickness are shown in Figure 3-12b. The direct bandgap of the 1L MoS₂ produces the strongest PL

intensity, while its intensity decreases with increasing MoS₂ thickness along with the direct-to-indirect bandgap transition. Two prominent exciton PL peaks at 1.83 eV and 1.98 eV are identified as the direct transition at the K-point in the MoS₂ Brillouin zone^{28, 103}. The main PL peak (Peak A) of 1L MoS₂ samples has a narrow width of 50 meV, with exciton energy at 1.90 eV, and few-layer samples display multiple emission peaks (labelled A, B, and I). Peaks A and B agree with the 1L emission that shift to the red and slightly broadens with increasing N, where Peak B possesses the energy 150 meV larger than that of Peak A. Peak I systematically red shifts and becomes less prominent with increasing N, approaching the indirect-gap energy of 1.29 eV for bulk^{14, 104}.

To explore the origin of the observed PL properties, the comparison between PL and absorption spectra has been done. The absorption spectra for MoS₂ crystals with different layer thickness are displayed in Figure 3-12c¹⁰². The two peaks in the absorption spectra at 1.88 eV and 2.03 eV correspond to the A and B exciton transitions in the PL spectra in Figure 3-12a. The energy separation between the A and B exciton peaks is ~0.15 eV in the 1L MoS₂ and gradually increased with increasing MoS₂ layer number, close to ~0.19 eV for the bulk MoS₂. This valence band splitting arises from the remarkable SOC effect and interlayer interactions in few-layer MoS₂ samples^{1, 9}. DFT calculations¹⁹ have been employed to explore the band structures for 4L, 3L, 2L, and 1L MoS₂, as shown in Figure 3-12a. The indirect bandgap gradually increases monotonically with the decreasing of layer number while the direct exciton transition energy at K point almost shows no changes. The variation of the electronic structure using the first-principles calculations in few-layer MoS₂ is in accord with previous PL and absorption data²⁸.

The stacking-dependent electronic features for 2L MoS₂ are also demonstrated in Figure 3-13. The larger emission intensity of A exciton and the larger energy difference between A and B excitons for AB-stacked 2L MoS₂ compared with AA stacking can be obviously found in Figure 3-13a, which agree with previous reports⁹⁴. Moreover, the calculated band structures for AA and AB 2L MoS₂ in Figure 3-13b and 3-13c clearly depict the splitting of top valence bands in AB stacking is larger than that of AA stacking, which in turn supports the experimental discoveries in Figure 3-13a. The PL spectra (Figure 3-14g) of twisted 2L MoS₂ samples show three prominent

Figure 3-12. Layer-dependent electronic band structure without spin-orbit coupling²⁸ (a), PL (b) and absorption (c) of MoS₂ crystals¹⁰⁵. Reproduced with permission from ref. [102]. Copyright 2014, RSC Publishing Group.

peaks at around 2.05 eV, 1.85 eV and 1.50 eV, corresponding to the two direct (A exciton-Peak I and B exciton) and indirect exciton peak II that originates from the interlayer exciton transition and depends sensitively on the interlayer electronic coupling strength: the smaller the indirect bandgap, the stronger the coupling strength. Figure 3-14h displays the energy difference between peak I and II in twisted bilayer samples. Unlike Peak I that remains almost unchanged, the energy for Peak II is the lowest for AA- and AB-stacked 2L MoS₂, and higher but nearly constant value for all other twist angles. Such trend shows the similarity to that of the interlayer coupling strength reflected in Raman vibrations (Figure 3-14f), indicating that the repulsive steric effects play a crucial role in the evolution of interlayer coupling between the bilayers for various stacking orders¹⁰⁶.

Figure 3-13. Stacking dependent PL feature (a) and band structure of bilayer MoS₂ with AA (b) and AB (c) stackings.

Figure 3-15a plots the PL spectra of a set of 3L MoS₂ samples with various stackings⁹⁴. The gray dashed lines indicate the stacking dependence of the PL peak separation between two prominent peaks P_A and P_B, which attribute to the direct A and B exciton transitions (Figure 3-15b). Interestingly, the splitting in AAA stacking samples is the smallest (~48 nm), followed by those with ABB (AAB) stacking (~56 nm), while ABA stacking has the largest splitting (62 nm). Similar trend is also found in our previous 2L systems with AA and AB stacking. Such stacking-dependent splitting patterns in few-layer samples arise from the SOC and the interlayer hopping effects in TMDs. In even-layer samples with inversion symmetry, both SOC and interlayer hopping effects contribute to the splitting between A and B peaks at K points. The different behaviors in splitting patterns have been reported in optical reflection spectra and transmission spectra for the 2H and 3R bulk phases of TMDs^{11, 107}.

Figure 3-14. (a-d) Optical images of 1L and 2L MoS₂ with different stacking angles. The insets are corresponding atomic models. (e) Raman spectra of a MoS₂ monolayer and bilayers with twist angles of 0° , 15° , 60° . (f) Raman peak separation between the A_{1g} and E_{2g}^1 in MoS₂ bilayers of different twist angles. (g) PL spectra of MoS₂ monolayer

and bilayers with twist angles of 0, 15, 60. (h) Dependence of PL peak energies on the twist angle for 44 MoS₂ bilayers¹⁰⁶. Reproduced with permission from ref. [103]. Copyright 2014, Nature Publishing Group.

Figure 3-15. (a) PL spectra of ABA-, ABB-, AAB-, AAA-stacked 3L MoS₂. (b) Stacking dependence of the PL peak separation between PA and PB of trilayer MoS₂ with error bars of experimental standard deviation for several samples.

By first-principle calculation, Figure 3-16 shows the spin-polarized band structures of ABA- and AAA-stacking 3L MoS₂ considering SOC effects. The band curves in red (blue) represent the spin-up (spin-down) states. SOC effects dominate the energy splitting in the top valence bands for ABA-stacking, while both SOC and interlayer hopping effects contribute to the splitting patterns for AAA-stacking 3L MoS₂, which corresponds to the observed stacking-dependent PL peaks separation in Figure 3-15a. Another interesting feature is the different spin-valley polarizations in different stackings: the valence band edges at K point in ABA stacking are dominantly from spin-up states with some mixing of spin-down states, while in AAA stacking, the VBM bands are completely spin-polarized. Our *ab initio* calculations indicate the enhanced spin-valley polarization in the AAA stacking contrast to the ABA stacking, which is similar to the observed spin-polarized states in the 3R phase TMDs by circularly polarized photoluminescence (CP-PL) measurements¹¹.

Our first-principles calculations also reproduce such scene for bilayer samples: the charge states are localized within each layer for AA-Stacking bilayer, while for AB-stacking the charges are distributed dispersedly among layers (see Figure 3-17). This suggests that the inter-layer hopping in AAA stacking is greatly suppressed and the

Figure 3-16. Calculated electronic band structures of ABA-(left), AAA-stacked (right) 3L MoS₂. The band curves in red and blue correspond to the spin-up and spin-down states.

circular polarization is not affected. Note that the above calculations do not include SOC effects. Due to the comparable SOC and interlayer hopping, the above simple view becomes vague and the charge density distributions become nonlocal. For tungsten dichalcogenides with giant SOC (~ 0.4 eV), the VBM bands are completely spin-polarized in AAA stacking that are the same as in monolayer and the Bloch states are localized in each layer, because the inter-layer hopping is greatly suppressed.

Figure 3-17 Stacking dependent charge density distribution of the top three valence bands of ABA-, AAA- and AAB-trilayer MoS₂.

Chapter 4 Thickness and stacking-dependent property in TMDs

4.1 Spin-valley polarization

Following the band structure discussions for various stacking configurations in few-layer TMDs, we then investigate how layer and stacking affect the spin and valley features. As reported, one of the most appealing applications of TMDs is the so called 'valleytronics'. The concept of valleys originates from that of spin and suggests the promising devices, analogous to spintronics, for next-generation electronics and optoelectronics. The key step towards valleytronics is to achieve the valley polarization through creating non-equilibrium charge carrier imbalance between K and K' valleys¹⁰⁸⁻¹¹¹. The principal mechanism usually involved is circularly polarized optical excitation^{3, 4}, in which the two valleys absorb left- (σ^-) and right- (σ^+) hand photons respectively, leading to a valley-selective circular dichroism (CD) within a honeycomb lattice due to the absence of inversion symmetry.

Therefore, in 1L TMDs without crystal inversion symmetry, the valley pseudospins can be distinguished by opposite signs at the corners (K and K') in the hexagonal Brillouin zone. The giant SOC separates the valence bands at each valley into the spin-up and spin-down states. Such inherent spin-valley coupling can significantly protect the valley polarization as the intervalley scattering requires a simultaneous spin flip. Only carriers with selective spin can be emitted under the valley optical selection rule, which have been widely demonstrated in the literature^{15, 109}. The colored band structure of 1L MoS₂ with top valence band and bottom conduction band marked in blue and pink is shown in Figure 4-1a and 4-1b depicts the schematic of valley-dependent selection rules for monolayer TMDs at K and K' points in crystal momentum space: σ^- (σ^+) circularly polarized light in blue (red) only couples to the band-edge transition at K (K') points. Therefore, the direct-bandgap transition at the two degenerate valleys, together with this valley-contrasting selection rule, suggest that one can optically generate and detect valley polarizations in a TMDs monolayer¹³.

Figure 4-1. (a) Three-dimensional band structure of 1L MoS₂ with top valence band and bottom conduction band marked in blue and pink. The centre hexagon is the Brillouin zone colour-coded by the degree of circular polarization, $\eta(\mathbf{k})$ ¹¹². Reproduced with permission from ref. [109]. Copyright 2012, Nature Publishing Group. (b) Schematic of valley-dependent selection rules at K and K' points in crystal momentum space: left (right)-handed circularly polarized light in blue (red) only couples to the band-edge transition at K (K') points

Beyond monolayer, few-layer TMDs introduce another intrinsic degree of freedom named as layer pseudospin. The interlayer hopping of electrons/holes further affects the spin–valley coupling in TMDs¹⁸⁻²⁰. The layer pseudospin refers to the carriers' location, either upper or lower layer in bilayer TMDs for instance. The natural AB-stacked bilayer TMDs, in which the lower layer is rotated by 180° with respect to the upper layer, possess the crystal inversion symmetry. Consequently, the layer rotation switches two valleys but leave the spin unchanged, which results in a sign change for the spin–valley coupling from layer to layer. In theory, the valley-dependent effect should vanish in the presence of inversion symmetry¹⁰⁹⁻¹¹¹. Figure 4-2a presents CP-PL spectra of thickness-dependent 3R- and 2H-MoS₂ collected at 4 K with σ^- excitation of 633 nm (1.96 eV), where σ^+ and σ^- denote right and left circularly polarized light, respectively. All the spectra are composed of sharp Raman and broad PL peaks, with the latter showing a peculiar thickness-dependent circular polarization. For 2H stacking, the intensity difference between the σ^+ and σ^- PL peak becomes smaller with increasing layer number, whereas that for 3R stacking does not show a clear layer number dependence. Therefore, the degree of circular dichroic polarization ρ , defined as $[I(\sigma^-) - I(\sigma^+)] / [I(\sigma^-) + I(\sigma^+)]$ under σ^- excitation, shows obviously different evolution

trends versus layer number for 2H and 3R stacking TMD crystals. In summary, the valley polarization ρ in 3R MoS₂ is almost independent on thickness, suggesting the strongly preserved excitons at the K (K') point, while ρ decreases significantly in 2H MoS₂.

Figure 4-2. (a) Circularly polarized PL spectra at 4 K for 1L, 2L, 3L and 4L 2H- (left) and 3R- (right) MoS₂, pumped by a left circularly polarized (σ_-) 633 nm laser. (b, c) Spin-resolved energy distribution curves (EDCs) for spin along the z axis, recorded at the inequivalent valleys of the K and K' points for 2H (b) and 3R (c) MoS₂¹¹. Reproduced with permission from ref. [11]. Copyright 2014, Nature Publishing Group.

In theory, inversion-symmetric even-layer 2H-MoS₂ should possess negligibly small ρ and yet the thickness-dependent ρ in the 2H stacking is rather unexpected. In fact, such a noticeable ρ in inversion-symmetric 2L TMDs has been widely reported in previous literature^{12, 22}. One plausible reason is the carrier localized effects, where the electrons/holes are localized in each layer rather than interlayer hopping²³. In detail, the

generated carriers under the circularly polarized laser (σ^- or σ^+) in the K (K') valley tend to localize within the upper (lower) layer, and the value of ρ decreases due to the intralayer-intervalley hopping and interlayer-intravalley hopping. However, the interlayer-intervalley hopping should be improbable owing to the giant momentum change and layer crossing barrier. As for 3R MoS₂, both interlayer and intralayer hopping are negligible and carriers are locked in each layer, leading to a larger ρ compared to that of 2H stacking. These results are also confirmed by spin- and angle-resolved photoemission spectroscopy (SARPES) in Figure 4-2b and 4-2c. The valence bands near the Fermi level at the K point for 2H-MoS₂ and 2H-WSe₂ are almost unpolarized. For 3R stacking cases, the SARPES (s_z) spectra at the K and K' points in Brillouin zone (Figure 4-2c) show the inversion of spin polarization. Therefore, this technique offers direct and powerful evidence of the valley/spin coupled state realized in bulk 3R-MoS₂. Figure 4-3a and 4-3b show the calculated spin polarizations P_z/P of the valence bands along (0, k_y , 0) for 2H-(Figure 4-3a)/3R-(Figure 4-3b) MoS₂, respectively. The white bands in Figure 4-3a are the summation of spin-up and spin-down states for 2H-stacked MoS₂, while the red and blue bands stand for the individual spin polarization contributions by SOC and interlayer hopping effect (Figure 4-3b). Therefore, both SARPES and calculated results provide a firm and clear image of the different spin-valley polarization behaviors for 2H and 3R stacking TMDs versus layer number¹¹.

Figure 4-3. Calculated spin polarizations P_z/P of the valence bands along (0, k_y , 0) for 2H-(a)/3R-(b) MoS₂¹¹. Reproduced with permission from ref. [11]. Copyright 2014, Nature Publishing Group.

The interplay among spin, valley pseudospins, and layer pseudospins opens an unprecedented platform toward manipulation of quantum states. We have measured the CP-PL spectra (valley and spin polarizations) in 1L, 2L (AA) and 3L (AAA) MoS₂ shown in Figure 4-5, where we can find the dropping of spin/valley polarization with layer number increasing. These results are consistent with what we demonstrated in Figure 4-2. Moreover, both spins and valleys have magnetic moments and can be manipulated by magnetic and optical means^{113, 114}. Layer pseudospin is associated with electric polarization and can be tuned by an electric field¹¹⁵. Numerous manipulations of degrees of freedom have been reported to exploit this quantum control in monolayer and bilayer TMDs.

In addition to valley and layer pseudospins demonstrated above, we proposed a new degree of freedom in our previous work - stacking in 2L and 3L TMD systems, where diverse stacking configurations can be facilely grown by CVD method. For circularly polarized photoluminescence (CP-PL), an extremely low laser power of ~60 μ W was used before a long-working-distance objective (Olympus, 50 $\times$ /NA0.45) to avoid the possible sample heating and the sample was kept at 77 K. The excitation laser with a linear polarization, either horizontal or vertical, transformed to a corresponding circularly polarized wave either left-hand (σ^-) or right-hand (σ^+), through an achromatic quarter-wave plate (Thorlabs, AQWP05M-600), while the emitted photoluminescence (σ^- or σ^+) passed through the same quarter-wave plate followed by a linear polarizer and finally the circular polarized photoluminescence is converted to linearly polarized wave which was finally collected by a silicon CCD. The schematic depiction of our CP-PL set-up is shown in Figure 4-4.

Based on previous discussions, certain stacking orders can break the inversion symmetry and reduce the interlayer coupling, which are prerequisites for valley- and/or spin-selective circular dichroism. Among all stacking configurations, intralayer-intervalley hopping between the K and K' valley is the most dominant valley relaxation path, followed by the interlayer-intravalley hopping. The latter path can preserve the momentum of the excitons and is dominated by interlayer coupling, which is in great contrast among various stackings, especially between the 2H and 3R stackings. In 2H stacking, this interlayer-intravalley hopping results in a reduction in

ρ , while this ρ is not affected in the 3R stacking, as the interlayer hopping is greatly suppressed in both bilayer and bulk 3R TMDs, as shown in our CP-PL spectra for AA-stacking bilayer and AB-stacking bilayer MoS₂ (Figure 4-6). These results affirm that the valley polarization is robustly preserved from the interlayer hopping in the 3R-stacked TMDs, where both the interlayer and intralayer hopping can be neglected for 3R-stacking TMDs in the discussions of ρ reduction.

Figure 4-4. Schematic depiction of the circularly-polarized PL (CP-PL) set-up in our experiments. The red (blue) curved arrow indicates the left-hand/right-hand circularly polarized laser light respectively, while the red (blue) lined arrow indicate the linearly polarized (parallel/perpendicular) laser light respectively. The schematic depiction is a simplified model of the Witec fiber system, where the collection fiber is a polarization-maintaining multimode fiber.

Our group firstly grew a series of 3L MoS₂ samples with various stackings and uncovered that this trilayer MoS₂ system also shows a strong stacking-dependent spin and valley polarizations. Figure 4-7 shows the CP-PL spectra for 3R-, AAA-, ABA (2H)- and, AAB-stacking 3L MoS₂ samples, which contain all the possible stacking configurations grown by CVD method²⁹. Note that ABB and AAB stacking are equivalent by spatial inversion. Hence, for 3R, AAA and ABA stacking MoS₂ under σ^- excitation at 77 K., there is only one peak situated at 1.91 eV under both σ^- and σ^+

detection, and yet with different polarization degrees: the largest for 3R (60%), followed by AAA stacking (50%) and the smallest for ABA stacking (30%). This observation demonstrates that valley optical selection rules in 3R-MoS₂ trilayer samples are consistent with previous reports¹¹. Comparable with monolayer, for AAA-stacked 3L MoS₂, the lack of inversion symmetry still holds, in which the spin and valley degrees of freedom are locked in AAA trilayer just like three individual monolayers, yielding strong CD. Interestingly, there are two peaks under σ^- detection and one peak under σ^+ detection for the ABB/AAB stacking. The energy of the corresponding two excitons are 1.91 eV (high energy, HE) and 1.86 eV (low energy, LE) respectively. Moreover, the HE peak displays a strong PL polarization ($\sim 90\%$) under σ^- and σ^+ detection, while the LE peak almost shows no spin-valley selectivity. We attribute the peaks located at ~ 1.76 eV to radiative recombination of bound excitons⁸⁵, i.e. neutral excitons bound to defects, consistent with the previous reported defects activated peaks at ~ 1.78 eV in monolayer MoS₂.

Figure 4-5. CP-PL spectra (valley and spin polarizations) in 1L, AA-stacking 2L and AAA-stacking 3L MoS₂.

Figure 4-6. CP-PL spectra of AA-stacking bilayer (a) and AB-stacking bilayer (b) MoS₂. Insets: corresponding optical images of 2L MoS₂ samples. All the spectra were collected using 633 nm laser in vacuum (10^{-3}) at low temperature (77 K).

To address this different dichroism behaviors, we have calculated the band structures of 3R (top) and AAB/ABB-stacking (bottom) 3L MoS₂ considering SOC effects, as shown in Figure 4-9. The spin-polarized band structures around the valley are also enlarged in Figure 4-10a. Due to different interlayer coupling and charge locking effect, the top valence band of 3R phase almost exclusively comes from the spin-up electrons in the upper layer, while for the AAB/ABB stacking, its top two valence bands are the mixing contributions of the upper and middle layer. The different PL polarization behaviors arise from the intrinsic stacking-modulated Bloch electrons at K(-K) valleys, as depicted in Figure 4-9. Here we focus on the spin textures at the band edge, which are marked with yellow rectangular blocks. The splitting between the conduction bands (Δc_1 , Δc_2) and valence bands (Δv_1 , Δv_2) are induced by interlayer coupling effects.

Figure 4-7. CP-PL spectra from five types of trilayer MoS₂ samples with 3R, AAA, ABA, AAB/ABB stacking respectively.

Figure 4-9a shows the energy level diagram of 3R-stacked 3L MoS₂. The three layers are coupled with each other by reduced interlayer coupling in 3R phase, resulting in non-trivial energy splitting to form 'triple monolayer'. The A-exciton transitions can only be excited by σ^- polarized light from -K valley and the Bloch wave functions are

localized in the upper layer. Due to the large energy splitting (~ 0.1 eV), the interlayer hopping is effectively suppressed and high circular valley polarization persists similar with the monolayer case. However, in AAB-stacking trilayer, the energy levels can be treated as the mix of coupled AB bilayers and decoupled AA bilayers, as shown in Figure 4-9b. Under σ^- excitation, the two detected σ^- signals ω_1 and ω_2 correspond to the electron-hole recombination in the upper layer at K valley and the middle layer at -K valley. At K valley, the spin can flip from the upper layer to the middle layer through the interlayer coupling by dissipation of Δv_1 (~ 20 meV). Within this process, σ^+ PL at ω_2 will emit, which contributes to the detected peak in Figure 4-9a. On the other hand, σ^+ at ω_1 needs to gain an energy cost of ~ 50 meV (Δc_1 for electron and Δv_1 for hole) to achieve the spin-flip from the middle layer to the upper layer at -K valley, which is greater than the thermal fluctuations kT . Therefore, the degree of circular polarization p at ω_1 emission is much larger than that of ω_2 ²⁹.

Figure 4-8. Schematics of calculated band structure of 3R-(a), AAA-(b), AAB-/ABB-(c) and ABA-(d) stacking trilayer MoS₂. The band curves in red and blue correspond to the spin-up and spin-down electronic states, respectively.

Figure 4-9. Schematic illustrations of spin and valley selection rules in 3R- (a) and AAB-stacked (b) 3L MoS₂ under σ^- excitation, respectively. The spin-up/spin-down bands are marked in red/blue. In (b), The orange (grey) balls/circles denote resonantly excited (after relaxed) electron-hole pairs under 633 nm laser.

Our first-principles calculations also reproduce such scene for bilayer samples: the charge states are localized within each layer for AA-Stacking bilayer, while for AB-stacking the charges are distributed dispersedly among layers (see Figure 4-10b).

Figure 4-10. (a) Schematics of calculated band structure of 3R and AAB-stacking trilayer MoS₂. (b, c) The charge density distribution diagrams of the top one/two valence bands and the conduction bands situated at 1.96 eV above the top valence band in 3R-/AAB-stacking trilayer MoS₂.

This suggests that the interlayer hopping in AAA stacking is greatly suppressed and the circular polarization is not affected. Note that the above calculations do not include SOC effects. Due to the comparable SOC and interlayer hopping, the above simple view becomes vague and the charge density distributions become nonlocal. For tungsten dichalcogenides with giant SOC (~ 0.4 eV), the VBM bands are completely spin-polarized in AAA stacking that are the same as in monolayer and the Bloch states are localized in each layer, because the inter-layer hopping is greatly suppressed.

4.2 Second harmonic generation

Bulk MoS₂ crystal with the space point group D_{6h} is inversion-symmetric which is broken when the thickness is reduced to monolayer. One consequence is to endow valley-selective optical transitions and can be used for valleytronics. It also results in nonlinear optical effects, for instance, thickness-dependent optical SHG have been reported in few-layer TMDs¹¹⁶⁻¹¹⁹, due to the non-trivial second-order nonlinearity associated with the broken inversion symmetry in odd few-layers. In this section, we show that this effect is highly sensitive to thickness, crystalline orientation, and stacking orders.

Figure 4-11 shows a MoS₂ sample with regions of different thickness for the study of thickness-dependent SHG properties. Based on the D_{3h} symmetry, the second-order nonlinear susceptibility tensor for TMDs has the relationship of $\chi^{(2)}_{y'y'y'} = -\chi^{(2)}_{y'x'x'} = -\chi^{(2)}_{x'x'y'} = -\chi^{(2)}_{x'y'y'} = \chi^{(2)}$ with nonzero elements. Here, x' , y' , z' are crystalline coordinates and x' is along the armchair direction, rotated 30° from the zigzag direction. It can be noted that the mirror symmetry is broken along zigzag direction, as shown in the lattice structure diagram of 1L MoS₂ (Figure 4-11b). It has been proven that the parallel (x) and perpendicular (y) components of the SHG field are proportional to $\sin(3\phi)$ and $\cos(3\phi)$, respectively, where ϕ is the angle between incident laser polarization direction (x) and the armchair direction in crystalline coordinates (x'). Hence, the power can be expressed as $P_x \propto \sin^2(3\phi)$ and $P_y \propto$

$\cos^2(3\phi)$, while the total power ($P=P_x+P_y$) is independent of ϕ ³².

Figure 4-11. Thickness-dependent second harmonic generation (SHG) in few-layer MoS₂. (a) Microscope image of a mechanically exfoliated MoS₂ flake from 1L to 4L. (b) Lattice structure of 1L MoS₂. Mo and S atoms are depicted as blue and yellow balls. (c) The normalized PL spectra of the signals from SHG in 1L MoS₂ (blue), the fundamental laser (red), and the pure substrate (gray, multiplied by a factor of 100). (d) The power of parallel (blue squares) and perpendicular (black circles) components of the SHG as a function of θ , the angle between the laboratory and the crystalline coordinates. The blue (black) solid line illustrates the theoretical $\sin^2 3\theta$ ($\cos^2 3\theta$) relationship. (e) The second harmonic power measured from different regions with layer number varying from 1L to 4L³². Reproduced with permission from ref. [32]. Copyright 2013, American Physical Society. (f) White-light image and SHG mapping of a CVD grown 1L MoS₂¹²⁰, respectively. The scale bars are 10 μm . Reproduced with permission from ref. [117]. Copyright 2015, John Wiley and Sons.

In the SHG experiments, the fundamental excitation pulse from a Ti-Sapphire laser centered at 810 nm is tightly focused to a spot of 2 μm in diameter, in the normal incident (along $-z'$) geometry and linearly polarized along the horizontal direction (defined as x in the laboratory coordinates), as shown in Figure 4-11a. As the photon energy of 810 nm laser is less than the bandgap of the sample, resonant band-to-band

absorption of the fundamental excitation light is not considered. Figure 4-11c shows the normalized SHG spectrum from the 1L MoS₂ (blue) region and the substrate (gray), together with that of the fundamental laser beam (red), and. The SHG intensity contrast of the 1L MoS₂ with respect to the substrate is more than 10⁴, which is much higher than that for linear PL signal (only about 0.3), where SHG signal shows expected quadratic dependence on the excitation power. The parallel (P_x) and perpendicular (P_y) components of the SHG were measured as a function of ϕ as shown in Figure 4-11d. The blue [black] solid line depicts the theoretical sin²(3 ϕ) [cos²(3 ϕ)] relationship from the D_{3h} symmetry. Through this ϕ -dependent SHG of the P_x and P_y, the magnitude of $\chi^{(2)}$ in 1L MoS₂ can be estimated to be around 10⁻⁷ m/V by solving the coupled-wave equations³⁰.

As a result, the 1L MoS₂ possesses a large $\chi^{(2)}$, which vanishes in bilayer 2H-MoS₂. Therefore, the investigation of how $\chi^{(2)}$ varies with the number of atomic layers shows great significance. The total power of the SHG from different layer regions of the MoS₂ flake are summarized in Figure 4-11e, with a fixed excitation power of 4 mW. Since the total power is independent of ϕ , the measurement will not be affected by the different crystal orientations within these regions. It has been found that $\chi^{(2)}$ of the 3L sample is about a factor of seven smaller than that in the 1L sample, while those in the 2L and 4L MoS₂ are about three orders of magnitude smaller. As TMD flakes with an even number of layers possess inversion symmetry, their second-order response should vanish theoretically. The smaller but nonzero $\chi^{(2)}$ observed in experiments can be possibly attributed to surface and interface effects. A similar layer-number dependence has also been observed recently in WS₂ and WSe₂³³. The bulk MoS₂ crystal (2H) shows its SHG power is about five orders of magnitude smaller than its monolayer counterpart, which stems from the inversion symmetry³².

Figure 4-12. Stacking-dependent SHG in artificially stacked 2L MoS₂. (a) The optical image of a 2L MoS₂ with a stacking angle of $\theta = 25^\circ$. (b) The schematic illustration of incident laser polarization in terms of the measured SHG polarization. The azimuthal angle φ is defined as the angle between the laser polarization and the armchair direction of the monolayer flake in (a). (c) A schematic for illustrating the vector superposition of the SH electric fields (a). (d-f) Polar plots of the polarization-resolved SH intensity as a function of φ measured from the 1L region (1) (d), 1L region (2) (e), and 2L stacking region (f)¹⁰. Reproduced with permission from ref. [10]. Copyright 2014, American Chemical Society.

SHG microscopy has been utilised to visualize the edge termination (Mo vs S) of grain boundaries and the crystalline orientations (Mo–S vs S–Mo) in as grown 1L MoS₂, owing to its high sensitivity to structural symmetry^{9, 32, 34}. This non-invasive optical technique with high output is generally applicable to a wide range of 2D materials besides TMDs¹²¹, including BN^{122, 123}, GaSe¹²³ and other hybrid structures^{44, 124}. Through mapping out a large amount of 1L MoS₂ samples with diverse orientation distributions, an understanding of grain growth and boundary formation through statistical analyses has been established. It has been found that the grain boundary formation in TMDs is driven by kinetics, without showing any preference for energetically favored structures. Figure 4-11f (left image) shows the optical

microscopic image of the 1L MoS₂ samples grown on sapphire substrate by low-pressure CVD. It is covered by MoS₂ triangles of the same optical contrast and all edges are straight. While the sample shows uniform contrast in the white-light image, the polarized SHG mapping of the same area indicates that it is formed by many MoS₂ triangular grains with different orientations (Figure 4-11f-right), where sharp boundaries exist between adjacent triangular grains. The contrast of various grains is originated from the anisotropic SHG response of 1L MoS₂ as described before. Briefly, when incident and collected lights are linearly polarized along the same direction, the SHG intensity is the largest when the direction of laser polarization is perfectly aligned to the armchair directions in 1L MoS₂. Therefore, by measuring the SHG anisotropic polarization patterns, the lattice orientations of all domains relative to the laser polarization can be readily determined, and hence the triangle edges with reduced SHG intensity can be predominantly identified as zigzag terminated by either Mo or S atoms¹²⁰.

Figure 4-13. Microscopic images (A) and SHG mappings (B) for a series of bilayer MoS₂ samples¹⁰ with stacking angles at $\theta = 2^\circ, 16^\circ, 30^\circ, 37^\circ$, and 54° . Reproduced with permission from ref. [10]. Copyright 2014, American Chemical Society.

Few-layer TMD samples also show strong stacking dependence in SHG response. The presence or absence of an inversion symmetry in bilayer TMDs with different stacking endows various second-order optical nonlinearity and this stacking angle dependence of the SHG can be utilized. *Hsu et al.*³⁷ have investigated the SHG from artificially stacked bilayer MoS₂ with different twist angles, in which the signal is a coherent superposition of the SH fields within each layer with a phase difference due to

the stacking angle. They investigated a bilayer MoS₂ with a rotation angle of $\theta=25^\circ$ between the 2 layers in Figure 4-12a. A back-reflection geometry is adopted and the pump laser was incident normally on the sample with its electric field along the x direction, parallel with the armchair direction of the 1L Flake 1 (Figure 4-12b). In this configuration, this SHG intensity is maximum for 1L Flake 1. Based on the polar plots of the polarization-resolved SHG intensity as a function of the ϕ as shown in Figure 4-12d and 4-12e, the individual 1L flake shows a six-petal feature, in which the petals lie along the perpendicular bisectors of each flake.

The SHG signal for the 2L stacking region (Figure 4-12f) also shows a six-petal pattern with its maximum signal lying in the middle of that of Flakes 1 and Flake 2. The SHG signal for the 2L region can be explained as the coherently interfered response between the two 1L flakes. The net SH electric field $E_s(2\omega)$ in the 2L region can be expressed using a vector superposition: $E_s(2\omega) = E_1(2\omega) + E_2(2\omega)$. The total SHG intensity in the stacking region is proportional to $|E_s(2\omega)|^2$, which can be described as $I_s(\theta) = I_1 + I_2 + 2\sqrt{I_1 I_2} \cos 3\theta$, where I_s , I_1 , and I_2 stand for the SHG intensity in the 2L stacking region, the 1L Flake 1 and Flake 2 respectively; and θ ($= 25^\circ$ in this case) is the stacking angle between layers (Figure 4-12c). Figure 4-13 shows a series of 2L MoS₂ with various stacking angles (2° , 16° , 30° , 37° , 54°) and the corresponding SHG intensity mappings. It has been proven that the SHG intensity in the bilayer region strongly dependent on the stacking angle. Based on the equation above, the SHG intensity varies as $\cos 3\theta$, which gives $I_s(\theta=0^\circ) = 4I_0$ (fully constructive) to $I_s(\theta=60^\circ) = 0$ (fully destructive) as the SH intensity from each flake is the same. Therefore, SHG also provides an efficient characterization tool for stacking orientation in bilayer TMDs system³⁷.

Chapter 5 Physical property tuning in TMDs

5.1 Strain and fragmentation effect in TMDs

In previous chapters, we have already discussed that the Raman vibrations and electronic band structures of TMD materials are very sensitive to thickness and stacking. Besides these two intrinsic parameters, external strain/stress can also have a prominent effect on physical properties of TMDs¹²⁵. Recently, both experimental and theoretical investigations of electronic band structure tuning in TMD crystals by strain engineering have been reported to some extent^{126, 127}.

It has been widely verified that strain/stress detection could be simply realized in 2D materials, due to its high sensitivity of phonon modes to external strain/stress. Moreover, the anharmonicity of molecular potentials induced phonon modes shift can be easily probed with our Raman spectroscopy. Recently, it has been revealed that the band structure of TMD materials could be engineered by strain/stress and thus strain/stress engineering could be used to increase the carrier mobility of TMDs, to fabricate tunable photonic devices, solar cells, as well as to control the magnetic properties^{128, 129}. So far, the 2D materials like MoS₂ are reported to sustain strains larger than 11%, which allows an efficient control of structure and intrinsic properties via strain/stress engineering.

Figure 5-1. (a) Schematic of the beam bending apparatus used to strain monolayer MoS₂. (b) Evolution of the Raman spectrum with strain from 0 to 1.6%. (c) PL spectra of a representative monolayer device as it is strained from 0 to 1.8% with subtracted PL background independent of strain. Reproduced with permission from ref. [123]. Copyright 2013, American Chemical Society.

Figure 5-1 shows that the uniaxial strain could be applied to monolayer or few-layer MoS₂ by controllably bending the polycarbonate beam in a four-point bending apparatus, which is also applied for other 2D materials. After sustaining strain, MoS₂ shows different evolutions of A' and E' modes with increasing strain (Figure 5-1b). Basically, in unstrained monolayer MoS₂, the A' mode at 403 cm⁻¹ comes from out-of-plane vibrations and the doubly degenerate E' mode at 384 cm⁻¹ due to in-plane vibrations of the crystal. With increased strain, the A' peak almost shows no shift in both frequency and intensity while the E' peak splits into two subpeaks with strain above 0.8% (labelled as E'⁺ and E'⁻ in this work), with the symmetry of the crystal broken by applied uniaxial strain. The PL spectra of a monolayer MoS₂ as with uniaxial strain from 0 to 1.8% are shown in Figure 5-1c, where the A exciton peak redshifts approximately linearly with strain and the intensity of the A peak decreases to a third of its original size with an applied strain of 2%. The observed redshift of the PL peak is contributed by the strain induced reduction of band gap, while the decrease in PL intensity of peak A with strain is considered as the direct to indirect bandgap transition from calculation.

Beside the demonstrated strain/stress engineering, the fragmentation mechanics in 2D materials are also of both fundamental and technological importance, as they reveal deformation physics on atom-thick layers with impact on various potential applications. For example, the dynamics of cracks in monolayer MoS₂ has been studied by popping the membrane using focused electron beam, indicating that the vacancy defects can modulate the toughness¹³⁰. Also, with the assistance of an AFM tip or an in-plane nanomechanical testing system, both the Young's modulus and the breaking strength of monolayer and multilayer TMDs are measured, demonstrating that TMDs are promising candidates for fabrication of flexible devices^{119, 131}. However, due to the fragile nature of TMDs from the presence of defects and unavoidable imperfections, fragmentation of TMDs is uncontrollable and tends to initiate from these pre-existing random defects, resulting in irregular morphologies, which have essentially limited their studies and applications.

Here we show a route to control the fragmentation of TMDs monolayers by exploiting polymer-based mechanical instabilities. When stretching a thermoplastic polymer, it first extends elastically until the yield stress, and then the consequent

downward bending of the stress–strain curve leads to mechanical instabilities within the polymer, thus resulting in neck formation with strong localized strain. The neck forms locally and then propagate along the polymer at a constant speed until the neck extends throughout the entire length of the polymer¹³². We take advantage of this strong localized yet propagating strain to fragment TMDs monolayers sandwiched between thermoplastic polymers, and demonstrate the formation of well-ordered atomically sharp and thin TMD nanoribbons. We systematically explore the surface morphology and crystal structure of these monolayer nanoribbons, and further demonstrate the universality of this method in several typical TMDs monolayers such as WS₂, MoS₂, MoSe₂, and WSe₂. Moreover, to evaluate the potential applications of the nanoribbon arrays by this physical fragmentation method, both FET measurement and electrocatalytic performance for the hydrogen evolution reaction (HER) are carried out. These results may enrich the fundamental study of TMD extreme and fragmentation mechanics and lead to the development of TMD material-based flexible devices for electrical, optoelectronic, sensing and catalytical applications.

Figure 5-2a illustrates the experimental steps for the formation of a parallel array of TMD nanoribbons. The starting monolayer WS₂ is transferred onto a polycarbonate (PC) substrate by conventional poly (methyl methacrylate) (PMMA)-mediated transfer process, followed by a consolidation process. After consolidation, the PMMA/WS₂ monolayers/PC is mounted in the clamps of a linear travel stage for the following necking process, and the tensile load is measured with a load cell. After an initial linear extension, the mechanical instabilities of the PC film results in the formation of neck, accompanied by relative large amount of strain localized in the necking region. When the neck encounters the sandwiched WS₂ monolayer, the localized strain reduces both the width and the thickness of PC, which subsequently pinches and fragments the localized WS₂ monolayer into a nanoscale ribbon. As the neck propagates further, the localized strain continues to fragment the monolayers into an ordered array of nanoribbons (Figure 5-2b). The observed fragmentation of TMD monolayers in this work is fundamentally different from previously reported fragmentations as follows: (1) Fragmentation is independent of the defects and crystal structure of the TMD monolayers. (2) Fragmentation is independent of the original size of the TMD monolayers (from a few microns to more than 100 μm). This is because that a controlled form of shear-lag fragmentation (SLF)^{130, 133, 134} is induced at the necking front, in other

words, the tensile strain is mainly focused on the propagating of necking front, thereby resulting in a localized brittle fragmentation.

Figure 5-2. (a) Schematic of the experimental steps to fragment monolayer WS₂. (b) Magnified fluorescence images of monolayer WS₂ nanoribbons with different orientations.

Raman and PL spectroscopy are used to map and monitor the strain induced structure evolution in monolayer nanoribbons. Figure 5-1b are the fluorescence images of two adjacent WS₂ monolayers before (located on SiO₂/Si surface) and after necking process. It clearly shows that monolayer WS₂ triangles break into an ordered train of nanoribbons with almost uniform sizes. The corresponding Raman and PL maps of the nanoribbons are shown in Figure 5-3a and 5-3b, respectively. The Raman and PL maps are integrated in terms of E'(Γ) + 2LA(M) peak ($\sim 350 \text{ cm}^{-1}$) and A exciton ($\sim 630 \text{ nm}$) to study the crystal structure and morphology of the monolayer WS₂. The alternate blue and white-color Raman/PL intensities represent the nanoribbons and voids, respectively.

Figure 5-3. (a, b) Raman/PL mapping of the monolayer WS₂ nanoribbons. (c) Representative Raman and PL spectra of monolayer WS₂ in different process steps, namely original (blue), after transfer (red), after consolidation (green) and after necking process (pink). (d) Frequencies of E_{2g}¹ and A_{1g} modes/peak energy of monolayer WS₂ in different process steps.

Figure 5-3c illustrates the Raman and PL single spectra of the monolayer WS₂ from as-grown to after-necking state. We first investigate the change of the Raman spectra of monolayer WS₂. In detail, the original WS₂ monolayer deposited on Si/SiO₂ surface presents two Raman feature peaks at 417.6 and 352.5 cm⁻¹ (Figure 5-3c), corresponding to A₁' mode due to out-of-plane vibrations and E mode due to in-plane vibrations, respectively. Specifically, the E mode contains E'(Γ) and 2LA(M) with close proximity, where both modes represent in-plane atomic vibrations yet with W and S atoms moving in the same (E'(Γ)) or opposite direction (2LA(M)). Therefore, we simply nominate the modes E'(Γ) + 2LA(M) as E mode hereinafter and discuss their peak evolution feature together at different processes. The E mode is softened to 349.2 cm⁻¹ after transfer and

consolidation processes, which is because a local uniaxial strain is introduced into monolayers during the PMMA-mediated transfer process¹³⁵. After necking process, the E mode blue-shifts to 352.6 cm^{-1} , owing to the stress relaxation of tungsten (W)-sulfur (S) bonds⁵. Furthermore, the strain during the whole process has less effect on the A_1' mode compared with E mode, attributing to the out-of-plane vibration feature of A_1' mode. The observed slight shift of E mode and A_1' mode during the whole process indicates that the crystal structure remains high quality. The similar evolvement process can be also found in PL spectra as shown in Figure 5-3c. After transfer and consolidation, the PL peak (A exciton) shows an evident red shift (Figure 5-3d). This phenomenon is consistent with previous results. After necking process, the released local strain results in a widening of bandgap and finally causes the blue shift of PL peak.

Furthermore, MoS_2 is a promising electrocatalyst for electrochemical hydrogen production. It is well established that HER efficiency depends strongly on the number of active sites, for instance, exposed edges in MoS_2 . Thus, introduction of edges to create more active sites is an effective way to improve the catalyst activity¹³⁶. In view of this, we explore the HER activity of the fabricated monolayer MoS_2 nanoribbons by our necking method. As shown in Figure 5-4, large enhancement of HER performance is detected in the monolayer MoS_2 nanoribbons. The polarization curve recorded on monolayer MoS_2 nanoribbons exhibits a current density of 1.63 mA cm^{-2} at a voltage of 0.4 V versus RHE. Its current density is nearly 3.4 times higher than 0.37 mA cm^{-2} of original CVD-grown monolayer MoS_2 triangles. This improvement in electrocatalytic activity is ascribed to the largely increased edge areas of monolayer MoS_2 nanoribbons and the fact to use this physical fragmentation method instead of chemical etching, as schematically illustrated in Figure 5-4a and 5-4b. Moreover, as shown in Figure 5-4d, the Tafel slope of the monolayer MoS_2 nanoribbons is 109 mV dec^{-1} , similar to 104 mV dec^{-1} of the origin monolayer MoS_2 triangles, which reveals that both the active sites located in origin and the resulting edges areas are active for HER activity. The Tafel slope of 109 mV dec^{-1} indicates that HER on monolayer MoS_2 nanoribbons is through the Volmer–Heyrovsky reaction as the rate-determining step.

Figure 5-4. (a, b) Schematic representations illustrate the function of the edges of monolayer MoS₂ triangle and monolayer MoS₂ nanoribbons as the active sites for HER. (c, d) HER polarizing curves and Tafel plots for supporting Au/graphene (cyan), monolayer MoS₂ triangles (red), and monolayer MoS₂ nanoribbons (black).

Since the proposed method relies on a physical breakup mechanism, it significantly broadens the repertoire of usable materials and is highly versatile. For example, other thermoplastic polymers³²⁻³⁴ such as polyetherimide, polyethylene terephthalate, polysulfone and polyethersulfone are also applicable in this method. After necking process, the width of the nanoribbons, the size and distribution of the wrinkles, and the spacing between the nanoribbons may vary with the polymers used, since the induced necking strain, Poisson's ratio and the elongation are different. Additionally, iterative necking processes can further downsize the width of the nanoribbons, and we can modify the morphology of these nanoribbons from "long strip" pattern into "square" or "triangular" pattern by controlling the necking directions, thus realizing various TMDs' shapes, which allows their applications such as high sensitivity sensors⁵ or nonlinear optics. Last but not least, compared to chemical etching³⁵, laser cutting³⁶ or micromolding technology³⁷, this method possesses the unique advantage in the

formation of sharp, clean and ordered edges benefiting from the nature of brittle fragmentation, offering a substantial impact on future developments of TMD material-based devices for electrical, optoelectronic, sensing and catalytical applications.

5.2 Pressure-induced phase transition in semimetallic WTe₂

Pressure is a clean and convenient tool to modify the physical properties of diverse TMDs materials^{137, 138}, via strengthening the vdWs interactions along c-axis and shortening the covalent bonds within the atomic plane. For instance, the typical first-order structural transition in MoS₂ (2H_c to 2H_a)¹³⁸, metallization in MoSe₂⁶ and superconductivity in T'-MoTe₂¹³⁹ have been reported under high pressure. Among the layered TMDs family, semimetallic WTe₂ have recently attracted considerable attention, with reports of the non-saturating large magnetoresistance (LMR)^{8, 140}, pressure-induced superconductivity¹⁴¹ and as the most promising candidate of a type-II Weyl semimetal¹⁴². Weyl Fermions were observed following the discovery of topological superconductors and semimetals, where they show low-energy excitation properties and have two types of Weyl points. A point-like Fermi surface are referred to as type-I, while a protected crossing appearing at the contact of electron and hole pockets are called type-II Weyl point. The type-II Weyl points in WTe₂ endows many novel physical properties that are different to those of type-I Weyl semimetals¹⁴². So far, the pressure-driven superconductivity in WTe₂ has been attributed to a possible structural instability or Lifshitz phase transition without structural transition. Therefore, the structural evolution of WTe₂ under high pressure is still unclear and needs to be further clarified.

In this section, we investigate the effects of hydrostatic pressure on both plane-parallel and plane-vertical orientation of vibrational properties in WTe₂, as well as the corresponding electronic properties. A first-order structural transition from the dT phase to a monoclinic T' phase occurs above 8 GPa, marked by the vanishing of the Raman band at 120 cm⁻¹ where the Raman active B₂ mode in the dT phase becomes Raman inactive (B_{2u} symmetry) in the T' phase. This B₂ Raman mode can only be observed in the dT phase with incident laser beam perpendicular to the c-axis of WTe₂ crystal, and it softens considerably with pressure, while all other Raman modes stiffen. Beyond the plane-parallel Raman studies generally conducted in 2D materials, our plane-vertical

measurements can detect the inactive Raman modes, which may become the indicator of defects, stacking, or phase transition as the characteristic peaks. To the best of our knowledge, it is the first report on the anomalous red-shift phenomenon of the dT-WTe₂ and the new T' phase under high pressure. We further show that these two phases have distinct electronic properties, especially in Weyl semimetallic states. Our findings offer the possibility to switch on/off the Weyl states in sole material via high pressure.

Unlike most other semiconducting TMDs with the hexagonal (2H) phase, WTe₂ exhibits a unique distorted octahedral coordination of the W atom, referred to as dT-polytype¹⁴³. Its space group (*Pmn*₂₁) endows the corresponding Raman tensors as

$$R(A_1) = \begin{pmatrix} a & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & c \end{pmatrix} \quad R(A_2) = \begin{pmatrix} 0 & d & 0 \\ d & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad R(B_1) = \begin{pmatrix} 0 & 0 & e \\ 0 & 0 & 0 \\ e & 0 & 0 \end{pmatrix} \quad R(B_2) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & f \\ 0 & f & 0 \end{pmatrix}$$

Therefore, A₁ and A₂ modes can be detected under plane-parallel configuration with incident laser along *c*-axis, while B₁ and B₂ modes can be observed with incident laser along *a*- or *b*-axis. In polarized Raman spectroscopy, A(BC)D are used to describe the excitation/collection configurations for sample measurements. In our case, A and D stand for the incident laser and output scattering direction, with respect to WTe₂ atomic plane. B and C stand for laser polarization and collection polarization direction, respectively. For perfectly plane-parallel aligned samples, A₁ symmetry is obtained in the $Z(XX)\bar{Z}$ and $Z(YY)\bar{Z}$ configurations, while A₂ symmetry is obtained in the $Z(XY)\bar{Z}$ configurations¹⁴⁴. In the case of plane-vertical configuration, B₂ modes can only be observed in $X(ZY)\bar{X}$ configuration, while for B₁ symmetry modes, they are forbidden under both $X(ZZ)\bar{X}$ and $X(ZY)\bar{X}$ configurations. As far as we know, the latter Raman geometries with plane-vertical orientation in WTe₂ have not been reported in the literature. Firstly, we address a full mode assignment in WTe₂ crystal for both plane-parallel and plane-vertical orientations via the polarized Raman spectroscopy. For the STEM experiments and plane-parallel property study, large-area monolayer WTe₂ samples with high quality are used to completely exclude the nonuniformity impact on Raman signals. As for the plane-vertical orientation, we vertically align the samples to achieve the $X(ZZ)\bar{X}$ and $X(ZY)\bar{X}$ geometries, so that the laser propagation direction

is within the *ab*-plane of bulk WTe₂ sample, as shown in Figure 5-5c.

Figure 5-5. (a, b) Scanning transmission electron microscope (STEM) images of 1L (a) and 2L (b) WTe₂. (c, d) Optical image of 1L CVD grown WTe₂ (c) vertically aligned bulk WTe₂ (d). The white rectangle in (c) highlights the corresponding Raman intensity mapping at 210 cm⁻¹, indicating its homogenous quality. The insert shows the atomic structures from the top view and the green arrows represent the reference sample orientation.

Figure 5-5a and 5-5b shows the Z-contrast STEM images of 1L and 2L WTe₂ in the dT phase which vividly reveal that the dT phase 1L WTe₂ consists of zigzag W chains along *a*-axis as skeleton with Te chains connected therein, in excellent agreement with the atomic model of 1L WTe₂. The STEM image of 2L WTe₂ indicates this stacking order is similar to that of 2H (AB) stacking for MoS₂ yet the atoms of top and bottom layers cannot perfectly overlap due to its distorted lattice structure. The optical images of 1L CVD grown and single crystal bulk WTe₂ samples are shown in Figure 5-5c and 5-5d, where the atomic planes (*010*) are parallel and perpendicular to the substrate, respectively. Figure 5-6a shows the Raman spectra of the monolayer and bulk WTe₂ samples with incident laser along *c*- (marked as P) and *a*-axes (marked as V) for the study of plane-parallel and plane-vertical anisotropies, respectively. All the Raman

signals with both $\vec{e}_i \parallel \vec{e}_s$ and $\vec{e}_i \perp \vec{e}_s$ configurations can be detected. For plane-parallel configuration (P), the peaks located at 89, 110, 117, 160 and 210 cm^{-1} (marked as P1, P2, P3, P4 and P5 in Figure 1d) can be assigned to A_2 , A_2 , A_1 , A_1 , and A_1 symmetry, respectively. Compared with plane-parallel case, the plane-vertical configuration exhibits a different set of Raman peaks, where the four peaks V1, V2, V3 and V4 located at 93, 123, 141, and 170 cm^{-1} are assigned as B_2 , B_2 , A_1 and A_1 symmetry respectively. The polarized Raman features of plane-parallel and plane-vertical configurations are further discussed both experimentally and theoretically in Table 5-1 by using various set-ups, which reaffirms the precise attributions of each mode. Our experimental frequencies of the observed peaks are excellent agreed with the calculated frequencies and the corresponding symmetry assignments match perfectly⁹⁴.

b	In-plane		Out-of-plane	
	$\vec{e}_i \parallel \vec{e}_z$	$\vec{e}_i \perp \vec{e}_z$	$\vec{e}_i \parallel \vec{e}_z$	$\vec{e}_i \perp \vec{e}_z$
A_1	$(a \cos^2 \phi + b \sin^2 \phi)^2$	0	$(b \cos^2 \theta + c \sin^2 \theta)^2$	0
	$\phi = 0^\circ, a^2$ $\phi = 90^\circ, b^2$		$\theta = 0^\circ, b^2$ $\theta = 90^\circ, c^2$	
A_2	0	$(-d \sin^2 \phi + d \cos^2 \phi)^2$	0	0
		$\phi = 0^\circ, d^2$ $\phi = 90^\circ, d^2$		
B_1	0	0	0	0
B_2	0	0	0	$(-f \sin^2 \theta + f \cos^2 \theta)^2$
				$\theta = 0^\circ, f^2$ $\theta = 90^\circ, f^2$

Figure 5-6. (a) Raman spectra of the monolayer (blue) and bulk (red) WTe₂ samples with incident laser along c- (marked as P) and a-axes (marked as V). The solid curves

are from experiments, and the gray curves (doted and solid) are corresponding Lorentzian fitting results. (b) Selection rules of the allowed Raman modes of in-plane and out-of-plane dT-WTe₂.

Symmetry	Calculation (rel.cm ⁻¹)	Experiment				Theoretical Raman intensities			
		Z(XX)Z (rel.cm ⁻¹)	Z(XY)Z (rel.cm ⁻¹)	X(Z'Z')X (rel.cm ⁻¹)	X(Y'Z')X (rel.cm ⁻¹)	Z(XX)Z (a.u.)	Z(XY)Z (a.u.)	X(ZZ)X (a.u.)	X(YZ)X (a.u.)
A ₁	7.14534					1.063764	0	2574.99	0
A ₂	25.81399					0	0.054425	0	0
B ₂	28.42782					0.002792	0	0	277.0799
A ₁	77.71408	80.11 ✓		83.71 ✓		38.5411	0	67.33722	0
B ₁	86.63641					0	0	0	0
B ₂	87.26287				93.67 ✓	0.000376	0	0.003386	0.866758
A ₂	87.69087		89.87 ✓			0	145.0431	0.000348	0
A ₂	110.3065		110.14 ✓			0	9.340124	0.000259	0
B ₁	110.5149					0	0.001036	0	0.000259
A ₂	112.9603					0	0.003913	0	0
A ₁	113.0253	114.69 ✓		121.21 ✓		43.59613	0	49.44458	0
B ₁	115.1443					0	0	0	0
B ₂	118.745					0	0	0.000214	0.103557
B ₂	122.6446				123.26 ✓	0.000212	0	0.001905	47.54472
B ₂	128.2021					0.000189	0	0.000189	8.333819
A ₁	128.4562	131.77 ✓				86.73353	0	1.500722	0
A ₁	131.3844					0.34405	0	7.075444	0
A ₁	132.9965			142.05 ✓	141.51 ✓	5.176224	0	9.610205	0
B ₂	133.4037					0	0	0	0.00018
B ₁	150.8618					0	0	0	0
A ₂	151.6023					0	0.015381	0	0
B ₂	156.0346				160.48 ✓	0	0	0	5.945633
A ₁	159.6056	161.08 ✓		162.26 ✓		57.84301	0	6.583512	0
A ₂	159.968		158.89 ✓			0	114.1113	0	0
B ₁	160.2771					0	0	0	0
B ₂	171.1383				170.16 ✓	0.000109	0	0	4.739992
A ₁	172.8187			170.08 ✓		0.024211	0	13.10635	0
B ₂	206.202				201.93 ✓	6.84E-05	0	0.000274	22.55213
A ₁	206.5278					193.9614	0	66.24763	0
A ₁	210.1813	208.89 ✓		213.13 ✓		235.3689	0	77.89723	0
B ₂	212.122					0	0	7.09E-05	3.619898
A ₁	230.5893					0.343939	0	5.427902	0
B ₂	231.2609				224.81 ✓	6.46E-05	0	0.000259	37.4272

Table 5-1. Comparison of the calculated and experimental of Raman active phonon modes (in cm⁻¹) for bulk WTe₂ structures, with different Raman configurations. “✓” means that the chosen mode is observed in experiment.

Figure 5-7. (a) Raman spectra of sample 1 from 1L to 12L and bulk regarding the peak of silicon, which can be used as layer identification. (b) Raman mappings in terms of the peak intensity and peak centre at 212 cm^{-1} , as well as the peak intensity at 520 cm^{-1} (silicon).

Next, we utilize Raman spectroscopy to extend the high-pressure study on plane-parallel and plane-vertical anisotropies of the vibrational properties, in which the *ab*-plane of bulk dT-WTe₂ are parallel (P type) or vertical (V type) to the diamond anvil surface. Figure 5-8b shows the Raman spectra of bulk dT-WTe₂ sample with the incident laser propagation along *c*- (P) and *a*- (V) axes at ambient pressure, respectively. The difference of Raman behaviors between P-type and V-type can be evidently noticed, that is, there is a particularly strong peak envelope at around 120 cm^{-1} showing up under V-type configuration. Figure 5-8b and 5-8c show the evolution of lattice vibrational properties of bulk dT-WTe₂ with the increasing of pressure for P- type (b) and V-type (c) sample orientation, respectively. In the case of P-type, all the observed Raman peaks gradually blue shift with no discontinuities as the increasing of hydrostatic pressure from 0 GPa to final 17.0 GPa, indicating no structural phase transition within the whole studied pressure range. The stiffening and broadening phenomenon of Raman modes under pressure has been well known, similar to other layered materials.

However, in the case of V-type, upon increasing pressure, the new Raman modes ($\sim 120\text{ cm}^{-1}$) of bulk dT-WTe₂ red shift while all other modes blue shift. More interestingly, the peaks at around 120 cm^{-1} nearly disappear with the pressure above 10.9 GPa. Both red-shift and vanishing of Raman peaks cannot be observed under the P-type configuration, which confidently declares that there is a phase transition point at ~ 10 GPa. Figure 5-9a and 5-9b are the statistic diagrams of peak center evolution of WTe₂ as a function of pressure for V-type (a) and P-type (b) configurations. Our experimental

observation on pressure-dependent Raman frequencies show good qualitative agreement with the calculated Raman frequencies as a function of pressure. The pressure-dependent lattice vibrational properties of the V-type WTe_2 are sketched in Figure 5-9a, where the peaks, V2 and V3, show an anomalous red shift as the pressure increases while other peaks show a blue shift. We can also find the consistent blue shift of all the Raman peaks in Figure 5-9b, and yet the change slope for peak P1 is smaller than that of other peaks. This insensitive property of Raman peak P1 to pressure vibration indicates this kind of peak represents the Raman vibration within atomic plane, where the pressure has a weaker impact on this plane-parallel vibration compared with plane-vertical vibration. This phase transition under high pressure (8 GPa) should strongly account for the dramatic change in magnetic and electronic properties of WTe_2 beyond a certain pressure as previously reported.

Figure 5-8. (a) Illustration of the diamond anvil cell loaded with parallelly- (P) and vertically- (V) aligned WTe_2 crystals. (b, c) The evolution of Raman vibrations with pressure for different sample orientations.

To further identify the possible phase transition under high pressure, we have performed the molecular dynamics (MD) simulation to examine the evolution of the

atomic structure of WTe_2 under 20 GPa (Figure 5-10) at 0 ps and 15 ps, respectively, which certified that the dT phase of WTe_2 cannot stably exist under 20 GPa and a phase transformation from dT to T' phase actually happens. Besides, we have also calculated the enthalpy difference as a function of pressure between the dT and T' structures of WTe_2 , as shown in Figure 5-9c. Before 8 GPa, the value of $H_{T'} - H_{Td}$ is small and positive, and then it rapidly changes to negative after the pressure increasing above 8 GPa, which further elucidates that the phase transition of WTe_2 is from dT phase to T' phase with the turning point pressure at around 8 GPa. Figure 5-9d shows the phonon dispersion curves for T'- WTe_2 at 12 GPa, where all the phonon frequencies are positive, indicating the T' phase can stably exist under high pressure. The instability of dT phase at 12 GPa is also discussed in Figure 5-9d and Figure 5-11, with imaginary frequencies based on our calculations. Therefore, the MD simulation, enthalpy with increasing pressure and phonon calculation for WTe_2 at 12 GPa are also consistent with that the application of pressure tends to stabilize the T' phase for MoTe_2 ¹³⁹.

Figure 5-9. (a, b) Evolution of Raman peaks with pressure for perpendicular (a) and parallel (b) to the laser polarizations. The transparent lines indicate the linear fit of Raman peak center as a function of pressure. (c) Calculated pressure dependence of the enthalpy difference between the dT and T' unit cells. (d) Calculated phonon dispersion

curve of T'-WTe₂ at 12 GPa.

Figure 5-10. (a, b) Side-view snapshots of WTe₂ at 0 and 15 ps under 20 GPa based on the molecular dynamics simulation indicating the transformation from dT to T' phase. (c) Vibrational schematics of two Raman active modes (V2 and V3) in bulk WTe₂ corresponding to the two red-shifted peaks in pressure-dependent Raman spectra. Both V2 and V3 modes become inactive after dT to T' phase transition.

Furthermore, in order to explain the anomalous Raman behavior with V-type configuration, we have performed the first-principles calculations of the phonon modes at the Brillouin zone (BZ) center within the framework of the density functional perturbation theory (DFPT)¹⁴⁵. Figure 5-10b depicts the vibrational schematics of two Raman active B₂ modes in V-type bulk dT-WTe₂ and T'-WTe₂ corresponding to the two red-shifted peaks in pressure-dependent Raman spectra (Figure 5-8c and Figure 5-9a). Compared with dT phase, T' WTe₂ undergoes an opposite sliding within adjacent layers, leading to the unit cell change from orthorhombic to monoclinic symmetry. This phonon softening of the peaks at 120 cm⁻¹ can be explained by the intermediate states engagement before the phase transition point. These states originate from the electron-phonon interactions, where inter-valence charge transfer between the WTe₂ layers plays an important role in the structural distortion of the crystal symmetry. Several materials have been previously reported to exhibit an intermediate state with soften phonon behavior while undergoing a transition from a semiconductor to a metallic state or when stress or strain is applied. To the best of our knowledge, it is the first report on the anomalous red shift of the dT -WTe₂ Raman modes. Our calculations indicate that the

two modes become inactive from dT to T' phase, in consist with our experimental findings that the peaks at around 120 cm^{-1} finally vanish at 10 GPa.

Figure 5-11. Phonon dispersion curves of dT- and T'-WTe₂ at 0 GPa and 12 GPa respectively. The dashed area highlights the imaginary frequencies of dT phase at 12 GPa, indicating its instability under high pressure.

We have also calculated their band structures with SOC for dT and 1T' phase of WTe₂ obtained from different pressures, as shown in Figure 5-12. At 0 GPa, four pairs of Weyl Fermions exist in dT phase, while these Weyl states vanish in the monoclinic T' phase at 10 GPa, due to the presence of inversion symmetry. Such difference in band structure may pave a potential way for Weyl state tuning in diverse 2D materials by phase engineering. The type II Weyl semimetal property in dT-WTe₂ was firstly reported by Alexey A. Soluyanov etc.¹⁴² and then A. Tamai etc. also demonstrated that the MoTe₂ with 1T' phase also held the similar property as dT-WTe₂¹⁴⁶. Moreover, one arc-tunable Weyl Fermion metallic state has been found in alloy materials, Mo_xW_{1-x}Te₂, in which they demonstrated that the Fermi arc length and topological strength can be modified by Mo concentration¹⁴⁷. In our work, we propose a possibility of switching on/off the Weyl

states in one material without doping.

Figure 5-12. (a) Calculated band structures of dT (Left) and T' (Right) WTe₂ with SOC at 0 and 10 GPa. (b) Artificially modification of the band structure of dT (Left) and T' (Right) WTe₂ along momentum space cut along the line K-K', where the Weyl points W1(-), (0.12314, 0.03455, 0) and W2(+)) (0.12185, 0.05280, 0) are given for dT.

In summary, we have investigated the high-pressure properties of WTe₂ single crystals by Raman micro-spectroscopy and *ab initio* calculations. WTe₂ shows strong plane-parallel/plane-vertical vibrational anisotropy, stemming from its intrinsic Raman tensor. Under pressure, the Raman peaks at $\sim 120 \text{ cm}^{-1}$ gradually soften upon increasing pressure and are totally suppressed above 10 GPa, indicating the phase transition from dT to T' phase. Reminiscent of the reported superconductivity emerging in WTe₂ at 10 GPa, one can expect that the phase transition from dT to T' phase at 10 GPa separates the LMR state and superconducting state. Our findings may provide a potential way to switch on/off the Weyl states in one material through high pressure.

5.3 Lithium intercalation induced phase transition in MoS₂

As TMD materials have relatively large interlayer distance ($\sim 6.5 \text{ \AA}$) and weak vdWs interactions among layers, alkali ions can be easily inserted into the abundant space therein¹⁴⁸. Lithium/sodium intercalation affords a convenient way to engineer properties for electronics and energy storage applications¹⁴⁹ and the large-scale production of single-layer TMD nanosheets¹⁵⁰. Selective Li intercalation has been used to obtain phase-engineered patterns to reduce the contact resistance in TMD transistors. Literature also reported that MoS₂-based device performance with 1T electrodes is highly reproducible and independent of the type of contact metal pads used¹⁵¹.

Up to now, two cardinal approaches have been employed to intercalate Li^+ into MoS_2 host lattices: immersing in organic lithium solutions (*n*-butyl lithium) and electrochemical intercalation¹⁵². The distinction is the Li^+ concentration in MoS_2 (i.e., Li_xMoS_2) and different bonding ways. In detail, through the former approach, electrons insert into the host phase, creating $[\text{MoS}_2]^-$ and leading to the formation of the octahedral 1T phase⁴, while the electrochemical intercalation proceeds into the 2H- MoS_2 lattice with a larger Li^+ concentration and can form diverse superstructures with the stabilization of lithium ions. The electrochemical method is also more controllable in terms of the amount of Li concentration. The exfoliation of TMDs such as MoS_2 and WS_2 using the well-known organolithium chemical method has been demonstrated to some extent¹⁵³, leading to the formation of the metallic 1T phase, where the 1T phase is stabilized by electron donation from the organolithium during intercalation. However, a good understanding of the transformative structures during intercalation in TMDs is still lacking.

Based on the previous studies, we demonstrate that the Li^+ -supported 1T lattice can be spontaneously distorted to a more stable phase (dT), which shows distinct lattice symmetry and Weyl state property compared with 1T- MoS_2 . After the Li ions are partially extracted from dT- MoS_2 lattice, high-resolution transmission electron microscopy (HR-TEM) has revealed that the 1T and 2H phases can coexist in the same TMD nanosheets and that the phase boundary between the two phases is atomically sharp with no visible defects¹⁵⁴. In our experiments, five button cells with 2H- MoS_2 powder and lithium plate acting as cathode and anode respectively are executed galvanostatic discharge/recharge through electrochemical workstation, which can controllably monitor the Li^+ intercalation/extraction process in MoS_2 . For the first four batteries, the terminate discharge potentials of MoS_2 cathode with respect to Li/Li^+ are 1.6 V, 1.1 V (80 mAh/g), 1.1 V (160 mAh/g), 0.9 V, which denotes Li^+ concentration in Li_xMoS_2 with *x* at 0.05, 0.37, 0.74, 1. For the fifth cell, it is recharged back to 2.4 V after discharging process, as illustrated in Figure 5-13a, which shows the galvanostatic discharge/charge curves with different cut-off points of the five button cells: A (*x*=0.05), B (*x*=0.37), C (*x*=0.74), D (*x*=1) and E (*x*=0.55). The insertion in Figure 5-13a vividly depicts the introduction process of Li^+ into 2H- MoS_2 lattice. We use copper foil coated with 2H- MoS_2 powder and lithium metal plate acting as cathode and anode respectively with typical electrolyte (LiPF_6) to construct button cells in glovebox. In addition, the

samples are obtained during the first discharge/charge cycle to avoid any possible dtchange to the MoS₂ structure caused by cycling. The reaction process of layered MoS₂ with Li⁺ and the correspondingly atomic structure evolution from hexagonal (2H) to distorted octahedral symmetry (dT) with gradual Li⁺ intercalation is vividly shown in Figure 5-13b. After electrochemical process, the MoS₂ cathodes are withdrawn from the button cells and then washed with acetone, ethanol and deionized water in sequence to efficiently remove electrolyte residuals. After that, these washed MoS₂ cathodes are ultrasonicated and centrifuged four times in deionized (DI) water and dropped on cleaned glass and copper grid for Raman, PL and HR-TEM testing. The more details about experimental set-up can be found in Figure 5-14.

Figure 5-13. Illustration of lithium intercalation and extraction process of 2H-MoS₂. (a) Galvanostatic discharge/charge curves for Li⁺ intercalation and extraction. A, B, C, D and E represent the cut-off points of the test button cells. (b) The atomic structure depiction of phase transition from hexagonal (2H) to distorted octahedral (dT) symmetry with gradual lithium ions intercalation.

Figure 5-14. Detailed experimental set-up for lithium electrochemical intercalation process of five different button cells, with MoS₂ acting as cathode and lithium plate as anode respectively.

Raman spectroscopy has been a potent approach to investigate the morphology variation and phase transition behaviors in 2D materials, especially the ULF Raman, which is highly sensitive to interlayer interactions and can reflect even the minute discrepancies of crystallographic structure¹⁵⁵. As for our gradually intercalated MoS₂, the structure of the unit cell is converted from trigonal prismatic coordination to octahedral coordination for single molecular layers, and meanwhile, the layer spacing and interlayer interactions vary during intercalation process. Therefore, we utilize ULF Raman spectroscopy to characterize this phase evolutionary process during intercalation and firstly uncover the different behaviors of 2H- and dT-MoS₂ within low frequency in Raman spectra. Figure 5-15a and 5-15b exhibit the high-frequency Raman spectra of pristine MoS₂ powder and lithium intercalated MoS₂ (battery A, B, C, D and E) with different Li⁺ concentration (Li_xMoS₂ at x=0, 0.05, 0.37, 0.74, 1, 0.55) respectively. For pristine 2H-MoS₂, it mainly consists of four Raman active modes E_{2g}² (32 cm⁻¹), E_{1g} (280 cm⁻¹), E_{2g}¹ (378 cm⁻¹) and A_{1g} (403 cm⁻¹) that have been extensively studied both experimentally and theoretically. The E_{2g}² mode belongs to the interlayer shear motion which can be observed within the extra low wavenumber region, while the E_{1g} mode depicts the similar in-plane-atomic vibration except for the Mo atoms staying motionless compared with E_{2g}¹ mode. Generally, the E_{1g} mode is forbidden under backscattering configuration due to the absence of valuable Raman tensor component within the atomic plane as shown below, where the E_{1g} mode can only be observed in edge plane measurements. In our experiments, we have distinctly observed the E_{1g} mode in 2H-MoS₂, which can be explained as the random lattice orientations of MoS₂ powder.

Figure 5-15. Raman features of intercalated 2H-MoS₂ cathodes with different lithium concentrations. (a-c) High-frequency (a, b) and ULF (c) Raman spectra of pristine MoS₂ powder and lithium intercalated MoS₂ with discharge potential at 1.6 V, 1.1 V (80 mAh/g), 1.1 V (160 mAh/g), 0.9 V, and recharge to 2.4 V respectively. (d, e) Calculated phonon dispersion curves for dT- (d) and distorted 2H- (e) MoS₂ respectively. The red arrows indicate the featured Raman peaks of dT and 2H-MoS₂. (f) The statistic diagrams of Raman peak centre (left) of E_{2g}¹ and A_{1g} modes and peak intensity (right) of E_{2g}² mode in (b) and (c).

In Figure 5-15a, the intensity of E_{1g} mode gradually descends with the driving down of the MoS₂ cathode potential, which denotes that the lattice of 2H-MoS₂ is correspondingly transformed. However, the three peaks marked with dashed lines become more and more prominent with the increasing of the introduced lithium ions. Specifically, these three peaks reach the highest intensity while the E_{1g} peak almost disappears for battery D (x=1). Combined with our first principle calculation as displayed in Figure 5-15d and 5-15e, the three peaks located at 196, 223, 350 cm⁻¹ in Figure 5-15a are the Raman peaks of dT-MoS₂, while the peaks at 383, 406 cm⁻¹ in Figure 5-15b are the Raman peaks of 2H-MoS₂ (E_{2g}¹ and A_{1g}). The Raman vibrational diagrams of these featured peaks are depicted in Figure 5-16. Meanwhile, the E_{2g}¹ and A_{1g} peaks commonly red shift and are broadened along with the discharge process as shown in Figure 5-15b and the statistic diagram of Raman peak center along with Li⁺ concentration in Figure 5-15f (left). This redshift and broadening effect should be

interpreted as the Mo-S bonds elongated and weakened to different extents by the slight coulomb interactions between sulfur atoms and lithium ions. An apparent change in peak center, peak intensity and line width for both E_{2g}^1 and A_{1g} peaks can be also observed after the MoS₂ cathodes being ultrasonicated and centrifuged four times. Here shows a common blue shift and broadened line width after ultrasonication and centrifugation due to the reduction in both thickness and lateral dimension⁷⁸, as well as a partial extraction of lithium ions.

Figure 5-16. The Raman vibrational diagrams of dT (a) and 2H MoS₂ (b) respectively. The three peaks located at 196, 223, 350 cm⁻¹ in (a) are the Raman peaks of dT MoS₂, while the peaks at 383, 406 and 32 cm⁻¹ in (b) are the Raman peaks of 2H MoS₂.

Figure 5-15c shows the ULF Raman spectra of pristine MoS₂ powder and lithium intercalated MoS₂. The two peaks located at 32 cm⁻¹ and -32 cm⁻¹ are the Stokes and anti-Stokes Raman modes, notated as E_{2g}^2 , corresponding to the interlayer rigidly shear vibration of 2H-MoS₂. During intercalation process, the intensity of E_{2g}^2 peak gradually decreases and then almost approximates to zero when discharging to 0.9 V, which is similar to E_{1g} mode. The intensity of E_{2g}^2 mode as a function of Li⁺ concentration is also shown in the statistic diagram in Figure 5-15c (right). Furthermore, the calculated phonon dispersion curves of dT- and 2H-MoS₂ are displayed in Figure 5-15d and 5-15e, where the three featured peaks of dT/2H from experiments are indicated with red arrows at Γ point in phonon dispersion diagrams. Therefore, our theoretical and experimental results are in good agreement which further confirms the phase transition from 2H to dT after complete lithium intercalation. Given the negligible ULF Raman peak in dT-MoS₂, the interlayer interactions among dT-MoS₂ are very weak and exhibit a single-layer-like property in this intercalated TMDs materials, which can be attributed to the enlarged layer space by inserted lithium ions. After recharging back to 2.4 V, the intensity of this E_{2g}^2 mode cannot entirely restore as that in previous 2H-MoS₂, which declares that the

interlayer interaction remains weak even after the lithium ions were largely extracted from MoS₂ interlayers. In addition, there is a slight redshift and reduced intensity of the E_{2g}² mode due to the enlarged layer distance.

To further investigate the variation of electronic properties from 2H phase gradually to dT phase during electrochemical intercalation process, we performed PL measurements using 532 nm (non-resonant) and 633 nm (resonant) excitation lasers separately. Bulk 2H-MoS₂ show indirect bandgap feature while its monolayer counterpart becomes a direct bandgap material with the PL peaks located at ~630 nm (B exciton) and 680 nm (A exciton) respectively. Figure 5-17a and 5-17b show the PL spectra using 532 nm (5-17a) and 633 nm (5-17b) excitation laser, for pristine 2H-MoS₂ powder and lithium intercalated MoS₂ (battery A, B, C, D and E) with different Li⁺ concentration (Li_xMoS₂ at x=0, 0.05, 0.37, 0.74, 1, 0.55) respectively. Figure 5-17a and 5-17b congruently exhibit red shift and reduced intensity of PL peaks from powder to battery C (x=0.74). We have also measured the absorption spectra accordingly as shown in Figure 5-17c, where the two absorption peaks (A and B excitons) also exhibit a common redshift from pristine powder to battery B (x=0.37). Besides, the absorption curves of battery C (x=0.74), D (x=1) and E (x=0.55) are close to that of glass which indicates almost no absorption for these lithium-treated MoS₂ samples

. Furthermore, this bandgap narrowing effect can be explained theoretically by band filling effect induced by electron doping. In detail, with the gradual Li atoms insertion, the Fermi level goes up and the gap between CBM and VBM gradually narrows, which in turn makes the redshift of PL peak reasonable. As for the fully phase-transited sample (battery D, x=1), there is almost no PL peak observed due to the metallic properties of dT phase. To explain this evolution, we have calculated the band structures of pristine 2H-MoS₂ (battery A, x=0.05) and dT MoS₂ (battery D, x=1) individually shown in Figure 5-17d and 5-17e. In band structure diagrams, the semiconducting and metallic properties of 2H- and dT-MoS₂ can be easily found by the sizable bandgap and overlapping of conduction and valence bands for 2H and dT phase, respectively. Similar with previous Raman features, the structure cannot considerably recover to 2H after recharging back as the battery E (x=0.55) mainly contains 2H and 1T phases. The statistic diagrams of the gradual bandgap evolution along with Li⁺ concentration is depicted in Figure 5-17f.

Figure 5-17. Photoluminescence of intercalated 2H-MoS₂ cathodes. (a, b) the PL spectra using 532 nm (a) and 633 nm (b) excitation laser respectively. (c) The absorption spectra of pristine 2H-MoS₂ powder and lithium intercalated MoS₂. (d, e) Calculated electronic band structures of the 2H (d) and dT (e) MoS₂ respectively. The solid and dashed red arrows in (d) indicate the direct and indirect excitons of 2H-MoS₂. (f) The statistic diagrams of the gradual bandgap change in (b) and (c).

HR-TEM is an intuitive tool to examine the crystal morphology and atomic structures, as well as provide real space imaging and precisely distinguish the atomic arrangements for different MoS₂ phases with single atom resolution. Therefore, it is used to morphologically characterize the phase transition process of 2H-MoS₂ during Li⁺ intercalation. Figure 5-18a gives the atomic HR-TEM images and Fast Fourier Transform (FFT) patterns of intercalated MoS₂ with different discharge potentials at 1.6 V (1[#]), 1.1 V (2[#]), 0.9 V (3[#]) and recharge to 2.4 V (4[#]) respectively. These HR-TEM mappings and FFT patterns vividly reveal that different phases dominant correspondingly different intercalation-treated MoS₂ samples with distinct atomic arrangements. In detail, as for 1.6 V-intercalated MoS₂ (Li_xMoS₂, x=0.05), there is only a very small amount of lithium ions inserted into 2H-MoS₂ layers and the perturbation to lattice is small, so the dominant phase is still 2H which exhibits honeycomb structures in HR-TEM image, as shown in Figure 5-18a (1[#]). The image inserted above corresponds to the FFT pattern of this hexagonal phase, which gives further confirmation of 2H lattice symmetry. We find the 1T lattice with octahedral symmetry in a 1.1 V-

intercalated MoS₂ sample (Li_xMoS₂, x=0.74), which has proven to be a metastable phase and yet can transitorily exist with the stabilization of high-concentration Li ions, vividly exhibited in Figure 5-18a (2[#]).

When the intercalation voltage drives down to 0.9 V (Li_xMoS₂, x=1), the 2H-MoS₂ has completed the phase transition to final dT structure which belongs to a distorted octahedral symmetry and its HR-TEM pattern shows a ribbon-like morphology consisting of Mo atoms. This dT phase possesses a $1 \times \sqrt{3}$ super-lattice structure, as displayed in Figure 5-18a (3[#]). From above experimental findings in HR-TEM, we consider that the Li⁺-supported 1T lattice can be further simultaneously distorted to the more stable dT-phase at an even larger Li⁺ concentration. From our previous Raman and PL features, we find that the phase cannot fully revert to 2H after the MoS₂ battery being recharged back to 2.5 V (battery E, x=0.55), which is also consistent with our HR-TEM result as shown in Figure 5-18a (4[#]). We can obviously find two main phases (2H and 1T) and their evolution boundary, which can be interpreted as the easy lattice transformation from dT to 1T when the stabilization support from Li⁺ becomes less. Therefore, the HR-TEM characterizations strongly support our previous Raman (ULF Raman), PL and first-principles calculation results³⁰⁻³³ of the gradual phase transition process from pristine 2H to final dT with lithium intercalation step by step and the irreversible feature after large lithium extraction.

Figure 5-18. (a) HR-TEM fingerprints and FFT patterns of intercalated 2H-MoS₂ with discharge potential at 1.6 V, 1.1 V, 0.9 V and recharge to 2.4 V, respectively. The atomic structures for 1T and 2H are inserted on the top of 4[#] TEM image. (b)

Transformation energy barrier of monolayer MoS₂ from 2H to 1T to dT phase by nudged elastic band (NEB) calculation.

Figure 5-19. Layer space (a) and relative energy per unit cell (b) in Li_xMoS₂ with different Li⁺ concentrations by first-principle calculation. (c, d) Atomic structures of the top views for dT-MoS₂ (c) and ReS₂ (d) monolayer.

Based on the discoveries in HR-TEM, the two phases of 1T and dT are found to distinctively exist in different intercalation-treated MoS₂ samples (discharging voltage at 0.9 V and 1.1 V), we further calculate the energy barrier of the transformation from 2H to 1T to dT phase by nudged elastic band (NEB) method. As shown in Figure 5-18b, the black curve with discrete transient states depicts the energy change of the phase evolution from 2H to 1T to dT without Li⁺ participation. The reaction coordinates at 1, 13 and 26 represent 2H, 1T and dT phase, which explicates that there is a large energy barrier from 2H to 1T phase transition, while the transition from 1T to dT phase can occur spontaneously as the energy of dT phase is lower than that of 1T phase. However, with the aid of Li⁺ participation (red curve), the energy barrier between 2H and 1T phase

is observably lowered down compared with the black curve without Li^+ , which makes the phase transition from 2H to 1T possible and facilitates the spontaneous transition from 1T to dT phase. This step-by-step mechanism calculated by NEB is a convincing explanation to the observation of 1T/dT phase in 1.1 V/0.9 V-intercalated samples in previous HR-TEM mappings in Figure 5-18a. Therefore, combining experimental discoveries and NEB calculation, we propose the 2H-1T- dT phase transition mechanism of MoS_2 with the gradual Li^+ intercalation for the first time, that is, the intercalated Li^+ can largely reduce the energy barrier of the phase transition from 2H to 1T and finally result in the low-energy phase transition from 1T to dT.

In summary, accompanied by the Raman (ULF Raman), PL, HR-TEM and first-principle calculations, our electrochemical methods have efficiently achieved the gradual phase transition engineering and accessed to the precise observations of the intercalation process and the corresponding structure evolutions in 2H- MoS_2 . In detail, we firstly demonstrated the extremely weak interlayer interactions in dT- MoS_2 contributed by the enlarged layer space and structural change after intercalation process, using ULF Raman and PL spectroscopy. Through intercalation, the few-layer dT- MoS_2 exhibited a single-layer-like property which should possess the physical and chemical features of both single and multiple layers. Moreover, during the process of intercalation, the gradual redshift and decrease in the PL emission have also been observed for the first time, followed by the PL vanishing of dT- MoS_2 . Moreover, combining experimental discoveries and NEB calculation, we proposed the 2H-1T- dT phase transition mechanism of MoS_2 with the gradual Li^+ intercalation for the first time. Finally, we uncovered that after Li^+ extraction, the MoS_2 samples mainly contain two phases (2H and 1T) verified by HR-TEM. This phase transition engineering can controllably modify the electronic and optical properties of MoS_2 , and other possible tunings such as thermal conductivity, mechanical property and chemical improvements are also of great value to study thereon.

5.4 Experimental details

Transfer of nanoribbons on various substrates (Chapter 5.1). After necking process, PMMA was removed using acetone and 2-propanol. The PC/nanoribbons were

then placed on Au or Si/SiO₂ wafer surface, followed by baking at 150 °C for 2 h in a vacuum oven, making the PC/nanoribbons adhere to the Au or Si/SiO₂ surface (Supplementary Fig. S7). The PC film was subsequently dissolved using dichloromethane and 2-propanol.

Annular dark field scanning transmission electron microscopy (Chapter 5.1). Samples were prepared for ADF-STEM imaging using the PMMA-assisted transfer method. After transfer of nanoribbons on Si/SiO₂ wafer, PMMA was spin coated onto the nanoribbons at the speed of 3000 rpm for 60 s, followed by baking at 170 °C for 5 minutes using a hotplate. Then the sample was carefully placed on the HF surface (49% HF: H₂O=1:4) for ~30 s, followed by rinsing in DI water six times. Then a TEM grid was used to fish out the sample, and the sample was air-dried and the PMMA was washed off with acetone and 2-propanol. STEM was carried out by Titan³ G2/TEM 60-300 (FEI) operated at 80 keV. In order to reduce irradiation damage, beam current was kept below 40 pA. A high-angle annular dark field (HAADF) detector was used to record ADF signal. While the ADF signal from light element was weaker for HAADF, low-angle condition (LAADF) was used to clear signal from sulfur atoms. For the most images in the text, the Gaussian Blur filter was applied to reduce the noise and enhance the visibility of detailed structure.

Electrochemical characterization (Chapter 5.1). A graphene film was first transferred onto Au (50 nm) as the substrate for promoting the electron transportation. Two monolayer MoS₂ flakes with the same size (5 mm*5 mm) and coverage were prepared for electrochemical measurement. One sample was the original monolayer MoS₂ flakes transferred on graphene/Au surface. The other sample was the patterned monolayer MoS₂ flakes by our necking method on graphene/Au surface. The graphene/Au substrate size was 1 cm*2 cm. Electrochemical measurements were carried out in a conventional three-electrode electrochemical cell using a Bio-Logic VMP3 potentiostat. An Ag/AgCl (3.5 M H₂SO₄) electrode and a Pt foil were used as the reference electrode and the counter electrode, respectively. The supported MoS₂ served as the working electrode. The catalytic performance was measured using linear sweep voltammetry between 0.2 V and -0.5 V versus reversible hydrogen electrode (RHE) with a scan rate of 5 mV/s. Before each testing, a flow of nitrogen gas was pumped more than a half hour to eliminate dissolved oxygen. All potentials were referenced to a RHE by a

value of $(0.209 + 0.059 \text{ pH}) \text{ V}$.

WTe₂ Sample preparation (Chapter 5.2). 1) The few-layer WTe₂ were synthesized by CVD method using WO₃ and WCl₆ (Sigma) as the W sources. The Te powder was used as the Te sources. The crystals were synthesized in quartz tube (1-inch diameter) with temperature from 700 to 850 °C. The mixed gas of H₂/Ar with 15 sccm and 150 sccm were used as the carrier gas, the silicon boat contained 30 mg mixed powders with WO₃:WCl₆: Te=1:1:1(weight ratio) was put in the center of the tube. The SiO₂/Si substrate was placed downstream. Another silicon boat containing 0.5 g Te powder was put on the upstream. The temperature ramps up to the 820 °C in 17 min, and keeping at the reaction temperature for about 5 min to 15 min. Then the furnace cooled down to room temperature gradually. 2) Bulk WTe₂ single crystals were prepared by chemical vapor transport method with iodide as the transporting agency. The stoichiometric amounts of W powder and Te lumps (300 mg) with iodide (30 mg) were sealed in a quartz tube under vacuum at 10⁻⁶ Torr, which was placed in a three-zone furnace. The reaction zone was prereacted at 750 °C for 24 h with the grown zone at 850 °C, preventing the transport of the samples. The reaction zone was then programed at a higher temperature of 950 °C with the growth zone at a lower temperature of 850 °C for seven days to give the temperature gradient in order to achieve the growth of single crystal. Finally, the furnace was naturally cooled down to room temperature and WTe₂ single crystals were collected in the growth zone.

High pressure measurements (Chapter 5.2). The high-pressure cell used in this experiment is based on a symmetric diamond anvil cell (DAC) having two diamonds with 400 μm culet size. The sample and pressure transmitting medium (methanol/ethanol, 4: 1) with a small ruby chip (10 μm) are loaded in a 150 μm hole drilled in a 250 μm thick T301 gasket preindented to 60 μm thickness. The high-pressure Raman spectra were collected using a Renishaw InVia micro Raman system under backscattering configuration, with excitation laser wavelength of 532 nm and 20X objective lens. The laser power is controlled below 0.4 mW to avoid possible laser-induced heating. The signal was dispersed by a 2400 g mm⁻¹ grating under the triple subtractive mode with a spectra resolution of 1 cm⁻¹. The acquisition time of each spectrum was 200 s. Frequency calibration of the Raman spectrum is realized using the characteristic 520 cm⁻¹ line of silicon. For WTe₂ sample loading in DAC, we use a very fine tip to cut the WTe₂ crystal, and adjust its orientation within the punched gasket to

obtain parallel and vertical alignments.

Molecular dynamics (MD) calculations (Chapter 5.2). For the MD simulation study, a 96-atoms $2 \times 2 \times 2$ supercell and $2 \times 2 \times 2$ MP k-point sampling grid. To adopt NPT ensemble, the simulation system is coupled to an Parrinello-Rahman barostat running with Langevin stochastic thermostat, as recently implemented in VASP code. The time step in the molecular-dynamics simulations was 1 fs and the external pressure maintains at 20 GPa. The Raman peak intensity of a particular normal mode ν is calculated as:

$$I^\nu \propto |e_i \cdot A^\nu \cdot e_s| \frac{1}{\omega_\nu} (n_\nu + 1), \text{ where } e_i (e_s) \text{ is the incident (scattered) light polarization,}$$

n_ν is the Bose-Einstein distribution and A^ν is the Raman susceptibility associated with the ν -th normal mode. To do the spin projection calculations, we computed the Wannier functions by the maximally localized algorithm, implemented in the package WANNIER90 using W s and d orbitals and Te p orbitals. The Weyl chirality is calculated by the software package WannierTools, which is based on the iterative Green's function.

2H-/1T-MoS₂ Sample preparation (Chapter 5.3). In our experiments, we use 2H-MoS₂ powder, carbon black and PCDF mixture with 8:1:1 mass proportion to assemble five testing cells, and these five testing cells were then executed galvanostatic discharge/recharge processes separately at 0.05 mA through electrochemical workstation to controllably monitor the Li⁺ intercalation/extraction process to MoS₂. For the first four batteries, the terminal discharge potentials of MoS₂ cathodes with respect to Li/Li⁺ are 1.6 V, 1.1 V (80 mAh/g), 1.1 V (160 mAh/g), 0.9 V respectively, which denoting the lithium intercalation process with gradually increasing Li-ion concentration. As for the fifth cell, after discharging to 0.9 V, we then recharge it with the MoS₂ cathode potential back to 2.4 V. All five batteries we terminated at their first discharge/charge cycle to avoid the possible structure changing caused by multi-cycles. After electrochemical process, the MoS₂ cathodes were withdrawn from the pouch cells and then washed with acetone, ethanol and DI water in sequence to efficiently remove electrolyte residuals around MoS₂. After that, these washed MoS₂ cathodes were ultrasonicated and centrifuged four times in DI water and dropped on cleaned glass (copper grid) for Raman, PL and HR-TEM testing.

Chapter 6 2D homo- and hetero- junctions based on TMDs

6.1 Current rectification in thickness- and stacking-induced TMD homojunctions

Beyond the mediating spin-valley coupling, stacking also correlates closely to the electronic and optoelectronic properties. The nature of TMDs, such as the appropriate bandgap, high carrier mobility and high current on/off ratios, makes TMDs as the ideal semiconductor material for the field-effect transistors, photovoltaics, photodetectors, and nonvolatile memories¹⁵⁶⁻¹⁵⁹. However, most of these devices are based on p-n junctions by heavy doping, Schottky junctions between metal and semiconductor, van der Waals heterojunctions by mechanical transfer, or other homojunctions associated with the strain, phase and layer number modulation. For example, the diode-like rectification effect and valuable drain-source current have been demonstrated in TMDs-based materials, such as layer-dependent MoX₂ homojunctions^{160, 161}, phase-modified 1T'-2H MoX₂ Schottky junctions⁷⁶, WS₂-WSe₂¹⁶², WX₂-MoX₂¹⁶³, graphene/BP-MoS₂¹⁶⁴ heterojunctions. So far, the homojunctions based on stacking have not been reported yet, even the comparison of the electronic and optoelectronic properties in these stackings.

In this work, we introduce a new type of stacking-dependent homojunctions consisting of alternant AA and AB stacked distributions in few-layer MoS₂ samples. These MoS₂-based homojunctions are intrinsically formed by one-step CVD growth without any heavy doping or mechanical transfer strategies¹⁶⁵, which guarantees a chemically homogeneous character and strong coupling among the layers. It has been discovered that AA and AB stacking in 2L MoS₂ can be facilely obtained with equivalent probability by CVD method. As shown in Figure 6-1a, the number of layers can be well defined by optical contrast image which indicates a trilayer feature of this flower-patterned MoS₂ sample. The bottom monolayer has uniform single-crystal morphology, whereas the bilayer region can be divided into the distinct phase domains. To investigate the intrinsic difference in lattice vibrations and band structures of various MoS₂ domains with different thickness and stacking configuration, we have performed the Raman and PL studies accordingly⁴⁷. Figure 6-1b and 6-1c show the Raman and PL mappings

regarding the intensity of E_{2g}^1 mode and B exciton, respectively. In both Raman and PL mappings, we can obviously distinguish the stacking distribution as alternant domains of AA and AB stackings. The AB stacking (denoted 2, 4, 6 in Figure 6-1a) shows a brighter contrast than AA stacking (denoted 1, 3, 5) in Raman mapping, which is consistent with the Raman curves collected from all the six triangles within bilayer region shown in Figure 6-1d.

For band structures, Figure 6-1c and 6-1e show PL mapping of B exciton intensity and PL single spectra of different domains within bilayer region respectively. In Figure 6-1c we can also find the sharp boundaries for all the different layer-dependent and stacking-dependent junctions. As monolayer has an extremely strong PL emission of A exciton, the B exciton emission is relatively much smaller compared to the bilayer and trilayer regions. Therefore, the monolayer region shows a darker contrast in intensity mapping as shown in Figure 6-1c. In Figure 6-1e, the three peaks located at around 630 nm, 680 nm and 850 nm are B, A and indirect (I) excitons, respectively. However, the A exciton almost shows no difference in both peak center and intensity between AA and AB domains, while there is a common blueshift for B and indirect excitons from AA to AB domain which indicates an enlarged spin-orbit-coupling valence band splitting for AB stacking caused by a stronger interlayer coupling effect compared with AA stacking. Figure 6-1f shows the absorption spectra for all the six domains in bilayer, where the blueshift of B and I exciton absorption peaks is in consistency with that of PL spectra in Figure 6-1e. Therefore, the absorption spectra further confirm the alternant phase distributions within bilayer region.

Figure 6-1. Optical characterizations of flower-patterned MoS₂. (a-c) The optical contrast image (a), Raman intensity (E_{2g}^1 mode, b) and PL (B exciton, c) mapping of flower-patterned trilayer MoS₂ sample. (d-e) High-frequency Raman (d), PL (e) and absorption (f) spectra of the flower-patterned MoS₂ sample within bilayer region.

Figure 6-2a displays the ULF Raman intensity mapping of the flower-patterned MoS₂ sample. The integrated peak used for mapping is the shear mode of bilayer MoS₂ (E_{2g}^2) covered with orange strip in Figure 6-2b, and the white-dashed line sketches the border of bottom monolayer in Figure 6-2a. The AA and AB domains show obviously different color contrast in mapping, while there is no signal arises from monolayer region as the ULF Raman only reflects the information of rigid motion between layers. In Figure 6-2b, all domains show two peaks at 22 cm⁻¹ and 38 cm⁻¹, which correspondingly represent the shear mode (SM) and layer breathing mode (BM) between two layers. In particular, domains 1, 3, 5 show a 3R stacking feature with the intensity of breathing mode larger than that of shear mode, while domains 2, 4, 6 own a much larger intensity of shear mode on the contrary which belong to 2H stacking based on our previous studies¹⁶⁶. Figure 6-2c shows the correspondingly atomic arrangements (top view) of 2H- and 3R-stacking bilayer MoS₂ by simulation with hollow sites (2H-) and filled S atoms (3R-) within repetitive hexagons.

Figure 6-2. (a, b) ULF Raman intensity mapping (a) and single spectra (b) of trilayer MoS₂ sample. The integrated peak for mapping is E_{2g}² shown as orange strip in (b) and the white-dashed line sketches the border of bottom monolayer. (c) Top-views of 2H- (top) and 3R- (bottom) stacking 2L MoS₂ by simulations.

On the foundation of above structural characterizations, we further study the electronic and optoelectronic performance of these novel intrinsic MoS₂ junctions with sharp and well-defined interface. However, before testing the electrical characteristics of the junctions, we have first characterized the electrical transport properties of 1L, 2L AA and AB MoS₂ to ensure ohmic contacts are achieved. A number of FETs for individual 1L, 2L AA and AB MoS₂ are fabricated on Si/SiO₂ substrate with Ti/Au film as source and drain contacts, as shown in Figure 6-3.

Figure 6-3. (a) Illustration diagram of the back-gate FET devices with three electrodes as drain, source and gate. (b) Optical image of the designed electronic devices with different pairs of junction shown in red instructions.

Figure 6-4 sketch the typical transfer characteristics (I_{ds} - V_{gs}) of monolayer (a), AA (b) and AB (c) FET devices with drain-source voltage (V_{ds}) at 1 V. The current increases as back gate voltage sweeps from negative to positive, which reveals a typical n type

behavior for these three MoS₂-based FETs and the corresponding on-off ratios are more than 10⁷ for all the monolayer, AA and AB bilayer samples. In reverse region of 2L MoS₂, the current increasing phenomenon could be attributed to gate-tuning band shift. The Fermi level is situated below the valence band maximum (VBM) under a negative gate voltage and thus extra holes are generated at the top of valence band. In addition, as the bandgap of bilayer MoS₂ (both AA and AB stacking) is smaller than that of monolayer MoS₂, this gate-tuning effect on band structure is stronger in bilayer case. Besides band shift, the possible p doping in 2L MoS₂ introduced during etching treatment (oxygen plasma) may also account for the current increasing in reverse region. The inserts show the optical images of one batch of FET devices for transfer and output characteristics measurements accordingly. The fabricated devices have a mutual channel length of 3 μm yet with different channel width, and the mobility of different MoS₂ devices can be derived from $\mu = g_m L / W C_{ox} V_{ds}$, where $g_m = dI_{ds}/dV_{gs}$ is the transconductance, L and W are the channel length and channel width, respectively, C_{ox} is the capacitance of the gate dielectric (270 nm SiO₂), and V_{ds} is the drain-source bias voltage. As a consequence, the calculated mobility is 1.24, 12.31 and 2.89 cm²V⁻¹s⁻¹ for monolayer, AA and AB stacking MoS₂ individually. Compared with mechanically exfoliated MoS₂ samples, this lower mobility can be attributed to the more defects introduced in MoS₂ flakes by CVD method. Figure 6-4d-4f are the according output characteristics (I_{ds}-V_{ds}) of monolayer (d), AA (e) and AB (f) FETs with applied gate-voltage bias changing from 0 V to 50 V in steps of 10 V. A linear I_{ds}-V_{ds} relationship is observed under all gate voltages for all the three types of samples, indicating that ohmic contacts are archived between MoS₂ and Ti/Au electrodes. These results are used to exclude the possible influences brought by the Schottky barrier and premised to our following electronic and optoelectronic performance measurement of stacking-dependent junctions.

Figure 6-4. (a-c) Transfer characteristics (I_{ds} - V_{gs}) of pure monolayer (a), 2L AA (b) and 2L AB (c) FET devices with drain-source voltage (V_{ds}) at 1 V. (d-f) Output characteristics (I_{ds} - V_{ds}) of monolayer (d), 2L AA (e) and 2L AB (f) FET devices with gate voltages applied from 0 V to 50 V.

Given that the ohmic contacts formed for all MoS₂ samples, we continue to probe the electronic behaviors of these new types of intrinsic homojunctions. The schematic of our back-gate electronic devices and corresponding optical image of as-designed devices with multiple electrodes based on our flower-patterned sample are shown in Figure 6-3. The details of device fabrication process and electrical measurement are presented in Methods section. Through working on different combinations of electrode pair, we have obtained the performances of various junctions (AA-1L, AB-1L and AA-AB) as indicated in optical image with black arrows. The channel length for all the three types of junctions is 4 μ m.

Figure 6-5a and 6-5b are the output characteristics of AA-1L and AB-1L junctions under different back-gate voltages, respectively. An obvious diode-like rectifying behavior is observed for both the AA-1L and AB-1L junctions, with current being much larger when the 2L AA or AB region is positively biased (1L region is grounded). The output current I_{ds} monotonically increases with the V_{gs} varying from 0 V to 50 V for both junctions, corresponding to the n type properties of MoS₂. More interestingly, our unique 2L AA-AB junction also demonstrates similar gate-tunable rectifying characteristics with the AB layer grounded, as shown in Figure 6-5c. It is noted that the

broad on-state current distribution of these three devices partially originates from the different channel widths. Figure 6-5d-5f show the photoresponse of AA-1L, AB-1L and AA-AB junctions respectively. All the I_{ds} - V_{ds} curves are measured both in the dark and under 532 nm laser illumination without applying gate voltage, and the y-axis-enlarged I_{ds} - V_{ds} curves in dark case are demonstrated as insets.

The rectification ratio (the current at bias of 2 V divided by the absolute value at bias of -2 V) of dark current for AA-1L junction is ~20, and this value decreases to ~10 for AB-1L junction. That is, both AA-1L and AB-1L junctions show a diode-like output characteristic with observable rectification ratio, and yet AA-1L junction displays a more remarkable rectifying behavior than that of AB-1L junction. No detectable open-circuit voltage (V_{oc}) is obtained for the AA-1L junction under 532 nm laser illumination with a power density of 10 mW/cm², and an asymmetric bias-dependent photocurrent is observed when the V_{ds} sweeping from -2 V to 2 V, as shown in Figure 6-5d. It is clear that the photocurrent at forward bias increases much faster than that at reverse bias, with the current at 2 V increasing from the dark current of 2 nA to 47.2 nA under illumination, while the current at -2 V changing from -0.1 nA to -0.6 nA. Thus, the rectification ratio of this AA-1L junction approaches 80 under illumination, four times as much as the dark case. Similar phenomena demonstrated in Figure 6-5e are achieved for the AB-1L junction. The current at 2 V (-2 V) changes from 3.6 nA (-0.37 nA) to 62.2 nA (-1.65 nA) as the laser excitation, resulting in an increase of rectification ratio from ~10 to ~40. Compared with AA-1L and AB-1L junctions, AA-AB junction exhibits a smaller rectification ratio of ~4.5 in the dark, indicating a weak rectifying effect formed in the bilayer junction. Under illumination, the forward photocurrent of AA-AB junction shows a similar tendency to the AA-1L and AB-1L junctions (the current at 2 V increases from 2.05 nA to 50.4 nA), whereas the reverse photoresponse is stronger than that of both the previously discussed junctions with the current changing from -0.46 nA to -3.85 nA at -2 V bias. Therefore, the rectification ratio increases to ~13, less than three times of the value in the dark.

Figure 6-5. (a-c) Drain-source current I_{ds} of AA-1L (a), AB-1L (b) and AA-AB (c) junctions as a function of drain-source bias voltage V_{ds} with different back-gate voltages V_{gs} . (d-f) Output characteristic and photo-induced current of AA-1L (d), AB-1L (e) and AA-AB (f) junctions under dark situation and 532 nm laser illumination shown in dark and green curves without gate-source bias. The inserts are the zoom-in plots of dark current curves.

Based on the ohmic contacts formed between all the three types of MoS₂ and Ti/Au electrodes, we can conclude that the rectification behaviors in all junctions are dominated by the stacking-related band structures of MoS₂. To explain the electronic and optoelectronic performances of the junctions, we carry out careful descriptions of the band alignments between different types of MoS₂ using the first-principles calculations, as shown in Figure 6-6. All the energy of conduction band minimum (CBM), valence band maximum (VBM) and Fermi level (nominated as E_{CBM} , E_{VBM} and E_f) for 1L, 2L AA and AB MoS₂ in Figure 6-6a are calculated by LDA+HSE considering the vdWs interactions with a mutual vacuum level. The bandgaps of 1L, 2L AA and AB MoS₂ are 2.26 eV, 1.87 eV, and 1.93 eV separately, and the corresponding Fermi levels are 6.50 eV, 6.17 eV and 6.22 eV respectively. There will be band bending to equilibrate the Fermi levels when the junction forms between any two types of MoS₂. Take AA-1L junction for example, the CBM of AA MoS₂ is located lower than that of the 1L and yet both the VBM and Fermi level are situated higher than that of the 1L. Therefore, after the 1L and AA MoS₂ forming a junction, a type I band profile is created, and the

conduction band offset (ΔE_C) is much larger than the valence band offset (ΔE_V), as shown by the left diagram in Figure 6-6b. When the 1L MoS₂ is grounded and AA MoS₂ is forward biased, the bands of AA domain move downwards relative to 1L and tend to form a type II-like band structure because of the small ΔE_V . The resulting band profile allows the electrons to flow from 1L to AA and the holes move in an opposite direction with no obvious barrier.

On the contrary, once we apply a reverse bias, the bands of AA MoS₂ will shift upwards with respect to 1L and this AA-1L junction remains type I character due to the large ΔE_C . Therefore, the large amount of electrons cannot easily transport from AA to 1L MoS₂ with a relatively large barrier caused by the band offset, while the holes can pass across the junction with no barrier. Therefore, the forward current increases rapidly with the increase of bias in the dark, whereas the reverse current is much smaller than that of forward case as the current is dominated by the electron flow for the n-type MoS₂, generating an evident rectification effect for AA-1L junction. However, the rectification ratio of AA-1L is significantly smaller than that of common type II diodes, which have a higher barrier for the reverse current. Under illumination, there will be no observable photovoltaic effect due to the lack of built-in field in the type I band structure. The photogenerated carriers trend to recombine in the AA MoS₂ (with a smaller bandgap) at zero bias, resulting in no net photocurrent. In the forward bias case, the photoexcited electron-hole pairs can be separated efficiently by the electric field, leading to a sensitive photoresponse. On the other hand, partial photoexcited electrons should be trapped in the AA MoS₂ region at the reverse bias, increasing the recombination rate with the flowing photoexcited holes and then reducing the photocurrent.

As a result, the large forward photocurrent and the negligible reverse photocurrent significantly increase the rectification ration of AA-1L junction. The detailed electronic band alignments and the movement of photoexcited carriers of AA-1L MoS₂ junction under different biases have been shown in Figure 6-7a. Similar explanation can be also deduced for AB-1L junctions, as interpreted by the middle diagram in Figure 6-7b and 6-7c, where the band offset for this junction decreases a little bit compared to AA-1L junctions, resulting in a larger reverse current both in the dark and under illumination. The combination of AB and AA MoS₂ also forms a type I junction, as shown in the right diagram in Figure 6-6b. However, the band offset for this bilayer junction is significantly

decreased as their CBM, VBM and Fermi level are very close to each other. Different from 2L-1L junctions, the band profile of AA-AB is easily tuned to type II-like alignment both at forward and reverse bias, as shown in Figure 6-7c. As a consequence, it shows a much weaker rectification effect when the AB region is grounded as ΔE_C is just a little larger than ΔE_V , and also a smaller rectification ratio under illumination due to the larger reverse photocurrent. Our calculation results are well consistent with all the previous experimental results.

In order to assess the robustness of our results, we further investigate photocurrent mapping for all types of junctions. The time-resolved photocurrent responses of the device are studied first, and the results of AA-1L, AB-1L and AA-AB bilayer junctions are shown in Figure 6-8(a-c), respectively. The switch of incident 532 nm laser is controlled by a mechanical shutter with an interval of 10 s, and the rise/fall times for all the junctions are ~ 0.5 s, which is a fast value for the CVD-grown atomically thin layers and ensures the convincing scanning photocurrent mapping measurement. Figure 6-8(d-f) display the photocurrent mappings for a different batch of samples with AA-1L (d), AB-1L (e), AA-AB (f) junctions, which have larger junction area than the flower sample for observing the intensity distribution more clearly. All the left panels are the optical images of the as-fabricated stacking-dependent junction devices and right panels show their corresponding scanning photocurrent intensity mappings collected from the rectangle regions in optical images. The wavelength of laser for photocurrent mappings is 532 nm with power below 10 μ W and the applied bias is 3 V. As we can see from the mappings for all stacking-dependent junctions, the photocurrents are mainly localized within the junction region along the ‘interline’ (versus ‘interface’) of 2L-1L or AA-AB domains. It is noted that there are no photocurrent responses near all the metal electrodes, clarifying that the photocurrents are driven by the electric field within junctions rather than the Schottky junctions between metal electrodes and MoS₂. Besides, the photoresponse at zero or reverse bias is too weak to detect for AA-1L and AB-1L junctions in the mapping measurement, and the intensity distribution of reverse photocurrent for AA-AB junction is not as clear as forward case because of the weaker signal. The mapping measurements confirm our deductions and demonstrate the intrinsic stacking-dependent semiconductor junctions in few-layer MoS₂ by direct experimental evidences.

Figure 6-6. Electronic band alignments of AA-1L, AB-1L, AA-AB junctions. (a) The individual band profile of 1L (left), 2L AA (middle) and 2L AB (right) MoS₂ before forming junctions. (b) The electronic band structure alignments of AA-1L (left), AB-1L (middle) and AA-AB (right) junctions.

Figure 6-7. (a-c) Electronic band alignments of AA-1L (a), AB-1L (b) and AA-AB (c) junctions calculated by LDA+VDW. The orange, green, blue lines represent the bands of 1L, AA, AB respectively. The left, middle and right columns show the band alignments

of the three junctions with zero, forward and backward bias. The gray arrows show the direction of electrons and holes flow after applying forward/backward bias.

Figure 6-8. (a-c) Time-resolved photocurrent response of the devices with AA-1L (a), AB-1L (b) and AA-AB (c) junctions, respectively. All the time intervals between laser light on and off states are 10 s. (d-f) The photocurrent mappings for a different batch of samples with AA-1L (d), AB-1L (e), AA-AB (f) junctions. The wavelength of laser for photocurrent mappings is 532 nm with power below 10 μ W and drain-source bias at 3 V.

In summary, we have successfully grown flower-patterned MoS₂ samples with alternant AA and AB stacking distribution within bilayer region by one-step CVD method and thereby introduced several new types of intrinsic junctions with various stackings, instead of either heavy doping or mechanical transfer strategy. By means of ULF Raman, PL and HR-STEM characterizations, we then uncovered the atomic arrangements of the two alternant stackings AA and AB as 3R and 2H. Through systematical electronic measurements, we firstly made sure that the contacts between Ti/Au electrodes and all types of MoS₂ are ohmic, and then observed and compared the distinct behaviors in different junctions induced by stacking configuration, that is, the AA-1L MoS₂ junctions show an excellent rectification behavior followed by AB-1L and AA-AB junctions. Under illumination, the negligible photocurrent at zero bias and the asymmetric photoresponse at forward and reverse biases for all the junctions can be ascribed to the original type I band alignment and the bands shift under different biases, which are coincidentally described by first-principle calculations. The scanning photocurrent mapping measurements further verified the stacking-dependent alignments of the 2L-1L and AA-AB MoS₂ junctions are the fundamentals to determine their

electronic performances. Such stacking-modulated performances of few-layer MoS₂ may broaden the applications of 2D materials in future electronics and optoelectronics.

6.2 Interlayer exciton study in strong-coupled WSe₂-MoSe₂ heterobilayers by pressure engineering

2D vdW HSs can be vertically constructed with different 2D TMD crystals, providing increasingly attractive properties and unique functionalities, which originate from different types of band alignment and their interlayer interaction^{38, 40, 42}. Specifically, interlayer excitons, raising from interlayer excitonic states between most of TMD vdWs HSs, possess longer electron-hole recombination lifetimes than intralayer excitons^{43, 44}. As a result, it plays a prominent role in the charge separation process and efficient photoabsorption in solar cells or photodetectors⁴⁸. Therefore, it is fundamental important to explore its dynamic mechanism through material variety¹⁶⁷, thickness¹⁶⁵, stacking sequence¹⁶⁸, electromagnetic field¹⁶⁹, and strain¹⁷⁰. However, these explorations have been usually hindered by two problems. One is the previously as-fabricated vdWs HSs by mechanical-stacking methods, which usually deliver weak or even no interlayer interaction due to unintentional contaminants. The other one is the weak external tuning methods, which induce limited changes in lattice parameters and physical properties for 2D TMD materials. For example, by strain engineering, one can only introduce up to 2% volume change¹²⁴. High pressure is a powerful tool, which can efficiently strengthen the vdW interactions for TMDs along c-axis and shorten the covalent bonds within atomic plane, leading to a prominent volume change during compression (e.g. 10%~20% at 10 GPa for TMDs). Under high pressure, the typical first-order structural transition (2H_c to 2H_a for MoS₂)²³, metallization, and pressure-driven superconductivity (WTe₂) have been discovered¹⁷¹. However, to our best knowledge, most high-pressure studies are mainly focused on pure TMD bulk materials^{172, 173}, leaving the interlayer coupling evolution and interlayer exciton dynamics in 2D TMD HSs less explored.

In this section, here, we firstly compare the different interband transitions and interlayer exciton behaviours in three types of 2D HSs with no interlayer interaction, weak interlayer interaction and strong interlayer interaction, respectively. We then designedly grow 2L WSe₂/MoSe₂ vdWs HS samples with clean interface and strong

interlayer coupling by a two-step CVD method. Through ULF Raman spectroscopy and first-principles calculations, we determine the stacking orientation of bilayer WSe₂/MoSe₂ HSs as 2H phase, where the intensity of shear mode is much larger than breathing mode with its frequency located between that of pure bilayer 2H WSe₂ and MoSe₂. Then, we perform systematic experimental and theoretical studies on interlayer coupling evolution of WSe₂/MoSe₂ HSs with increasing hydrostatic pressure up to 10 GPa.

Figure 6-9 depicts the scheme of type-II band structure alignments of 2D HSs with different interlayer interaction strength. For (i), a hetero-bilayer sample with no interlayer interaction shows only pristine PL emissions from individual layers, which applies to samples prepared by the transfer processes where cross-contamination during transfer or the large interlayer distance severely hinders the interlayer coupling; By annealing at high vacuum¹⁷⁴, the interlayer interaction can be improved, indicated by an additional PL peak due to interlayer transition (ii). Epitaxial grown samples⁴¹ with well-defined layer stacking will result in much stronger interlayer interaction (iii). In this case, the energy bands of the two layers tend to tightly hybridize and form a more effectively charge-separating bilayer system, giving rise to purely strong interlayer exciton emission I, formed by electrons and holes in different layers. Their corresponding PL peak I is observed at energy lower than that of pristine PL of pristine monolayer TMDs.

Figure 6-9. Top: Scheme of type-II band structure alignment of 2D heterostructures (HSs) with three types of interlayer interaction, (i) no interlayer interaction, (ii) weak interlayer interaction, (iii) Strong interlayer interaction (our HS sample). Bottom: PL sketches of these three types of 2D HSs with different coupling. The red and blue curves are pristine intralayer exciton emissions from individual layers. The green curves are interlayer exciton peaks formed by electrons and holes in different layers.

Figure 6-10 proposes our designed research outline of interlayer exciton dynamics in this 2D TMD HSs with strong interlayer coupling via high pressure, which will induce a dramatic change in electronic band structures and hence interlayer coupling between layers. In this optimized HS, there is no pristine PL from individual layers and all the electrons and holes tend to form interlayer excitons instead.

Figure 6-10. Our designed research outline of interlayer exciton behaviour in 2D HSs via high pressure.

To obtain this kind of hetero-bilayer with a strong interlayer interaction, we fabricated WSe₂-MoSe₂ HSs by employing a two-step CVD epitaxial method, by growing a WSe₂ monolayer on top of the MoSe₂ monolayer. The simplified schematic diagrams of the growth processes and sample structure in both top and side views are shown in Figure 6-11a. MoSe₂ is grown first by a typical CVD method with MoO₃ and Se powders serving as precursors, and then WO₃ powders are introduced subsequently to grow the WSe₂ layers with modified reaction temperature and flow of carrier gas. The detailed growth techniques are demonstrated in the Methods section¹⁷⁵. The growth of WSe₂ usually starts from the edge of MoSe₂, and can form both vertical and lateral WSe₂-MoSe₂ HSs. Our sample consists of 2L WSe₂ at the edges followed by 2L

WSe₂/MoSe₂ with 1L MoSe₂ at the center. The optical image of our as-grown WSe₂-MoSe₂ HS samples on Si/SiO₂ substrate is shown in Figure 6-11b. Hereinafter, we only focus on the interlayer coupling study of bilayer vertical WSe₂-MoSe₂ HS region in all samples (Figure 6-11c).

Figure 6-11. (a, b) Designed two-step growth (a) and optical contrast image (b) of as-grown WSe₂-MoSe₂ HS sample on Si/SiO₂ substrate of WSe₂-MoSe₂ HSs on Si/SiO₂ substrate (top and side view), by CVD. (c) Schematic diagram of WSe₂-MoSe₂ HS samples in top view (left) and side view (right).

To probe the band structure and structural characterization of our WSe₂-MoSe₂ HS samples, we employed PL and high-frequency Raman spectroscopy. Figure 6-12a shows the PL spectra of the WSe₂-MoSe₂ HSs, 1L MoSe₂ and 1L WSe₂, where the peaks at 720 nm and 760 nm correspond to the PL emission of 1L WSe₂ and 1L MoSe₂, while the peaks centered at 770 nm and 845 nm refer to the high and low energy PL emissions of 2L WSe₂-MoSe₂ HSs. Notably, neither of these two PL peaks in 2L WSe₂-MoSe₂ occur at the same energy as those of individual monolayer MoSe₂ and WSe₂, and that the energy of both peaks is smaller than either of the constituent monolayers. We assign these two PL peaks in 2L WSe₂-MoSe₂ HSs as interlayer exciton A and B, which

originate from direct (I_d) and indirect (I_{in}) interlayer interband transitions, illustrated in top-left diagram. These low-energy interlayer exciton emissions in 2L WSe₂-MoSe₂ without intralayer emission from individual layers indicate a strong interlayer interaction and electron-phonon coupling in our CVD grown HSs. This could be attributed to the clean and tightly controlled interface between two individual monolayers. In Figure 6-12b, the high-frequency Raman spectra for different regions are shown for comparison. The featured peaks for 1L WSe₂ (red curve) and 1L MoSe₂ (blue curve) are located at 250 cm⁻¹ and 240 cm⁻¹, corresponding to the Raman vibrations of A_{1g} for WSe₂ (W(A_{1g})) and MoSe₂ (M(A_{1g})), respectively. The black curve is the Raman response of 2L WSe₂-MoSe₂ HSs, containing both the featured peaks of MoSe₂ and WSe₂ as expected. The PL and Raman intensity mappings are shown in Figure 6-12c, collected from the corresponding region in Figure 6-12a, by integrating the intensity of PL peaks at 760 nm (top left, MoSe₂) and 845 nm (top right, WSe₂-MoSe₂ HS), Raman peaks at 240 cm⁻¹ (bottom left, MoSe₂) and 250 cm⁻¹ (bottom right, WSe₂), respectively. The sharp boundaries between two different domains (2L WSe₂-MoSe₂ and 1L MoSe₂) in all the images confirm the good quality of our CVD grown WSe₂-MoSe₂ HS samples.

Figure 6-12. (a, b) PL (a) and Raman (b) spectra of the WSe₂-MoSe₂ HSs, 1L MoSe₂ and 1L WSe₂. The two peaks of WSe₂-MoSe₂ in a are direct (A) and indirect (B) interlayer interband transitions, as illustrated in top-left diagram. (c) Top: PL mapping of the cubic region in Figure 6-11b, regarding the intensity of the PL peaks at 760 nm (left, 1L MoSe₂) and 850 nm (right, 2L WSe₂-MoSe₂), respectively. Bottom: Raman mapping by integrating the intensity of Raman peak at 240 cm⁻¹ (left, MoSe₂) and 250 cm⁻¹ (right, WSe₂), respectively.

As the layer stacking configuration is critical to the interlayer interaction, we have

use the ULF Raman spectroscopy technique that we developed¹⁷⁶⁻¹⁷⁸ to determine the stacking order between the WSe₂ and MoSe₂ layers. Figure 6-13a shows the ULF Raman spectra of 2L 2H-MoSe₂, 2L 2H-WSe₂, 2L 3R-WSe₂ and 2L WSe₂-MoSe₂ HS, where the two peaks at around 20 cm⁻¹ and 35 cm⁻¹ correspond to the in-plane shear mode (SM) and out-plane breathing mode (BM), respectively. These two modes of 2L WSe₂-MoSe₂ HS are located at ~17.3 cm⁻¹, ~35.3 cm⁻¹, and their vibrational schematics are drawn in Figure 6-14. The Raman frequencies of both SM and BM for WSe₂-MoSe₂ HSs are located between that of 2L WSe₂ and 2L MoSe₂.

Figure 6-13. (a) ULF Raman spectra for WSe₂-MoSe₂ HSs, 2L 2H MoSe₂, 2L 2H WSe₂ and 2L 3R WSe₂ samples. The dashed lines indicate the peak position of shear mode (SM) and breathing mode (BM) for WSe₂-MoSe₂ HSs. (b) High resolution Z-contrast STEM images of the corresponding sample region in b. (c) Enlarged STEM image of the corresponding region in g, showing the typical honeycomb structure for 2H stacking.

In particular, the intensity of the shear mode is much stronger than that of the breathing mode, indicating typical 2H stacking sequence based on our previous studies⁹⁴. The corresponding calculated ULF Raman results are also summarized in Figure 6-14b. To further support our ULF Raman results and simulations, we conduct aberration-corrected STEM as displayed in Figure 6-13b and 6-13c. The contrast in the high-resolution STEM images fundamentally relies on the atomic weight and the number of layers. In the region of hetero-bilayer, the brightest dots are the W atoms in the top layer with the overlaid Se atoms in the bottom layer, and the less bright dots are the Mo atoms in the bottom layer with the overlaid Se atoms in the top layer. The enlarged STEM image (Figure 6-13c) shows more clearly the typical honeycomb structure for 2H stacking, as we discussed before in 2L MoS₂ system²⁹.

Figure 6-14. (a) Raman vibrational diagrams of SM, BM, E_{2g}^1 and A_{1g} mode in 2H WSe₂-MoSe₂ HSs. (b) Statistic table of Raman frequency and intensity for 2L MoSe₂, 2L WSe₂ and WSe₂-MoSe₂ HSs from experiments and calculations. (c) Schematic diagrams of the lattice structure of 2H WSe₂-MoSe₂ heterobilayer in both side view and top view by simulations.

We further studied the interlayer exciton behaviours in WSe₂-MoSe₂ HSs under high pressure, as shown in the Figure 6-15. The details of sample transfer and loading to high pressure DAC are described in the Methods section. Figure 6-15a and 6-15b show the PL intensity contour mapping (a) and PL spectra evolution (b) of WSe₂-MoSe₂ HS samples under pressure. PL peaks A, B and C, D are used respectively for the mapping in Figure 6-15a below and above 1.2 GPa. Upon increasing pressure, the A and B exciton peaks in PL spectra exhibit different evolutions; from 0 GPa to 0.64 GPa, the direct exciton peak A shows a blue shift while peak B shows red shift. An obvious pressure-induced changeover is observed between 0.64-1.6 GPa, where the A and B PL peaks are replaced by two high energy peak C and D. We note that these results are distinctly different from the previous report on high pressure study of bilayer MoS₂¹³⁷, as interlayer excitons cannot be formed in the 2L MoS₂ due to efficient electron/hole sharing between layers. As a result, the phenomena related to interlayer exciton behaviors are missed. The photon energies of the PL peak A, B, C and D as a function of pressure are shown in Figure 6-15c. For the pressure range of 1.6-3.5 GPa, both C and D PL peaks show red shift with increasing pressure. We will discuss in detail the band structure evolution and interband transition selection under different pressures later.

Figure 6-15. (a, b) The PL intensity counter mapping under different pressures (a) and PL spectra evolution (b) of the WSe₂-MoSe₂ HS samples under pressure. PL peaks A, B and C, D are used before and after 1.6 GPa. (c) Interlayer exciton energies of the PL peaks A, B, C, and D as a function of pressure are shown by solid circles, and the dashed lines are linearly fitted results.

The pressure-dependent Raman intensity contour mapping and Raman spectra evolution are shown in Figure 6-16a and 6-16b, where the out-of-plane mode (A_{1g}) is found to be more sensitive than that of in-plane mode (E_{2g}^1) and the structure remains undamaged under high pressure. In detail, upon the application of pressure, the Raman modes at around 240 cm^{-1} containing the A_{1g} mode of MoSe₂ and WSe₂ ($M(A_{1g})+W(A_{1g})$), exhibit typical monotonically shift toward higher frequency with no anomalies up to 9 GPa, accompanied with slight peak width broadening. However, the E_{2g}^1 mode at around 290 cm^{-1} of MoSe₂ ($M(E_{2g}^1)$), shows almost no pressure-dependent Raman shift. Since the A_{1g} modes involve mostly out-of-plane atomic vibrations while the E_{2g} modes are in-plane atomic motions, our Raman results suggest that pressure mainly affects the layer coupling and has little effect on the individual layers. This conclusion is supported by our theoretical calculation that shows the interlayer distance change is almost 10 folds larger than that happens in atomic plane (Figure 6-17). Combining with the energy band structure calculation, it reinforces our conclusion that the drastic change in PL spectra is caused by the increased interlayer interaction. Figure 3f summarizes the Raman evolution of WSe₂-MoSe₂ HS samples under pressure.

Figure 6-16. (a, b) The Raman intensity counter mapping under different pressures (a) and Raman spectra evolution (b) of the WSe₂-MoSe₂ HS samples under pressure. (c) The Raman frequency of M(A_{1g})+W(E_{2g}¹) and M(E_{2g}¹) as a function of pressure are shown by solid spheres, and the dashed lines are linearly fitted results.

To address the mechanism of the interband transition changeover in 2L WSe₂-MoSe₂ HSs under pressure, we performed the first-principles calculations of the electronic band structures for 2L HS sample under pressure of 0-2.7 GPa (Figure 6-17a), where the competition of electronic bands and VBM changeover from K to Γ points at around 1.0 GPa could be clearly observed. The inset displays the calculated lattice parameters (a , c/a) with pressure. Under ambient pressure, the predominant interband transitions, A and B, represent the two original PL peaks in Figure 6-15b, where the direct interband transition (A) is from K valley (VBM) with calculated gap energy of 1.38 eV. The CBM is located at Y point, which contributes to the indirect transition peak (B) with a lower energy of 1.30 eV (Figure 6-17b). It is worth emphasizing that these results completely agrees with the two coexistent coupling peaks observed in our CVD grown 2L WSe₂-MoSe₂ HS samples, being different from previous reports on TMD heterostructures by mechanical exfoliation¹⁷⁹.

Figure 6-17. (a) Theoretic study: self-competition of electronic bands in $\text{WSe}_2\text{-MoSe}_2$ HSs under high pressure by Poisson-Boltzmann equation (PBE). Inset: Corresponding lattice parameter change (a , c/a) with increasing pressure. (b, c) Calculated band structure for 2L $\text{WSe}_2\text{-MoSe}_2$ HSs under pressure of 0 GPa (b) and 2.7 GPa (c).

All bands shift upwards yet with different rate under pressure, where the large upward shift of top band at Γ point and bottom band at K point results in the changeover of VBM from K to Γ point and PL peaks from direct band to indirect band transition (A to C). At the same time, the other relaxation path still holds indirect transition from CBM at Y point to new VBM at Γ point (D). Therefore, PL peaks C and D originated from the indirect X- Γ and Y- Γ interband transitions become dominant under high pressure (Figure 6-17c). We also plot the photon energy evolution of the PL peaks A, B, C, and D as a function of pressure in Figure 6-18a, extracted from our calculated band structures in Figure 6-17a. We can clearly see that the blue shift of A peak and red shift of B peak below 1.0 GPa, and the red shift of both C and D peaks above 1.0 GPa. Moreover, the steep change of photon energy at round 1.0 GPa can be also found in our calculated band structures. Hence the calculated results in Figure 6-18a is strongly supportive of our experimental PL results. We also carried out pressure-dependent

absorption measurement to track the band gap change during compression process (Figure 6-18b), where the dashed line indicates the initial peak position of excitonic absorption at K point (peak A). From 0 GPa to 0.64 GPa, we can clearly find the slight blue shift of band edge and excitonic absorption peak, followed by a steep change in both energy and peak width from 0.64 GPa to 1.6 GPa. The absorption transition from direct path (A, K point) to indirect path (C, Γ -Y) at 1.60 GPa further confirms the efficient phonon assisted process and hence the strong electron-phonon coupling in our CVD grown HSs. Finally, the excitonic absorption peak disappears at 4.16 GPa, indicating the quenching of PL emission at higher pressure. These results of absorption spectra under different pressures are also in consistent with above PL spectra and calculation.

Figure 6-18. (a) Photon energies of the PL peaks A, B, C, and D as a function of pressure, extracted from the calculated band structures. (b) Absorption spectra of the WSe₂-MoSe₂ HS samples under pressure. The dashed line indicates the energy evolution of excitonic absorption peak at K point (peak A).

In summary, we report 2L WSe₂-MoSe₂ HS samples with strong interlayer coupling by our designed two-step CVD growth and its identification of atomic arrangements as 2H stacking, by ULF Raman spectroscopy, HR-STEM, and first-principles calculations. Through experimental and theoretical high-pressure study, we find that the interlayer coupling between two individual layers in 2L WSe₂-MoSe₂ HSs can be mechanically modulated, where both direct and indirect interlayer excitons in WSe₂-MoSe₂ are sensitive to external pressure. Importantly, the self-competition of electronic bands and changeover of interlayer excitons from K (A, B) to Γ point (C, D) under pressure are

observed in both PL and absorption spectra for the first time, which reveals the efficient phonon assistance and strong coupling between WSe₂-MoSe₂ heterobilayer grown by CVD. This study provides a means to reversibly tune interlayer interaction and electron-phonon coupling in TMD HSs via high pressure and will also guide the design of their future applications in pressure sensing and actuating systems.

6.3 Experimental details

Devices fabrication and electrical measurements (Chapter 6.1). The few-layer MoS₂ samples patterned by e-beam lithography are firstly etched using Argon plasma. The Ti/Au (5/50 nm) electrodes are deposited using the thermal evaporator, followed by a lift-off process. For all the electronic and optoelectronic measurements of MoS₂, the as-prepared devices are loaded in a vacuum probe station. DC electrical measurements are performed using Agilent B1500A. 532 nm YAG laser with an intensity $100 \pm 2 \text{ mW cm}^{-2}$ is used as the excitation source for photocurrent test.

Photocurrent mapping (Chapter 6.1). We use a Witec CRM200 Raman system equipped with a solid-state YAG laser at 2.33 eV (10 μW) and a Variable-Gain Low-Current Amplifier (FEMTO, DLPCA-200) to transfer and detect the photocurrent signals. The size of the laser beam is around 250 nm which is focused on the sample using an objective (Olympus, 100 $\times$ /NA0.95) and the input bias is 3 V for all junctions while scanning the sample. The scanning step size is four points per micrometer and integration time for each point is one second.

WSe₂-MoSe₂ Sample preparation (Chapter 6.2). 1) The 2L WSe₂-MoSe₂ HS samples are obtained by a modified two-step CVD grown method, with atomic MoSe₂ layers grown first, followed by the second growth of WSe₂ layers. Briefly, MoO₃ powder and Se powder are used as the precursors for MoSe₂. SiO₂/Si wafer serves as the growth substrate and is placed face down with respect to the MoO₃ powder at the center of the furnace. The furnace is ramped to 750 °C in 15 min and held for 20 min for the growth. Meanwhile the Se powder was put upstream at a lower temperature zone (the temperature is about 200 °C) for evaporation. Fifty SCCM mixture of H₂/Ar (with 15% H₂) served as the carrier gas and a reducing atmosphere during the entire process. The

as-grown MoSe₂ on SiO₂/Si substrate was then transferred into another CVD setup for subsequent WSe₂ growth, which is similar to the previous MoSe₂ growth. The only differences are (i) WO₃ replaced MoO₃ as the precursor, (ii) the reaction temperature was set to 900 °C, and (iii) 100 SCCM H₂/Ar was applied instead of 50 SCCM.

High pressure measurements (Chapter 6.2). The high-pressure cell used in this experiment is based on a symmetric diamond anvil cell (DAC) having two diamonds with 400 μm culet size. The sample and pressure transmitting medium (silicon oil) with a small ruby chip (10 μm) are loaded in a 150 μm hole drilled in a 250 μm thick T301 gasket preindented to 60 μm thickness. The high-pressure PL/Raman spectra were collected using a Witec CRM200 system under backscattering configuration, with excitation laser wavelength of 532 nm and 20X objective lens. The laser power is controlled below 0.4 mW to avoid possible laser-induced heating.

Chapter 7 Conclusion and future work

7.1 Conclusion of this thesis

In this thesis, the fundamental studies of the growth mechanism, crystallographic structure, optical property and electronic performance for transition metal dichalcogenides (TMDs) were demonstrated. As a featured part of this thesis, thickness and stacking engineering in ultra-low-frequency (ULF) phonon vibrations and electronic bandstructures for TMD materials (especially MoS₂) were discussed in detail, through ULF Raman spectroscopy, circularly-polarized photoluminescence (CP-PL) measurement, scanning transmission electron microscopy (STEM) and first-principles calculations. In addition, external modifications on physical/chemical properties of TMDs, such as strain and fragmentation, lithium intercalation, hydrostatic pressure engineering, and temperature variation were also investigated in this thesis. Thickness-/stacking-induced MoS₂ homojunctions (1L-2L AA, 1L-2L AB and 2L AA-2L AB) were obtained by typical one-step CVD method, all of which displayed excellent current rectification effect and fast photocurrent response. Besides TMD single crystals studied above, TMD heterostructures (2L WSe₂-MoSe₂) with strong interlayer interaction were fabricated by an epitaxial two-step CVD method. The direct and indirect interlayer exciton transitions in TMD heterostructures were investigated under hydrostatic pressure. Last, we offer our perspectives and future challenges in TMDs research field.

7.2 Future work

Scaling transistors' dimensions has been the thrust for the semiconductor industry in the last 4 decades. However, scaling Si-based integrated circuits beyond 7 nm has become exceptionally challenging^{53, 180}. Fortunately, the emergence of atom-thick 2D materials with exotic properties in recent times has opened up new avenues in device design and would extend the life of Moore's law. Beyond semi-metallic graphene, TMDs possess tunable band gap, significant photoresponse, favorable transport performances, leading to applications in the electronic circuit requiring low stand-by power, diverse optoelectronic devices, and next-generation nanoelectronics^{57, 63, 181, 182}.

The newest development in this highly competitive area of study is to assemble these 2D materials in a 3D stack, layer by layer in a precisely chosen sequence, known as vdWs heterostructures, which hold great promise for novel devices with designed electronic properties beyond their monolayer counterparts, due to the unique coupled spin-valley physics of its constituent monolayers^{49, 51, 183}. For instance, pioneering experiments have demonstrated the type-II band alignment in these heterostructures with bound electrons and holes localized in individual monolayers, that is, interlayer excitons (see Figure 7-1). Owing to the atomically sharp interfaces, interlayer excitons possess longer electron-hole recombination lifetimes than intralayer excitons, which make them ideal candidates for realization of bosonic many-particle states, triplet superconducting states, as well as light detection and harvesting.

Figure 7-1. The schematic structure and band diagram of a photoexcited interlayer exciton.

Despite the exciting achievements, there still exist highly relevant and important issues which need to be addressed. Firstly, the heterostructures are mainly fabricated by stacking TMDs layer-by-layer using mechanical cleavage and transfer techniques. Using such low-yield technique, the stacking orientation cannot be precisely controlled and this cannot be used for real applications. Furthermore, it often results in defects and contaminants. Secondly, the character of these charge transfer states, as well as the general problem of the charge transport properties across the heterostructure, requires knowledge of the band structure and band alignment of the heterostructure. Although optical signatures of the charge transfer state and general optical properties of

heterostructures are currently being examined, to date, the electronic structure of these TMD HSs has not been extensively explored. Specifically, it is experimentally unknown whether the optical transitions will be spatially direct or indirect in such hetero-bilayers.

Therefore, we will adopt a one-step growth strategy for the fabrication of high-quality vertically stacked heterostructures of TMD/TMD in our future work. By means of ULF Raman spectroscopy, we will identify the stacking configurations in TMD HSs, and establish the one-to-one correspondence between the macroscopic stacking patterns and the atomic stacking orders, combining with the first-principles calculations. By utilizing CP-PL measurements, we will investigate the stacking-dependent coupling behaviors in the electrical structures arising from the SOC and interlayer coupling, and reveal the valley polarization and charge separation behaviors of the interlayer excitons. High pressure is a clean and powerful tool to induce dramatic changes in lattice parameters and physical properties in 2D materials, by which we will investigate the pressure-induced interlayer exciton dynamic in TMD HSs. Our study will deepen the understanding of the distinct observed PL spectra and the lifetime of interlayer excitons in TMD HSs and provide useful guidance for future optoelectronics fabrication using various stacked vdWs heterostructure blocks.

Figure 7-2. The architecture of future work based on 2D vdWs heterostructures.

Equally important is that the physical understanding about the interactions between each layer and behavior of carriers at the interface will be investigated using the first-principles calculations. We believe that our theoretical study will shed light on the unusual properties and new physical phenomena in such heterostructures. Based on vdWs HSs consisting of layered TMDs components $\text{MX}_2\text{-WX}_2$, our future work will mainly focus on investigating the behaviors of interlayer excitons at the interfaces and explore the collective quantum phenomenon involving spin/valley and stacking with new possible physics therein. This is a significant step to go beyond 2D materials and engineer a class of man-made materials that combine the unique properties of constituent components that result in more exotic properties (Figure 7-2). We expect the successful outcome of our future work will become an important milestone in the current extensive competition of developing future 2D electronics. In summary, we plan to accomplish the following objectives:

1. Achieve the featured phonon modes for different stacked TMD heterostructures

and establish a one-to-one correspondence between macro image and atomic arrangement, by ULF Raman spectra and first-principles calculations; Develop a fast and non-destructive method to identify the stacking configurations in 2D TMDs and their heterostructures.

2. Explore the spin-valley polarization behaviors in different stacked TMD heterostructures by CP-PL and modify their intrinsic excitons and trions by gate tuning method.

3. Investigate the interlayer coupling evolution in TMD heterostructures under high pressure.

4. Fabricate photonic, electronic, optoelectronic and photovoltaic devices based on 2D TMD heterostructures.

5. Study the ferroelectric and ferromagnetic properties in 2D Bernal blocks and heterostructures.

6. Illuminate the nature of the interlayer excitons and the optical signatures of the charge transfer states.

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