

Synthesis, Characterisation, and Properties of Monolayer MoS₂, WS₂, and Their Vertical Heterostructures

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*Submitted in conformity with the requirements
for the degree of DPhil in Materials Science*

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September 2018

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Abstract

Synthesis, Characterisation, and Properties of Monolayer MoS₂, WS₂, and Their Vertical Heterostructures

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In pursuit of DPhil Degree, Trinity Term, 2018

Transition metal dichalcogenides (TMDs) are semiconducting two-dimensional (2D) materials with direct bandgaps for the monolayers. Recently, much attention has been attracted to its synthesis, properties and applications in nanoelectronics and optoelectronics. The DPhil project focused on growing 2D materials developing chemical vapour deposition (CVD) approaches to grow 2D materials, including molybdenum disulphide (MoS₂), tungsten disulphide (WS₂), and hexagonal boron nitride (hBN), based on which vertical layered heterostructures (VLHs) were fabricated *via* sequential transfer. Furthermore, a range of characterisation techniques were employed to investigate the structural, vibrational, optical and thermal properties of both these monolayers and multilayer stacks.

An atmospheric pressure CVD (APCVD) method was first developed to grow monolayer MoS₂ crystals on silicon substrates with an amorphous oxide layer (SiO₂/Si). A gradient of morphologies ranging from strictly triangular to highly dendritic shapes were attained with the growth dynamics controlled by tailoring the local concentrations of the precursors. In addition, the growth procedure was programmed and the conditions were optimized for large domain size. The monolayer MoS₂ dendrites show good electrocatalytic performance toward hydrogen evolution reactions (HER). Subsequently, this manner was applied to synthesise monolayer MoS₂ on crystalline strontium titanate (SrTiO₃) substrate. The crystal shape was dependent on the surface terminations of the

substrate, explained by the greatest interfacial van der Waals (vdW) bonding between MoS₂ monolayers and SrTiO₃ at the maximum commensuration of their lattices. The as-grown MoS₂ was annealed either under vacuum or in sulphur environment, leading to either degradation or defect annihilation, respectively, as indicated by Raman and photoluminescence (PL) spectroscopy and X-ray photoelectron spectroscopy (XPS).

The focus of the following studies were on the interlayer interactions between TMD monolayers and the optical properties of the as-constituent WS₂:hBN:MoS₂ and WS₂:hBN:WS₂ VLHs. The involvement of hBN separators restricts the interlayer charge transfer and instead enables Förster energy transfer, switching the observation of PL quenching to enhancement. The level of PL enhancement could be determined by the layer number of hBN, the excitation power, the lattice strain, and the temperature, which were revealed by PL spectroscopy and transient absorption spectroscopy, as well as by theoretical modelling. The layer number of hBN adjusts the separation distance and thereby the interlayer coupling between the TMD monolayers; at higher excitation power, the possibility of interlayer energy transfer increases due to the higher exciton density, which results in a larger quantum yield (QY) of the heterosystem; the presence of strain induces shifts in the bandgap of TMDs and alters the relative offsets in the band structure generating the type II heterojunction where the interlayer interactions take place; the nonradiative decay channels are suppressed at cryogenic temperatures, and the efficiency of PL emission can be improved. These VLHs hold potential for advanced devices with desirable optical performance.

Acknowledgements

My DPhil studies could not be accomplished without my supervisor, colleagues, families, and friends. First of all, I would like to sincerely acknowledge my supervisor, Prof Jamie H. Warner. His great wisdom and strict attitudes toward science have deeply infected me, and will have long-term impact on my future research life. He offered me a large platform for self-development in Materials Science, and whenever I am faced with difficulties, his guidance and considerate advice would provide me with power and confidence. His brilliant insights in my projects and helpful suggestions enabled me to move forward in scientific researches, and all my fruitions link tightly with his excellent supervision. Thanks to him, I have got precious opportunities and generous funding to visit and collaborate with a number of research groups worldwide, as well as attending international conferences.

I appreciate the Department of Materials, University of Oxford. The well-organized education system contributes to my progress. The colloquiums and seminars presented by famous scholars across the world have broadened my academic horizons. Besides, The Queen's College, which I am in, enriched my extracurricular activities. It hosts fantastic formal dinners, parties, welfare tea, and movie nights. It also facilitates interdisciplinary communications, spreading knowledge of a variety of majors in the University of Oxford. The scholarship and part-time jobs it offered have allowed me a more colourful life.

My acknowledgement is also given to my collaborators. Prof Martin C. Castell's group, Prof Mauro Pasta's group, and Prof Harish Bhaskaran's group in the University of Oxford provided me with sufficient technical support, *i.e.*, materials characterisation, and discussions. Furthermore, it has been my honour to collaborate with Prof Michael S. Strano's group (MIT), Prof Jeffery C. Grossman's group (MIT), Prof Tian Jiang's group (NUDT), Prof Ju Li's group (MIT), and Prof Junying Zhang's group (BUAA). We have made up what the other lacks, for a common better

understanding of science, especially the theoretical modelling performed by Dr Daichi Kozawa, and the optical measurements of my materials by Dr Ke Wei, Mr Yizhi Wang, and Mr Yu Liu. The academic visits in MIT are very memorable for me, by which I experienced their different but pleasant group cultures, joined their meetings, and visited their highly developed laboratories.

Moreover, I would like to express my gratitude to my colleagues and friends. Our group members are zealous and the academic environment is friendly. Communicating with them about their projects has increased my interests in the field of 2D Materials. Dr Youmin Rong, Dr Shanshan Wang, Dr Zhengyu He, Dr Yüewen Sheng, and Dr Xiaochen Wang helped me to attain hands-on skills of CVD growth, wet transfer, and data computing, which are of importance for my DPhil studies. Besides, it was fantastic to know Ms Sha Li, Ms Yingqiu Zhou, Ms Qu Chen, Mr Hefu Huang, Dr Haijie Tan, Dr Ye Fan. They not only offered me helpful suggestions on my research, but also filled joy into my life. All the junior students, like new blood, supplied enthusiasm into my daily work.

Last but not least, I want to thank my parents and grandparents for their unconditional love and understanding. Our hearts are gapless and our mutual emotions wrap me with warmth wherever I am. To fully support me, they made compromises and sacrificed inclination, and this will never be forgotten. Specifically, my family member, Miaoyu, has devoted invaluable companion to me during these years. I wish him infinite sweetness and inexhaustible sunshine throughout his life. I am also very grateful to my beloved boyfriend, Lin Cheng, who lightened my starry dawn at the first sight, is always sharing my happiness and sadness, bringing me passion and prospect, and will definitely be forever.

Publications

The studies accomplished during the course of this project is listed herein. The result chapters in this thesis are all based on the first-author publications.

Chapter 4

1. **Xu, W.**; Li, S.; Zhou, S.; Lee, J. K.; Wang, S.; Sarwat, S. G.; Wang, X.; Bhaskaran, H.; Pasta, M.; Warner, J. H. Large Dendritic Monolayer MoS₂ Grown by Atmospheric Pressure Chemical Vapor Deposition for Electrocatalysis. *ACS Appl. Mater. Interfaces* **2018**, *10*, 4630–4639.

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Table of Contents

Chapter 1	Introduction	12
1.1	Project Aims	12
1.2	Thesis Scope	12
Chapter 2	Literature Review	16
2.1	Introduction	16
2.2	Crystal structure	18
2.3	Electronic structure	19
2.4	Optical properties	21
2.4.1	Photoluminescence of TMD monolayers	21
2.4.2	Photoluminescence of TMD heterostructures	23
2.4.3	Influential factors of photoluminescence	27
2.5	Vibrational properties	41
2.6	Electrocatalytic properties	45
2.7	CVD synthesis	51
2.7.1	CVD synthesis of TMD monolayers	52
2.7.2	Discussions	61
2.8	Applications of 2D TMDs	71
2.9	Conclusion	75
Chapter 3	Methodology	77
3.1	Introduction	77
3.2	CVD Synthesis and Transfer of 2D materials	77
3.2.1	Substrate preparation	77
3.2.2	CVD synthesis of monolayer MoS ₂	77
3.2.3	CVD synthesis of monolayer WS ₂	79
3.2.4	CVD synthesis of hBN	81
3.2.5	Transfer of 2D materials and fabrication of VLHs	82
3.2.6	Thermal annealing	84
3.3	Optical Microscopy	85
3.4	Scanning Electron Microscopy	85

3.5	Raman and Photoluminescence Spectroscopy	86
3.6	Atomic Force Microscopy	87
3.7	X-ray Photoelectron Spectroscopy	88
Chapter 4	<i>Large Dendritic Monolayer MoS₂ Grown by APCVD for Electrocatalysis</i>	89
4.1	Introduction	90
4.2	Results and Discussion	91
4.3	Conclusion	106
Chapter 5	<i>Epitaxial Growth and Thermal Degradation of Monolayer MoS₂ on SrTiO₃ Single Crystals for Applications in Nanoelectronics</i>	107
5.1	Epitaxial Growth of Monolayer MoS ₂ on SrTiO ₃ Substrates	108
5.1.1	Introduction	108
5.1.2	Results and discussion	110
5.1.3	Conclusion	122
5.2	Thermal Degradation of Monolayer MoS ₂ on SrTiO ₃ Supports	123
5.2.1	Introduction	123
5.2.2	Results and discussion	125
5.2.3	Conclusion	133
Chapter 6	<i>Vertical Stacked 2D WS₂:hBN:MoS₂ Heterostructures</i>	135
6.1	Introduction	136
6.2	Results and Discussion	138
6.3	Conclusion	155
Chapter 7	<i>Vertical Stacked 2D WS₂:hBN:WS₂ Heterostructures</i>	156
7.1	Introduction	157
7.2	Results and discussion	158
7.3	Conclusion	166
Chapter 8	<i>Conclusion and Outlook</i>	167
8.1	Conclusion	167
8.2	Future Outlook	169
Appendix		172
References		186

Chapter 1 Introduction

1.1 Project Aims

The objective of this doctorate project is to systematically design, understand and optimise the chemical vapour deposition (CVD) approach for growing atomically thin 2D materials, including MoS₂, WS₂, and hBN. In terms of MoS₂, the synthesis was programmed to control the growth mode and produce various domain shapes exhibiting desirable catalytic performance. The comprehension of the substrates effects was also developed by employing both amorphous and crystalline growth surfaces. Given the application requirements, the thermal behaviour of MoS₂ was monitored and the crystallinity was resurged *via* specific annealing method. To explore the interlayer interactions between MoS₂ and WS₂ monolayers, vertical heterostacks were built up through sequential transfer with the interlayer distance being tuned by the adjustable layer thickness of the hBN separator. The structural, optical, as well as electrochemical properties of these 2D nanomaterials have been investigated utilising a range of characterisation techniques.

1.2 Thesis Scope

The thesis covers the research that has been performed through my 4-year course for DPhil degree in the Department of Materials, University of Oxford. It unfolds with a literature review (Chapter 2), summarizing the recent progress on the study of monolayer MoS₂ and WS₂, hBN, and

SrTiO₃. These contents are essential for my DPhil studies, which set up the fundamental knowledge and indicate the challenging and outstanding issues in this research field. In Chapter 3 there presents the basic CVD setup for growing monolayer MoS₂, monolayer WS₂, and few-layer hBN, followed by the introduction of the characterisation techniques adopted in my research.

My work begins with the atmospheric pressure CVD (APCVD) growth of monolayer MoS₂ on the Si substrates coated with a thin layer of amorphous SiO₂ (*i.e.*, SiO₂/Si), as shown in Chapter 4. This study aims to controllably synthesise MoS₂ crystals with morphologies ranging from strictly triangular to highly dendritic shapes by customising the local chemistry during the growth. The CVD growth is well programmed so that large domain size with uniform Raman and PL signals is achieved, beneficial to the material characterisation and scalable production in the future. More importantly, the growth is switched from thermodynamic mode to kinetic mode with tailored atomic ratio of the precursor species, which initiates the diffusion-limited aggregation for generating dendritic structures. The MoS₂ dendrites are desirable as electrocatalyst in hydrogen evolution reactions (HER), and the electrochemical measurements demonstrated its improved working efficiency compared to other morphologies. As for defect engineering, a thermal annealing procedure is developed to restore the sulphur vacancies. On one hand, this can improve the crystallinity and optical properties of the monolayer MoS₂; on the other hand, this enables correlating the electrocatalytic performance of MoS₂ with its edge density and domain shape.

To understand the interfacial interactions between the CVD-grown monolayer MoS₂ and its substrate, the APCVD strategy is alternatively applied on crystalline SrTiO₃ substrates (Chapter 5). The crystal shapes and orientations of MoS₂ are dependent on their epitaxial interaction with the surface terminations of the substrates. The domain shapes have been inspected by scanning electron microscopy (SEM) and analysed based on statistical methods. The strains and defects in MoS₂ induced by the epitaxial growth and cooling on different substrates have been analysed using Raman and PL spectroscopy. Sequentially, the thermal behaviour of the monolayer MoS₂ grown on SrTiO₃

substrates was investigated *via* annealing in vacuum. The products annealed at a gradient of temperatures were examined using SEM, scanning tunnelling microscopy (STM), XPS, and Raman and PL spectroscopy. For reviving the deteriorated optical properties of MoS₂ caused by the annealing, a follow-up treatment was employed in sulphur atmosphere, by which the sulphur vacancies can be filled and the Raman and PL signals have been largely increased.

My research then centres on studying the interlayer interactions in TMD van der Waals heterostructures. Interlayer charge transfer and interlayer excitons have been discovered in WS₂:MoS₂ heterobilayers, but for the first time the interlayer interactions between MoS₂ and WS₂ monolayers with controllable separation distance are investigated in this project (Chapter 6). The stacks have been assembled with all CVD-grown materials, by sequentially transferring monolayer WS₂, certain nm-thick hBN, and monolayer MoS₂ on top of one another, giving WS₂:hBN:MoS₂ vertical layered heterostructures (VLHs). The interactions between the semiconducting WS₂ and MoS₂ monolayers are tuned owing to the variable thickness of the insulating hBN spacers. Additionally, the exciton density is changed by inputting different excitation powers. The optical properties of these heterostacks have been examined by PL spectroscopy and transient absorption spectroscopy, and have been found to depend on the thickness of hBN, the excitation power, the strain, as well as the temperature. These are studied using both experimental and theoretical methods. Förster energy transfer has been demonstrated to occur between the WS₂ and MoS₂ monolayers with interlayer separation, which is predominant over the charge transfer, resulting in the observation of PL enhancement. This would also be applicable for other TMD heterostructures, and could be useful in applications such as light amplifiers.

My last project focuses on the interlayer interactions and optical behaviour of WS₂:hBN:WS₂ VLHs (Chapter 7). The heterostacks have been studied with PL spectroscopy and transient absorption spectroscopy, and the mechanism explaining the observations has been probed by model simulations. The PL yield is influenced by the thickness of the hBN spacer and the temperature. This work shows

the feasibility of tailoring the PL emission under adjustable experimental conditions, and reveals the possibility of achieving enhanced PL with identical TMD materials.

Chapter 8 concludes my research findings and achievements in the each of the projects implemented in my DPhil course. Lastly, a plan for future work has been proposed.

Chapter 2 Literature Review

2.1 Introduction

Two-dimensional (2D) materials have attracted tremendous interest in the recent year due to the unique properties that exist upon thinning down their bulk forms.^{1–4} The most extensively studied 2D material is graphene, which possesses rich physics in a condensed matter system.⁵ The zero energy gap of pristine graphene gives it semi-metal attributes in a variety of electronic applications.^{6,7} Expanding the functionality of 2D materials beyond graphene requires access to insulating and semiconducting 2D systems. TMDs are a class of materials with the formula MX_2 , where M is a transition metal element from group IV–VI, and X is a chalcogen (S, Se or Te). The TMDs involved in this thesis consist of transition metal elements in group VIB and chalcogen elements in group VIA, as highlighted in Figure 2.1. The 2D exfoliated versions of TMDs offer properties that are complementary to yet distinct from those in graphene, correlated with the atomic layer structure.^{7,8} Importantly, the sizable bandgaps of $\approx 1\text{--}2$ eV exhibited by 2D TMDs open up a wide range of new applications, such as optoelectronics and solar cells.^{7–11}

Amongst the preparation methods, chemical vapour deposition (CVD) is the leading approach for bottom-up growth of 2D materials, by which large-area and high-quality products fulfilling the requirements for industrial applications can be obtained.¹² A significant milestone in the development of TMDs was the creation of functional heterostructures assembled by vertically stacking different

2D materials. The layered structures have demonstrated a range of fascinating physical phenomena, and can be applied onto transparent and flexible substrates for broader applicability. It is also promising to attain customized properties by tailoring the constituents. This will pave an avenue for the creation of novel devices.^{13,14} Nevertheless, there are many issues remained to be resolved or understood so far. For instance, the CVD growth mechanism explaining the difference in domain morphologies is not completely clear, and the science behind the performance of 2D heterostructures is still under investigation.

In this chapter, a review of 2D TMDs, especially MoS₂ and WS₂, are present based on previous research work. More specifically, the discussions will involve their crystals structures, electronic structures, CVD growth strategies, properties, and potential applications.

Periodic Table of the Elements

The periodic table displays elements with their atomic number, symbol, name, and atomic mass. A legend box in the top center defines the fields: Atomic Number, Valence Charge, Symbol, Name, and Atomic Mass. The table includes elements from Hydrogen (1) to Oganesson (118), plus the Lanthanide and Actinide series at the bottom.

Legend:

- Alkali Metal
- Alkaline Earth
- Transition Metal
- Basic Metal
- Semimetal
- Nonmetal
- Halogen
- Noble Gas
- Lanthanide
- Actinide

Figure 2.1. Period table showing the diversity of TMDs. The transition metals that are highlighted in grey predominantly crystallize into layered structures with three chalcogen elements, whereas those highlighted in cyan tend to form non-layered structures. The elements of the TMDs studied in this thesis are marked by deep red squares. Reprinted with permission from ref. 15. Copyright ThoughtCo 2017.

2.2 Crystal structure

Bulk TMD materials are layered structures, with each monolayer consisting of three covalently-bonded X–M–X atomic planes. Adjacent layers are weakly coupled by van de Waals forces. However, different polymorphs are present because of the variations in stacking order and atom coordination. The well-studied polytypes are 1T, 2H, and 3R, where the letters represent the crystal symmetry systems of trigonal, hexagonal and rhombohedral, respectively, and the digits indicate the number of layers in each unit cell.^{16,17} The crystallographic unit cell of 1T-TMDs is composed of only one layer. The transitional metal atoms in 1T-TMDCs are arranged in octahedral coordination (O_h). Two atomic planes are aligned vertically along the *c*-axis, giving a stacking sequence of AbC, AbC..., in which the capital letters and the letters with lower case stand for the chalcogen atom and the metal atom, respectively. 1T-TMDs exhibit metallic behaviours. They are metastable and can only be obtained through synthetic approaches.^{18,19} In contrast, 3R-TMDs can be found in natural minerals. The crystallographic unit cell of 3R-TMDCs are made up of two layers with the stacking order AbA, BcB, CaC, AbA.... Semiconducting 2H-TMDCs are the most abundant polytype in nature. It has the same intralayer coordination configuration with the 3R counterparts, *i.e.*, the metal atoms are arranged in trigonal prismatic coordination, while shows different interlayer coupling manner, which is AbA, BaB, AbA....²⁰ The detailed crystal structure of 2D TMDs are shown in Figure 2.2.

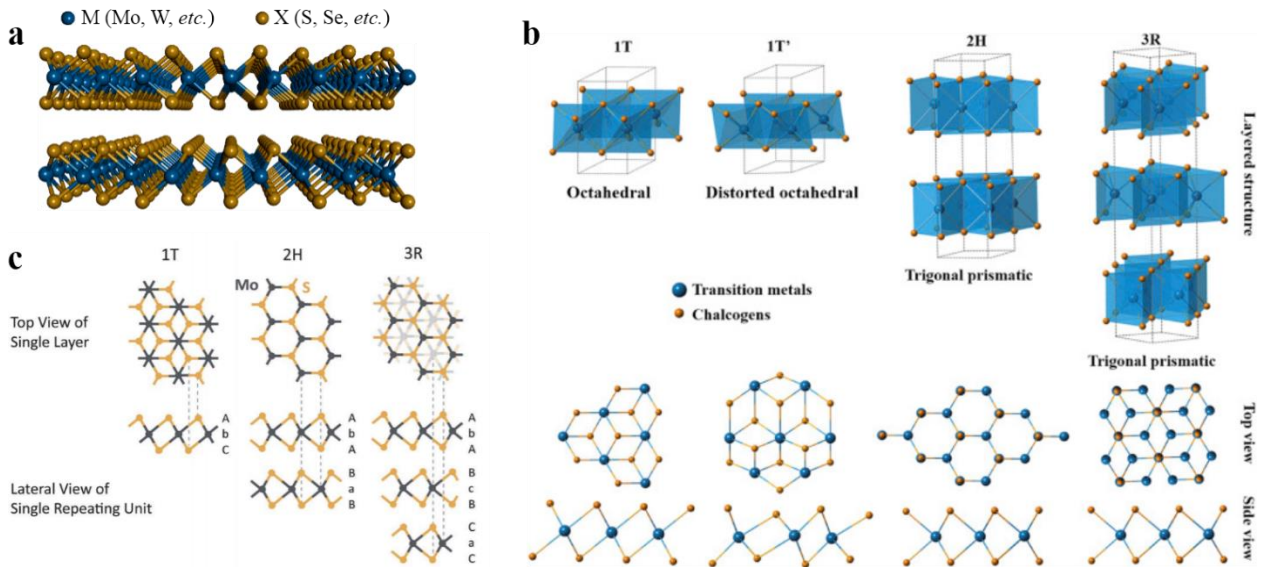


Figure 2.2. Crystal structure of 2D TMDs. (a) Perspective view of a MX_2 bilayer. (b) Top panel – schematics of structure polytypes of TMDs: 1T (octahedral coordination, one X-M-X unit per unit cell), 1T' (distorted octahedral), 2H (trigonal prismatic coordination, two X-M-X units per unit cell), and 3R (trigonal prismatic coordination, three X-M-X units per unit cell). The chalcogen atoms (X) and transition metal atoms (M); bottom panel – the side view and top view of corresponding 1T, 1T', 2H, and 3R structures. (c) Schematics of three polytypes of TMDs, 1T, 2H, and 3R. The dashed lines show how the top views and the lateral views match with each other. (b) Reprinted with permission from ref. 17. Copyright Elsevier B.V. 2016. (c) Reprinted with permission from ref. 20. Copyright Royal Society of Chemistry 2015.

2.3 Electronic structure

As predicted by first principles and tight-binding approximations and measured using a variety of spectroscopic tools, TMDs have similar features regarding their band structures. The electronic structures of atomically thin TMDs are determined by the elemental composition, atomic arrangement, and dimensionality.²¹ It is known that the electronic distributions are spatially related to the atomic structure.¹ Specifically, for MoS_2 , density functional theory (DFT) calculations reveal that the conduction-band states at the K-point mainly result from the localized d orbitals on the Mo atom, which is sandwiched within the S–Mo–S structure and remain almost unchanged by interlayer coupling, so that the direct excitonic transitions at the K-point is nearly independent of the layer number. However, the states near the Γ -point are attributed to combinations of the antibonding p_z

orbitals on the S atoms and the d orbitals on the Mo atoms, which can extend to the outer surface of the MoS₂ monolayer. Thus the hybridization of these orbitals is strongly influenced by the interlayer coupling due to quantum confinement, which in turn leads to the changes in band structure with layer number.^{1,2,22,23} For many TMDs, the indirect bandgap of the bulk material gradually shifts to be direct for the monolayer. This indirect–direct bandgap transformation with decreasing layer number has been supported theoretically by first-principle calculations,^{1,2,23,24} and affirmed experimentally by angle-resolved photoemission spectroscopy (ARPES) and optical spectroscopic methods (Figure 2.3a,b). A small difference in the band structure was revealed by ARPES between exfoliated and CVD monolayer MoS₂, though they both showed direct gaps (Figure 2.3c,d).²⁵ This might stem from the CVD-induced strain as well as defects (see Section 2.4, 2.5, and 2.7). The transition to a direct bandgap in the TMD monolayer yields distinct physical properties, and is important for a variety of applications, which will be discussed later in more detail.

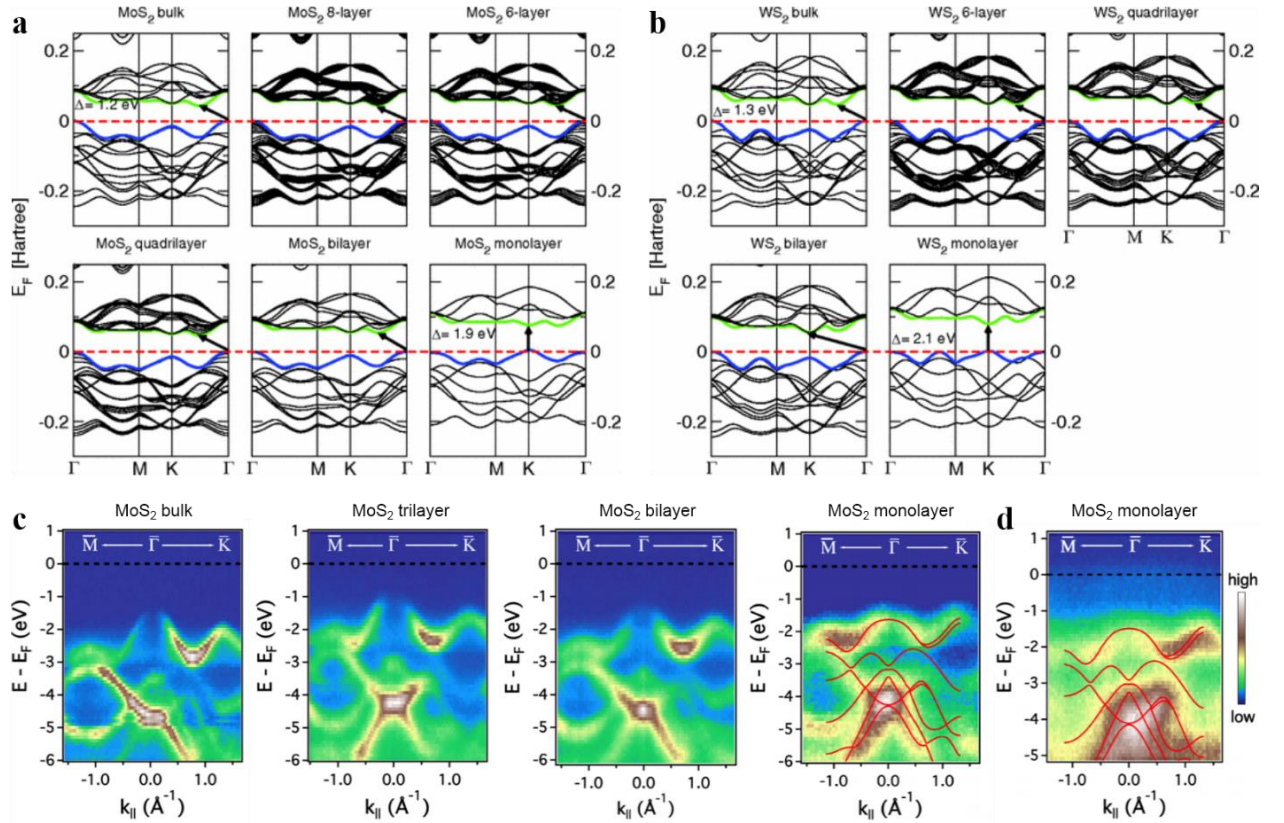


Figure 2.3. DFT-calculated band structures of (a) MoS₂ and (b) WS₂, respectively, including their bulks, monolayers, as well as polylayers. The horizontal dashed lines indicate the Fermi level. The arrows indicate

the fundamental bandgap (direct or indirect) for a given system. The top of valence band (blue/dark grey) and bottom of conduction band (green/light grey) are highlighted. (c) ARPES band map along the $\bar{M}$ - Γ - $\bar{K}$ high symmetry lines of exfoliated bulk, trilayer, bilayer, and monolayer MoS₂, and (d) of CVD monolayer MoS₂. (a,b) Reprinted with permission from ref. 23. Copyright American Physics Society 2011. (c,d) Reprinted with permission from ref. 25. Copyright American Physics Society 2013.

2.4 Optical properties

The electronic band structures of TMD semiconductors directly influence their optical properties. The direct bandgap in TMD monolayers enable them to absorb or emit photons with a much higher efficiency than the multilayers or the bulk.^{1,2} For MoS₂, the change in film thickness has impacts on the PL yield,^{1,2} photoconductivity,²⁶ as well as absorption behaviour.²⁷

2.4.1 Photoluminescence of TMD monolayers

Photoluminescence (PL) spectroscopy is an extensively used tool to gain information on the band structure and optical performance of materials. Since the radiative recombination rate increases significantly with the decreasing thickness of 2D TMDs, strong PL is observed in TMD monolayers owing to their direct bandgaps.^{1,2,28} The indirect–direct bandgap transition enables the intensity of the PL emission to enhance significantly from a bilayer to a monolayer (Figure 2.4a,d).^{2,29} The PL quantum yield (QY) also increases greatly with the decreasing layer number (Figure 2.4a,f).^{2,21,30} The pronounced peak in the PL spectrum of monolayer WS₂ is located at 2.0 eV, corresponding to the emission of A excitons.²⁸ However, there are two peaks for monolayer MoS₂, which are located at 1.8 eV and 2.0 eV.¹ The energy variation is attributed to the splitting at the valence band maximum in monolayer MoS₂ due to the spin–orbit effect. The direct gap transitions at the K point in the Brillouin zone between the maxima of split valence bands and the minimum of the conduction band, known as A1 and B1 transitions, can generate A and B excitons, respectively, upon laser excitation, giving the dominant features in both the PL and the optical absorption spectra of MoS₂.^{31–33} Few-layer MoS₂ shows additional peaks relating to the indirect-gap transition and

direct-gap hot luminescence.² Calculations have shown that the exciton binding energies are very high because of the reduced dielectric constants compared to the bulk, as well as the 2D confinement.³⁴ It is worth mentioning that the photon energy in the PL spectrum corresponds to the optical bandgap, which is the difference between the fundamental bandgap and the exciton binding energy. As presented in Figure 2.4c,g, the PL peak energy of MoS₂ and WS₂ decreases with the layer number, resulting from the shifts in the band structure. Larger improvements have been observed in suspended MoS₂² and the MoS₂ supported by hBN instead of SiO₂ substrate.³⁵ However, the as-measured QY of MoS₂ is massively lower than the near-unity values that are expected for a direct-gap semiconductor.²¹ These suggest that the real optical performance of 2D TMDs are related to their interactions with the material or substrate in contact, and more work is needed to understand the mechanism, to control the optical behaviour, and to increase the QY for future optoelectronic applications.

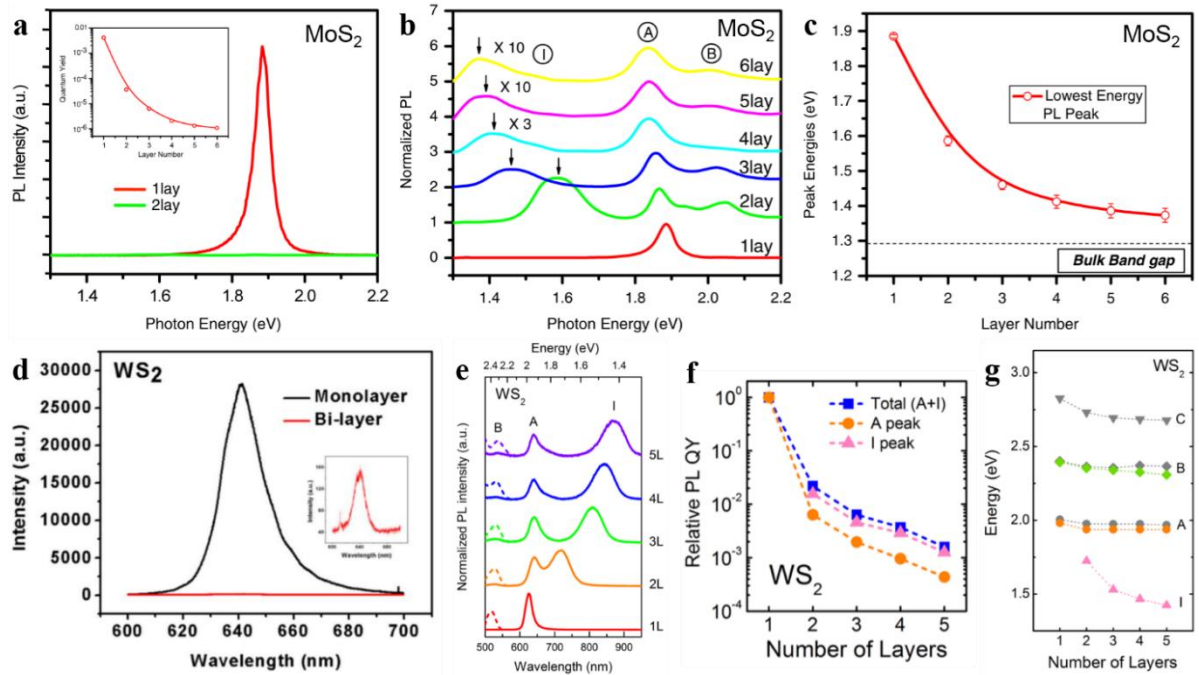


Figure 2.4. (a) PL spectra for mono- and bilayer MoS₂. Inset: PL QY with the layer number of MoS₂. (b) Normalized PL spectra by the intensity of peak A of mono- to six-layer MoS₂. Peaks I for quadri- to six layers, arising from an indirect gap emission (also for WS₂), are magnified with the corresponding spectra displaced for clarity. (c) Bandgap energy of MoS₂, inferred from peak A for a monolayer and from peak I for bi- to six layers. The dashed line represents the indirect bandgap energy of bulk MoS₂. (d) PL spectra for mono- and bi-layer WS₂. (e) Normalized PL spectra for mono- to five-layer WS₂. (f) Relative PL QY vs. number of layers for WS₂. (g) Energy (eV) vs. number of layers for WS₂.

of mono- and bilayer WS₂. Inset: the magnified PL peak of bilayer WS₂. (e) Normalized PL spectra of mono- to five-layer WS₂. The hot electron peaks B are magnified and shown as dashed lines for clarity, which are typically 100–1000 times weaker than the band edge emission peaks. (f) PL QY with the layer number of WS₂, normalized to the PL QY of a WS₂ monolayer. (g) PL (coloured) and absorption (grey) peak energies of WS₂ as a function of layer number. (a–c) Reprinted with permission from ref. 2. Copyright American Physics Society 2010. (d) Reprinted with permission from ref. 29. Copyright Nature Publishing Group 2015. (e–g) Reprinted with permission from ref. 30. Copyright American Chemical Society 2012.

2.4.2 Photoluminescence of TMD heterostructures

Thanks to the availability of diverse 2D TMDs, a wide variety of TMD heterostructures can be designed and fabricated by compiling individual layers into vertical heterostructures without the constriction of lattice matching (Figure 2.5a). Such multilayered TMD possess intriguing electronic and optical properties at the atomic level. This is based on the interlayer coupling of charge carriers across the heterojunction, which offers a new degree of freedom in band engineering. Furthermore, the layer-by-layer stacking method could generate a new class of semiconductor heterostructures with customized constituent layers and therefore tailorable performance.³⁶

Theoretical work predicted a type II band alignment for TMD heterostructures (Figure 2.5b).^{37–40} This would permit charge transfer to take place at the heterojunction, which was confirmed by Hong *et al.* in a van der Waals heterostructure formed by MoS₂ and WS₂ monolayers. Upon optical excitation of the MoS₂ A-exciton, the electron (e[−]) was retained in the MoS₂ layer while the paired hole (h⁺) was transferred to the WS₂ layer (Figure 2.5a,c). The separate electron–hole pair had a much lower emission efficiency, so that PL quenching was observed at the overlapping regions with respect to either of the monolayer (Figure 2.5d).⁴¹ The quenched PL intensity relative to either the TMD monolayer due to charge separation is a common phenomenon and was also verified in MoS₂/WSe₂⁴² (and WSe₂/MoS₂⁴³), MoSe₂/WSe₂⁴⁴ and MoTe₂/MoS₂⁴⁵ bilayer stacks. The hole transfer from the photoexcited MoS₂ layer to the WS₂ layer was

demonstrated by the absorption spectra shown in Figure 2.5e–g. Although only MoS₂ A-exciton transitions are optically excited, transient absorption spectra in the MoS₂/WS₂ heterostructure are dominated by a resonance feature (red circles in Figure 2.5e,f) corresponding to the WS₂ A-exciton transition (blue line in Figure 2.5g), which is clearly distinguishable from the resonance feature corresponding to the MoS₂ B-exciton transition in an isolated MoS₂ monolayer (green squares in Figure 2.5e,f and magenta line in Figure 2.5g). As measured by femtosecond pump–probe spectroscopy, the charge transfer was found to occur within 50 fs after the photoexcitation.⁴¹ Ceballos *et al.* also reported the charge separation and formation of indirect excitons in MoS₂/MoSe₂ heterostacks. When excitons were injected in the MoSe₂ layer, an ultrafast transfer of electrons from MoSe₂ to MoS₂ layers was proved within subpicosecond, despite the strong Coulomb attraction from the holes in the resonantly excited excitons. On the contrary, selectively injecting excitons in the MoS₂ layer led to the transfer of holes to MoSe₂ on a similar time scale. The charge transfer process was followed by the generation of spatially indirect excitons with the electrons and holes residing in separate layers. The lifetime of these indirect excitons was longer than that of the direct excitons in MoS₂ and MoSe₂ monolayers (Figure 2.5h).⁴⁶ The extended lifetime is responsible for a significant spectral broadening of the excitonic transitions compared to the individual layers in reflectance contrast measurements.⁴⁴ Moreover, Yu *et al.* showed that the interlayer exciton relaxation in MoS₂/WS₂ heterostructures is independent of the stacking epitaxy or orientation,⁴⁷ while a contradictory result was obtained by Zhang *et al.* through the investigation of epitaxially grown MoS₂/WS₂ stacks. They argued that the coupling is strongest for A–A and A–B stacking configurations corresponding to 0° and 60° lattice orientation, respectively, and attributed this to the shortest interlayer distance with the top layer S atom in MoS₂ right above the bottom W atom in WS₂.⁴⁸ However, their conclusion was drawn by comparing the heterobilayer directly grown *via* CVD approach with the transferred counterpart. It was ignored that without a proper post-transfer treatment, such as thermal annealing, the latter one

was very likely to have contaminated interface which would hinder the interlayer coupling. The annealing effects will be discussed later in more detail.

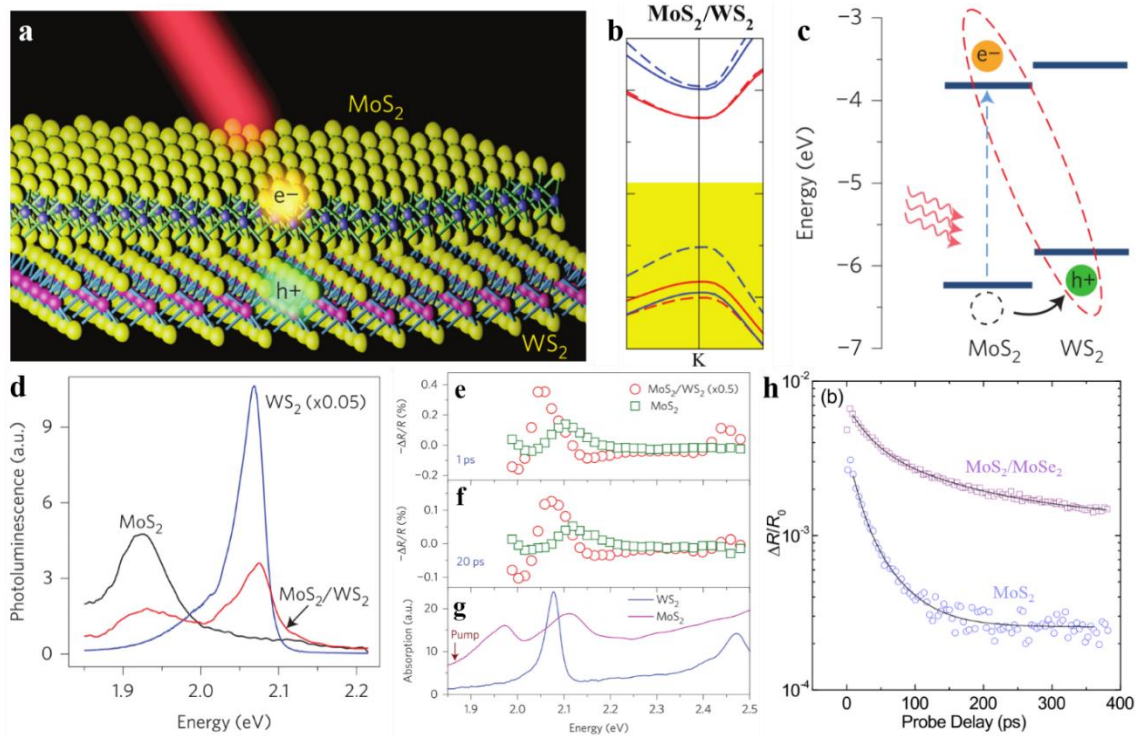


Figure 2.5. (a) Illustration of a MoS₂/WS₂ heterostructure. The electrons and holes created by photoexcitation are separated into different layers. (b) Band structures at the K point for a MoS₂/WS₂ heterostructure. (c) Schematic of the theoretically predicted type II band alignment of a MoS₂/WS₂ heterostructure. (d) PL spectra of a MoS₂ monolayer, a WS₂ monolayer and a MoS₂/WS₂ heterostructure. (e,f) Transient absorption spectra for MoS₂/WS₂ (red circles) and MoS₂ (green squares) at 1 ps and 20 ps pump–probe delays, respectively. (g) Linear absorption spectra of monolayers of MoS₂ (magenta line) and WS₂ (blue line). (h) Differential reflection signal as a function of the probe delay measured from the heterostructure (purple squares) and the MoS₂ ML (blue circles). The black lines are biexponential fits. (a,c–g) Reprinted with permission from ref. 41. Copyright Macmillan Publishers Limited 2014. (b) Reprinted with permission from ref. 37. Copyright American Physics Society 2013. (h) Reprinted with permission from ref. 46. Copyright American Chemical Society 2014.

For MoSe₂/WS₂ heterostructures, though the excitation of the MoSe₂ layer only led to interlayer charge transfer, Förster-type energy transfer was observed and claimed as the dominant relaxation pathway when the WS₂ layer was excited. The energy transfer process was mediated by strong dipole–dipole interaction between the two monolayers, with the excitons in WS₂ resonantly

exciting higher-order excitons in MoSe₂. The decay rate was estimated to be in picosecond to subpicosecond time scales, which was comparable to that of the charge transfer in similar TMD heterobilayers as aforementioned.⁴⁹

Furthermore, the interlayer coupling in TMD heterostructures is highly sensitive to the spacing between the isolated monolayers (Figure 2.6). This implies the possibility of tuning the interlayer coupling by changing the interlayer distance. Yu *et al.* indicated that close coupling could not be achieved solely *via* mechanical stacking, yet van der Waals heterostructures consisting of two interacting TMD monolayers could be obtained after a thermal annealing treatment. In this way the charge transfer was much more efficient as revealed by the significantly quenched PL intensity (Figure 2.6a) along with an improved absorption for epitaxial and annealed non-epitaxial heterostructures relative to the monolayer MoS₂, as indicated by the dashed red lines and black arrows in Figure 2.6b.⁴⁷ Tongay *et al.* reported that the degree of interlayer coupling in WS₂/MoS₂ heterobilayers could be enhanced with the anneal time. As a function of the coupling strength, the PL emission gradually evolved from an additive spectrum where the MoS₂ and WS₂ monolayers contribute individually, to a coupled spectrum where the PL was dictated by the charge transfer across the heterojunction (Figure 2.6c–e).⁵⁰ Besides, Chiu *et al.* demonstrated the transition of MoS₂/WSe₂ stacks from being uncoupled to being strongly coupled by thermal annealing (Figure 2.6f,g), which was performed in an H₂/Ar environment (atmosphere pressure; H₂:Ar = 1:4) at 300 °C for 4 h.⁴² It was also found that the interlayer interactions could be readily suppressed by intercalating dielectric layers, *e.g.*, hBN in WSe₂/MoS₂ heterobilayers, which led to reduced coupling as the layer number of hBN increased (Figure 2.6h,i).⁴³ However, the PL emission could even be enhanced *via* Förster-type energy transfer in MoSe₂/hBN/WS₂ heterostructures (Figure 2.6j). Recently, Calman *et al.* has presented the observation of indirect excitons at room temperature in van der Waals TMD heterostructures, with the MoS₂ monolayers separated by

atomically thin hBN. The lifetime of the indirect excitons was orders of magnitude longer than that of direct excitons in monolayer MoS₂, and their energy could be controlled by gate bias.⁵¹

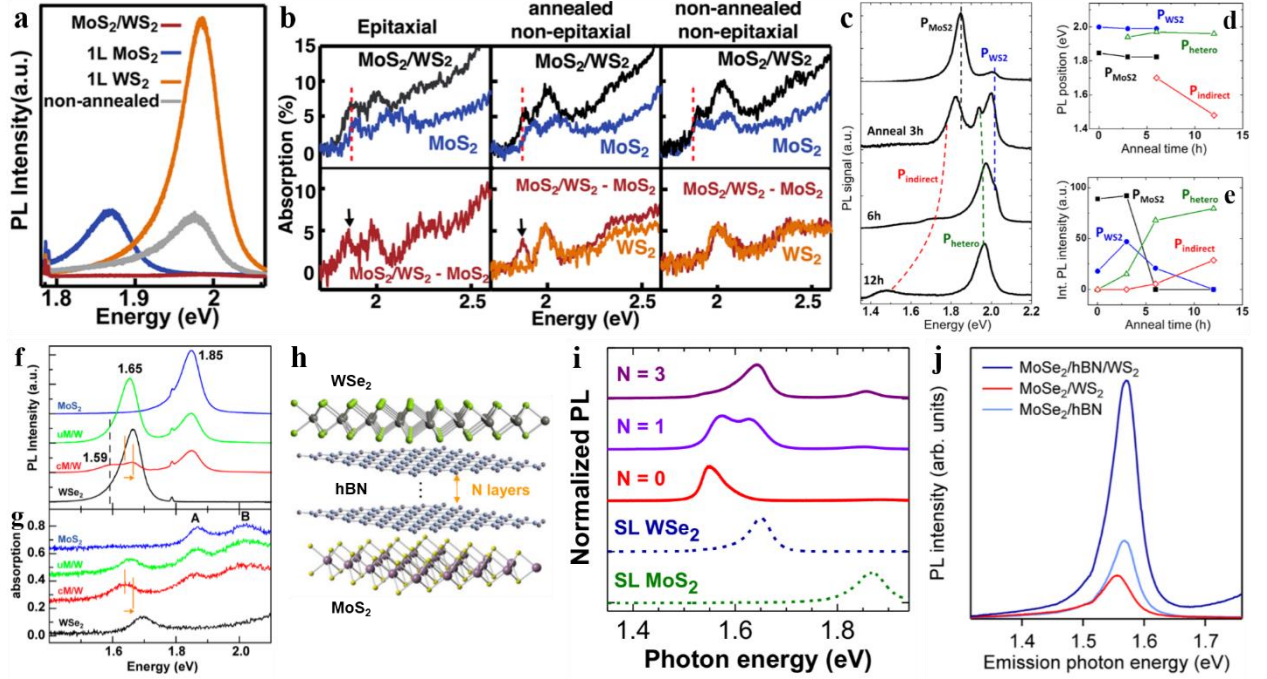


Figure 2.6. (a) PL and (b) absorption spectra (upper panel) of a MoS₂/WS₂ heterostructure along with the difference between the absorption spectra of MoS₂/WS₂ and MoS₂ (lower panel). (c) PL spectra of a transferred WS₂/MoS₂ heterostructure with different anneal times. (d) PL peak position and (e) integrated PL intensity as a function of the anneal time. (f) PL and (g) absorption spectra of a MoS₂/WSe₂ heterostructure. uM/W: non-coupled MoS₂/WSe₂; cM/W: coupled MoS₂/WSe₂. The dashed line indicates an interlayer PL emission. Orange lines and arrows: anti-Stoke shift for clarity. (h) Schematic atomic structure and (i) normalized PL spectra of WSe₂/(hBN)/MoS₂ heterostructures with increasing layers of the hBN spacer. (j) PL spectra for the MoSe₂ emission upon excitation in resonance with WS₂ A exciton emission. (a,b) Reprinted with permission from ref. 47. (c–e) Reprinted with permission from ref. 50. (f,g) Reprinted with permission from ref. 42. (a–g) Copyright American Chemical Society 2014. (h,i) Reprinted with permission from ref. 43. Copyright National Academy of Sciences 2014. (j) Reprinted with permission from ref. 49. Copyright American Chemical Society 2016.

2.4.3 Influential factors of photoluminescence

2.4.3.1 Strain

2D materials are known to be single photon emitters, which is associated with a shift of the bandgap and the formation of a potential well.^{52–56} Theoretical calculations showed that the electronic structure of semiconducting TMD monolayers could be engineered by strain, given its ability to directly change the lattice constant of TMD crystals, *e.g.*, through mechanical bending (Figure 2.7a,b). The bandgap energy would be decreased for lattice expansion whereas increased for lattice contraction (Figure 2.7c,d).^{57,58} These implied a route to control the PL emission of monolayer TMDs *via* applying strain. The strain effects have been investigated by Conley *et al.* on MoS₂. In monolayer MoS₂, the PL intensity obviously reduced with increasing uniaxial tensile strain, and the emission energy for A excitons also decreased with an approximate linear dependence (Figure 2.7e,f). The dramatic decrease in PL intensity was attributed to the direct-to-indirect bandgap transition,⁵⁹ which agreed well with the theoretical predictions.^{60,61} However, the peak related to indirect transition was not observed even under the highest strain, which could be a strong rebuttal of this argument. As regards bilayer MoS₂, both the emission energies for A exciton and indirect transition dropped linearly. However, the PL intensity was found to be unaffected under tensile strains up to 0.6%. Similar effects have been demonstrated for monolayer WS₂, except for the observation of indirect transition peak (Figure 2.7g–i). Additionally, the dissociation energy of trions was also lowered with the strain (Figure 2.7j).⁶² A recent research showed that the monolayer MoS₂ on SiO₂/Si substrate experienced a $\approx 0.3\%$ biaxial tensile strain during the CVD growth, and the A exciton and A⁻ trion peaks are both red-shifted with the biaxial strain in a linear fashion.⁶³ The biaxial tensile strain could also be controllably introduced by applying a pressure difference across suspended membranes, which enabled the investigation on large strains in monolayer MoS₂. The strain dependence of the PL intensity and PL peak position for different excitonic components are consistent with other reports, and are barely influenced by the material synthesis approach (Figure 2.7k,l).⁶⁴

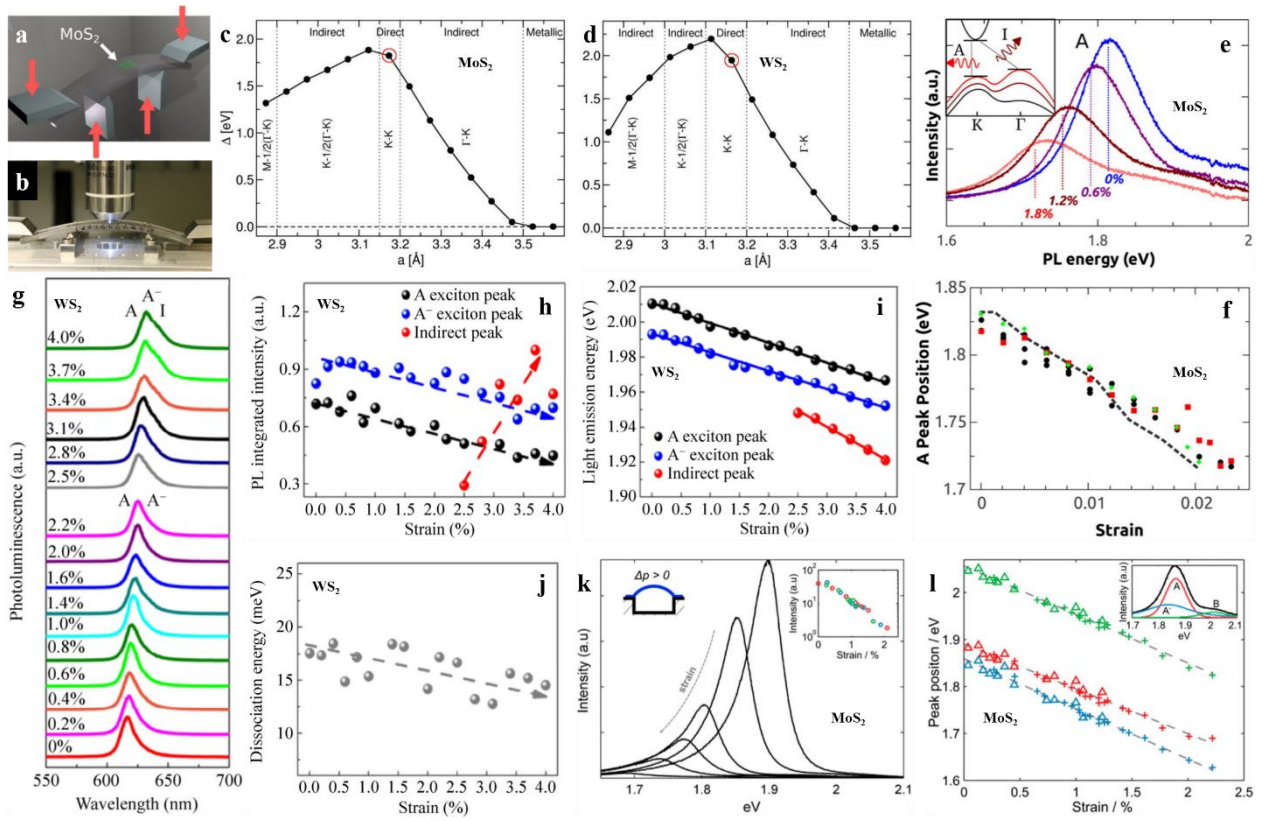


Figure 2.7. Strain effects on the PL of MoS₂ and WS₂ monolayers. (a) Schematic and (b) photograph of an apparatus to bend MoS₂. Bandgap evolution of monolayer (c) MoS₂ and (d) WS₂ subject to isotropic strains, with the red circles showing equilibrium structures. (e) PL spectra of monolayer MoS₂ under increasing uniaxial tensile strains. Inset: band structure schematic. (f) PL A peak position of monolayer MoS₂ vs. uniaxial tensile strain (colours show the three samples) along with the theoretically calculated values (dashed line). (g) Normalized PL spectra of monolayer WS₂ under increasing uniaxial tensile strains. (h) PL integrated intensities, (i) peak emission energies, and (j) dissociation energy of monolayer WS₂ vs. uniaxial tensile strain. (k) PL spectra of monolayer MoS₂ under different biaxial tensile strains. Inset: A peak intensity vs. biaxial tensile strain. (l) PL peak positions of the excitonic species in monolayer MoS₂ vs. biaxial tensile strain, where the crosses and triangles represent the CVD and exfoliated samples, respectively. (a,b,e,f) Reprinted with permission from ref. 59. Copyright American Chemical Society 2013. (c,d) Reprinted with permission from ref. 58. Copyright American Physics Society 2013. (g–j) Reprinted with permission from ref. 62. Copyright Tsinghua University Press and Springer-Verlag Berlin Heidelberg 2015. (k,l) Reprinted with permission from ref. 64. Copyright American Chemical Society 2016.

The bandgap of TMD heterostructures is also subject to strain. Based on first-principles calculations, Su *et al.* predicted that the MoS₂/MoSe₂ heterobilayers would undergo a semiconductor–metal transition and exhibit a direct bandgap by an in-plane compressive strain

ranging from 1 to 3%, while the indirect bandgap character of the MoS₂/WSe₂ system was maintained under any strain.⁶⁵ However, experimental results demonstrated that the excitonic behaviour in an epitaxially grown MoS₂/WS₂ stack varied with tensile and compressive strains (Figure 2.8a). The PL peaks for MoS₂ and WS₂ show linear red shifts with increasing tensile strain (Figure 2.8b) and linear blue shifts with increasing compressive strain (Figure 2.8c). However, the MoS₂ and WS₂ exhibit contrasting trends in the change in PL intensity under tensile and compressive strains (Figure 2.8d,e). This was ascribed to the fact that the electronic band structure transitions for the two monolayers were differently affected by the strain (Figure 2.8f,g).⁶⁶ Further, theoretical calculations showed that for both of the monolayers and the heteroregion, the strain-induced bandgap modification is similar along the zigzag and the armchair directions (Figure 2.8h).⁶⁷ For MoSe₂/WSe₂ heterobilayers, the two PL peaks observed correspond to the direct and indirect transitions, respectively (Figure 2.8i), and are both red-shifted linearly with the uniaxial tensile strain (Figure 2.8j).⁶⁸ Considering that this study only focused on the strain-induced band structure of the individual monolayers rather than of the heterobilayer, more experimental work is required to validate the role of strain in altering the type II heterojunction.

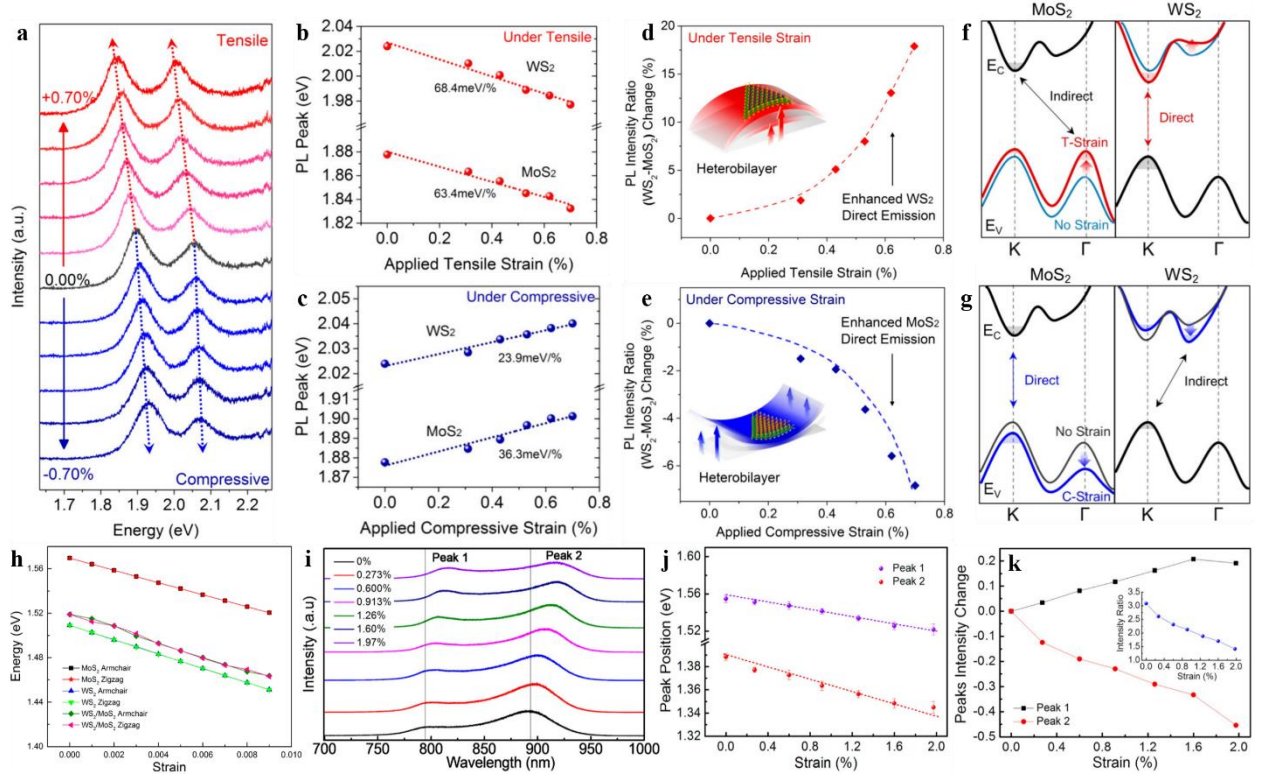


Figure 2.8. Strain effects on the PL of TMD heterobilayers. (a) PL spectra of a MoS₂/WS₂ heterobilayer under different uniaxial strains. PL peak position of the coupled MoS₂ and WS₂ monolayers in the heterobilayer vs. uniaxial (b) tensile and (c) compressive strain. The dependence of the relative PL intensity between WS₂ and MoS₂ in the heterobilayer on (d) tensile and (e) compressive strain. Schematic band structure of MoS₂ and WS₂ monolayers under (f) tensile (red) and (g) compressive (blue) strain. (h) Theoretical evolution of the bandgap of WS₂ and MoS₂ monolayers, and a WS₂/MoS₂ heterostructure under uniaxial tensile strain along zigzag and armchair directions. (i) PL spectra of a MoSe₂/WSe₂ heterobilayer showing the direct transition peak (Peak 1) and the indirect transition peak (Peak 2) under different uniaxial tensile strains. (j) PL peak positions with linear fits and (k) PL peak intensities for the direct and indirect transitions in MoSe₂/WSe₂ heterobilayer as a function of strain. Inset of panel (k): PL intensity ratio of Peak 2 to Peak 1. (a–g) Reprinted with permission from ref. 66. Copyright American Chemical Society 2017. (h) Reprinted with permission from ref. 67. Copyright American Institute of Physics 2016. (i–k) Reprinted with permission from ref. 68. Copyright American Chemical Society 2016.

2.4.3.2 Doping

Since the quantum confinement induces strong many body effects, the PL of atomically thin TMDs is very sensitive to their carrier densities. The optical properties of 2D TMDs can therefore be governed by electrical gating, as it is an effective approach to manipulate the carrier type and

density in these semiconductors. The observation of such effects is owing to the large exciton binding energy and small energy difference between the two conduction band extrema in 2D TMDs.⁶⁹ Ross *et al.* reported the electrostatic tunability of PL in exfoliated monolayer MoSe₂ via a standard back-gated FET. The neutral and charged excitons showed opposite changes in the PL intensity with varying gate voltage. At zero voltage, the PL spectrum was dominated by neutral exciton X^0 (along with X^I which was attributed to the excitons states trapped to impurities). With increasing or decreasing gate voltage, the intensity of X^0 peak decreased continuously. In contrast, another peak corresponding to the X^- or X^+ emission was enhanced, which was believed as an effect of the electrostatic charging of MoSe₂ induced by the applied bias (Figure 2.9a–c). The PL peak position increases with reducing temperature, and interestingly, the peak separation of trion was observed from ≈ 130 K.⁷⁰ Similar trends are displayed by monolayer WSe₂, while the changes in both the intensity and binding energy of X^- show higher rates than X^+ (Figure 2.9d).⁷¹

The electric field effects of MoS₂ were studied at room temperature using a FET based on exfoliated monolayer MoS₂. However, the PL intensity presents different response toward gate voltage compared to monolayer MoSe₂. The emission intensity of neutral exciton emissions decreases monotonically with the gate bias though a reaching the saturation of electrons at 50 V, while the trion emission intensity remains almost the same. The total PL intensity followed the trend of the neutral exciton (Figure 2.9i,j). Additionally, the split of X^0 and X^- peaks was also observed at low temperature.⁷² Moreover, Shang *et al.* reported similar observations for the X^0 peak and total PL intensity in exfoliated monolayer WS₂, while that of X^- reduces slightly when a negative or positive gate voltage was applied (Figure 2.9f,g). With the change from negative to positive gate voltage, the photon energy of X^0 increases yet that of X^- decreases, and the dissociation energy of X^- is enhanced at an increasing rate (Figure 2.9h). It is notable that the CVD monolayer WS₂ shows decreasing PL intensity but the photon energy keeps constant when the gate voltage varies from -40 to $+40$ V (Figure 2.9e).⁷³ Therefore it is likely that the excitonic

properties of TMDs against gate bias basically rely on the chalcogen element, *e.g.*, S or Se). This could result from the fine difference in the band structure, but to confirm, more systematic studies are required. In addition, the binding energy of charged excitons was found to increase with the gate voltage, presumably caused by quantum-confined stark effect.⁷⁴ Further increase in the vertical electric field can even tune the bandgap of TMDs, which could be reduced or even closed by applying sufficiently high electric field, as predicted by the theoretical calculations.^{75–78} Bilayer TMDs would behave differently from the monolayers. In addition to the lower photon energy of bilayer WS₂, the PL intensity was enhanced whereas that of monolayer WS₂ was quenched under a lateral electric field (Figure 2.9k,l). In spite of this, the PL variation in both monolayer and bilayer TMDs could derive from the transfer of photoexcited electrons from one conduction band extremum to another, modifying the resultant recombination pathways.⁶⁹

Similarly, the PL emission of 2D TMDs can also be modified *via* functionalization methods. Charge transfer between TMDs and electron donor or acceptor can effectively tune the PL emission, which have been realized in earlier studies by chemical doping.^{79–83}

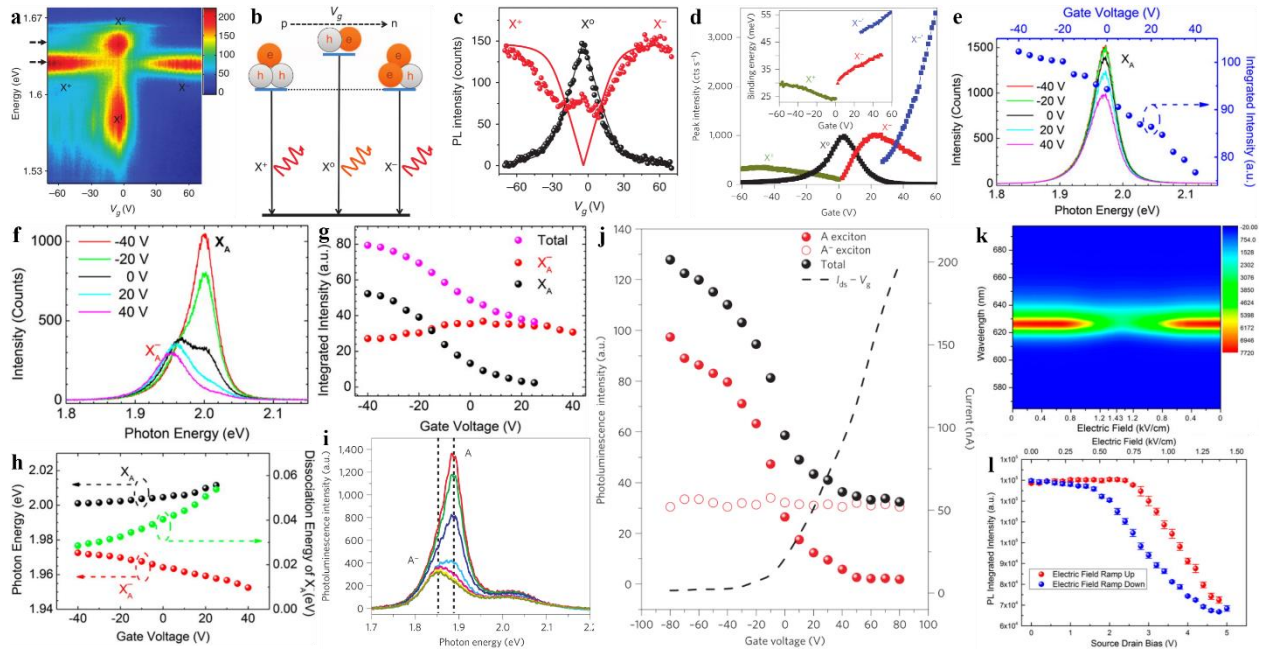


Figure 2.9. Effects of electric field on the PL in monolayer TMDs. (a) PL map (colour scale in counts) as a function of back-gate voltage. Neutral excitons (X^0), impurity-trapped excitons (X^1), negative excitons

(X^-), and positive excitons (X^+) are indicated. (b) Schematic of the gate-dependent excitons and trions and their transitions. (c) Fitted PL intensity curves for the exciton and trion vs. gate voltage at the dashed arrows in panel (a). (d) PL intensity of the exciton and trion vs. gate voltage. Inset: trion binding energy vs. gate voltage. (e) PL spectra of CVD monolayer WS_2 at different back-gate voltages (left axis) and integrated PL intensity (right axis) vs. gate voltage (upper axis). (f) PL spectra of exfoliated monolayer WS_2 at different back-gate voltages. (g) Emission energies of X_A and X_{A^-} (left axis) and dissociation energy of X_{A^-} (right axis) vs. gate voltage. (h) Integrated intensities of X_A , X_{A^-} , and the total emission vs. gate voltage. (i) PL spectra in monolayer MoS_2 at different back-gate voltages. (j) Drain–source current (right) and integrated PL intensities of A and A^- and their total contribution (left) in monolayer MoS_2 vs. gate voltage. (k) PL map of monolayer WS_2 under a lateral electric field. (l) Integrated PL intensity of monolayer WS_2 vs. lateral electric field. (a–c) Reprinted with permission from ref. 70. (d) Reprinted with permission from ref. 71. (a–d) Copyright Macmillan Publishers Limited 2013. (e–h) Reprinted with permission from ref. 73. (i,j) Reprinted with permission from ref. 72. Copyright Macmillan Publishers Limited 2012. (k,l) Reprinted with permission from ref. 69 (e–h, k, l) Copyright American Chemical Society 2015.

2.4.3.3 Structural disorders

Considering that single-photon emissions can be observed from localized excitons in 2D materials,^{52,55,56,84} the PL emission of TMDs is also affected by the structural configurations, including defects, grain boundaries (GBs), *etc.* For monolayer MoS_2 , two types of GBs showed different PL emissions. As proved by the PL mapping, the PL emission intensity was doubly enhanced at the tilt GB. In contrast, the PL intensity was clearly quenched at the mirror twin GB. The distinct PL response between the two kinds of GBs was found to depend on the local doping because of the different structural configurations. In mirror GB, the dominant structures are 8-4-4 defects (the number of atoms in a ring) and are rich in metal atoms, leading to n-type doping and thereby PL quenching. On the contrary, the atomic structures are dominated by the sulphur-rich 5-7 defects in the tilt GB, which therefore resulted in p-type doping and PL enhancement (Figure 2.10a–c).⁸⁵

It was reported that the edges of CVD-grown monolayer WS_2 could show non-uniform PL compared with the central regions. The PL mapping of a monolayer WS_2 single crystal clearly indicates the spatial dependence of PL emission. At the WS_2 edges, the PL intensity showed dramatic

enhancement, and the peak position was greatly red-shifted (Figure 2.10d). Further study attributed the PL enhancement and red shift of the peak at domain edges to the formation of biexcitons. This was confirmed by the superlinear dependence of the PL peak intensity for the biexcitons on excitation power (Figure 2.10e). It was also found that a thermal annealing treatment of the sample led to quenching in the PL peak intensity with a blue shift (Figure 2.10f), which was mainly due to the decreased A^- and AA peaks but increased A^0 peak as revealed by the peak deconvolution. The narrowed PL peak of the annealed sample was explained by the resultant dominance of A^0 peak.⁸⁶

Cracks in monolayer TMDs also exhibit distinct PL. It was reported that the crack generated by thermal annealing showed PL enhancement in monolayer MoS_2 .⁸⁷ Apart from the p-type doping induced by the adsorbed oxygen at the cracks, this was also due to the decreased non-radiative decay rate, as the PL intensity of the crack showed little dependence on the temperature. Surprisingly, the PL peak position of the crack regions was also independent of the temperature despite the negative temperature dependence of semiconductor bandgaps, which may suggest that different physical origins should account for the PL upon changing temperatures.

Other defects also have an impact on the PL emission of 2D TMDs, such as sulphur vacancies. The methods to create defects in the TMDs include and controlling the environment and applying oxygen plasma. For instance, the monolayer WS_2 can be made defective through exposure to water vapour under vacuum. Another peak originating from defects was observed at lower energy apart from the peak corresponding to excitons and trions. As revealed by the systematic temperature-dependent PL measurements, this peak was associated with the bound excitons being trapped by surface impurities, which led to a highly localized state for the excitons. Such defects-related excitons were expected to be trapped by either shallow or deep potentials.⁸⁸ Alternatively, defects in monolayer WS_2 were generated by oxygen plasma treatment, which gave access to investigating the dependence of PL on the defect density (Figure 2.10 h,i).⁸⁹ The spectral weight of the PL component arising from defects increased linearly with the plasma time after 15 s. The defects activated

photoluminescence was also observed in monolayer MoS₂, MoSe₂, and WSe₂, with significant peaks for bound excitons at a cryogenic temperature of 77 K. Also, the bound exciton (X_B) and free exciton (X₀) emissions are enhanced with the increase in irradiation dose, as indicated by the black arrows in Figure 2.10g.⁹⁰ It was noted that the absorption of gas species would only occur at the original defect sites, such as S vacancies.^{89,90} The binding energy of the localised excitons in monolayer MoS₂ was found to have a low binding energy of 20 meV.⁹¹ These studies indicate that the PL of monolayer TMDs is highly sensitive to its surrounding atmosphere.

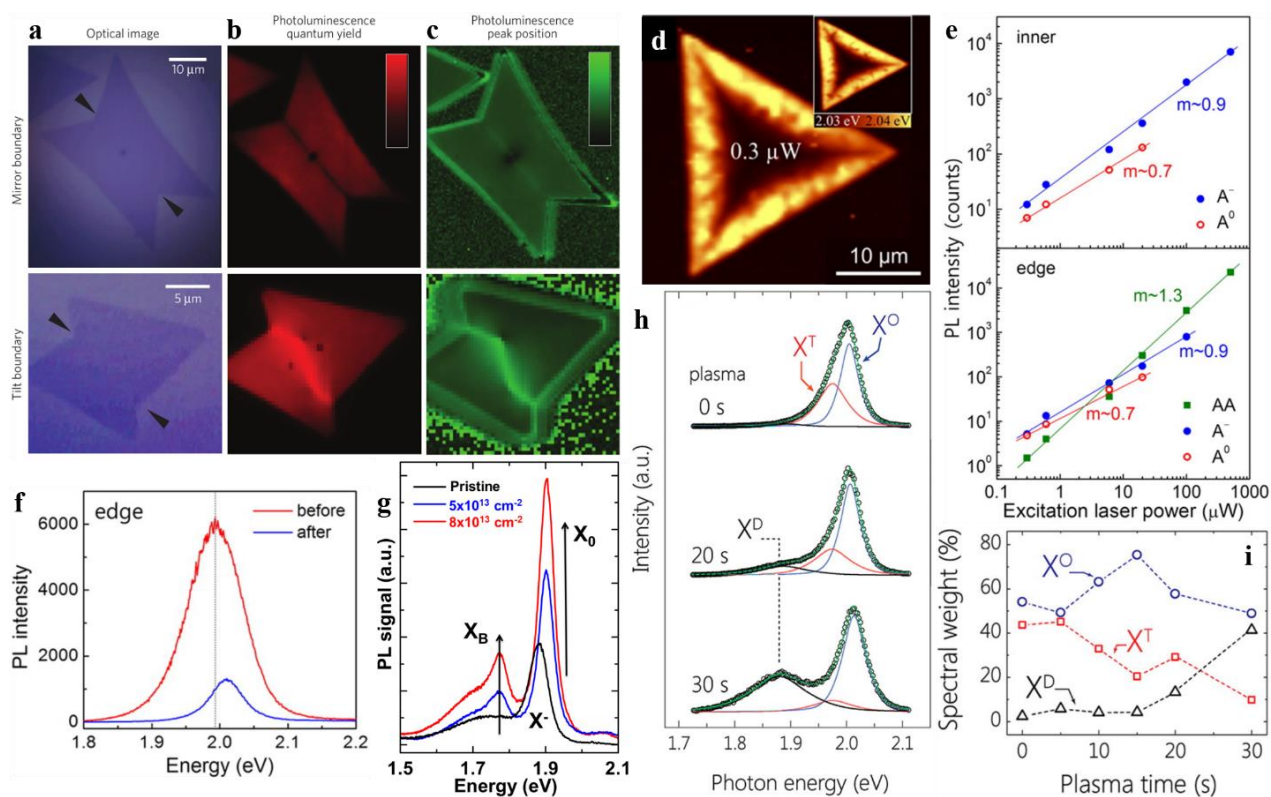


Figure 2.10. (a) Optical microscopic images, (b) PL QY map, and (c) PL peak position map with colour scale 1.82–1.87 eV of MoS₂ islands containing a mirror boundary (upper panel) and a tilt boundary (lower panel). (d) PL intensity map of a monolayer WS₂ domain at 0.3 μW excitation power. Inset: the corresponding PL peak position map. (e) PL peak intensities of neutral excitons (A⁰), trions (A⁻), and biexcitons (AA) vs. excitation power. Solid lines: power fits; m values: numeric powers. (f) PL spectra of the edge of monolayer WS₂ before and after heat treatment. (g) PL spectrum of monolayer MoS₂ at different irradiation doses. (h) Normalized PL spectra of monolayer WS₂ vs. plasma treatment time. (i) Spectral contributions of the exciton species vs. plasma treatment time. (a–c) Reprinted with permission from ref. 85. Copyright Macmillan Publishers Limited 2013. (d–f) Reprinted with permission from ref. 86. Copyright American Chemical

2.4.3.4 Excitation power

The interactions between excitons are ignorable when the excitation density is sufficiently low, known as the linear optical response regime, while high excitation power would induce many-body effects in 2D TMDs owing to the enhanced quantum confinement.² However, sublinear dependence of exciton density on the laser power was found, as the decay channel could be changed at high excitation fluence. This may be indicative of exciton–exciton interactions. Since the lifetime of excitons varies with the decay channel, the radiative pathways of excitons can be probed by time-resolved photoluminescence (TR-PL) measurements. A new decay component with much shorter lifetime appeared with increasing excitation power in monolayer WS₂. This was attributed to an exciton–exciton annihilation process, where the emission energy relating to the recombination of one exciton is transferred non-radiatively to another exciton.⁹² Further increase in the excitation power causes enhanced density of the excitons and shortens the average distance between them. Therefore the wave functions of two excitons can overlap and fuse together, so that a four-body with higher energy (*i.e.*, biexciton) is formed, leading to a new feature in the PL spectra of 2D TMDs.⁹³ In this case, one of the excitons would decay radiatively and emit a photon with energy smaller than a normal exciton due to the binding energy of biexciton, while the other exciton would return to its original energy state and decay as a normal exciton. Shang *et al.* reported the first observation of biexcitons in monolayer WS₂. Figure 2.11a shows the low-temperature PL of monolayer WS₂ at three different excitation powers. Two main features were observed in the PL spectra at low excitation power. The high-energy peak corresponded to the emissions of both excitons and trions, and the low-energy peak was attributed to localized states (LS) resulting from the surface adsorbates. At high power excitation, the spectral weight of LS

was reduced while there appeared a new peak between LS and trion in energy. Figure 2.11b presents the power dependence of the peak intensity corresponding to excitons, trions, LS, and biexcitons. Both the exciton and the trion exhibited linear power dependence, and the LS was sublinearly dependent on the excitation power. Notably, the biexciton peak presented a quadratic power dependence.⁷³ Nonetheless, it is worth mentioning that this rule is not applicable to all excitation power regimes. A more general rule is a quadratic relationship between the PL intensities of biexciton and exciton.^{94,95} The binding energy of biexciton can be obtained by calculating the difference in the PL emission energy between excitons and biexcitons. Atomically thin TMDs have been demonstrated to possess large biexciton binding energies, *e.g.*, ≈ 36 meV for bilayer WS₂⁹⁵ and 52 meV for monolayer WSe₂⁹⁶. The stability of biexcitons has also been studied at different temperatures. It was found that the biexciton emission intensity in monolayer WSe₂ started to diminish greatly above 40 K, suggested an increasing dissociation rate with temperature.⁹⁶ The biexciton population decay dependent on temperature was also observed in bilayer WS₂, where the dissociation energy was estimated to be ≈ 26 meV.⁹⁵ However, Kim *et al.* reported the biexciton emission at room temperature. Moreover, the edges were demonstrated to be preferential sites for biexciton generation, attributed to the large amount of charge carriers from the excessive growth promoters. However, this was inconsistent with the conventional knowledge indicating that only neutral excitons participate in the biexciton formation process. Another contradictory observation was the enhanced emission of biexcitons under positive gate bias, which led to a larger ratio of charged to neutral excitons.⁸⁶ Both these experimental findings raise a question about how the biexciton form in monolayer TMDs. Although theoretical work predicted that the biexciton in monolayer TMDs can be made up of a trion and a hole,⁹⁷ more experiments are necessary to confirm this argument.

2.4.3.5 Temperature

It is known that the electronic structure of semiconductors is highly sensitive to the lattice temperature.⁹⁸ Given the bandgap shrinkage for TMDs at elevated temperature, their PL emission is possible to be tuned *via* temperature control. More specifically, the dependence of the TMD bandgap on the temperature is described by an empirical equation:

$$E_g(T) = E_g(0) - S\hbar[\coth\left(\frac{\hbar\omega}{2kT} - 1\right)]$$

, where $E_g(T)$ is the bandgap at temperature T , $E_g(0)$ is the bandgap at 0 K, $\hbar\omega$ is an average phonon energy, and S is a dimensionless coupling constant.⁹⁸ Considering that the exciton binding energy is barely affected by the temperature, this equation is also applicable to describe the PL emission energy.

Tongay *et al.* studied the temperature dependence of PL in monolayer TMDs, including MoS₂ and MoSe₂. The PL intensity was gradually reduced and the peak was broadened with the increase in temperature (Figure 2.11c). These phenomena are typically attributed to the exponential enhancement in the nonradiative electron–hole recombination process, which decreases the probability of radiative transition. The PL peak also displays red shift as a function of temperature. The reduction in bandgap was because of the increased electron–phonon interactions as well as the slightly decreased bonding length. For bilayer MoS₂ and WS₂, the emission energies of the direct A and B excitons and indirect excitons varied differently with the temperature. While the A and B peaks are red-shifted, I peak shows a blue shift as the temperature increases. These spectral shifts were likely to be interpreted by two reasons, which were the lattice constant increase induced by thermal expansion and the enhanced electron-phonon coupling. DFT calculation showed that the lattice constant change was responsible for the temperature dependence of the indirect bandgap, whereas the temperature dependence of the direct bandgap should be ascribed to the enhanced electron–phonon coupling. Not only the emission energy, but also the emission QY is influenced by the temperature. Due to the increased non-radiative rate at

higher temperatures, the PL intensity quenching is observed for monolayer and few-layer MoS₂,⁹⁹ monolayer MoSe₂,¹⁰⁰ and monolayer WS₂ (Figure 2.11d,e).⁶⁹ However, opposite temperature dependence was displayed by multilayer MoSe₂, with the PL intensity being enhanced at higher temperature. This could be due to layer decoupling as a result of the lattice expansion along *c*-axis. The discrepant trends for few-layer MoS₂ and MoSe₂ might stem from their distinct differences between the direct and indirect bandgap. Unlike the well-separated indirect and direct gaps in bilayer MoS₂, the indirect and direct bandgaps in few-layer MoSe₂ would become degenerate when the interlayer spacing increased.¹⁰⁰ For CVD-grown MoS₂/WS₂ heterobilayers, the overall PL intensity also increases with the decrease in temperature. More specifically, due to the lattice contraction upon being cooled, both the peaks for MoS₂ and WS₂ exhibit obvious blue shifts (1.89 eV for MoS₂ and 2.02 eV for WS₂ at 77 K). Additionally, smaller full width at half maximum (FWHM) of the MoS₂ PL peak is observed at low temperatures. This could be explained by the suppressed acoustic phonon scattering, which causes a linear decrease in the FWHM of PL peak with reducing temperature. An extra peak at ≈ 1.94 eV was noted in the low-temperature PL spectra, which should arise from the recombination of interlayer carriers. The recombination efficiency is much weaker at room temperature as this peak can hardly be seen at 300 K (Figure 2.11f).⁴⁸

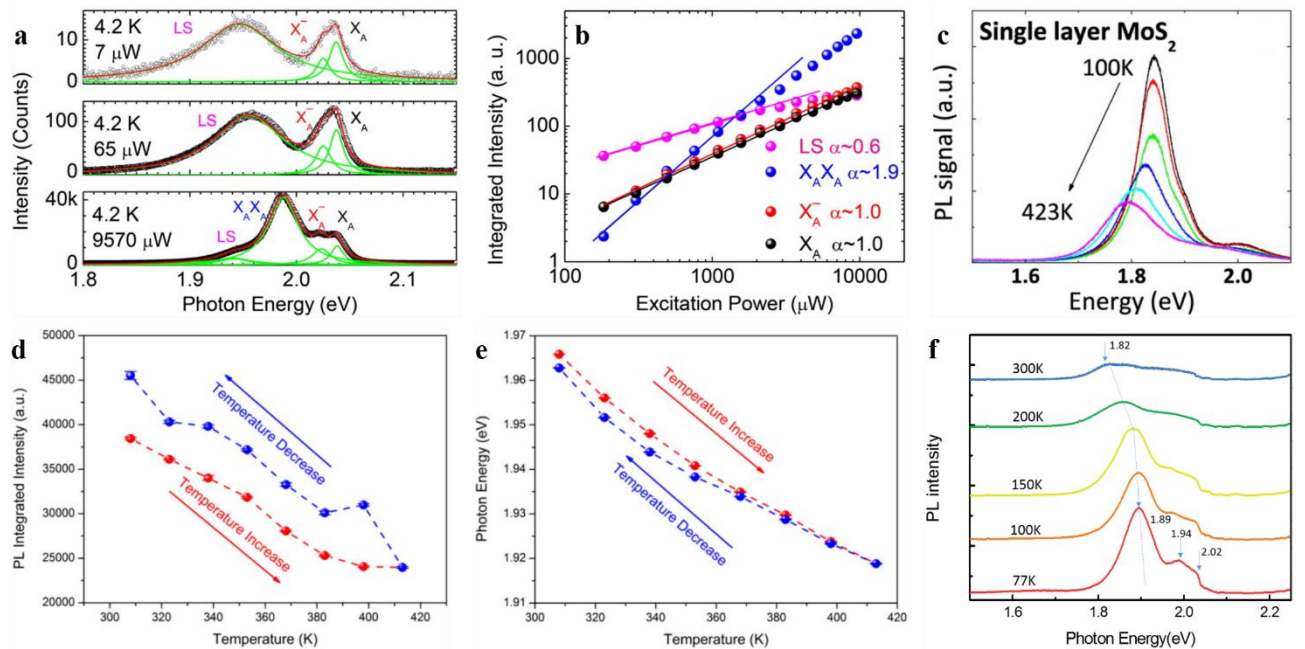


Figure 2.11. (a) PL spectra of monolayer WS₂ at different excitation powers at 4.2 K, where the red and green curves represent the total fits and subpeaks for exciton (X_A), trion (X_A⁻), biexciton (X_AX_A), and localised states (LS), respectively. (b) Log-log plots of integrated PL intensities of the four emission components vs. excitation power. Solid curves: linear fits; α values: slopes. (c) PL spectra of monolayer MoS₂ under increasing temperatures. (d) Integrated PL intensity and (e) PL photon energy of monolayer WS₂ vs. temperature. (f) PL spectra of CVD-grown MoS₂/WS₂ heterobilayer under different temperatures. (a,b) Reprinted with permission from ref. 73. (c) Reprinted with permission from ref. 100. Copyright American Chemical Society 2012. (d,e) Reprinted with permission from ref. 69. (a,b,d,e) Copyright American Chemical Society 2015. (f) Reprinted with permission from ref. 48. Copyright Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim 2016.

2.5 Vibrational properties

The vibrational properties of MoS₂ and WS₂ associated with their phonon dispersions have been calculated by *ab initio*,¹⁰¹ and those of MoS₂ have been investigated experimentally by Raman spectroscopy.¹⁰² Raman spectroscopy is non-destructive technique to explore the structural and vibrational properties of TMDs. It relies on the inelastic scattering of materials of monochromatic light. More specifically, when a monochromatic light source illuminates on a sample, the majority of the light is elastically scattered, which has the same energy with the excitation source. This is known as Rayleigh scattering. Nonetheless, some of the light is inelastically scattered with a different energy due to its interactions with the vibrational atoms of the sample. Raman spectroscopy records the intensity of this inelastically scattered light and the corresponding frequency shift with respect to the incident light source, and thereby offering identification and quantitation of materials. For atomically thin TMDs, E_{2g}^1 and A_{1g} are the two typical Raman signatures.¹⁰² Although both of these peaks are related to intralayer lattice vibration modes, the A_{1g} mode corresponds to the out-of-plane lattice vibration in which metal atoms stay still and two chalcogen atoms move perpendicularly against the atomic plane in opposite direction, while the E_{2g}^1 mode corresponds to in-plane vibration where two chalcogen atoms and metal atom move in the opposite direction within the atomic plane.

The E_{2g}^1 and A_{1g} Raman peaks of MoS₂ are located at $\approx 382\text{ cm}^{-1}$, and $\approx 406\text{ cm}^{-1}$, respectively (Figure 2.12a). The A_{1g} mode is much more affected by the long-range interlayer Coulombic interactions with its neighbouring materials, compared to the E_{2g}^1 mode. Therefore, the A_{1g} peak frequency of MoS₂ would be greatly shifted in varied environment, while leaving the E_{2g}^1 peak frequency nearly unchanged. Consequently, the lattice strain, doping type, and doping level can be indicated by the Raman peak positions. As regards the doping of MoS₂, the A_{1g} mode is more sensitive than the E_{2g}^1 mode as a result of the strong interaction between electrons and phonons.^{103–107} For n-type doping, a red shift of the A_{1g} peak position is observed with a larger peak width when the dopant concentration increases (Figure 2.12e,f).¹⁰⁴ Hence this offers a route to uncover the substrate-induced doping in the TMD adlayers.¹⁰³

The strain in MoS₂ can instead be reflected by the E_{2g}^1 peak.^{59,108,109} A red or blue shift would occur for the E_{2g}^1 peak under a tensile or compressive strain, while the A_{1g} peak is barely affected (Figure 2.12g,h). However, large tensile strain ($>0.8\%$) can cause a E_{2g}^1 peak split, which may arise from the breaking of the crystal symmetry.⁵⁹

The relative Raman peak positions are widely used to determine the layer number of MoS₂. For decreasing layer thickness, the A_{1g} peak shows a red shift as the lower van der Waals forces results in a smaller effective restoring forces on atoms. On the contrary, the E_{2g}^1 peak undergoes a blue shift, which originates from the long-range Coulomb interlayer interactions that enhances the dielectric screening or the in-plane configuration change due to the stacking effects. The frequency difference of monolayer MoS₂ ranges from 17.5 to 21.0 cm^{-1} . This value increases with the MoS₂ thickness, till it reaches 25.2 cm^{-1} for the bulk material (Figure 2.12b). Besides, the integrated intensities of the two Raman peaks and the ratio between them are also dependent on the layer thickness of MoS₂, with the monolayer showing a E_{2g}^1/A_{1g} ratio of ≈ 1 (Figure 2.12c). The line widths of these Raman modes for different MoS₂ layer numbers are presented in Figure 2.12d.¹⁰²

The second-order Raman signature of TMDs can be revealed upon resonant excitation. Figure 2.12i shows the Raman spectrum of monolayer WS₂. The most prominent peak in the spectrum lies at 352 cm⁻¹, which was interpreted as the second-order mode of longitudinal acoustic (LA) phonons at the Brillouin zone edge. The strong 2LA(M) response is believed to arise from the doubly resonant Raman process involving resonant vertical electronic excitation and the scattering of two phonons with opposite momentum in a conduction band with particular shape. The 2LA(M) mode is hence tightly related to the band structure, and the intensity ratio of 2LA(M) to A_{1g} was found to be correlated with the layer number of TMDs.¹¹⁰

Although two methods have been developed to identify the layer number of TMDs, *i.e.*, the frequency difference between E_{2g}¹ and A_{1g} modes, and the intensity ratio of 2LA(M) to A_{1g}, they both have drawbacks. The peak position difference between the two Raman modes can be affected by many other factors, including doping and strain as aforementioned; the use of the 2LA(M) mode is limited to WS₂ because achieving double resonance in other TMDs would require laser with particular wavelength which is not always feasible. Recently, the interlayer Raman signature at low frequencies starts to attract research interest and is believed to be a more efficient indicator of the TMD layer number. The low-frequency Raman spectra of MoS₂ also vary with the layer number, where two vibration modes can be observed, *i.e.*, layer breathing mode (LBM) and shear mode (SM). They describe the perpendicular and in-plane movements of the atomic plane with the adjacent layers moving in opposite directions and show strong dependence on the layer number.¹¹¹

Furthermore, the Raman spectra of vertical heterobilayers typically show additive peaks from both of the monolayers. Figure 2.12j is an example in which the WS₂/MoS₂ stack exhibits four peak, corresponding to WS₂ 2LA(M)+E', WS₂ A₁', MoS₂ E', and MoS₂ A₁' Raman modes.

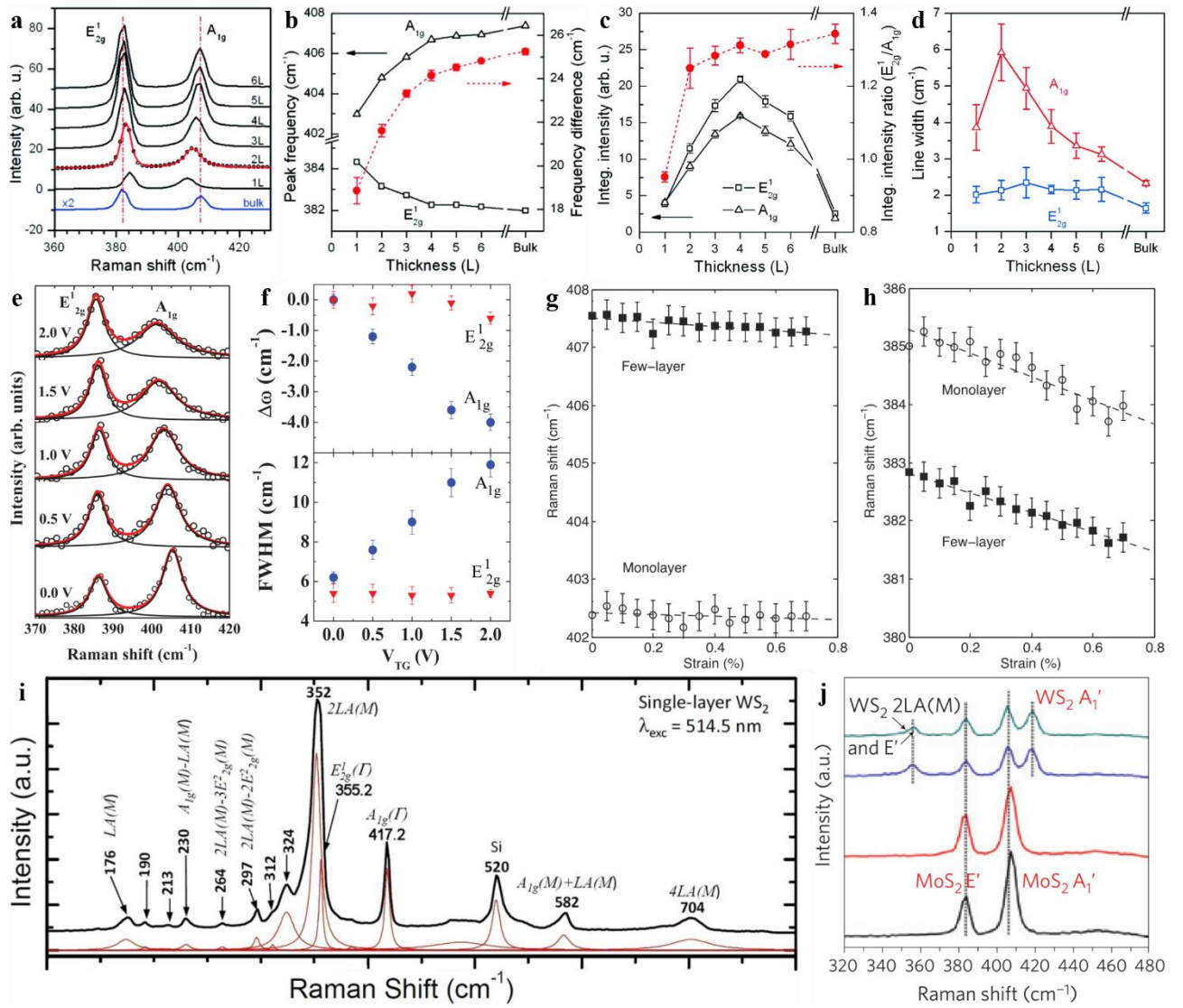


Figure 2.12. (a) Raman spectra of MoS₂ with different layer numbers. Dependence on the MoS₂ layer thickness of (b) E_{2g}^1 and A_{1g} Raman mode frequencies and their difference, (c) integrated intensity of E_{2g}^1 and A_{1g} Raman modes and their ratio (E_{2g}^1/A_{1g}), and (d) line widths of the two Raman modes. (e) Raman spectra of monolayer MoS₂ at different top-gate voltages (V_{TG}). (f) Change in the phonon frequency $\Delta\omega$ and FWHM of the two Raman modes vs. V_{TG} . Frequency of the (g) A_{1g} and (h) E_{2g}^1 Raman modes of monolayer and few-layer MoS₂. (m) Raman spectra of monolayer WS₂ with Lorentzian fits. (n) Raman spectra of monolayer MoS₂ and WS₂/MoS₂ heterobilayers at two different positions (from bottom to top). The dashed lines show the positions of the MoS₂ and WS₂ Raman peaks. (a–d) Reprinted with permission from ref. 102. Copyright American Chemical Society 2010. (e,f) Reprinted with permission from ref. 105. Copyright American Physics Society 2012. (g,h) Reprinted with permission from ref. 109. Copyright American Physics Society 2013. (i) Reprinted with permission from ref. 110. Copyright Nature Publishing Group 2013. (j) Reprinted with permission from ref. 112. Copyright Macmillan Publishers Limited 2014.

2.6 Electrocatalytic properties

Great potential has been shown by TMDs as alternative materials to noble metals for hydrogen generation *via* the electrolysis of water.¹¹³ Specifically, MoS₂ exhibits good catalytic behaviour in hydrogen evolution reactions (HER). This is basically attributed to the fact that the hydrogen adsorption free energy (ΔG_H) of MoS₂ edges is as low as ≈ 0.1 eV, which is close to that of platinum (Pt) and demonstrates the facilitated processes of H* adsorption and H₂ desorption. On another hand, the exchange current density of MoS₂ edge sites is comparable to those of noble metals, giving rise to a higher electron transfer rate and kinetic HER activities.

Theoretical work has predicted some key points in optimizing the HER performance of monolayer TMDs.^{114,115} Till now, a number of strategies have been developed to increase the HER catalytic activities, such as by generating extra active sites,^{116–118} increasing the conductivity of the nanosheets,¹¹⁹ heteroatom doping,¹²⁰ and so on. Additionally, the effect of supports on the hydrogen adsorption free energy of MoS₂ has been investigated using DFT. It was found out that for the Mo-terminated MoS₂, strong adhesion to the support would result in a weaker hydrogen binding energy, suggesting that the catalytic activity at the Mo-edge could be tuned by choosing the support.¹²¹

As for HER, the reactive sites in MoS₂ include the edge sites and sulphur defects. Figure 2.13b presents the surface sites on a 2H-phase MoS₂ nanosheet. The edge sites marked by green balls are catalytically active while the basal plane sites marked by blue squares are inert for HER. The geometric and electrochemically active surface areas are also indicated. Rougher surfaces normally have more available edge sites and thus higher catalytic activity per projected geometric surface area, and the catalysts in which the basal planes are oriented perpendicular to the surface should also show enhanced activities. The number of edge sites exposed has been directly correlated to the HER activities in non-continuous MoS₂ nanosheets,¹²² with the exchange current density increasing linearly with the MoS₂ edge length (Figure 2.13a), so that increasing the edge site density is an effective method to improve the electrocatalytic performance of MoS₂. This has been executed by

growing designed MoS₂ structures, such as MoS₂ nanoflowers^{123,124}, nanoplatelets (Figure 2.13c),^{125,126} dendrites (Figure 2.13d),¹²⁷ and vertically aligned layers (Figure 2.13e)¹²⁸. Typically, the number of active sites can be optimised by controlling the preparation temperature of MoS₂ (*e.g.*, Figure 2.14j).^{126,127,129} Large amounts of MoS₂ edge sites could also be attained *via* the synthesis on highly porous scaffolds (Figure 2.13e). In this regard, conductive support is desired for an efficient electrical communication between the catalytic edge sites and the underlying electrode.^{130–135} The interactions of MoS₂ with the matrix will be discussed later.

Earlier studies have also found that different polymorphs of MoS₂ exhibit distinct HER activities. Apart from the domain edges, the electrochemically active sites on 1T-MoS₂ also include the basal plane, while it is inert for 2H-MoS₂, limiting its role in HER. Figure 2.13h,i present that the 1T phase MoS₂ (1T-MoS₂) shows improved HER performance compared to the 2H phase MoS₂ (2H-MoS₂), and is less sensitive to the edge oxidation because of the large amount of reactive sites in its basal plane.^{134,136} In addition, the Nyquist plots obtained by electrochemical impedance spectroscopy (EIS) reveal that the metallic 1T-MoS₂ has a lower intrinsic resistance than the semiconducting 2H-MoS₂ (Figure 2.13j), which can facilitate the electron transfer in the HER process. The edge oxidation leads to a higher in-plane resistance of both the 1T- and 2H-MoS₂, observed as the relatively larger *x*-axis intercept at the high frequency region, but the charge transfer resistance is much more increased for 2H-MoS₂, indicated by the larger radius of the semiarc at the low frequency region. The transition of MoS₂ from 2H to 1T phase has been realized, whereby the hopping efficiency of electrons in the vertical direction is increased.^{123,137} Improvements could be made through introducing sulphur defects as additional catalytic sites for the HER along with a strain. The combination of S vacancies and uniaxial tensile strain is illustrated in Figure 2.13g. This is particularly useful for the continuous region of 2H-phase MoS₂ to activate its basal plane. The defect engineering is feasible through several strategies.^{116–118,138–140} For instance, Li and Tsai *et al.* treated the CVD-grown MoS₂ with Ar/H₂ plasma to generate numerous S vacancies.¹³⁹ It was confirmed that the free energy of hydrogen proton

absorption on MoS₂ surface decreases with the increasing number of the in-plane S vacancies (Figure 2.14a,b), and the applied strain further tunes the HER activity (Figure 2.14c).^{138,139} Cracks in monolayer 2H-MoS₂ could be created by O₂ plasma or H₂ annealing (Figure 2.14h,i). The increment in edge sites allows an improved HER performance (Figure 2.14j). Figure 2.14d,e show that the individual and combined effects of S vacancy and uniaxial tensile strain in CVD-grown monolayer 2H-MoS₂. The strained MoS₂ with S vacancies exhibits the best performance, suggesting that these two factors have synergistically contribute to the enhancement in the HER activity. However, high S-vacancy density accompanied by a large tensile strain would give rise to a low stability (Figure 2.14c). Li *et al.* further investigated the quantitative relationship between the density of S vacancy and the HER activity of monolayer 2H-MoS₂ (Figure 2.14f,g). The largest S-vacancy density of 14% corresponds to a reduced HER activity compared to that in the range of 7–10%, which may stem from the compromised crystalline quality close to the S vacancies. To deeply understand the kinetic behaviour of S vacancies, Li and Du *et al.* employed scanning electrochemical microscopy to systematically investigate their roles in enhancing the HER activity. As revealed by the calculation results, the electron transfer rate is increased by 4 times with the involvement of S vacancies.¹⁴¹

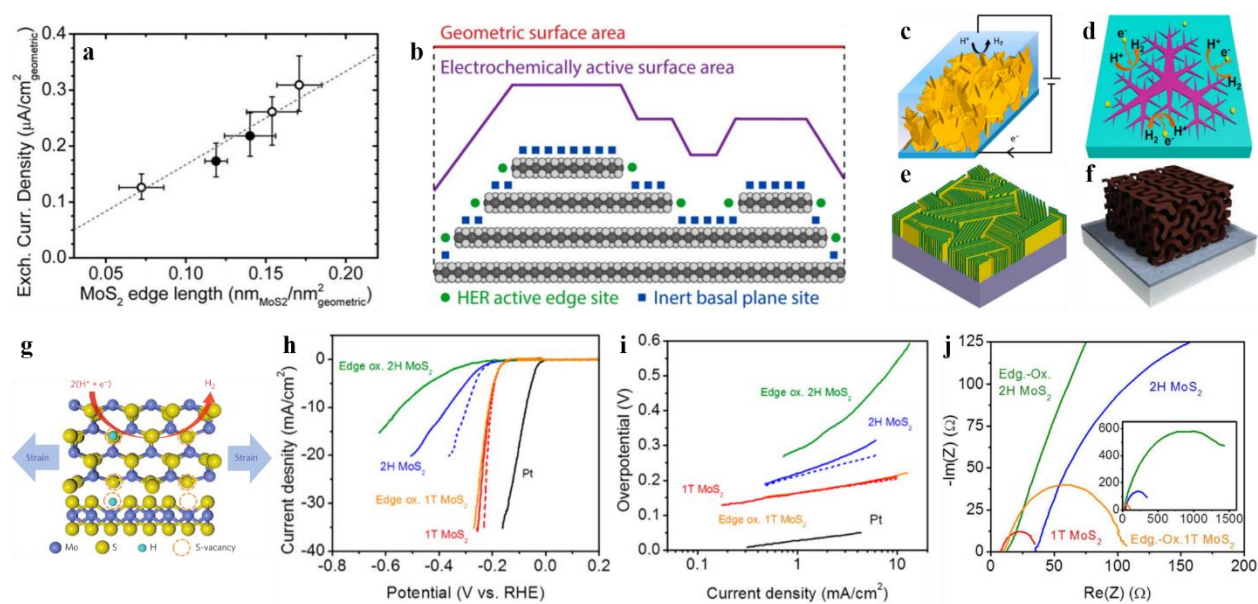


Figure 2.13. HER activities of MoS₂. (a) Exchange current density vs. MoS₂ edge length, in which the open and filled circles represent the samples annealed to 400 and 550 °C, respectively. (b) Schematic diagram of

the catalytically active surface area and projected geometric surface area for 2H-MoS₂. Schematics of MoS₂ (c) nanoplatelets, (d) dendrites, (e) vertically aligned layers, and (f) mesoporous structure. (g) Schematic of the top (upper panel) and side (lower panel) views of MoS₂ with strained S vacancies on the basal plane. (h) Polarization curves of 1T- and 2H-MoS₂ nanosheets before and after edge oxidation. Dashed lines: *iR*-corrected polarization curves. (i) Tafel plots obtained from the LSV curves in panel (h). (j) Nyquist plots of 1T- and 2H-MoS₂ before and after oxidation. (a) Reprinted with permission from ref. 122. Copyright American Association for the Advancement of Science 2007. (b) Reprinted with permission from ref. 136. (c) Reprinted with permission from ref. 126. Copyright American Chemical Society 2016. (d) Reprinted with permission from ref. 127. (b,d) Copyright American Chemical Society 2014. (e) Reprinted with permission from ref. 128. (f) Reprinted with permission from ref. 135. Copyright Macmillan Publishers Limited 2012. (g) Reprinted with permission from ref. 139. Copyright Macmillan Publishers Limited 2016. (h–j) Reprinted with permission from ref. 134. (e,h–j) Copyright American Chemical Society 2013.

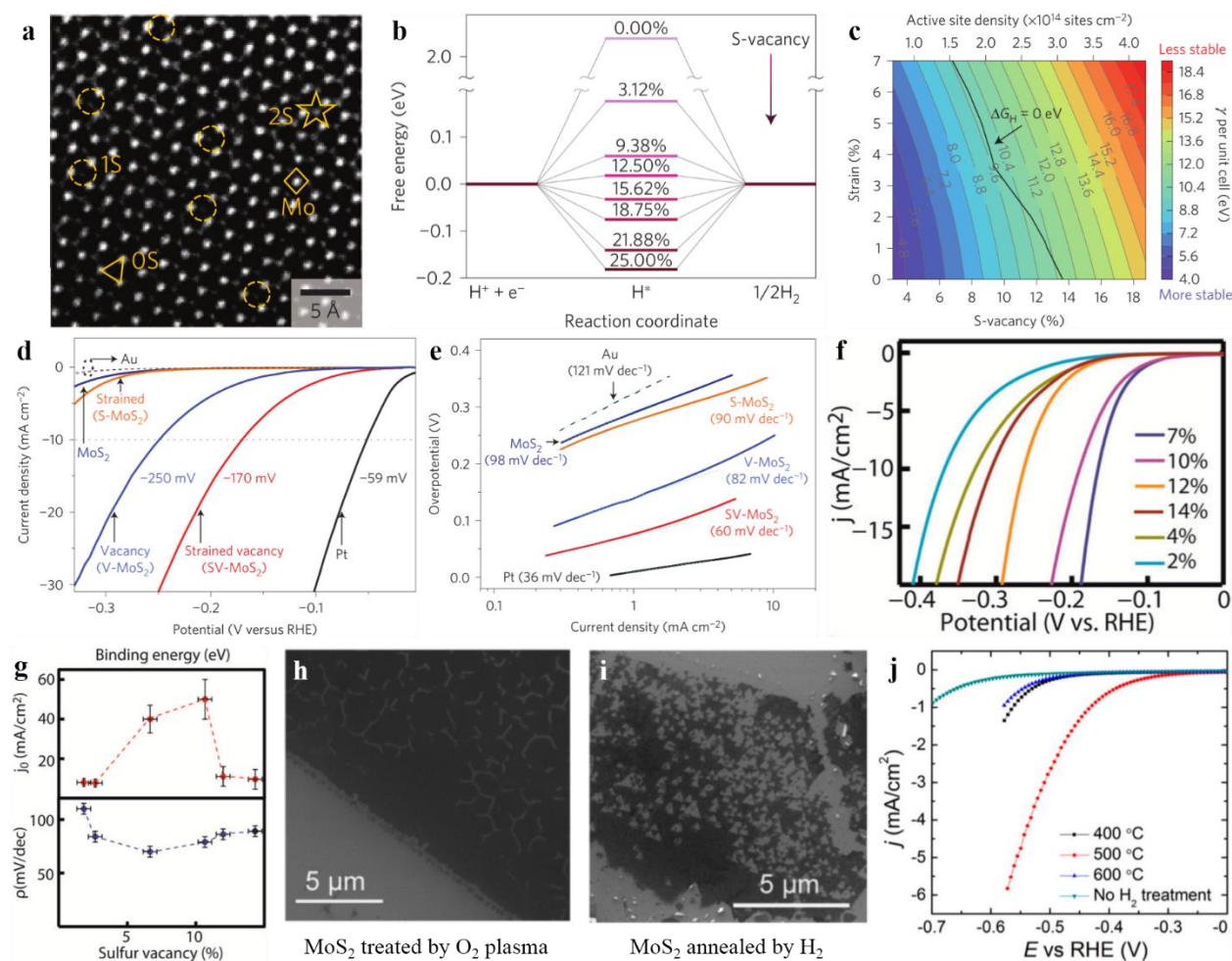


Figure 2.14. HER activity of CVD-grown monolayer 2H-MoS₂. (a) ACTEM image of an unstrained MoS₂ monolayer with ≈11.3% S-vacancy. Rhombus dots: Mo atoms; star: two atoms (2S); dotted circle: a single S atom below the Mo plane (1S); triangle: zero S atoms (0S). (b) Free energy vs. reaction coordinate of HER for

different densities of the S-vacancy. (c) Coloured contour plot of surface energy per unit cell γ (with respect to bulk MoS₂) vs. S-vacancy and uniaxial tensile strain. (d) LSV curves for the Au substrate, Pt electrode, as-transferred MoS₂ (0% strain and 0% S vacancies), strained MoS₂ without S vacancies (S-MoS₂), unstrained MoS₂ with S vacancies (V-MoS₂), and strained MoS₂ with S vacancies (SV-MoS₂). The labelled potential values correspond to current density of 10 mA cm⁻² (dotted line). (e) Corresponding Tafel plots of the LSV curves in panel (d). (f) Polarization curves of MoS₂ films with different S-vacancy densities. (g) Exchange current densities (upper panel) and Tafel slopes (lower panel) of MoS₂ films vs. the S-vacancy density. SEM images of the MoS₂ (h) treated by O₂ plasma and (h) annealed by H₂. (j) Polarization curves of MoS₂ for different H₂ annealing temperatures. (a–e) Reprinted with permission from ref. 139. Copyright Macmillan Publishers Limited 2015. (f,g) Reprinted with permission from ref. 116. (h–j) Reprinted with permission from ref. 118. (f–j) Copyright American Chemical Society 2016.

Recently, a field effect modulation method was launched for a lower contact resistance between the electrode and the catalyst, which could promote the injection of electrons into the active sites. By applying a gate voltage of 5 V to an HER device based on individual MoS₂ nanosheet, the overpotential decreases to 38 mV, which is comparable to that of Pt (Figure 2.15a,b). This reflects the fast electron transfer, resulting from the Fermi level of the n-type MoS₂ shifted towards the bottom of the conduction band under the positive electric field.¹¹⁹ Figure 2.15c,d, show that the electrocatalysis of MoS₂ is also dependent on its layer number, as a result of the electron hopping over an interlayer potential barrier (0.119 V). This also implies that monolayer MoS₂ is more capable than few-layer MoS₂ as a catalyst in HER.¹⁴²

Apart from the use of individual TMDs for HER, 2D heterostructures have shown advantages including fast charge transfer, flourish surface electron state, and low contact resistance. The HER performance of TMD semiconductors is very likely to be further enhanced through the combination with conducting materials, such as carbon-based nanomaterials and metals.^{113,130–133,143–145} For example, Shi *et al.* first grew monolayer MoS₂ on highly conductive Au foils by LPCVD method. In this work the improved catalytic performance was allowed by the strong electron coupling between MoS₂ and the conductive substrate.¹⁴⁴ Tang *et al.* reported the design and synthesis of 3D mesoporous

graphene/n-doped MoS₂ vertical heterostructures *via* a two-step CVD method.¹³⁰ The modified morphology, interface, and edge sites led to an increased rate for the HER. Another powerful approach was assembling the individual TMDs into an alloy, exemplified by the rGO/W_xMo_{1-x}S₂ heterostructures showing an onset potential of 96 mV and a Tafel slope of 38.7 mV dec⁻¹ in the HER (Figure 2.15f,g), and a high stability was demonstrated (Figure 2.15i). The high reactivity observed in W–Mo alloys, compared to pure WS₂ and MoS₂ phases, was attributed to the lowering of the activation energy barrier in HER. The bandgap of both the pristine TMDs and the W_xMo_{1-x}S₂ alloy was decreased due to the interlayer electronic-coupling with rGO, and the density of states (DOSs) calculations suggesting high electron mobility indicate the role of rGO in improving the conductivity (Figure 2.15e). The EIS results in Figure 2.15h show that the electric resistance of the rGO/W_xMo_{1-x}S₂ is between those of the rGO/WS₂ and rGO/MoS₂.¹⁴⁶

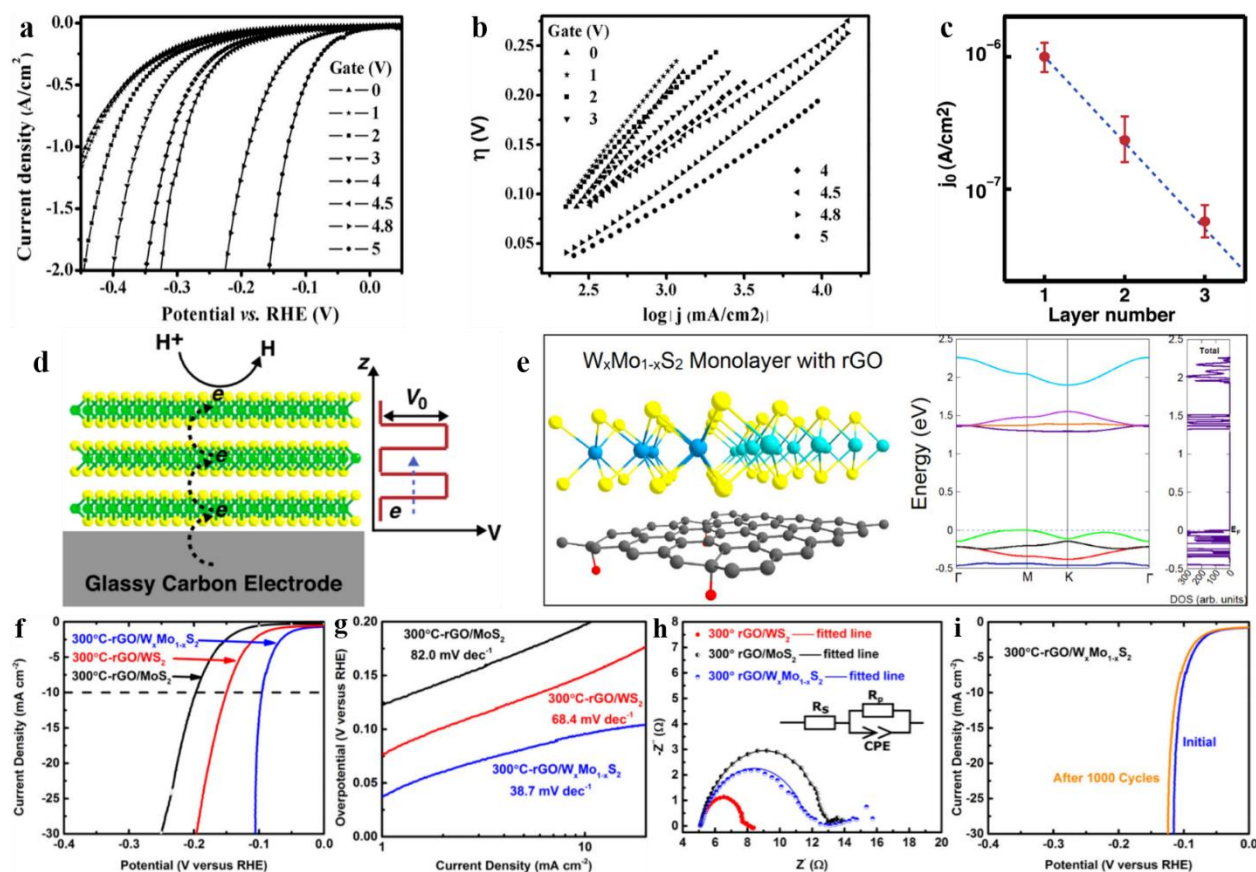


Figure 2.15. (a) Polarization curves of MoS₂ nanosheets at different back-gate voltages. (b) Corresponding Tafel plots of the LSV curves in panel (a). (c) Exchange current density (logarithmic scale) of MoS₂ films as a function of layer number with a linear fit. (d) Electron hopping in the vertical direction of MoS₂ layers. The

right side illustrates the potential distribution in the multilayer film and the hopping of electrons through the potential barrier in the interlayer gap. (e) Effect of alloying on the band structure and DOSs of an rGO/W_{0.4}Mo_{0.6}S₂ heterostructure. (f) Polarisation curves, (g) the corresponding Tafel plots, and (h) Nyquist plots of the 300 °C-annealed films on glassy carbon with the fitting circuit in the inset of panel (h). (i) Polarisation curves of the 300 °C-annealed rGO/W_xMo_{1-x}S₂ film on glassy carbon at the first cycle and after 1000 cycles. (a,b) Reprinted with permission from ref. 119. Copyright Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim 2017. (c,d) Reprinted with permission from ref. 142. Copyright American Chemical Society 2014. (e–i) Reprinted with permission from ref. 146. Copyright American Chemical Society 2017.

On the basis of these methods, advances of the HER performance for 2D materials have been achieved in several aspects, namely a lower onset potential, higher current density, and smaller Tafel slope. Notwithstanding, more efforts are required for the practical electrocatalysis of TMDs, such as extending the range of electrolytes. Utilising seawater beyond acid solutions would be a straightforward and environmental protective way for hydrogen generation.

2.7 CVD synthesis

Till now, a variety of methods have been developed for producing 2D TMDs, such as hydrothermal synthesis,^{147,148} mechanical^{1–3,102,149–151} and liquid-phase exfoliation,^{152–155} and physical vapour deposition (PVD).^{156,157} Notwithstanding, limitations shown by these approaches include small domain size, low throughput, poor quality, hard control over the layer number, and strict requirements on the experimental conditions. Considering the demand for fundamental study and future industrial uptake, chemical vapour deposition (CVD) is the most advantageous technique in many aspects, such as the high yield, high quality of the products, controllable growth for large area films with a desired thickness, and so on.¹² The CVD synthesis of MS₂ (M = Mo or W) can be generalised into two routes. Route I is based on solid-state reactions. In most cases, the M or M oxide is deposited on the substrate surface prior to a sulphurisation process for conversion into MS₂. In contrast, only gaseous precursors are utilized in route II, where the precursors are

vaporized before they are transported to the substrate region and form MS_2 . Large-area, high-quality and uniform monolayer MS_2 is achievable by route II.^{158–160} Its advantages over route I include the better control on the introduction of precursors, the more thorough reaction in the vapour phase, the more tailorable growth recipe, and the less complicated fabrication process. Compared to low pressure CVD (LPCVD), the reaction under atmospheric pressure CVD, *i.e.*, APCVD, is preferable because it sets a lower standard for the growth apparatus. The prospect of TMD applications may lie with the CVD approach providing access to the wafer-scale production of single crystalline monolayers. This section recapitulates the CVD growth of monolayer MS_2 and related heterostructures. The emphasis is put on route II, as it is the method utilised in my DPhil projects.

2.7.1 CVD synthesis of TMD monolayers

The first attempt of growing monolayer MS_2 through route I was accomplished by Zhan *et al.*, using the setup in Figure 2.16a. An atomically thin Mo layer was deposited on SiO_2 by electron beam evaporation, after which it was sulphurised into MoS_2 films. As shown in Figure 2.16c, most areas (dark grey) of the synthetic products are few-layer MoS_2 , while the area marked by an arrow (light grey) is mono- or bilayer MoS_2 .¹⁶¹ Following this method, Laskar *et al.* grew monolayer MoS_2 on sapphire at elevated temperature. The selection of crystalline substrate and increased sulphurisation temperature led to higher crystallinity of the resulting MoS_2 .¹⁶² Even though this technique offered an opportunity for large-area synthesis of MoS_2 , the film uniformity fully relied on the pre-deposition of the Mo layer. Taking this into consideration, a recent work improved the growth of MoS_2 by exploiting soda-lime glass as the substrate, though still with the conventional precursors of Mo foil and sulphur. A 6-inch uniform MoS_2 monolayer film consisting of $>400\ \mu\text{m}$ large domains was obtained within a short time of 8 min. The high efficiency and high uniformity were due to the

homogenously distributed sodium catalysts on the glass substrate. In addition, an etching-free transfer process was developed relying on the hydrophilicity of the glass.¹⁶³

Apart from transition metal, transition metal oxides (MO_x) could also been implemented for the production of MS_2 through sulphurisation. For instance, MoO_2 microcrystals were employed by Wang *et al.* as a growth template. The adopted CVD system is presented in Figure 2.16b. The MoO_3 precursor was first deposited on SiO_2/Si substrate *via* thermal evaporation, which was then reduced by S vapour into MoO_2 . Further sulphurisation of the crystalline MoO_2 gave birth to MoS_2 with the layer thickness varying with the reaction time. Allowed by the relatively weak adhesion between MoS_2 and MoO_2 , the resulting MoS_2 layer was peeled off after the reaction and transferred onto any substrate. The MoS_2 prepared by 3 h annealing and post-growth transfer is displayed in Figure 2.16d.¹⁶⁴ Subjected to the MoO_2 crystals that were isolated and small, this method would not be viable for producing continuous films with large domain size. Moreover, the crystallinity of MoS_2 was inevitably damaged in the transfer process. The thermal evaporation technique was then quickly developed for the growth of monolayer WS_2 domains *via* sulphurisation of WO_3 atomic layers pre-deposited on a SiO_2/Si substrate. Similar to the set-up in Figure 2.16b, the reaction proceeded at atmospheric pressure.²⁸ Despite the increased yield and good crystallinity of the as-grown WS_2 (Figure 2.16f,g), the continuity over large area was compromised (Figure 2.16e), which could be due to the low uniformity of the as-deposited WO_3 layer. These studies indicate that thermal evaporation technique raises a dilemma on weighing between the thickness and continuity of the resulting TMD films.

Concerning this issue, atomic layer deposition (ALD) technique was used as a renovation for the metal-oxide deposition. As a distinctive CVD approach, the ALD involves a cyclic flow of precursors pulsed into the growth chamber, between which an inert gas is additionally exploited to separate two or more different reactions. The as-derived WO_3 thin films had controllable thickness and large-scale uniformity. More specifically, the WO_3 film was obtained by the gas-phase reaction

between O_2 plasma and W-based species through an ALD process. Gaseous H_2S was then introduced to sulphurise the WO_3 , till it was fully transformed into WS_2 continuous film with large area and high quality. By tuning the number of the ALD cycles, the thickness of the WS_2 product was accurately tailored from mono- to few-layer over a wafer scale (Figure 2.16h–m).¹⁶⁵ Notwithstanding, reactive substrates are essential for the deposition of WO_3 and the reactants in the ALD are not very accessible, which would limit the scope of application.

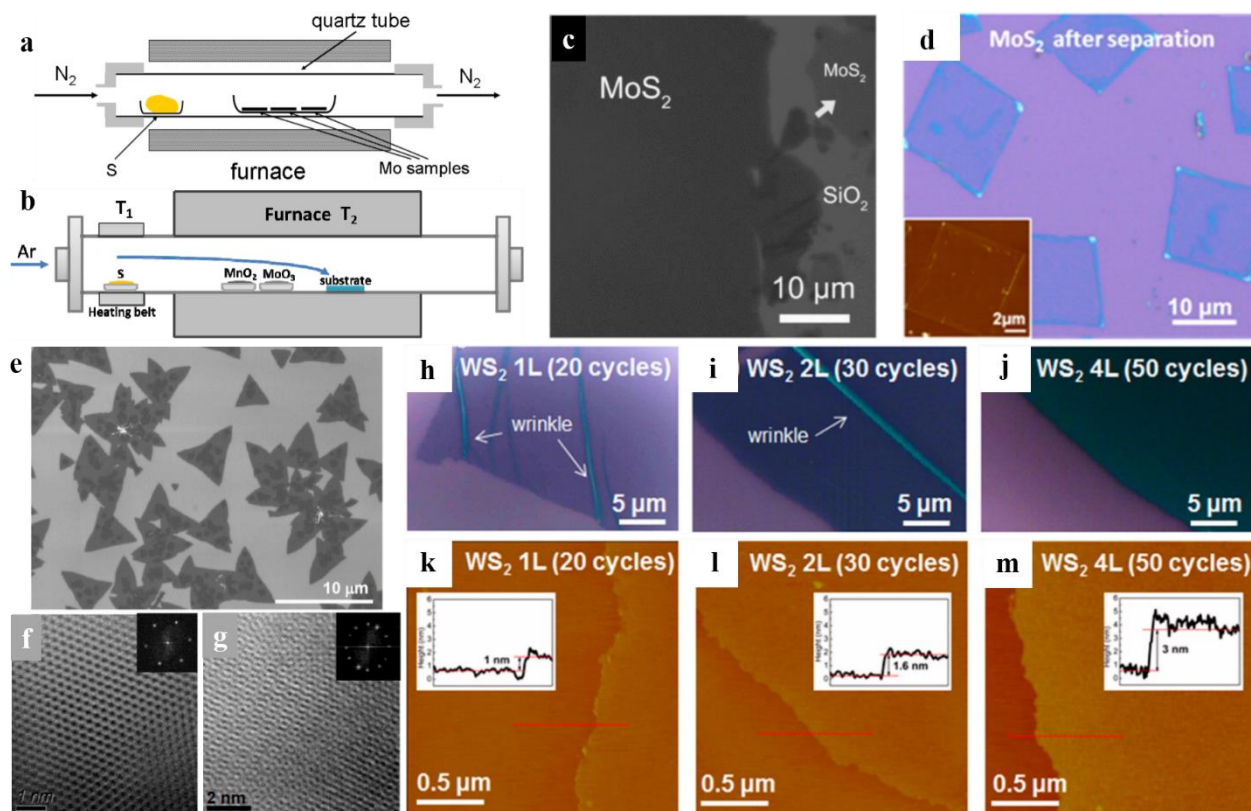


Figure 2.16. CVD synthesis of MoS_2 . (a,b) Schematics of the CVD setups, where S and Mo (a) and MoO_3 (b) were employed as the original precursors, and the resulting MoS_2 thin layers are shown in the optical microscopic images in (c) and (d), respectively. (e) SEM image of the CVD-grown WS_2 using S and WO_3 as the precursors. HRTEM images of the (f) monolayer and (g) bilayer regions in panel (e). (h) Monolayer, (i) bilayer, and (j) four-layer WS_2 derived from the WO_3 precursor pre-deposited by ALD technique, with the corresponding AFM images and height profiles (insets) shown in (k–m), respectively. (a,c) Reprinted with permission from ref. 161. Copyright Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim 2012. (b,d) Reprinted with permission from ref. 164. (e–g) Reprinted with permission from ref. 28. (h–m) Reprinted with permission from ref. 165. (b,d–m) Copyright American Chemical Society 2013.

In terms of route II, the APCVD growth of monolayer MoS₂ with both the precursors of MoO₃ and S reacting in the vapour phase was initiated by Lee *et al.* The substrate of either SiO₂/Si or sapphire was placed face-down over the MoO₃ powder, and was pre-treated with seed promoters, *e.g.*, aromatic molecules, which helped to enhance the wettability of the substrate surface for high throughput and served as nucleation sites in the reaction to facilitate the production of MoS₂. It was believed that the gaseous MoO₃ was first reduced by the S vapour into an intermediate compound, MoO_{3-x}, which then reacted with S to form 2D MoS₂ on the substrate surface. The growth occurred at a relatively low temperature in flowing nitrogen (N₂). Star-shaped MoS₂ domains with a lateral size of ≈ 160 nm formed around the seed crystals, which merged into form monolayer to few-layer regions. The as-prepared MoS₂ was used to fabricate FET devices, where it exhibited n-type behaviour due to the interactions with the substrate during the growth.¹⁶⁶ This work is followed by modifications of the seed promoters. The typical CVD setup and temperature programming process are shown in Figure 2.17a,b, respectively. By using PTAS seeding promoter, highly crystalline and uniform MS₂ monolayers with larger domain size of ≈ 50 μ m were obtained (Figure 2.17c,d). This seeding strategy also expanded the range of applicable substrates, including three-dimensional (3D) corrugated substrates (*e.g.*, quartz, sapphire, Si, mica, *etc.*) and 2D substrates (graphene, hBN, *etc.*), as presented in Figure 2.17e–i.^{167–169} To avoid seeding with foreign substances, Najmaei *et al.* managed to use the MoO₃ precursor as the growth initiator. In lieu of using the powder form, the MoO₃ was dispersed into highly crystalline nanoribbons *via* hydrothermal reactions and applied onto a SiO₂/Si substrate. The resulting domains have monolayer thickness with a sharp-edged triangular morphology and a domain size of ≈ 10 μ m. They also systematically investigated the different factors affecting the growth. It was shown that the domain morphology is mainly determined by the relative concentration of S, while the nucleation density is mainly attributed to the relative concentration of MoO₃. The MoS₂ was found preferentially nucleate in the proximity of structural imperfections, such as edges, scratches, and rough surfaces. This encouraged the idea

of patterning the substrate to create heterogeneous sites with a particular shape, which can thereby navigate the nucleation of MoS₂ into designated positions and promote the growth into continuous films.¹⁷⁰ Given the contamination and defects introduced by the seeds, high cleanness and flatness of the substrate surface were believed to be crucial for attaining high-quality monolayer MoS₂. By employing ultraclean SiO₂/Si substrates as well as fresh precursors in an APCVD process, van der Zande *et al.* synthesised monolayer triangular MoS₂ domains with large lateral sizes up to $\approx 120\ \mu\text{m}$.⁸⁵

One of the disadvantages of the approaches mentioned above is that the concentration gradient of MoO₃ changed greatly on the facing-down substrate, so that the sample did not have uniform thickness, nucleation density or domain size. More importantly, the MoO₃ and S vapours interacted before reaching the substrate and their concentrations were quenched as the reaction proceeds, which restricts the control on the growth. Thus for industrial uptake, a stable and controllable supply of the gaseous precursors is necessary to grow large-area uniform MoS₂ films. This was realized by Zhang *et al.* by loading the two precursors separately (Figure 2.17j). A SiO₂/Si chip was placed horizontally with its face up, and LPCVD method was utilized for the growth. Continuous polycrystalline MoS₂ monolayer was produced on a centimetre scale, where the self-terminated growth mechanism ensured a homogenous film thickness (Figure 2.17k,l).¹⁷¹ Another demonstration was provided by Ji *et al.*, while fluorophlogopite mica (KMg₃AlSi₃O₁₀F₂) crystal was employed as the substrate in the LPCVD. Again, the independent temperature control of the precursors contributed greatly to the formation of centimetre-scale uniform MoS₂ monolayer. In addition, the newly-prepared mica substrate was also found vital for the monolayer growth, thanks to its chemical inertness, atomic flatness, and hexagonally arranged lattice structure. The impact of substrate was also noticed in this study. The MoS₂ grew epitaxially on the crystalline mica substrate, based on the good lattice alignment between them. The resulting domains show two preferential orientations with a 180° twist (indicated by the dashed rhombic in Figure 2.17i), while in-plane strain still existed due to the

small lattice mismatch of $\approx 2.7\%$.¹⁶⁹ The growth of centimetre-scale monolayer MoS₂ film was also developed by Wang *et al.* Owing to the vertical placement of the SiO₂/Si with respect to the gas flow, the concentration gradient of the precursor vapours was relatively stable across the entire substrate surface, leading to a high uniformity of the MoS₂ film, even under atmospheric conditions.¹⁷²

The CVD synthesis of MoS₂ was also realized by other types of precursors. Yu *et al.* used molybdenum chloride (MoCl₅) and S as the precursors in LPCVD. Uniform MoS₂ films were grown on the substrates of SiO₂/Si and sapphire. The film thickness of either monolayer or bilayer could be tailored by adjusting the experimental parameters, such as the amount of MoCl₅, the chamber pressure, and the reaction temperature. As a ‘gas phase reaction-precipitation’ process, the growth was believed to follow a self-limiting mechanism, where the interaction between the MoS₂ and its substrate played an important role.¹⁷³ Instead of Mo-based solids, Michail *et al.* used sodium molybdate (Na₂MoO₄) solution as the Mo precursor, which is non-toxic and eco-friendly in contrast to MoO₃ and MoCl₅. Two growth regimes were achieved by controlling the concentration of the Na₂MoO₄ solution pre-deposited before the APCVD process, *i.e.*, homogeneously distributed monolayer MoS₂ domains at low concentration or continuous MoS₂ films at high concentration.⁶³

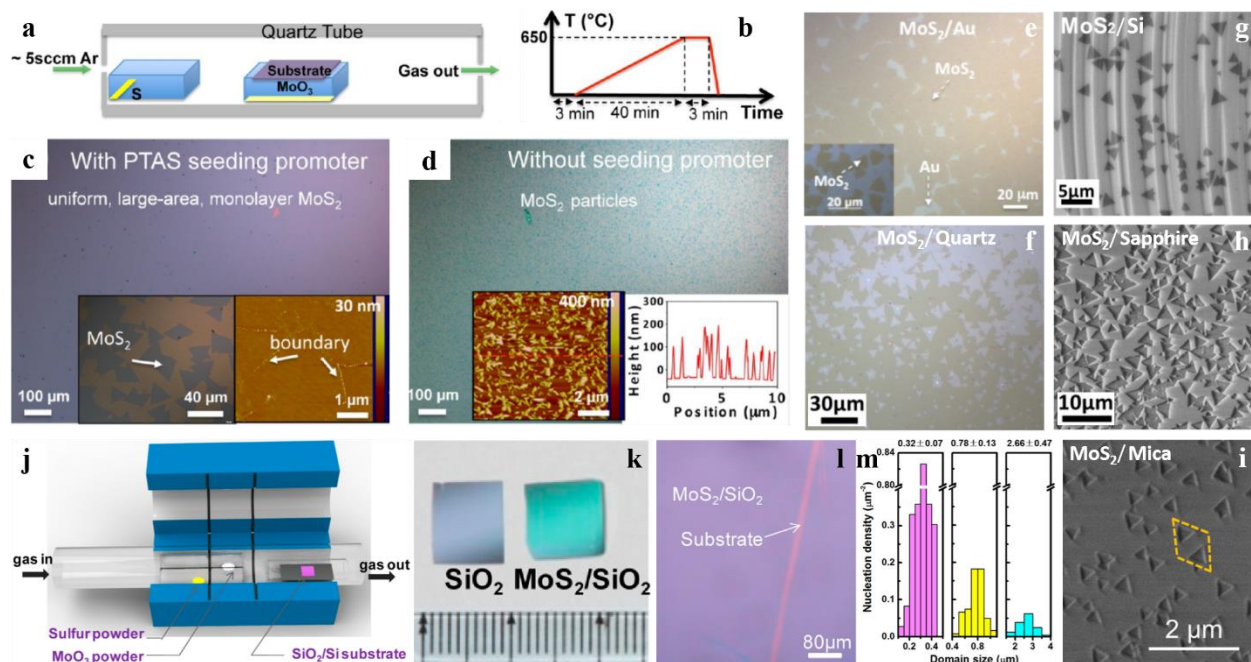


Figure 2.17. CVD synthesis of MoS₂. (a) Schematic of the CVD setup and (b) temperature programming process for a typical growth of the MoS₂ in panel (c–e). (c,d) Optical microscopic images of the MoS₂ obtained with (c) and without (d) the PTAS seeding promoter. Insets: (c) optical microscopic image of the triangular MoS₂ domains at the edge of the MoS₂ monolayer (left) and AFM image measured from the continuous region (right); (d) AFM image of the MoS₂ particles (left) and the corresponding height profile (right). (e,f) Optical microscopic images and (g,h,i) SEM images of the monolayer MoS₂ grown on different substrates. (j) Schematic of a three-temperature-zone CVD system for growing the MoS₂ in panel (k,l). (k) Photograph showing the different contrasts between a bare SiO₂/Si substrate and the one covered by a MoS₂ monolayer. (l) Optical microscopic image of a continuous MoS₂ film. (m) Statistical relation of the nucleation density with the domain size for the monolayer MoS₂ grown on mica. The number above each graph is the corresponding average domain size. (a–e) Reprinted with permission from ref. 168. (f–h) Reprinted with permission from ref. 167. (j–l) Reprinted with permission from ref. 171. (a–e,j–l) Copyright American Chemical Society 2014. (i,m) Reprinted with permission from ref. 169. (f–h,i,m) Copyright American Chemical Society 2013.

The successful CVD synthesis of MoS₂ inspired the attempts to grow monolayer WS₂ starting from the sulphurisation of WO₃ on insulating substrates, *e.g.*, sapphire, quartz, and SiO₂/Si. Compared to the MoO₃ precursor used for growing MoS₂, an increased temperature is required for the WO₃ precursor in the vapour phase reaction. Following the LPCVD synthesis of MoS₂ on mica substrate,¹⁶⁹ Zhang *et al.* demonstrated that this strategy for producing large-area monolayer was likewise viable for WS₂, using the setup presented in Figure 2.18a. Sapphire (Al₂O₃) was employed

as the substrate, with its hexagonal (0001) plane in analogy to the structure of mica. To accelerate the reduction of WO_3 into WO_{3-x} , hydrogen (H_2) was introduced apart from the S vapour during the growth as a more effective reducing agent. It was intriguing to find that the WS_2 domains obtained with or without H_2 exhibited different morphologies, because the involvement of H_2 could instigate a transition from dynamic growth mode, where the WS_2 crystals might form while aligning themselves with the substrate lattice (Figure 2.18b), towards kinetic growth mode, where the lattice alignment was not allowed by the time and resulted in the most thermodynamically stable, *i.e.*, triangular-shaped WS_2 (Figure 2.18c).¹⁷⁴ An alternative method to improve the reduction of WO_3 was achieved by Cong *et al.* In this work the concentration of S vapour was enhanced in a one-end quartz tube accommodating the two precursors and the substrate. The as-prepared monolayer WS_2 domains showed large sizes up to $\approx 200\ \mu\text{m}$, but with a low coverage, presumably due to the non-epitaxial SiO_2/Si substrates and/or the atmospheric-pressure environment.¹⁷⁵

The WS_2 produced by the aforementioned methods was either large domains without a large-scale continuous film or a continuous film consisting of small domains. This could be attributed to the inertness of the insulating substrates. For the first time Gao *et al.* adopted conductive Au as the substrate, giving access to a self-limited growth of WS_2 . In this method, the Au substrate played a catalytic role in the dissociation of S_2 and the sulphurisation of WO_3 , and decreased the required amount of the WO_3 precursor. In addition, since the solubility of W is negligible in Au, the formation of WS_2 multilayers derived from W segregation or precipitation was suppressed. The growth support of Au foil contributed to a low nucleation density, high uniformity and crystalline quality, and the largest ever domain size of $400\ \mu\text{m}$ in the synthesis of 2D TMDs (Figure 2.18d). As presented in Figure 2.18e,f, the roll-to-roll/bubbling production of large-area monolayer WS_2 films and their heterostructures with graphene was achieved on flexible polyethylene terephthalate (PET) substrates. Furthermore, the as-grown WS_2 monolayer was assembled into field-effect transistors (FETs) that showed high flexibility and transparency (Figure 2.18g,h). It was therefore suggested that the choice

of metallic substrate would provide potential opportunities for the application of WS₂ in flexible devices and roll-to-roll manufacturing as has been developed for graphene.¹⁷⁶

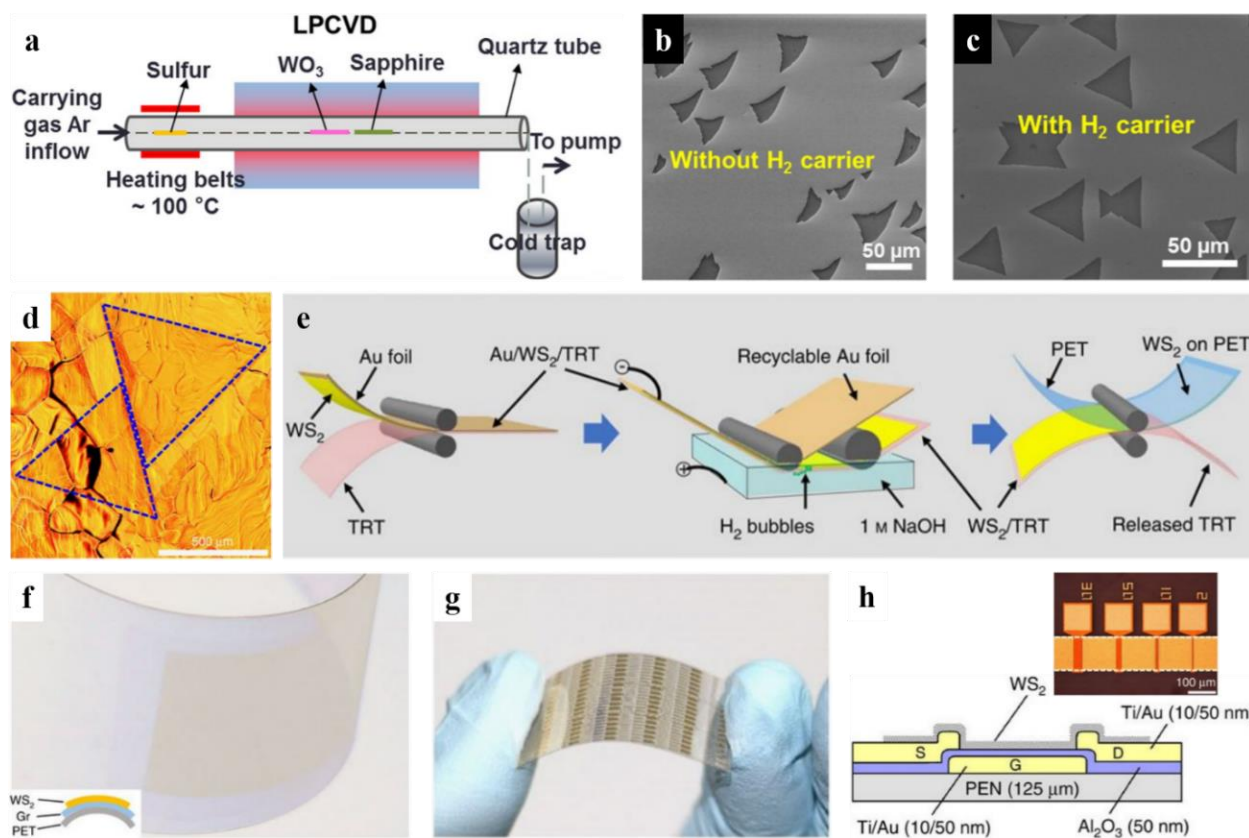


Figure 2.18. CVD synthesis of monolayer WS₂. (a) Schematic of a typical CVD setup. (b,c) SEM images of the monolayer WS₂ domains without (b) and with (c) H₂ as a carrier gas. (d) Optical microscopic image of the millimetre-sized WS₂ domains grown on Au foil. (e) Schematic of a roll-to-roll/bubbling process for producing large-area WS₂ films. (f) Photograph of a $\approx$ 2-inch flexible transparent film of monolayer WS₂/graphene (Gr) heterostructure on a PET substrate using the roll-to-roll/bubbling method in panel (e). Inset: schematic of the layered structure. (g) Photograph of large-area flexible monolayer WS₂-based FET arrays fabricated on a PEN substrate. (h) Schematic cross-section of a WS₂ buried-gate FET. Inset (top-right): the corresponding optical microscopic image, where the monolayer WS₂ film indicated by dotted white lines was patterned to form FET channels. (a–c) Reprinted with permission from ref. 174. Copyright American Chemical Society 2013. (d–h) Reprinted with permission from ref. 176. Copyright Macmillan Publishers Limited 2015.

Considering the high cost of Au for large-scale production of TMD monolayers in industry, Kang *et al.* proposed a novel CVD method with gas-phase metal organic (MO) precursors and H₂ to prepare MS₂ monolayers on SiO₂/Si substrates. In this MOCVD, Mo(CO)₆ or W(CO)₆ and (C₂H₅)₂S

were introduced as the precursors under a low pressure. Under optimised conditions, the MoS₂ film showed high uniformity over a wafer scale (4-inch), with an average domain size of $\approx 1\ \mu\text{m}$. The success was attributed to the layer-by-layer growth mechanism, which is key for synthesising highly uniform monolayers. It was speculated that the growth mode was determined by the partial pressure of the Mo species (P_{Mo}). The film was grown layer-by-layer at low P_{Mo} , where the atoms could attach to the MoS₂ nuclei along lateral directions, forming a uniform MoS₂ monolayer. In contrast, island growth mode was launched by high P_{Mo} , leading to a mixture of layer thicknesses. The concentration of H₂ was found to have impacts on both the domain size and the crystallinity of the resulting MX₂. At high H₂ concentration, the domains were single-crystalline with a triangular shape, but the domain size was small. In contrast, coalescence occurs at low H₂ concentration between the adjacent large domains. Additionally, the influences of S concentration on the nucleation density, grain size, morphology of MoS₂ were also indicated. By optimizing the H₂ concentration along with the S-based precursor, the as-grown continuous MS₂ monolayers exhibited high-quality lattice stitching between adjacent grains. The low density of defects at the grain boundaries allowed comparable electrical performance of the CVD MoS₂ with that of the exfoliated samples.¹⁷⁷ Sheng *et al.* reported the feasibility of APCVD technique to synthesise centimetre-scale monolayer WS₂ films with H₂ as an extra reducing agent. Good continuity and high quality were simultaneously attained by optimising the H₂:Ar ratio during the growth.¹⁵⁸

2.7.2 Discussion

The progress in the CVD growth of 2D materials has aroused some hot topics, including the domain morphology, lattice orientations with respect to the substrate, and annealing behaviours. These are directly linked with their properties and performance for future applications, and are worth deeper discussions.

The control of TMD domain morphologies would not only contribute to the understanding of the CVD growth mechanism but also correlate with their electrochemical properties, especially for 2H-MoS₂ that is catalytically active at the edge sites. Existing studies have verified three possible routes to modulate the shape of CVD MoS₂, which all relate to the growth conditions. Wang *et al.* reported the shape evolution of the MoS₂ domains prepared by APCVD on SiO₂/Si substrate (Figure 2.19a). The change in domain shape was proposed to result from the varied Mo:S ratio on the substrate surface along the direction of gas flow (Figure 2.19b). However, the crystal shape only changed in a small range (between hexagonal and triangular, as presented in Figure 2.19a), with different domain sizes limited within 50 μm . The low yield of each domain shape would also hamper the individual use.¹⁷⁸ In another work, the gas flow rate was tuned during the APCVD to attain dendritic MoS₂ flakes (Figure 2.19c), while the multilayer thicknesses of the MoS₂ caused a much quenched PL intensity compared to monolayer MoS₂ (Figure 2.19d). Additionally, the flake thickness showed a low uniformity. The dendritic-shaped monolayer MoS₂ could also be obtained by employing SrTiO₃ substrate.

At room temperature (RT), SrTiO₃ crystallises in the cubic perovskite structure. The Ti⁴⁺ ions are six-fold coordinated by O²⁻ ions, whereas each of the Sr²⁺ ions is surrounded by four TiO₆ octahedra, within which a hybridization of the O-2p states with the Ti-3d states leads to a pronounced covalent bonding whereas Sr²⁺ and O²⁻ ions exhibit ionic bonding character. Such mixed ionic-covalent bonding in SrTiO₃ makes it a unique electronic material. In comparison, sapphire, a crystalline form of aluminium oxide (Al₂O₃), belongs to the trigonal crystal system; however, SiC has three common polytypes, *i.e.*, 3C that adopts cubic zinc blende structure whereas 4H and 6H adopt hexagonal structure. The physical properties of these substrate materials are summarised and can be compared in Table 2.1.

Table 2.1. Physical properties of SrTiO₃, sapphire (Al₂O₃), and SiC.

Property	Value		
	SrTiO ₃	Al ₂ O ₃	SiC*
Lattice constant at RT (Å)	3.905	a = 4.785	a = 3.073–4.360
		c = 12.991	c = 10.053 or 15.120
Atomic density (g cm⁻³)	5.12	3.98	3.21
Melting point (°C)	2080	2030–2050	2730
Mohs hardness	6.0	9.0	9.0–9.5
Dielectric constant (ϵ_0) at RT	300.0	a-axis: 9.40	9.60–9.72
		c-axis: 11.58	
Thermal conductivity at RT (W m⁻¹ K⁻¹)	12	∥ to c-axis: 23.1	360–490
		⊥ to c-axis: 25.2	
Coefficient of thermal expansion (×10⁻⁶ K⁻¹)	9.4	5.2–5.9	4.0
Refractive index	2.31–2.38	1.78	2.55

* The exact values of SiC depend on the polytype.

Nevertheless, the disadvantages of using SrTiO₃ as the substrate for CVD growth in earlier studies include the small domain size of <10 μm, the varying branching degree across the substrate dependent on the relative local concentrations of the MoO₃ and S precursors, the requirement of vacuum conditions, and the high standard of the single-crystalline SrTiO₃ substrate to develop diffusion-limited-aggregation process for growing MoS₂ dendrites.¹⁷⁹ A regioselective synthesis of monolayer MoS₂ dendrites was realized on LaAlO₃ (100) single crystals that contained adjacent twin domains formed through second-order phase transition. The unique dendritic shapes demonstrated a strong substrate modulation effect. Apart from the utilisation of a low-pressure system, the nucleation density was not consistent even within a small region due to the undulated substrate surface, and the resulting dendrites showed only a small size with non-uniform thicknesses.¹⁸⁰ Dendritic MoS₂ monolayer was also synthesised on silicon carbide single crystal substrate, *i.e.*, SiC(0001), *via* APCVD. The dendrite morphology of MoS₂ was found to be affected by the lattice symmetry of SiC.

Native SiC gave birth to six-fold symmetric backbones, extending with many hierarchical branches harbouring similar angles of $\approx 60^\circ$ (Figure 2.19e,f), while the SiC substrate intentionally etched into groove arrays resulted in two-fold symmetric MoS₂ dendrites (Figure 2.19g). The fractal dimensions of these two types of MoS₂ dendrites were calculated based on box-counting method, as displayed in Figure 2.19h,i.¹⁸¹ A very recent study attempted to synthesise monolayer MoS₂ dendrites by pre-treating the SiO₂/Si substrate with tapes (Figure 2.19j). The formation of the dendritic shape was associated with the existing twin defects in the MoS₂. The S vacancies accommodated at the grain boundaries were proved by the locally enhanced PL intensities (Figure 2.19k). The fractal dimension varied with the tape type as it induced different defects in the synthesis stages, and for a certain tape, the S:Mo vapour concentration ratio dictated the growth mode and hence the domain morphology (Figure 2.19l). Nonetheless, this method complicated the preparation procedure, and gave access only to small MoS₂ domains with a high defect level.¹⁸² Therefore a facile strategy for producing large-area MoS₂ dendritic structures with uniform monolayer thickness and the ability to produce various domain morphologies with a high yield for each are lack of investigation.

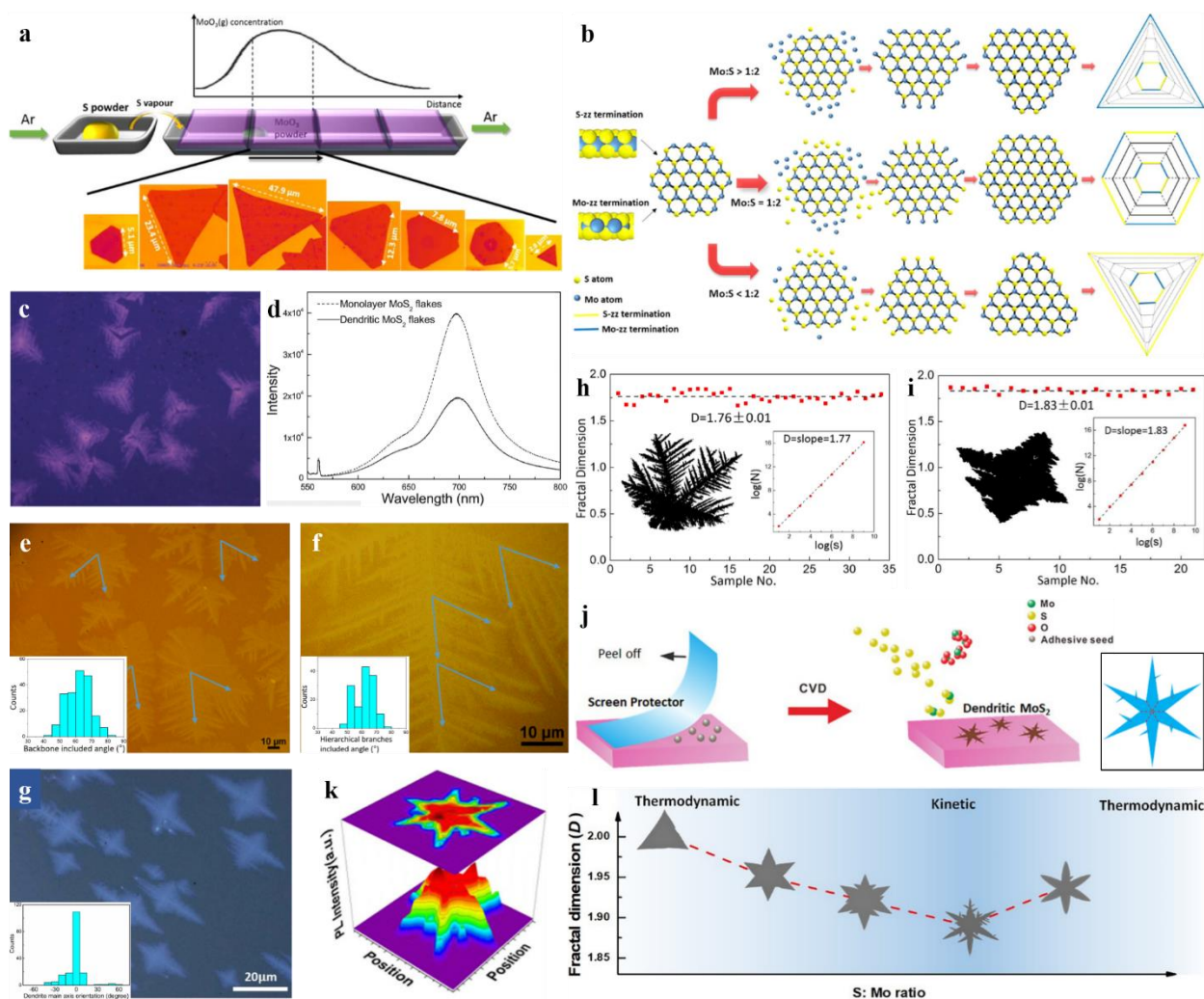


Figure 2.19. Domain morphologies of CVD MoS₂. (a) Evolution of the domain shape depending on the SiO₂/Si substrate position in a CVD growth. (b) Schematic of the relationship between Mo:S atom ratio and the domain shape. (c) Optical microscopic image of few-layer dendritic MoS₂ flakes. (d) PL spectra of monolayer MoS₂ and the few-layer MoS₂ dendrites in panel (c). (e–g) Optical microscopic images of dendritic monolayer MoS₂ with six-fold (e,f) and two-fold (g) symmetric backbones. Insets: angles between (e) the backbones, (f) the hierarchical branches, and (g) the main axis orientation. (h,i) Statistics for the two types of dendritic MoS₂ flakes in panel (e,f) and panel (g), respectively, where the fractal dimension is estimated by box-counting method. (j) Schematic of the synthesis of MoS₂ dendrites by introducing adhesive seeds on SiO₂/Si substrate. Inset: schematic of a dendrite whose grain boundaries are marked by red dashed lines. (k) PL intensity map of the MoS₂ dendrite shown as the inset in panel (j). (l) Evolution of fractal dimension represented by domain shapes vs. S:Mo ratio, which is associated with the growth mode transition. (a,b) Reprinted with permission from ref. 178. Copyright American Chemical Society 2014. (c,d) Reprinted with permission from ref. 179. Copyright Elsevier B.V. 2015. (e–i) Reprinted with permission from ref. 181. (j–l) Reprinted with permission from ref. 182. (e–l) Copyright American Chemical Society 2017.

The growth substrate has also been found determinant for the CVD TMDs. Li *et al.* reported the regioselective nucleation of dendritic MoS₂ on corrugated LaAlO₃(100). The corrugation was incurred by a second-order phase transition during the growth. In the meanwhile a domain wall was developed, and divided the corrugation into two adjacent regions so that isolated the steps on the substrate. The side with steps induced higher nucleation density and smaller MoS₂ domain size.¹⁸⁰ In another regard, the MoS₂ monolayer synthesised by CVD on amorphous substrate such as SiO₂/Si is polycrystalline due to the merging of randomly oriented domains. The grain boundaries can be detrimental to the optical and electrical properties of 2D TMDs.⁸⁵ It is thus crucial to predefine the orientations of the isolated domains toward uniform continuous films for potentially achieving ultimate performance in devices. This is most likely to be realised through epitaxial growth on a crystalline substrate, which could be dictated by vdW forces or electrostatic interactions at the TMD–substrate interface.^{183–185} An example is the epitaxy of monolayer MoS₂ domains on mica as aforementioned in Section 2.7.1, where two opposite orientations are preferentially formed (Figure 2.17i). Besides, monolayer polycrystalline MoS₂ has been obtained on single-crystalline sapphire (0001), *i.e.*, *c*-plane sapphire, by both LPCVD¹⁸⁴ and APCVD¹⁸⁵ approaches. The as-grown triangular domains showed two prevalent directions, where the vdW interaction was stronger between the MoS₂ adlayer and the substrate so that induced lattice alignment.^{184,185} The MoS₂ monolayer film made up of coalescing single grains with only a few crystal orientations exhibited good electrical conductivity and relatively large mobility in the FETs.¹⁸⁵ Experimental work along with theoretical calculations confirmed the substrate-mediated growth of monolayer MoS₂ on *c*-plane sapphire. The preferential orientations of the MoS₂ domains were observed at about 0° and 30°.¹⁸⁴ However, another study determined the dominant orientations to be at 0° and ±60° (Figure 2.20b,c), where the lattices of MoS₂ and *c*-plane sapphire exhibit good commensuration (Figure 2.20d).¹⁸⁵ The two orientations on the left side are commensurate with lattice rotation angles $\theta = 0^\circ$ and 60° , where the two with lattice rotation angles $\theta = 30^\circ$ and 90° on the right side show larger lattice mismatches and are less observed. The

discrepancy could stem from the use of as-received sapphire substrates without any pretreatments in the former work, so that the surface was not likely to be as atomically smooth as the one in the latter work and would interfere the epitaxial growth of MoS₂. Moreover, *c*-plane sapphire is able to govern both the nucleation and the growth of WSe₂. As manifested in Figure 2.20e,f, the base edges of the WSe₂ domains tend to align with the steps on the sapphire surface, and the few-layer regions were formed in a layer-over-layer growth mode rather than the layer-by-layer mode which is more common for 2D TMDs.¹⁸⁶ But the density and alignment of the initially formed MoS₂ nuclei showed low uniformity on such surfaces.^{180,186}

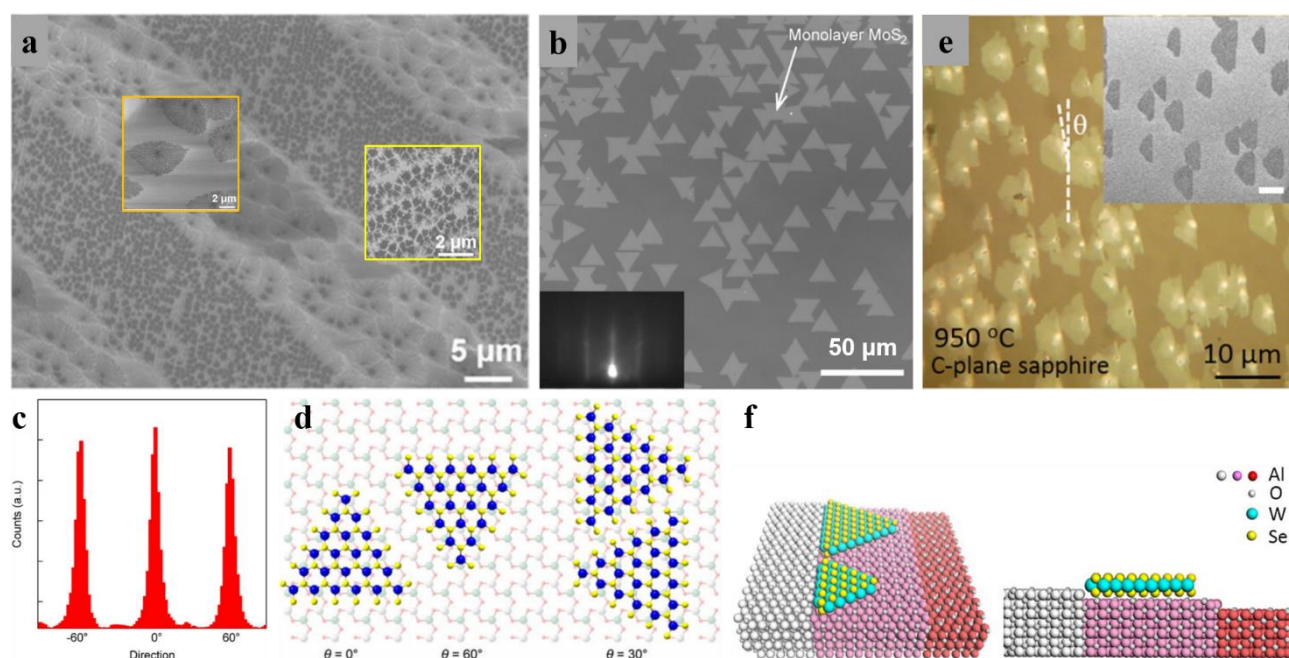


Figure 2.20. Substrate effects on the domain orientation and morphology. (a) SEM image of dendritic MoS₂ on LaAlO₃(100). Insets: SEM images corresponding to the adjacent regions with relatively low nucleation density and large domain size (orange) and high nucleation density and small domain size (yellow). (b) Optical microscopic image of monolayer CVD MoS₂ domains on *c*-plane sapphire and the RHEED pattern (inset) showing the long-range structural order. (c) Histogram of the orientation distribution based on the area in panel (b). (d) Top view of the relative lattice orientations between monolayer MoS₂ domains and the *c*-sapphire substrate. (e) Optical microscopic and SEM (inset) images of CVD WSe₂ domains on *c*-plane sapphire substrate. (f) Atomic models illustrating the aligned nucleation of WSe₂ on *c*-plane sapphire. (a) Reprinted with permission from ref. 180. Copyright IOP Publishing Ltd 2016. (b–d) Reprinted with permission from ref. 185. (e,f) Reprinted with permission from ref. 186. (b–f) Copyright American Chemical Society 2015.

As the crystallinity of 2D TMDs is tightly associated with their properties, the thermal behaviour of TMDs is of significance for high-temperature applications. This has been studied during the synthesis process of MoS₂ or immediately after its growth under different conditions. Several substrates have been used as they could have different reactions with the MoS₂ adlayer at elevated temperatures. MoS₂ nanosheets on SiO₂/Si substrate were completely decomposed *via* thermal annealing in air at 400 °C and transformed into MoO₃ primarily due to the atmospheric O₂ and moisture. Although the few-layer MoS₂ could be thinned to a monolayer at 330 °C (Figure 2.21a,b), the irremovable MoO₃ fragments induced hole injection and influenced the performance of the FETs fabricated. Longer annealing time led to simultaneous etching and thinning and triangular pits were formed with identical orientation in the MoS₂ nanosheets (Figure 2.21 c,d).¹⁸⁷ This was suggestive of anisotropic etching, and could also be observed by directly exposing mono- or bilayer MoS₂ to oxygen at annealing temperatures ranging from 300 to 340 °C. In this case, the uniformly orientated triangular etch pits originated from the native defect sites on the basal plane surface of MoS₂ but was not stimulated by the substrate effects, *e.g.*, charged impurities or surface roughness. As evidenced in Figure 2.21e, the (10 $\bar{1}$ 0) Mo edge is more stable compared to the ($\bar{1}$ 010) S edge, and is decorated by S atoms in one of two possible configurations. The pit size was found to correlate linearly with the oxidation time (Figure 2.21f). Figure 2.21g–j show that the E_{2g}^1 and A_{1g} Raman peaks would be shifted and the A_{1g} peak intensity would be increased with the oxidation time and the number of MoS₂ layers. It was also noted that p-type doping of the MoS₂ occurred above 200 °C, but the MoO₃ was only formed above 340 °C, and the complete conversion to MoO₃ occurred at 400 °C.¹⁸⁸ However, higher chemical stability was observed for the monolayer MoS₂ on Au (111) substrate. The STM images in Figure 2.21k,l demonstrate the little affected surface quality of the monolayer MoS₂ after air exposure at room temperature for a few hours, followed by a mild annealing to 227 °C in ultrahigh vacuum (UHV, base pressure of $<2 \times 10^{-10}$ mbar) to remove physisorbed species, and MoS₂ lattice even appeared to be well preserved up to ≈ 627 °C in UHV.¹⁸⁹ In the absence of oxygen or hydrogen,

the thermal decomposition of few-layer MoS₂ on oxide or nitride substrates would not occur below at an increased temperature, 850 °C.¹⁹⁰ Bulk MoS₂ is much more robust for the H₂/O₂-free thermal decomposition, which was believed to be a desulphurisation process in basically two steps, *i.e.*, MoS₂ → Mo₂S₃ → Mo, in agreement with the theoretical calculations by DFT. To be more specific, the MoS₂ firstly decomposed into Mo₂S₃ at >1203 °C, which was unstable and led to the sequential removal of two S atoms and then the last S atom till Mo metal was produced.¹⁹¹ It is notable that thermal annealing at lower temperatures such as 270 °C could improve the adhesion between the few-layer MoS₂ and the SiO₂/Si substrate, as the lifting of trapped impurities at their interface gave rise to a larger contact area.¹⁹²

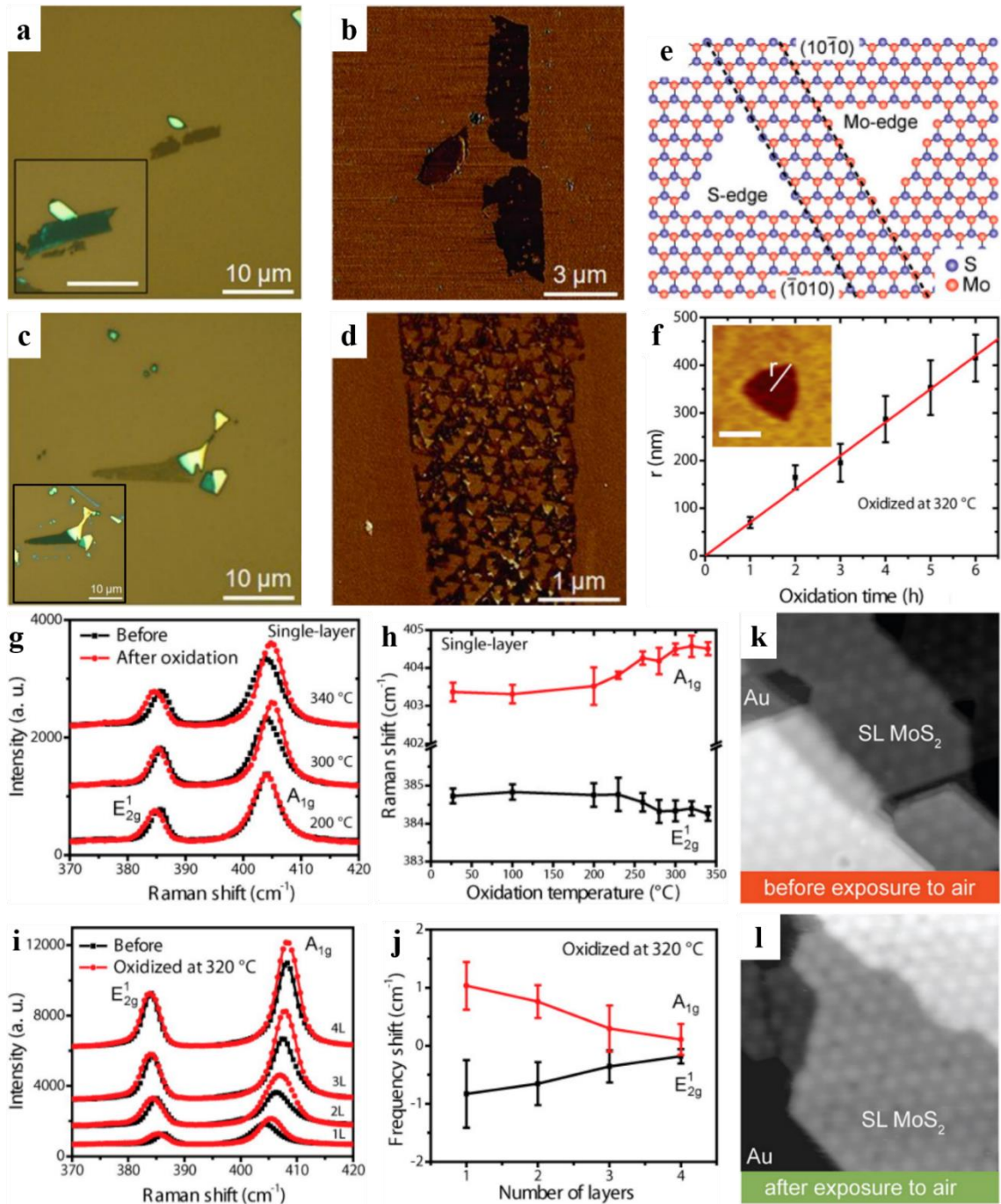


Figure 2.21. (a,c) Optical microscopic images showing the thermal thinning (a) and simultaneous thinning and etching (c) of a bilayer MoS₂ flake into a monolayer before (inset) and after being annealed at 330 °C for 10 h (a) and 15 h (c). (b,d) AFM phase images of the annealed MoS₂ flakes corresponding to panels (a,c), respectively. (e) Schematic of the MoS₂ hexagonal lattice with triangular pits. The black dashed lines indicate the $(\bar{1}010)$ S and $(10\bar{1}0)$ Mo edges. (f) Average distance r from the centre to the apex of triangular pits vs. the oxidation time. Red line is the linear fit. Inset: AFM image of a typical triangular pit formed on monolayer MoS₂ after 4 h oxidation. Scale bar: 300 nm. (g) Raman spectra of monolayer MoS₂ before and after oxidation at 200, 300, and 340 °C for 2 h, and the (h) extracted peak shifts vs. oxidation temperature. (i) Raman spectra of mono-, bi-, tri-, and quadri-layer MoS₂ after oxidation at 320 °C for 2 h, and the (j) extracted peak shifts vs.

MoS₂ layer number. (k,l) STM images of monolayer MoS₂ before (k) and after (l) exposure to air. Imaging areas: 35 nm × 35 nm. (a–d) Reprinted with permission from ref. 187. Copyright Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim 2013. (e–j) Reprinted with permission from ref. 188. Copyright American Chemical Society 2013. (k,l) Reprinted with permission from ref. 189. Copyright American Chemical Society 2015.

2.8 Applications of 2D TMDs

The scaling limits of conventional silicon-based technology in the last decades suggest exploitation of atomically thin semiconductors, such as 2D TMDs, as suitable elements for next generation integrated circuits, provided manufacturing and integration challenges can be addressed. The direct bandgap in TMDs renders them superior to graphene in various applications, including electronics, gas sensors, energy storage devices, and so on. This section introduces the electronic and optoelectronic devices based on MoS₂ and/or WS₂, with hints of future improvements in their functionalities.

Benefiting from the thickness dependent bandgap of MS₂, they are deemed to be prospective materials for electronic devices. It has been demonstrated that high carrier mobilities can be achieved in the MoS₂-based back-gate transistors by involving a high- κ dielectric buffer layer. Hafnium oxide (HfO₂) was used as a gate dielectric encapsulating monolayer MoS₂ (Figure 2.22a), whereby the carrier mobility of MoS₂ was increased from 0.5–3 to over 200 cm² V⁻¹ s⁻¹ with a high on/off current ratio of 1×10^8 (Figure 2.22b),^{3,149,193} while the simulation results showed that the ultimate on/off ratio of such MoS₂ transistors should exceed $>10^{10}$.¹⁹⁴ In order to boost the carrier mobility, Lee *et al.* utilised a high- κ (Al₂O₃) dielectric layer to fabricate MoS₂ phototransistors with top-gate configuration, and a large carrier mobility up to 80 cm² V⁻¹ s⁻¹ was achieved with monolayer MoS₂. It was also uncovered that the different transfer characteristics as a consequence of the thickness-modulated optical energy gap.¹⁹⁵ Moreover, the electric double layer transistors (EDLTs), *i.e.*, FETs gated by ionic liquids, showed performance up to two orders of magnitude higher than that of conventional FETs (*e.g.*, bottom-gate FETs with SiO₂ dielectric)

via the accumulation of carriers.^{196,197} Integrated circuits composed of multiple MoS₂ transistors were proved to be capable of amplifying electrical signals and performing logic operations.^{150,198}

Benefiting from the thickness dependent bandgap of MS₂, they are also deemed to be prospective materials for optoelectronic devices. In this regards, existing studies have affirmed the superb performance of MoS₂ over graphene. Yin and Li *et al.* fabricated a phototransistor based on mechanically exfoliated monolayer MoS₂, which exhibited an on/off ratio of $\approx 10^3$ and a carrier mobility of $0.11 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The switching behaviour of photocurrent generation and annihilation could be completed within $\approx 50 \text{ ms}$, much more rapid than that using monolayer graphene (tens of ps),¹⁹⁹ and the photoresponsivity was improved to 7.5 mA W^{-1} from 1 mA W^{-1} in graphene-based devices.²⁰⁰ The MoS₂ nanosheets have also showed potential in light-emitting diodes (LEDs). Hybrid structures have been prepared by coupling a high work function hole-injection layer of MoS₂ and an electron extraction blocking layer of MoO₃. The electrons built up at the oxide/emissive layer interface generated a local field, promoting the hole injection and therefore the formation of excitons, which led to an enhanced light emitting performance and efficiency.^{201,202} Photodetectors based on WS₂ have been fabricated with different configurations. Because CVD technique offers a viable route to the scalability of devices, many studies have been utilising this method to synthesise the constituent materials. As a paradigm, few-layer WS₂ films grown by CVD were used for photosensor devices, showing a fast response, good responsivity and stability.²⁰³ With the intention to improve the performance of photodetectors, MoS₂/WS₂ heterostructures were constructed with two types of architectures. The vertical device exhibited a novel rectifying and bipolar behaviour, and could also work as photovoltaic cell and high efficiency self-driven photodetector with a photo-switching ratio of 10^3 owing to the presence of built-in potential in the heterostructure. The planar device displayed better optoelectronic performance compared to the multilayer MoS₂ and WS₂ devices, regarding its high field-effect on/off ratio, high electron mobility, and high photoresponsivity.²⁰⁴

Graphene (Gr) possesses finite DOS from the Dirac cones of the valence and conduction bands, thus incorporating graphene as the electrodes rather than conventional metal (*e.g.*, Au) would permit the modulation of photoresponsivity *via* electrostatic gating and light input. This triggered the fabrication of all 2D ultrathin photodetectors such as the lateral architecture of Gr–WS₂–Gr, where monolayer graphene functioned as the electrodes and monolayer WS₂ functioned as the active semiconductor.²⁰⁵ Another paradigm is the vertical stacked tunnelling cross-bar devices with the structure of Gr/WS₂/Gr. Owing to the different dielectric environments and doping levels of the top and bottom graphene electrodes, a potential difference existed in the vertical dimension so that a strong electric field was generated perpendicular to the WS₂ layer and modified its band structure.²⁰⁶ Graphene electrodes were also laterally applied to vertical WS₂/MoS₂ heterobilayers to fabricate high-performing ultrathin photodetectors (Figure 2.22g). The carrier transportation dynamics of Gr–WS₂/MoS₂–Gr photodetector under positive back-gate potential and light irradiation are illustrated in Figure 2.22e,f, and the irradiation power dependence of its output characteristics is also given (Figure 2.22h). The photoresponsivity of the as-assembled photodetector was increased by about an order of magnitude compared to both the homobilayer and the Au–WS₂–MoS₂–Au planar devices, and by two orders of magnitude compared to monolayer WS₂ and MoS₂ devices, reaching 10³ A W⁻¹ at an illumination power density of 1.7 × 10² mW cm⁻² (Figure 2.22i). The significant improvement in performance was attributed to the strong Coulomb interaction between the WS₂ and MoS₂ layers. The efficient charge transfer at the WS₂/MoS₂ interface and long trapping time of the photogenerated carriers resulted in a large photoconductive gain.²⁰⁷ A two-step CVD approach was designed to obtain large-scale periodic arrays consisting of vertically layered MoS₂ and WS₂ films for photodetection. The as-prepared MoS₂/WS₂ heterostructures showed sharp interface and were fabricated into photodetectors, which exhibited high photoresponsivity, as well as flexible optoelectronics.²⁰⁸ Furthermore, centimetre-scale graphene and MoS₂ monolayers, both grown by CVD, were vertically stacked on a flexible PET substrate, which displayed semitransparency and high stability upon

bending to a curvature of 1.4 cm. The injection of photoexcited electrons from MoS₂ to the graphene channel gave rise to a combination of high responsivities with μA range photocurrent and a large photoconductive gain, surpassing those in graphene and/or TMD-based photodetectors in the visible range.²⁰⁹ However, the drawbacks of CVD-grown WS₂ include low optical absorption (2–10%) and poor carrier mobility (0.01–0.91 cm² V⁻¹ s⁻¹). To resolve this, pulsed-laser deposition (PLD) approach was developed to produce multilayer WS₂ films over a centimetre scale. It exhibited stable broadband photoresponse with the largest range (370–1064 nm) reported in WS₂ photodetectors. Thanks to the high optical absorbance (40%–85%) and high carrier mobility (31 cm² V⁻¹ s⁻¹), an improved responsivity of 0.51 A W⁻¹ was reached by these photodetectors in ambient environment, far exceeding those using CVD-grown WS₂ ($\mu\text{A W}^{-1}$), and the responsivity could be further increased to 0.70 A W⁻¹ under vacuum.²¹⁰ Additionally, photoconductors were fabricated based on the heterostructure of monolayer WS₂ and methyl-ammonium lead triiodide (CH₃NH₃PbI₃) perovskite films. The PL of the perovskite was quenched due to the interfacial charge transfer. More importantly, the dark current of these bilayer photodetectors was remarkably suppressed, leading to greatly increased photocurrent (Figure 2.22c,d) and photodetectivity.²¹¹ It was also demonstrated that the performance of MoS₂ photodetector could be enhanced *via* the charge transfer of photoexcited electrons from organic dye molecules to MoS₂.^{212,213} The performance improvement could also be modulated by choosing the dyes with different molecular structures and optical absorption bandwidths.²¹³ Recently, ultrabroadband MoS₂ photodetectors have been obtained with the spectral response from blue (445 nm) to mid-infrared light (2717 nm). This largest ever reported range was achieved by engineering the bandgap of MoS₂ through the introduction of S defects.²¹⁴

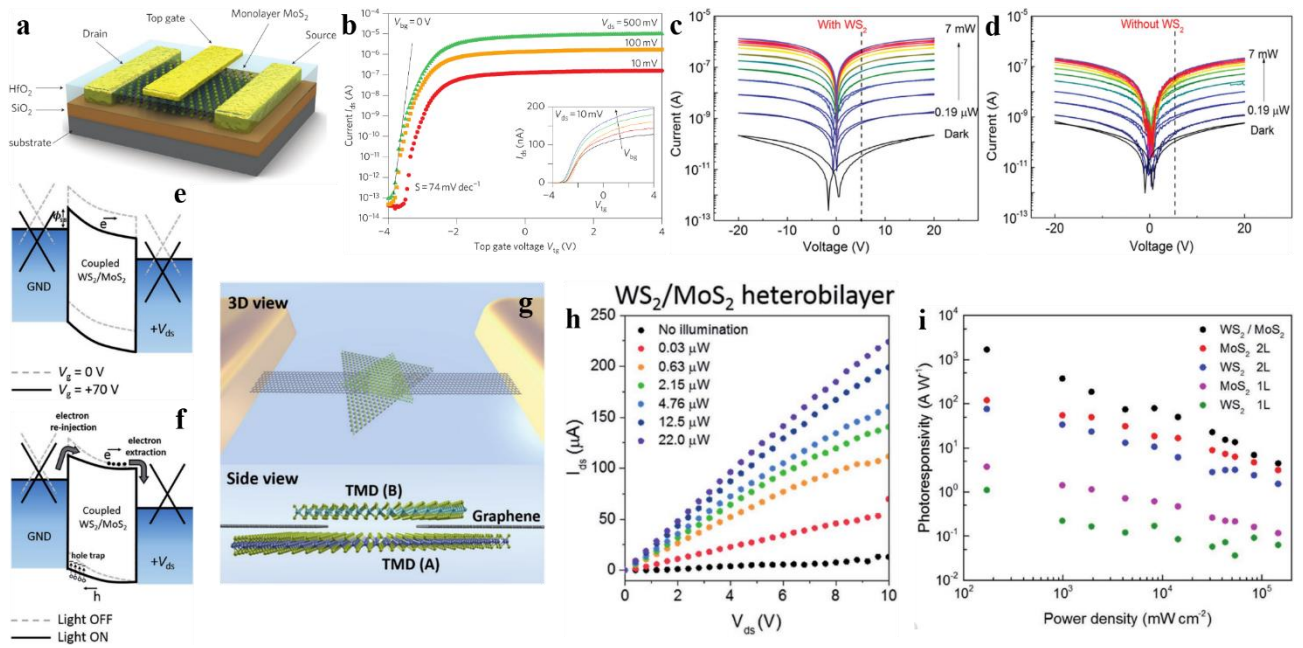


Figure 2.22. (a) Schematic of a MoS₂ monolayer transistor, where the HfO₂ acts as a gate dielectric and mobility booster. (b) I_{ds} – V_{tg} curve recorded for different bias voltages. Inset: I_{ds} – V_{tg} for values of $V_{bg} = -10, -5, 0, 5$ and 10 V. (c) I – V curves of the WS₂/perovskite photoconductor measured in dark and under illumination with different white-light intensities, and the (d) corresponding I – V curves measured on the perovskite single layer. Band schematics of a Gr–WS₂/MoS₂–Gr device (e) under positive back-gate potential and (f) under light irradiation. (g) Schematic of the Gr–WS₂/MoS₂–Gr photodetector. (h) I_{ds} – V_{ds} measurements at different light irradiation powers for Gr–WS₂/MoS₂–Gr photodetectors. (i) Photoresponsivity of Gr–WS₂/MoS₂–Gr photodetectors vs. irradiation power density. (a,b) Reprinted with permission from ref. 149. Copyright Macmillan Publishers Limited 2011. (c,d) Reprinted with permission from ref. 211. Copyright WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim 2016. (e–i) Reprinted with permission from ref. 207. Copyright WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim 2017.

2.9 Conclusion

In summary, the recent development of 2D TMDs has verifies its potential in both fundamental research and industrial applications. This is allowed by their unique structure and diverse functionalities. The non-zero bandgap offers promise to complement graphene especially in electronic devices. Many aspects of these materials are found tunable *via* accessible routes, such as the morphology and properties, which make it attractive be studied in depth. Firstly, producing high-quality and uniform 2D TMDs over a large scale is of great interest, which can be fulfilled

by CVD strategies. A variety of methods have been reported for the synthesis of large-area TMD monolayer. However, there is still lack of investigation on the control of TMD domain shape to achieve desired performance. For this goal, a better comprehension of the growth mechanism, correlating with the experimental parameters and the substrate influences are worth being further explored. In addition, considering the susceptibility of 2D TMDs to the environment, their stability requires supplementary work. Moreover, the 2D heterostructures based on TMDs have been demonstrated previously to show exceptional behaviours. Although the TMD heterostructures can be fabricated directly by CVD growth, this approach limits the tailorability of the configuration, and therefore the understanding of the interactions between the TMDs and the feasibility of manipulating their properties toward future applications. While mechanically layer stacking may resolve this issue, access to clean interfaces is crucial to be achieved before drawing any conclusions. Some of these will be addressed in the following chapters.

Chapter 3 Methodology

3.1 Introduction

The purpose of this chapter is to introduce the experimental apparatus utilized in my research projects. The detailed information will involve the CVD system for growing different 2D materials, the corresponding growth parameters, and the operating procedures of various characterisation techniques.

3.2 CVD Synthesis and Transfer of 2D materials

3.2.1 Substrate preparation

The substrates used to grow 2D materials, including amorphous SiO₂ (300 nm)/p++ Si (2 cm × 2 cm × 0.5 mm, University Wafer) for MoS₂ and WS₂ monolayers, single-crystalline SrTiO₃ (7 × 2 × 0.5 mm, PI-KEM) doped with Nb at 0.5% by weight with epi-polished (111), (110), and (001) surfaces for MoS₂ monolayers, and copper foil (1 cm × 1 cm × 25 μm, Alfa Aesar) for hBN, were sonicated for 10–15 min in acetone and isopropanol solutions successively. When aiming to get dendritic monolayer MoS₂, four pieces of the SiO₂/Si substrates were cemented together to build a cuboid box with all the SiO₂ sides facing out, for which each piece of the SiO₂/Si substrates was diced according to the desired shape of the resultant MoS₂ domains.

3.2.2 CVD synthesis of monolayer MoS₂

The monolayer MoS₂ domains were grown by hydrogen-free APCVD with the precursors of molybdenum trioxide (MoO₃, powder, ≥99.5%, Sigma-Aldrich) and sulphur (S, powder, ≥99.5%, Sigma-Aldrich). Either p-doped silicon (Si) coated with a 300 nm thick oxide layer (amorphous SiO₂) or crystalline SrTiO₃ was used as the substrate. Double-walled quartz tubes were employed for the CVD synthesis to avoid cross-reaction between the precursors. Two separate furnaces were utilised for individual temperature control. The MoO₃ (15 mg) loaded in the inner tube (0.6 inch diameter) was placed in the central zone of the low-temperature furnace, and the S (600 mg) in the outer tube (1 in. diameter) was placed 1.7 cm from the left open end of the high-temperature furnace. The substrate was located at the centre of furnace 2, as shown in Figure 3.1. The growth system was first flushed with 500 sccm argon (Ar) for 30 min to drive off the oxygen. Then, the furnaces were ramped to ~180 and ~200 °C, so as to create a sulphur-rich environment. Next, furnace 2 was heated up to 800 °C, and meanwhile, the temperature of MoO₃ was increased to 300 °C. Once the target temperature was reached, MoS₂ began to nucleate with the 150 sccm Ar flow. This stage lasts for 20 min, after which the flow rate was reduced to 50 sccm for a 25 min growth. The temperature of S was increased slowly from 180 to 200 °C since then to maintain the concentration of S vapour at a nearly constant level. The growth time could be extended to 39 min to obtain bilayer dendrites, with the second-layer islands located on top of the large-area dendritic monolayer. To attain high uniformity and large domain size, we, for the first time, designed a follow-up procedure that enabled atom migrations, where the MoO₃ temperature was reduced to 270 °C and the gas flow rate was dropped to 5 sccm for a lower precursor feedstock, with a quenched substrate temperature of 700 °C to decrease the sublimation of MoS₂ species formed on the substrates. The time for obtaining a large domain size was optimized to be 15 min. Finally, the synthesis ended up with cooling fast.

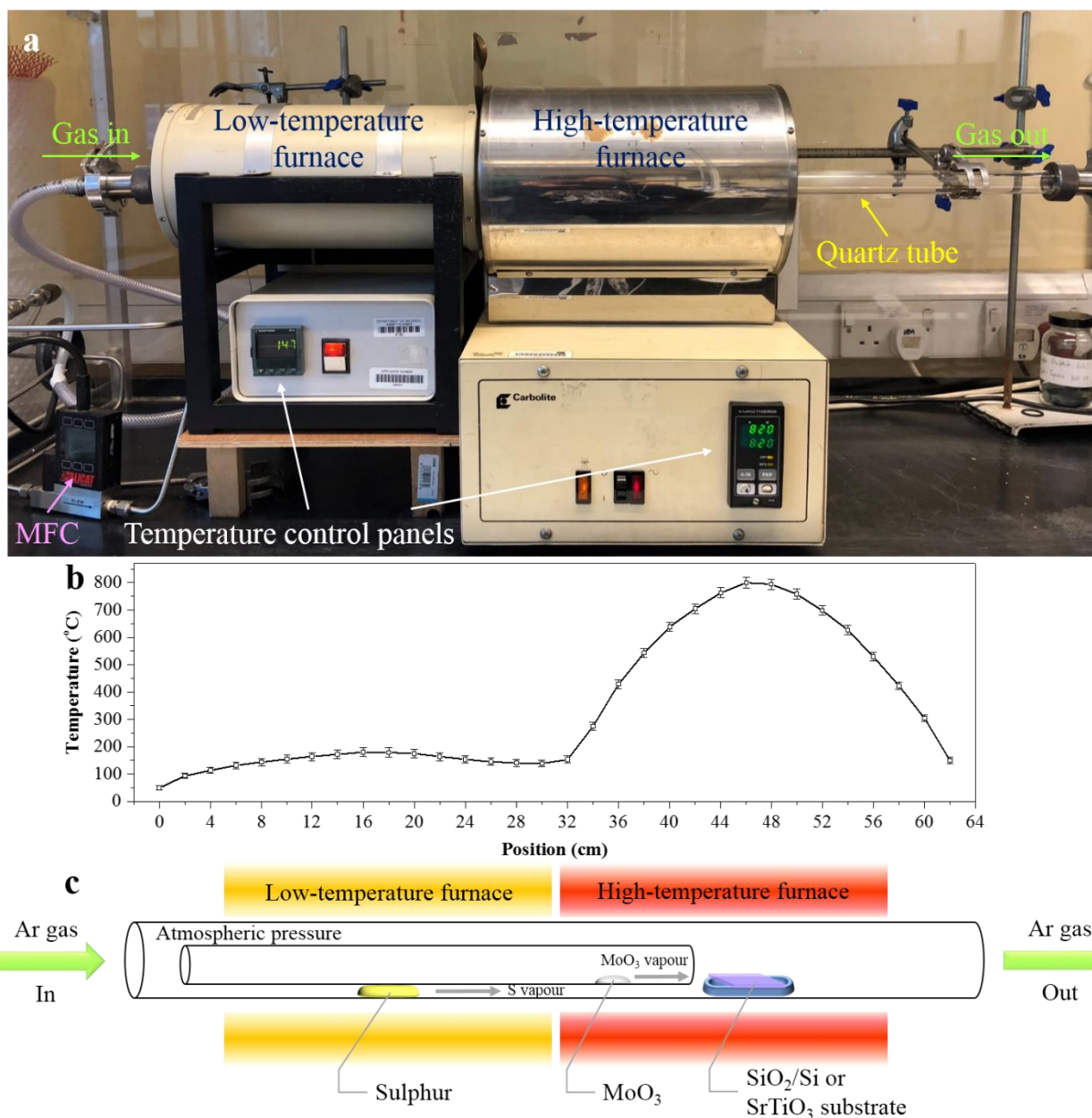


Figure 3.1. CVD synthesis of monolayer MoS₂. (a) Digital photograph. (b) Temperature profile during the main growth stage and the (c) corresponding schematic diagram of a typical CVD setup.

3.2.3 CVD synthesis of monolayer WS₂

A similar strategy was adopted to produce monolayer WS₂. The monolayer WS₂ domains were grown by hydrogen-free chemical vapour deposition in atmospheric pressure with the reactants of tungsten trioxide (WO₃, powder, 99.9%, Sigma-Aldrich) and sulphur (S, powder, ≥99.5%, Sigma-Aldrich). To avoid solid-phase reactions between the two precursors, 200 mg WO₃ was first placed

in a smaller quartz tube, which was then mounted into a larger quartz tube with 400 mg S preloaded. While loading the precursors and the substrate, the S and WO₃ were put at the centres of the low- and high-temperature furnaces, respectively, and a 300 nm SiO₂/Si chip was positioned 9.5 cm downstream of the WO₃. Argon was introduced with a flow rate of 250 sccm to transport the precursor vapours onto the substrate surface. Two furnaces were used for independent temperature control. The S reached its target temperature of 180 °C 10 min before WO₃ was finally heated to 1070 °C (ramp rate: ≈ 30 °C min⁻¹ for sulphur and ≈ 40 °C min⁻¹ for WO₃). The reaction then lasted for 3 min, after which the sample was rapidly cooled down to room temperature.

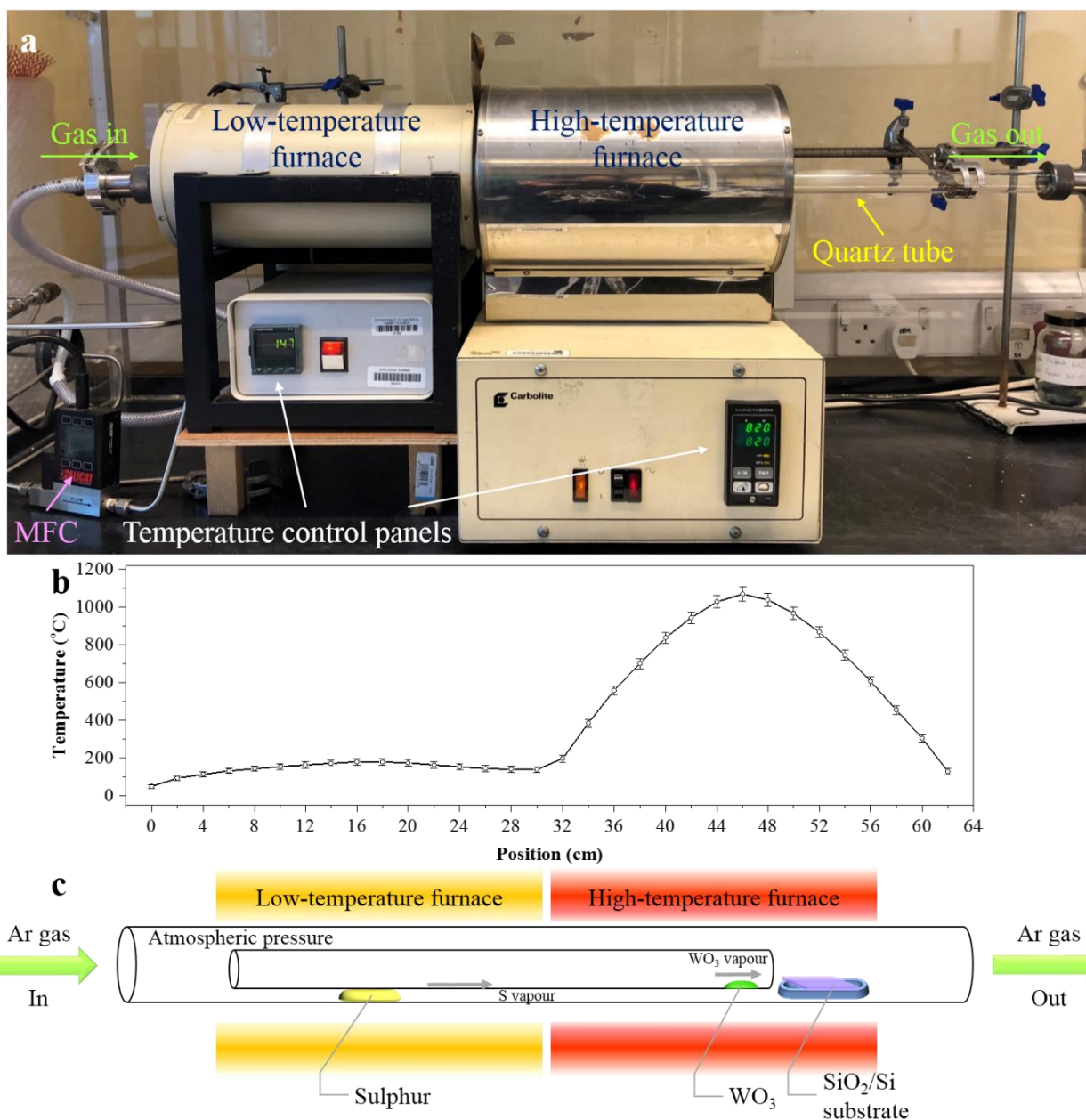


Figure 3.2. CVD synthesis of monolayer WS₂. (a) Digital photograph. (b) Temperature profile during the main growth stage and the (c) corresponding schematic diagram of a typical CVD setup.

3.2.4 CVD synthesis of hBN

The hBN films were also synthesized *via* CVD method on copper foil, using ammonia borane (H₃NBH₃, powder, ≥97%, Sigma-Aldrich) as the precursor. In order to smoothen the reaction surface, the substrate was first annealed at 1000 °C for 1 h. Then the precursor (7 mg) was evaporated at ≈130 °C and carried by 120 sccm hydrogen. The growth was carried out at 1050 °C in another furnace.

The growth time was precisely controlled to obtain continuous films with different thicknesses (15 min for monolayer hBN and 17 min for bilayer hBN). The sample was cooled rapidly after the growth.

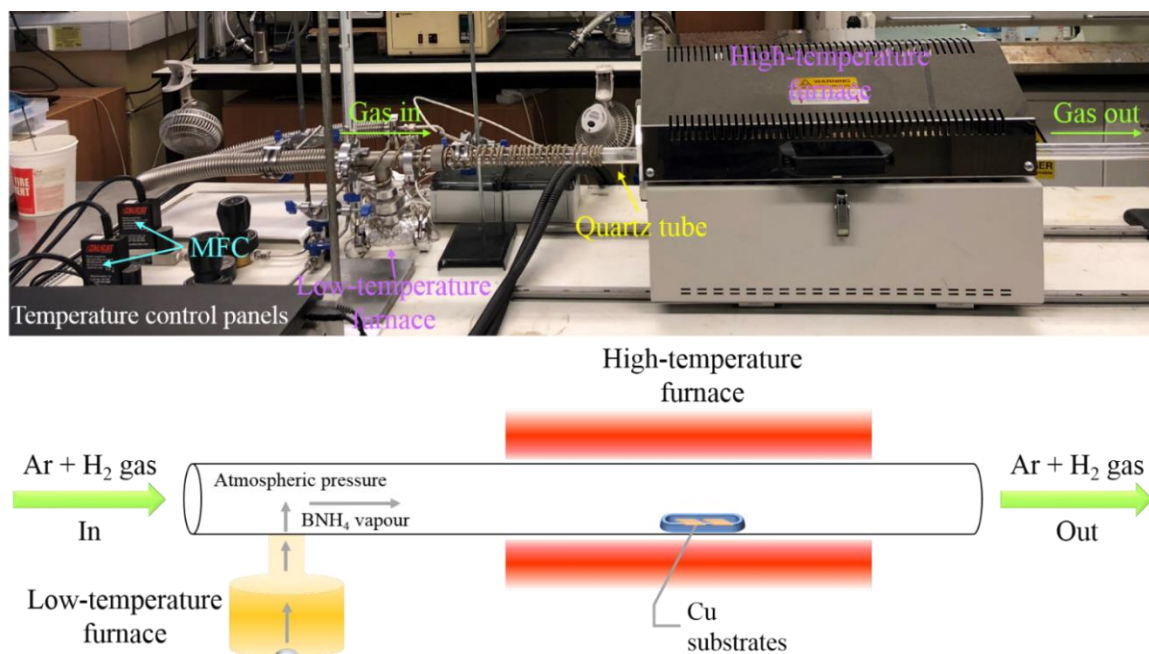


Figure 3.3. Photograph and schematic diagram of the typical CVD setup for the growth of hBN films.

3.2.5 Transfer of 2D materials and fabrication of VLHs

The transfer procedures were illustrated in Figure 3.4. The as-grown MoS₂ or WS₂ sample was first spin-coated with a thin film of poly(methyl methacrylate) (PMMA, 8 wt% in anisole, 495k molecular weight) at 4500 rpm for 60 s, followed by a 90 s curing process at 180 °C. The SiO₂ layer was etched off by floating the sample on a 1 M potassium hydroxide (KOH, Sigma-Aldrich) aqueous solution in a 50 °C water bath. It is worth mentioning that the planar strain in the MoS₂ or WS₂ nanosheets was released in this process. As soon as the film of PMMA/MS₂ detached from the SiO₂/Si substrate, it was rinsed in deionized (DI) water three times for 1 h each. A standard transfer method could be adopted in most cases (Figure 3.4a–c), where a piece of SiO₂/Si or glassy carbon (Sigma-Aldrich), precleaned *via* sonication in acetone and isopropanol for 15 min each, or a new TEM grid (a supported 200 nm thick Si₃N₄ film perforated by an array of 2 μm diameter viewing holes, Agar Scientific Y5358), was submerged into the deionised (DI) water to fish out the film. However, a

newly developed sliding transfer method was necessary when there is MS_2 on the target substrate (Figure 3.4a,d,e), normally in the fabrication of vertical stacks, so as to preserve the underlying MS_2 and ensure the interface cleanness. More specifically, a piece of clean cover glass was submerged into the DI water to fish the film, and then a few drops of IPA were applied onto the cover glass to expel the residual water before the film slid slowly onto the designated substrate. The as-transferred sample was left overnight in a ventilation environment. After totally dried, it was baked at 150 °C for 25 min to enhance the interface adhesion. At last, the sample was soaked in a 55 °C acetone bath for 48 h to dissolve the PMMA coating. Vertical heterostructures were made by repeatedly stacking different layers following either of the standard or the sliding transfer method without/with MS_2 on the target substrate, respectively. The layer-by-layer assembly of WS_2 :hBN: WS_2 VLHs is shown as an example in Figure 3.5. The alignment between the upper and lower layers was achieved by the optical microscope prior to the transfer process, and aided by naked eyes when the film slid onto the substrate.

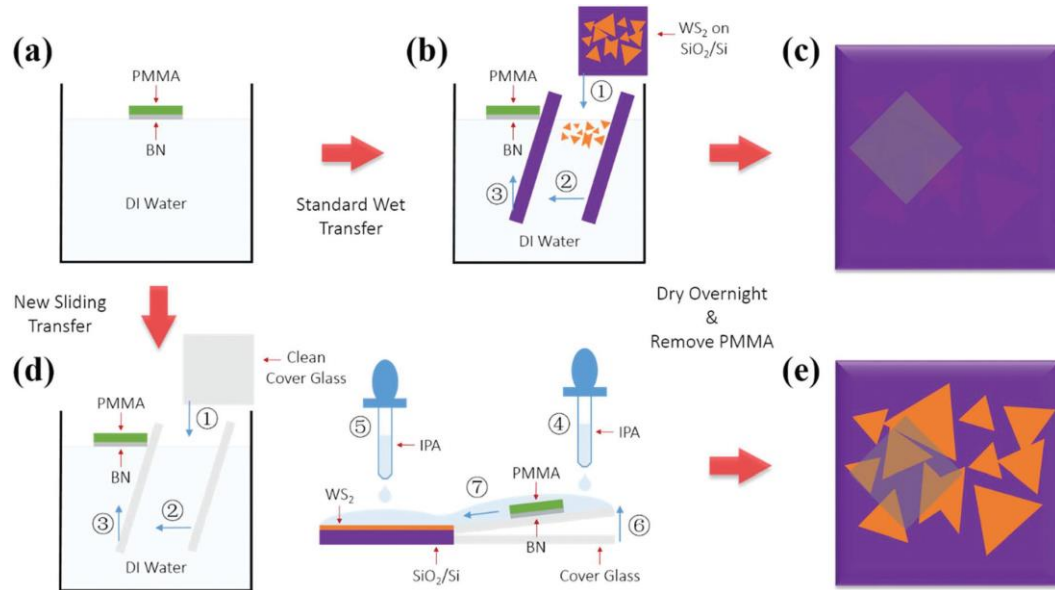


Figure 3.4. Schematic illustration of the non-aqueous sliding transfer method and the standard aqueous wet transfer process. (a) After all the cleaning processes, the PMMA/hBN stack was floating on DI water. (b) The standard wet transfer involves (1) suspending the $\text{WS}_2/\text{SiO}_2/\text{Si}$ in the DI water, (2) pushing it towards the stack and (3) scooping the stack onto the $\text{WS}_2/\text{SiO}_2/\text{Si}$. (c) It was found that most of the WS_2 crystals were washed off when soaked in DI water. (d) The sliding transfer process includes (1) dipping a piece of clean cover glass

into DI water, (2) pushing it towards the stack, (3) scooping the stack onto the cover glass, (4) wetting the cover glass with some isopropanol (IPA), (5) dropping IPA onto the WS₂/SiO₂/Si chip and keep it horizontal on the desk, (6) resting one side of the cover glass on the edge of the chip and lifting the other side up slightly and (7) allowing the stack to slide down very slowly. (e) All the WS₂ crystals remain intact after removing the PMMA.

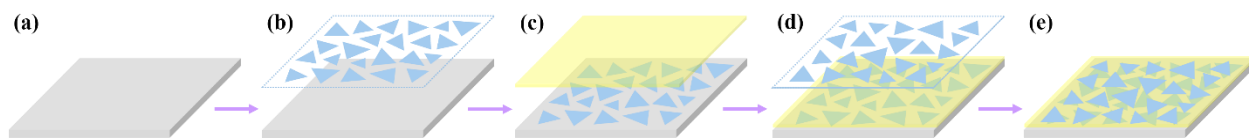


Figure 3.5. Schematic illustration of the transfer steps for the fabrication of WS₂:hBN:WS₂ vertical layered stacks. (a) A piece of clean SiO₂/Si substrate. (b) Transfer of a monolayer of WS₂ domains. (c) Transfer of an hBN continuous film on top of the as-prepared WS₂/SiO₂/Si. (d) Transfer of a second monolayer of WS₂ domains on top of the as-prepared hBN/WS₂/SiO₂/Si. (e) The as-fabricated WS₂:hBN:WS₂ stacks. Please note that each layer was coated with PMMA prior to the transfer, which was then removed in acetone after it was completely dried on the new substrate as described in the text; the sliding transfer method depicted in Figure 3.4d is necessary for transfer steps (c–e), while the standard transfer method could only be used for step (b).

3.2.6 Thermal annealing

Both to further eliminate the PMMA residues after the acetone bath and to fill the S vacancies, the sample was annealed in the presence of S vapour carried by Ar flow. In this process, the S powder (150 mg) and the sample were sealed in a quartz tube and were positioned at the centres of two furnaces, similar to the CVD growth. After the system had been flushed by the 500 sccm Ar flow for 30 min, the furnaces were ramped up to 200 and 276 °C, as calibrated with a thermocouple. The S vapour was then transported with the 300 sccm Ar flow downstream to the sample for 60 min. This was followed by a slow cooling process to avoid the formation of strain. The VLHs were assembled by repeating this transfer procedure.

As for studying the thermal degradation behaviour of the MoS₂ monolayer, the sample was alternatively annealed in vacuum. After being loaded into the ultrahigh vacuum-scanning tunnelling microscopy (UHV-STM) chamber, the samples were heated by resistively passing a direct current through them. The temperature was measured through a viewpoint with an optical pyrometer. The

temperature was ramped up and down at a rate of $2.5\text{--}5.5\text{ }^{\circ}\text{C min}^{-1}$, and the annealing process typically lasted 0.5–1 h.

3.3 Optical Microscopy

Optical microscopy (OM) is useful for characterisation of large TMD domains, and particularly, is featured with unique layer-dependent optical contrast. Two OM set-ups were employed in my DPhil projects, namely the Mitutoyo objective lens with a $50\times$ magnification attached to the CMOS camera (DCC1645C Thorlabs high-resolution 1280×1024 CMOS camera with a colour sensor), and the one implemented into the Raman system which will be introduced in Section 3.5. The former one is capable of providing optical microscopic images with good contrast and resolution of the prepared MS_2 on SiO_2/Si or SrTiO_3 substrate. Hence it was used to preliminarily examine the CVD-grown MS_2 in terms of the uniformity in layer thickness, the domain size, and the nucleation density, as well as the vertically stacked heterostructures. The latter one is inferior regarding the optical contrast and resolution, but it sufficed for recognising the overlapping region in the heterostacks with regard to the monolayer MS_2 components that required Raman and PL measurements. It is mentionable that hBN is not visible on either copper (after synthesis) or SiO_2/Si substrate (after transfer) because of its high transparency. The contrast and brightness of the optical microscopic images could be manually enhanced to manifest more clearly the information of interest with an image processing tool called “ImageJ”.

3.4 Scanning Electron Microscopy

Scanning electron microscopy (SEM) is a useful tool to examine the surface topography of materials. This derives from its image generation mechanism, where the contrast originates from the secondary electrons (SEs) excited by the incident beam on the sample surface and only those SEs

generated within a few nanometres of the surface can escape. In this project, Hitachi S-4300 field emission scanning electron microscope was operated to characterize micrometre-scale features of the CVD-grown 2D MoS₂, WS₂, hBN, and their vertically stacked heterostructures, including the nucleation density, the domain shape and size, the film continuity, as well as the layer number. It was mounted onto the sample stub firmly with carbon sticky pads so as to diminish any unwanted charge-up. The accelerating voltage was set to be 3 kV coupled with a beam current of 10 μ A. The choice of such a low accelerating voltage is for gaining clearer surface structures with less electron charging and irradiation damage to the samples.

3.5 Raman and Photoluminescence Spectroscopy

Raman and photoluminescence (PL) spectroscopy were employed in this research project to investigate the layer number, lattice strain, doping level, and interlayer contact of MoS₂, WS₂, hBN, and their heterostacks. The spectra were collected with a JY Horiba LabRAM ARAMIS imaging confocal Raman microscope, which couples a Raman spectrometer with a standard optical microscope. This permits simultaneous visualization of the sample under high magnification and acquisition of the Raman or PL signals at a micrometre-sized laser spot. The excitation light was a 532 nm laser with an estimated laser spot size of $\approx 1 \mu\text{m}$. Before the measurements, the Raman spectrometer was calibrated by a standard silicon chip (520.7 cm^{-1}) to exclude any instrumental error that would otherwise give inaccurate data. Two gratings can be selected, *i.e.*, 600 g mm^{-1} (600 grooves per mm grating) and 1800 g mm^{-1} . The density of grooves is proportional to the resolving power of the spectrometer, but is inversely proportional to the wavelength coverage. In the Raman mode, 1800 g mm^{-1} was used for a better spectral resolution. Although only a relatively small range of wavelengths can be covered, this is sufficient for the characteristic vibrational modes of MoS₂, WS₂, and hBN. To can supply a good signal-to-noise ratio and avoid any sample damage due to the laser-induced thermal effects, the Raman spectrum was normally taken from 200 to 600 cm^{-1} for

MoS₂ and WS₂ samples and from 1300 to 1500 cm⁻¹ for hBN samples, all with an acquisition time of 5 s and an accumulation number of 5. For the PL spectrum, a coarser resolution is required and was collected with 600 g mm⁻¹ grating. The acquisition time and accumulation number were adjusted according to the investigation purposes and the optical properties of the material to be measured. The intensity of Raman peaks was used to normalize the PL signal as they were covered in the same spectral range, whereby the quantum efficiency of MoS₂ and WS₂ could be shown. To investigate the homogeneity of the CVD-grown materials, Raman and PL mappings were conducted by collecting multi-point spectra across lateral dimensions (XY coordinates) in a fixed step size. Thanks to the SWIFTTM mapping mode embedded in the HORIBA Raman system, the acquisition time at each spot can be decreased to 0.1 s without compromise in characterisation quality. The step size was set to be $\approx 1 \mu\text{m}$, being similar to the diameter of the excitation laser spot. A smaller step size would cause convolution effects especially on the edges of the 2D domains, while a larger step size would decrease the resolution of the spatial mapping.

3.6 Atomic Force Microscopy

Atomic force microscopy (AFM) is the most unambiguous characterisation method to provide information on the thickness and surface morphology of 2D materials. Since the SiO₂/Si or SrTiO₃ substrates have good surface flatness as well as rigidity, both the as-grown and transferred samples supported by them can be used for AFM characterisation. The measurements were carried out utilizing Asylum Research MFP-3D in a tapping mode (AC mode) with a silicon AC-160TS cantilever (Olympus, spring constant of $\approx 42 \text{ N m}^{-1}$ and resonant frequency of $\approx 300 \text{ kHz}$). An optical microscope was combined to the equipment for visualizing the sample areas. Various imaging modes can be recorded simultaneously, including the topological imaging mode and the phase mode. The topological imaging mode can display the height difference between the surfaces of the material and the substrate, and was used to measure the sample thickness. The phase imaging mode is sensitive to

the elasticity of materials, so it can help on differentiating the tiny domains that are not easy to be visualized under the low magnification of the optical microscope. The AFM images and height profiles were generated by 'Gwyddion' software.

3.7 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) is a surface-sensitive quantitative spectroscopic technique that measures the elemental composition. It can offer information on the empirical formula, chemical state and electronic state of the elements existing within the material. XPS spectra were obtained by irradiating the sample with a beam of X-rays while simultaneously measuring the kinetic energy and number of electrons that escape from the top 0 to 10 nm of the sample, which is larger than the thickness of the material to be analysed. The samples were characterised by Thermo Scientific K-Alpha XPS instrument with a microfocused monochromated Al X-ray source (1486.6 eV). The source was operated at 12 keV and spot size was $\approx 400 \mu\text{m}$. The analyser operates at constant analyser energies of 200 eV for survey scans and 50 eV for detailed scans. A combined low energy/ion flood source was used for charge neutralization. The data acquisition and analysis was conducted with Thermo Scientifics Advantage software. Peak fitting (Lorentzian/Gaussian 30%) was applied following removal of the background. Normalized atomic percentages were determined from peak areas of the elemental main peaks detected on the survey scan following background subtraction and application of Thermo sensitivity factors.

Chapter 4 Large Dendritic Monolayer MoS₂ Grown by APCVD for Electrocatalysis

The edge sites of MoS₂ are catalytically active for the hydrogen evolution reaction (HER), and growing monolayer structures that are edge-rich is desirable. Here, we show the production of large-area highly branched MoS₂ dendrites on amorphous SiO₂/Si substrates using an atmospheric pressure chemical vapour deposition and explore their use in electrocatalysis. By tailoring the substrate construction, the monolayer MoS₂ evolves from triangular to dendritic morphology because of the change of growth conditions. The rough edges endow dendritic MoS₂ with a fractal dimension down to 1.54. The highly crystalline basal plane and the edge of the dendrites are visualized at atomic resolution using an annular dark field scanning transmission electron microscope. The monolayer dendrites exhibit strong photoluminescence, which is indicative of the direct bandgap emission, which is preserved after being transferred. Post-transfer sulphur annealing restores the structural defects and decreases the n-type doping in MoS₂ monolayers. The annealed MoS₂ dendrites show good and highly durable HER performance on the glassy carbon with a large exchange current density of 32 $\mu\text{A cm}_{\text{geo}}^{-2}$, demonstrating its viability as an efficient HER catalyst.

4.1 Introduction

MoS₂ is a layered material with a promising catalytic behaviour toward the hydrogen evolution reaction (HER).^{116,126,139,141,215,216} The electrocatalytic activity typically occurs at edge sites of MoS₂ and at defects of sulphur atoms (*i.e.*, unsaturated states and vacancies).^{116–118,122,139–141,216} Metallic 1T-phase MoS₂ normally displays superior HER performance compared with the semiconducting 2H-phase MoS₂ because of the additional reactive sites across the basal planes that are electrochemically inert for 2H-MoS₂,^{123,134,216} and further improvement can thus be achieved through a phase transition from 2H to 1T.^{137,217} The catalytic activity of 2H-MoS₂ increases linearly with the number of edge sites,¹⁴² whereas it decreases linearly with the layer number because of the reducing electron hopping efficiency.¹⁴² Alternative ways to increase the HER catalysis of MoS₂ include chemical doping and defect/strain engineering, which modulate the lattice structure and electronic states^{120,139,141,218–224} and hybridising with other materials^{133,145,225–231}.

There are a variety of methods to produce MoS₂ for electrocatalysis, such as electrochemical intercalation,¹⁵³ chemical exfoliation,^{123,134} solvothermal reaction,²³² and chemical vapour deposition (CVD).^{126,164,166,178} Improving the catalytically active CVD-grown thin films of MoS₂ usually centres around enriching the edge numbers, for example, by growing vertically aligned films or porous structures with exposed edges.^{126,128,135,137,216,233} Monolayer MoS₂ that is effective for the HER can also be obtained by CVD,^{127,144} provided that the films are not fully continuous and are instead composed of numerous isolated flakes that have abundant edges. Controlling the CVD growth parameters to achieve dendritic-shaped MoS₂ domains increases the number of catalytic sites relative to areal coverage.^{127,179}

Although it has been reported that the morphology of monolayer MoS₂ is variable by modifying the heated temperature and carrier gas flow rate in CVD,^{127,234,235} the change in the domain shape is constricted within a narrow range, and the lateral size is small. Few-layer dendritic MoS₂ has been synthesized in a previous study by changing the carrier gas flow rate in the CVD process,¹⁷⁹

while the photoluminescence (PL) of these dendrites is significantly weaker compared to their monolayer counterparts because of their indirect bandgap.² Low pressure CVD has been adopted to grow dendritic MoS₂ monolayers on a single crystal substrate of SrTiO₃ (STO(100)), but the domain size is limited to $\sim 10\ \mu\text{m}$, and high coverage has not been achieved simultaneously with the increase in the branching degree,¹²⁷ which restricts the density of active edge sites. Therefore, further work on producing highly fractal MoS₂ is of interest to enhance HER efficiency, especially for CVD-grown MoS₂.

In this project, a three-stage atmospheric pressure CVD (APCVD) technique was utilised to synthesise highly uniform monolayer MoS₂ dendrites on amorphous SiO₂/Si substrates with a large domain size. The ambient condition ensures a facile and green synthesis with lower reaction temperature and simplified experimental equipment. Each aspect of the CVD process can be controlled individually and allows the growth of large monolayer domains. The flake evolves from a triangular to highly dendritic shape by customizing our home-built substrate. The electrochemical catalytic behaviours of these large-area MoS₂ dendrites with different crystal morphologies are characterized on the glassy carbon. The effects of transfer and sulphur annealing were explored on the PL and HER performance of monolayer MoS₂, which also grant us the ability to investigate the sole contribution of edges to the HER activities.

4.2 Results and Discussion

Figure 4.1a depicts the APCVD used in the present work for growing monolayer MoS₂. The temperature control in this system was realised by *in situ* calibration utilising a thermocouple, with the quartz tubes loaded. Large-area MoS₂ nanosheets are produced by a three-stage growth (Figure 4.1b). Sufficient precursor feedstocks are provided by a high gas flow rate during the initial stage to form nuclei. After that, the main growth starts under a lower gas flow rate and proceeds by consuming the excess precursors at local sites. Then, the gas flow rate is further decreased so that the atoms

residing on the domain surfaces can migrate freely to the adjacent edges. The temperature is simultaneously decreased to reduce both the feedstock of MoO_3 and the sublimation of as-produced MoS_2 .

The relative concentrations of the gaseous precursors vary greatly on different substrate surfaces. The atom ratio of Mo/S can determine the shape of the resulting MoS_2 domains.¹⁷⁸ Herein, monolayer MoS_2 flakes with various morphologies are controllably synthesized in a single growth by adjusting the position of the substrate chips. The low Mo/S ratio on the bottom substrate typically gives rise to MoS_2 dendrites with a high branching degree (Figure 4.1d,f), whereas normal triangular MoS_2 crystals are grown at the same time on the other three substrates (Figure 4.1c,e). Figure 4.1f presents an abundance of edge sites accommodated by the dendritic pattern. As the growth system is rich in sulphur, the nucleation density of MoS_2 relies on the concentration of MoO_3 , which is very low in close proximity to the tube wall. Lateral growth is favoured at the nuclei with lower densities, giving a larger domain size of the dendritic MoS_2 on the bottom substrate. The optimized CVD procedure and substrate construction allow the production of large-area, highly dendritic MoS_2 monolayers with the arm length up to $\approx 390\ \mu\text{m}$.

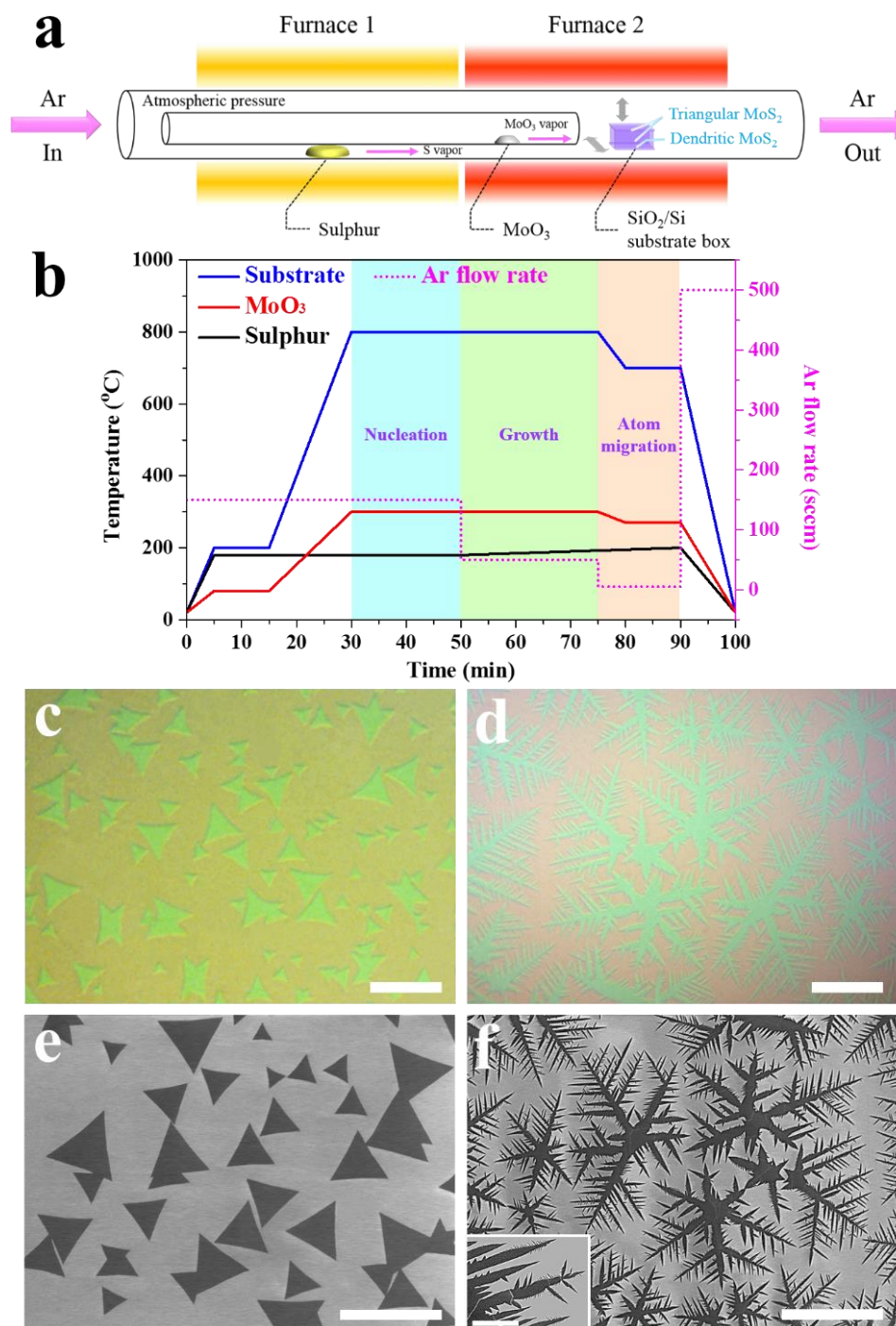


Figure 4.1. (a) CVD setup for the synthesis of MoS₂ domains. (b) Profiles of the temperature and carrier gas flow rate programmed for the formation of large-area MoS₂ monolayer flakes with varied morphologies. (c,d) Optical microscopic images and (e,f) scanning electron microscopy (SEM) images for the as-grown triangular and dendritic MoS₂, respectively. Scale bar: 200 μm . The inset of panel (f) shows the fine detail of a dendrite tip; scale bar: 10 μm .

The shape of the MoS₂ domain is also tunable by altering the distance of the SiO₂/Si chip to the gas flow. The branching degree is dependent on the local ratio of Mo/S, which is in turn determined by the location of the substrate surfaces.¹⁷⁸ The construction of the self-supported substrate box is flexibly tailorable. The inside and outside chips can be shifted along the directions indicated with the grey arrows in Figure 4.1a, and the bottom chip would be moved up or down while changing its width, which is perpendicular to the gas line. Figure 4.2a illustrates the spatial concentration of the sulphur vapour, which is affected by both the distance to the source (radial degradation) and the distance along the quartz tube (linear degradation) because of the temperature gradient in the furnaces. The decreasing heights correspond to the evolving domain morphologies shown in Figure 4.2 from panel b to i. It is notable that the growth on the bottom substrate is independent of the presence of the other three. Because the temperature of the SiO₂ surfaces is kept identical, the Mo/S ratio is dependent on and sensitive to the height of the substrate (green arrow). When reducing the chip width (blue arrows), the substrate is closer to the inside wall of the quartz tube at a lower height, where the concentration ratio of Mo/S is smaller. It is found that a larger relative concentration of the sulphur results in a higher branching degree of the MoS₂ products. The shape evolution is noticeable with a decrease of every 2.0 ± 0.5 mm in width, from 2 cm for strictly triangular MoS₂ (Figure 4.2b) to 0.6 cm for highly dendritic MoS₂ (Figure 4.2i). Further narrowing the substrate would cause insufficient feeding of the precursors and scale down the macroscopic area of the sample. The branched monolayer MoS₂ in Figure 4.2e–i contains a large density of grain boundaries and hence is likely to show distinct optical and electrical properties.⁸⁵

The complexity and roughness of the fractal pattern is of interest because it is correlated to the HER activities of MoS₂. It can be evaluated by the fractal dimension of the crystal pattern. The box-counting method is usually applied for the calculation, based on the number of boxes that are in contact with the domain edges as a function of the scaling factor.²³⁶ The fractal dimension for monolayer MoS₂, indicated by the slope of the linear regression, increases from 1.15 (triangular

outline, Figure 4.3a) to 1.54 (highly dendritic outline, Figure 4.3h). This demonstrates that through the adjustment of substrate construction, the edge of MoS_2 is increasingly rough with the shape change, therefore holding potential for enhanced HER performance.

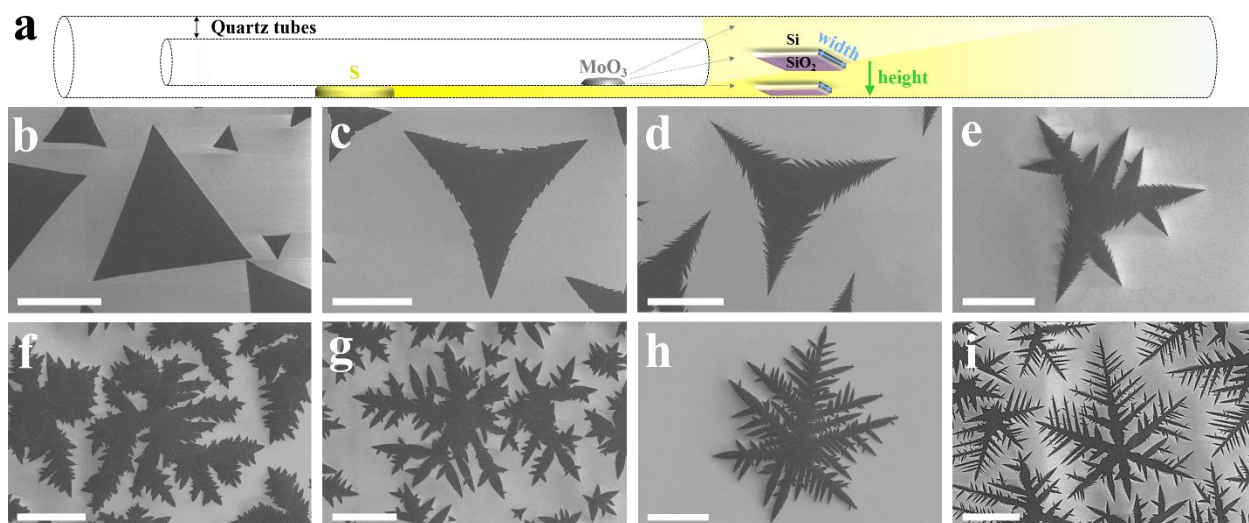


Figure 4.2. Shape evolution of the as-synthesized MoS_2 on bottom SiO_2/Si substrate. (a) Schematic diagram of the substrate positioning relative to the precursor vapours. (b–i) SEM images of the resulting monolayer MoS_2 . The domain evolves from the normal triangular shape in panel (b) to the highly dendritic shape in panel (i). Scale bar: $100\ \mu\text{m}$.

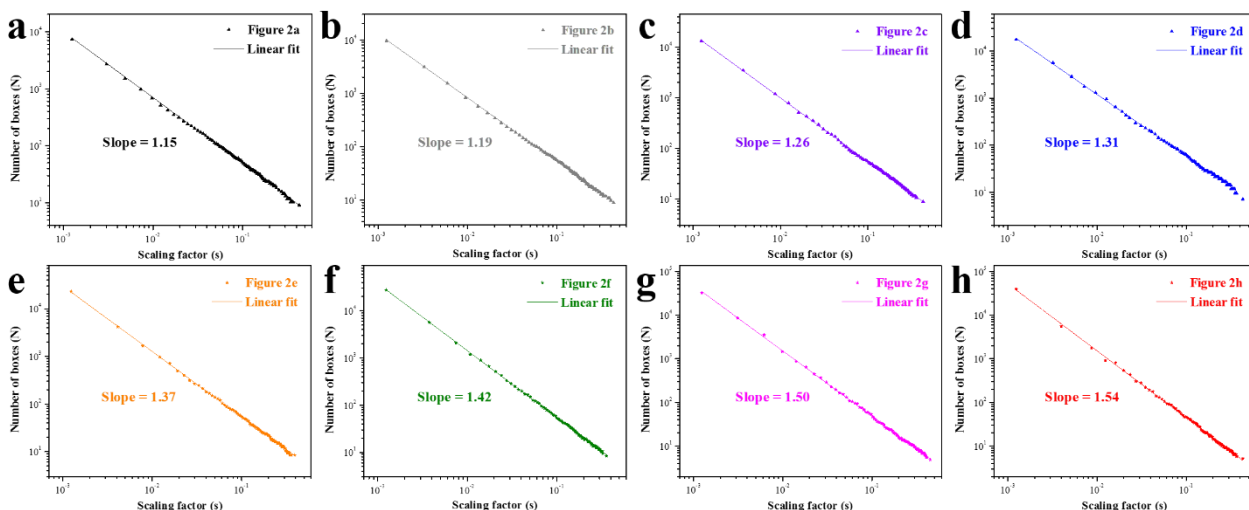


Figure 4.3. Linear regression for the evolving crystal morphologies. The logarithmic plots in (a–h) correspond to the SEM images in Figure 4.2b–i. The slopes indicate the fractal dimensions of the domain patterns, varying from 1.15 in panel (a) for triangular MoS_2 , to 1.54 in panel (h) for highly dendritic MoS_2 .

The configurations of the as-grown MoS₂ are carefully inspected in Figure 4.4, where each hierarchical level is indicated by one arrow colour. Unlike crystalline substrates such as SrTiO₃,²³⁷ on which the preferential diffusion paths are specified and restricted by the well-organised surface structures, highly anisotropic surface energies are offered by the amorphous SiO₂/Si substrate. This could promote the branching concurrent with the expansion of the domain area. In another aspect, the higher flux of sulphur vapour around the bottom substrate triggers a growth transition from the thermodynamic mode to the kinetic mode. The precursor molecules attach to the existing crystal with the anomalous diffusion of precursors, and the growth is preferred along the lowest-energy diffusion paths on the substrate, instead of the crystal edges.²³⁸ Consequently the islands develop into large fractal-like structures (Figure 4.4d). A moderate precursor flux results in thermodynamic growth, and at equilibrium, triangular MoS₂ domains are produced (Figure 4.4a). In another case, the growth mode could switch intermittently near the transition threshold, and accordingly, MoS₂ grows laterally *via* the attachment of precursor molecules along domain edges (under thermodynamic control) while shooting out arms along the crystal facets (under dynamic control). By virtue of this combined regime, branched structures are generated with more compact body, wider arms, and less hierarchical morphology (Figure 4.4c) relative to the sharp dendrites. The determination of the growth mode is highly sensitive to the concentrations of precursor vapours at specific locations, which explains the feasibility of achieving various branching degrees. As illustrated in Figure 4.4, the offshoots and side sprouts show parallel alignments for either side of the arms. However, the offshoots in any hierarchical level grow forward away from the central core/axis, while the side sprouts grow backward pointing to the main body. Interestingly, the angles measured by the arm axes are all ~60° between the primary backbones and the secondary arms (I & II), the secondary and the tertiary arms (II & III), the tertiary and the quaternary arms (III & IV), as well as the side sprouts and their affiliated arms (SS and A), regardless of their positions (*e.g.*, Figure 4.4b). The results are summarized in Figure 4.4f, with the error bars <8.2%. We also observed three-fold symmetric backbones for the triangular

domains and six-fold symmetric backbones for the dendrites, both centred at the nucleation core. Therefore, the growth mechanism in our scenario cannot be interpreted purely by the classical diffusion-limited aggregation (DLA) model, giving random dendritic configurations.²³⁹ Because certain lattice directions are energetically favourable (*e.g.*, zigzag or armchair direction) at the growth front, backbones would prefer to develop from the nucleation core with symmetries, and similarly, side branches tend to form a 60° angle to the arm at deflection sites when the growth is driven by kinetics. This could apply to other TMD materials with the same low-energy pathways. The high crystallinity of the as-grown MoS₂ monolayers are verified by the annular dark-field scanning transmission electron microscopy (ADF-STEM) imaging shown in Figure S1 (Appendix), regardless of the domain shape. The dendrite edges indicate that the domain has zigzag edge terminations in both S and Mo directions, as expected considering the presence of six arm branches from the core of the dendrite.

The growth of dendritic structure was derived from the twin defects which exist in the nucleation (and early growth) stage(s).²⁴⁰ Then the highly excessive concentration of the S vapor compare to the Mo vapor on the substrate surface initiated a diffusion-limited aggregation, for which the mass transport coefficient is greatly larger than the reaction rate constant ($h_g \gg k_s$) so that the diffusion of reactive species is the rate-limiting step in the CVD, resulting in the large MoS₂ dendrites. It is notable that the Reynold's number remains below 600 ($Re < 600$) in our CVD system by controlling the total velocity of the argon (Ar) gas flow. This ensured a consistently laminar rather than turbulent flow, and allowed the growth of uniformly monolayer domains. The six-fold symmetric backbones of the monolayer dendritic MoS₂ domain is attributed to the amorphous substrate surface, whereby the growth of the MoS₂ adlayer would not be dictated by the lattice symmetry of the substrate, and more importantly, as the intrinsic characteristic of MoS₂, the six-fold cyclic defects that account for the branching of the MoS₂ nuclei. It can therefore be

deduced that the six-fold symmetry could be expected for the backbones of such monolayer dendritic TMDs on any other amorphous substrate surfaces.

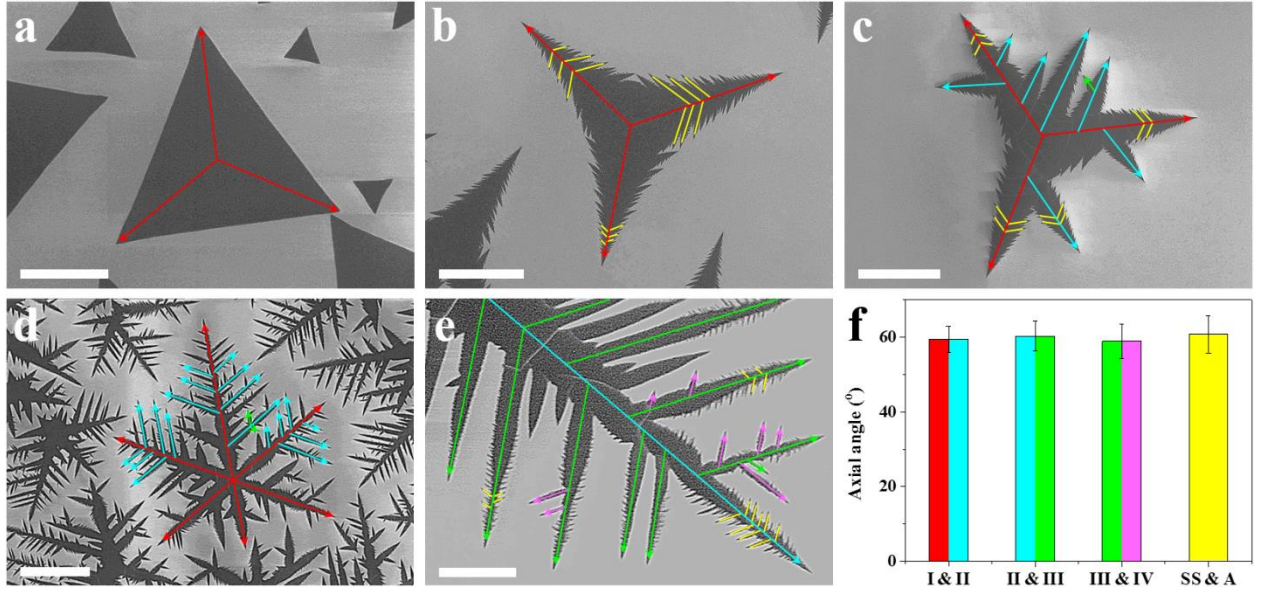


Figure 4.4. Analysis of the CVD-grown monolayer MoS₂ with (a) strict triangular, (b) star triangular, (c) branched, and (d) highly dendritic morphologies. The hierarchical structures are marked by arrows, *i.e.*, red for the primary (I) backbone, cyan, green, and pink for the secondary (II), tertiary (III), and quaternary (IV) arms. The side sprouts (SS) are marked by yellow lines. (f) Histogram of the axial angle between different hierarchical arms (I and II, II and III, III and IV), and between the arms and their side sprouts (SS and A). The first three columns are bicoloured according to the hierarchy levels of the arms, which is consistent with panel (a–e), and while considering the high similarities, the results for the side sprouts affiliated with arms II to IV are generalised in the yellow column. Scale bar: (a–d) 100 μm ; (e) 20 μm .

Raman and PL spectroscopies were performed to explore the physical properties of the MoS₂ grown on SiO₂/Si substrates. Figure 4.5a shows the two characteristic Raman modes of MoS₂, E_{2g}^1 ($\sim 384.0\text{ cm}^{-1}$) and A_{1g} ($\sim 403.6\text{ cm}^{-1}$). The E_{2g}^1 mode corresponds to the in-plane Mo–S phonon and is preferentially excited for terrace terminations, whereas the A_{1g} mode corresponds to the out-of-plane Mo–S phonon and is preferentially excited for edge terminations. The relative intensities between A_{1g} and E_{2g}^1 can therefore provide information on the texture of MoS₂.^{126,128} For both triangular and dendritic domains, the integrated intensity ratios of $A_{1g}/E_{2g}^1 \approx 1$ conform well to the reported value of monolayer MoS₂,¹⁰² indicating that terrace sites are predominant in the

nanosheets.¹²⁸ However, the dendritic MoS₂ shows a slightly higher A_{1g}/E_{2g}^1 ratio, which is suggestive of a rougher surface. Strong PL is observed in these monolayers (Figure 4.5b),¹ and the PL intensities of both morphologies are comparable. It is noteworthy that the PL intensity and the peak position have minor deviations (intensity $\pm 5.4\%$; peak position $\pm 3.6\%$), mainly because of the temperature profile in the CVD furnaces for centimetre-scale synthesis,²⁴¹ which are yet negligible (intensity $\pm 0.8\%$; peak position $\pm 0.5\%$) within single domains. We further extract the quantitative information about the as-grown MoS₂ dendrites in Figure 4.5c by fitting the data to Gaussian functions with three peaks originating from B exciton, A exciton, and A⁻ trion. The neutral excitons of A and B arise from two different transitions within the direct bandgap of monolayer MoS₂, whereas the A⁻ trion is a bound state of two electrons and one hole (namely, A exciton + a free electron) *via* Coulomb interactions due to the n-type doping from charged SiO₂ surfaces.²⁴² The Raman and PL maps in Figure 4.5e–g,j–l show the integrated intensity and the peak position over the energy range corresponding to the peaks in the Raman (Figure 4.5a) and PL spectra (Figure 4.5b) and verify that our CVD-grown MoS₂ is highly uniform. The frequency difference between A_{1g} and E_{2g}^1 modes can be used to precisely determine the layer number of MoS₂, and the values lying within the range of 18.5–19.0 cm⁻¹ confirm the monolayer nature across the domains (Figure 4.5h,m).¹⁰² The thicknesses are also confirmed by atomic force microscopy (AFM) measurements (Figure S2, Appendix A).

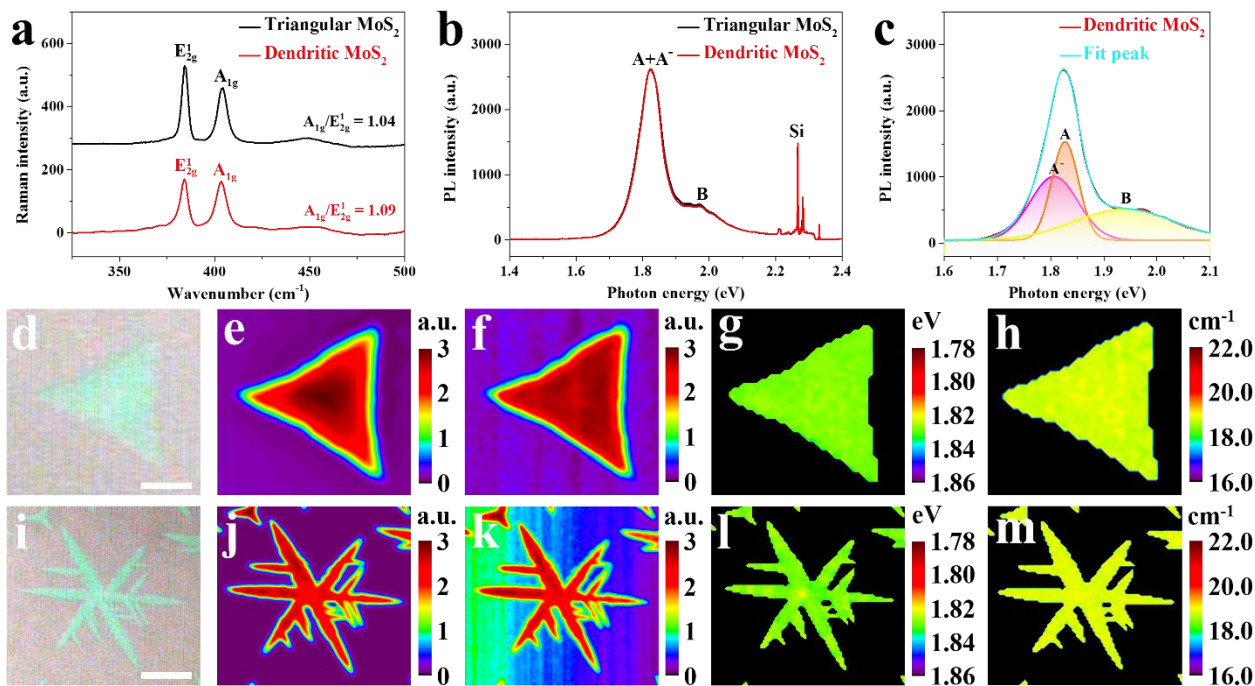


Figure 4.5. Raman and PL studies of the as-grown MoS₂ on SiO₂/Si substrates. (a) Raman and (b) normalized PL spectra of the triangular MoS₂ and dendritic MoS₂. (c) Deconvoluted PL spectrum of the dendritic MoS₂ with Gaussian fitting (PL components: B exciton, A exciton, and A⁻ trion). (d,i) Optical microscopic images of triangular MoS₂ and dendritic MoS₂ for measurements. Total (e,j) PL and (f,k) Raman integrated intensities, (g,l) PL peak positions, and (h,m) frequency differences between A_{1g} and E_{2g}¹ Raman peaks of (e–h) triangular and (j–m) dendritic MoS₂. Scale bar: 30 μm.

Nanostructured MoS₂ is an active electrocatalyst for the HER. The catalytic response was found to correlate linearly with the number of edge sites.¹²² Therefore, dendritic MoS₂ is promising to exhibit improved HER performance in comparison with other monolayer morphologies. We transferred the CVD-grown MoS₂ onto the conductive glassy carbon as the working electrode in the HER. Figure 6a,b shows the as-transferred triangular and dendritic MoS₂ flakes on the glassy carbon. The electrocatalytic activities of MoS₂ depend on several factors, including the phase,^{123,134,216} layer number,¹⁴² structural disorders,^{116,118,139–141,216} and strain,^{139,141,218} apart from the density of edge sites.^{116,117,122,126,216} 2H-phase MoS₂ is produced by the CVD method, and the inbuilt strain is released through a wet transfer process. The release of strain is evidenced by comparing the PL spectra of dendritic MoS₂ grown on the SiO₂/Si substrate (red curves in Figure 4.5b,c) with those of dendritic

MoS₂ transferred to the glassy carbon (purple curves in Figure 4.6c,e). The PL peak position is blue-shifted by 17.1 meV (6.3 nm) after the transfer, which corresponds to ~0.27% strain for MoS₂ monolayers.²⁴³ Monolayer MoS₂ exhibits the optimal catalytic performance because of the high electron hopping efficiency, which decreases significantly with more layers added.¹⁴² However, sulphur vacancies are inevitably generated during the transfer. Therefore, the individual contribution of edge sites to the catalytic efficiency can be analysed only if the influences of defects are minimized. To this end, we conduct thermal annealing for the transferred MoS₂ in a sulphur vapour environment. The PL of the MoS₂ dendrites is probed before and after annealing. It is found that the PL intensity is increased (Figure 4.6c), and the peak width is narrowed together with a red shift (Figure 4.6d) after the annealing treatment. Figure 6e,f presents the detailed Gaussian fits before and after annealing, respectively. The enhanced PL peak intensity suggests that the crystallinity of MoS₂ is improved.¹¹⁸ Besides, the annealing results in less localized states (LSs), which are associated with defects such as sulphur vacancies.²⁴⁴ The change in the peak intensity ratio of A/A^- reflects the varied relative population density of excitons and trions.²⁴² The increased A/A^- ratio after annealing indicates a reduced concentration of electrons in the material. These observations show that sulphur atoms have been incorporated into the crystal lattice of MoS₂ during the annealing process. It fills the sulphur vacancies and causes p-type doping in the MoS₂ nanosheets. However, it should be mentioned that defects cannot be entirely restored so that the LS peak of the annealed sample is still not negligible in the Gaussian fitting.

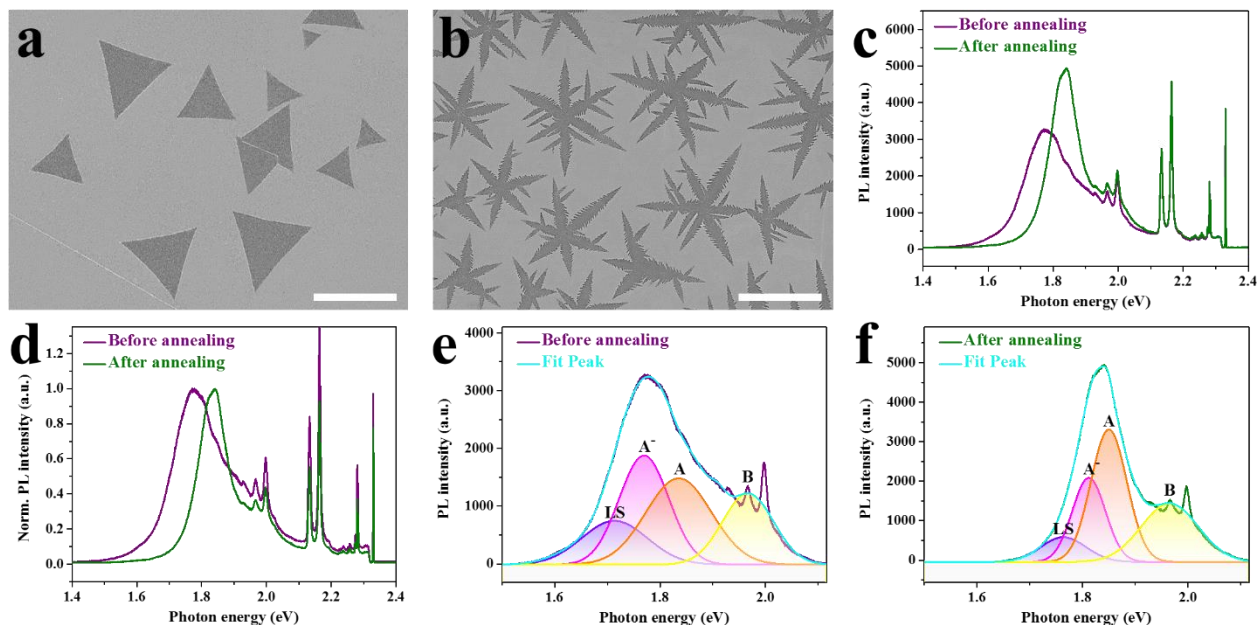


Figure 4.6. SEM images of the as-transferred (a) triangular MoS₂ and (b) dendritic MoS₂ on glassy carbon plates. (c) PL spectra and (d) normalized PL spectra before (purple curves) and after (green curves) annealing. (e,f) Deconvoluted PL spectra using Gaussian fitting into four PL components, *i.e.*, B exciton, A exciton, A⁻ trion and LSS. Scale bar: 30 μ m.

Precycling has been done before the electrochemistry measurements to precisely examine the native HER properties of monolayer MoS₂ as this could be necessary for transferred sample to reach stabilities.¹¹⁶ The electrochemical tests were performed in a three-electrode system using the monolayer MoS₂ transferred on the glassy carbon as the working electrode, a Pt wire (or alternatively, a carbon rod) as the counter electrode, and Ag/AgCl/KCl (3 M) as the reference electrode. A defined working area of the sample was immersed into a 0.5 M H₂SO₄ N₂-purged solution for HER activities. The potentials were calibrated to a reversible hydrogen electrode ($E(\text{RHE}) = E(\text{Ag/AgCl/KCl (3 M)}) + 0.21 - 0.059 \cdot \text{pH}$). Cyclic voltammetry was applied at a scan rate of 100 mV s⁻¹ to clean the sample surface till the current signal was stable.¹¹⁶ Then, LSV was conducted under quasiequilibrium conditions at 1 mV s⁻¹. The MoS₂ was not grown directly on glassy carbon substrates, as the smoother surface of SiO₂ is beneficial to high uniformity and large-scale synthesis, especially for 2D monolayers.^{242,245} The linear sweep voltammetry (LSV) results in Figure 6.7a indicate that the

dendritic MoS₂ displays an enhancement of the HER activities with increased current density (j or j_{geo}), and the performances are improved even after 1000 times cycling. A sensible interpretation could be that the existing sulphur vacancies tend to aggregate and proliferate in the strained structure during the cycling process,²⁴⁶ by which the active site density is increased inside the basal plane of 2H-MoS₂. However, the HER performance then degrades rapidly upon further cycling. In contrast, MoS₂ exhibits high durability after the transfer and sulphur annealing, though lower HER activities are observed initially (Figure 4.7d). This is owing to the successful elimination of the strained sulphur vacancies, which are unstable reactive sites in the MoS₂ monolayers. A long-term cycling test up to 30 000 times was applied to the branched MoS₂, and it proved the excellent stability of the postannealed MoS₂ monolayers. The MoS₂ dendrites also show a lower Tafel slope (Figure 4.7b,e), suggesting that a lower overpotential would be required for a certain increase in the current density. As largely influenced by the strain in sulphur vacancies,¹⁴¹ the Tafel slope increases after the transfer and annealing treatments, indicating reduced HER efficiencies, while it was little relevant to the domain coverage if annealed in H₂S atmosphere.¹²² Additionally, the difference in Tafel slopes is smaller between the dendritic and triangular MoS₂ after sulphur annealing, which could result from the exclusion of strained sulphur vacancies associated with domain edges. Exchange current density (j_0) is used to describe the efficiency of electron transfer in catalysts at zero overpotential (η). It can be calculated by fitting the linear portion of the Tafel plot ($\log j$ vs. η) at large values of η .^{122,247} A large exchange current density of 37 $\mu\text{A cm geo}^{-2}$ is reached by the as-transferred (*i.e.*, nonannealed) dendritic MoS₂, incorporating plenty of strained sulphur vacancies, while the annealing-derived highly crystalline MoS₂ with much less structural defects shows an exchange current density of 32 $\mu\text{A cm geo}^{-2}$ for the dendrites and 14.5 and 0.8 $\mu\text{A cm geo}^{-2}$ for the branched and triangular structures, respectively. These values match well with the literature regarding the HER (0.13–38.9 $\mu\text{A cm geo}^{-2}$), and the behaviour of our highly crystalline dendrites is among the best reported for monolayer MoS₂ catalysts that were not engineered to be integrally defective or heterostructured with other materials,

irrespective of morphologies, substrates, and preparation methods.^{122,126,250,251,127–129,135,139,232,248,249}

The larger exchange current densities were attributed to the massive amount of active catalyst materials in the bulk MoS₂ compared to the monolayers we have grown and/or the substantial defects that were deliberately incorporated.^{139,222,251} The exchange current density of MoS₂ has also been increased beyond 38.9 $\mu\text{A cm geo}^{-2}$ *via* hybridisations.^{225,230} Considering that the areal coverage of the MoS₂ dendrites is 12% higher because of its large domain size, determined by the SEM images in Figure 4.1e,f, the exchange current density of the dendritic MoS₂ is ~ 37 times larger than that of the triangular counterpart. EIS is also employed to analyse the catalytic property of MoS₂ (Figure 4.7c,f). The semiarc at the low frequency region is an indicator of the kinetic control in the electrode process, and any mass transfer control is excluded, which is consistent with other studies,^{116,127,216} which would otherwise give an additional straight line with a 45° angle at the low frequency region. It is revealed by the smaller radius of the semiarc that dendritic morphology with significantly increased edge density permits a decreased charge transfer resistance (R_{ct}) across the MoS₂–electrolyte interface. This can facilitate the rate-determining step in the HER, *i.e.*, proton discharge (Volmer reaction: $\text{H}_3\text{O}^+ + \text{e}^- \rightarrow \text{H}_{\text{ads}} + \text{H}_2\text{O}$) in our case, and thereby improve the catalytic activity of MoS₂.²⁵² As the x-axis intercept at the high frequency region represents the ohmic impedance of the reaction system,²⁵³ the dendrites show a lower electrical resistance (R_s), which is in agreement with the larger areal coverage (a) of 12% based on Ohm's law ($R = \rho l a^{-1}$, where ρ is identical for polycrystalline MoS₂ and l is the fixed monolayer thickness). Moreover, the sulphur annealing for either domain shape leads to a slightly higher R_s , stemming from the reduction in sulphur vacancies that act as n-dopants in MoS₂. Figure 4.7g–i links the edge density (E_D) with the HER behaviour. The change from a triangular to highly dendritic domain shape corresponds to an increase in E_D , whereby the HER performance of monolayer MoS₂ is enhanced. The exchange current density and the onset potential correlate almost in a linear fashion with E_D (Figure 4.7g,i, respectively). The trend of j_0 vs. E_D is similar to that in earlier studies.^{118,122} However, the decrease in the Tafel

slope is more obviously smaller at high E_D (Figure 4.7h), as it relies on the Volmer reaction whose rate consistently limits these HER processes.

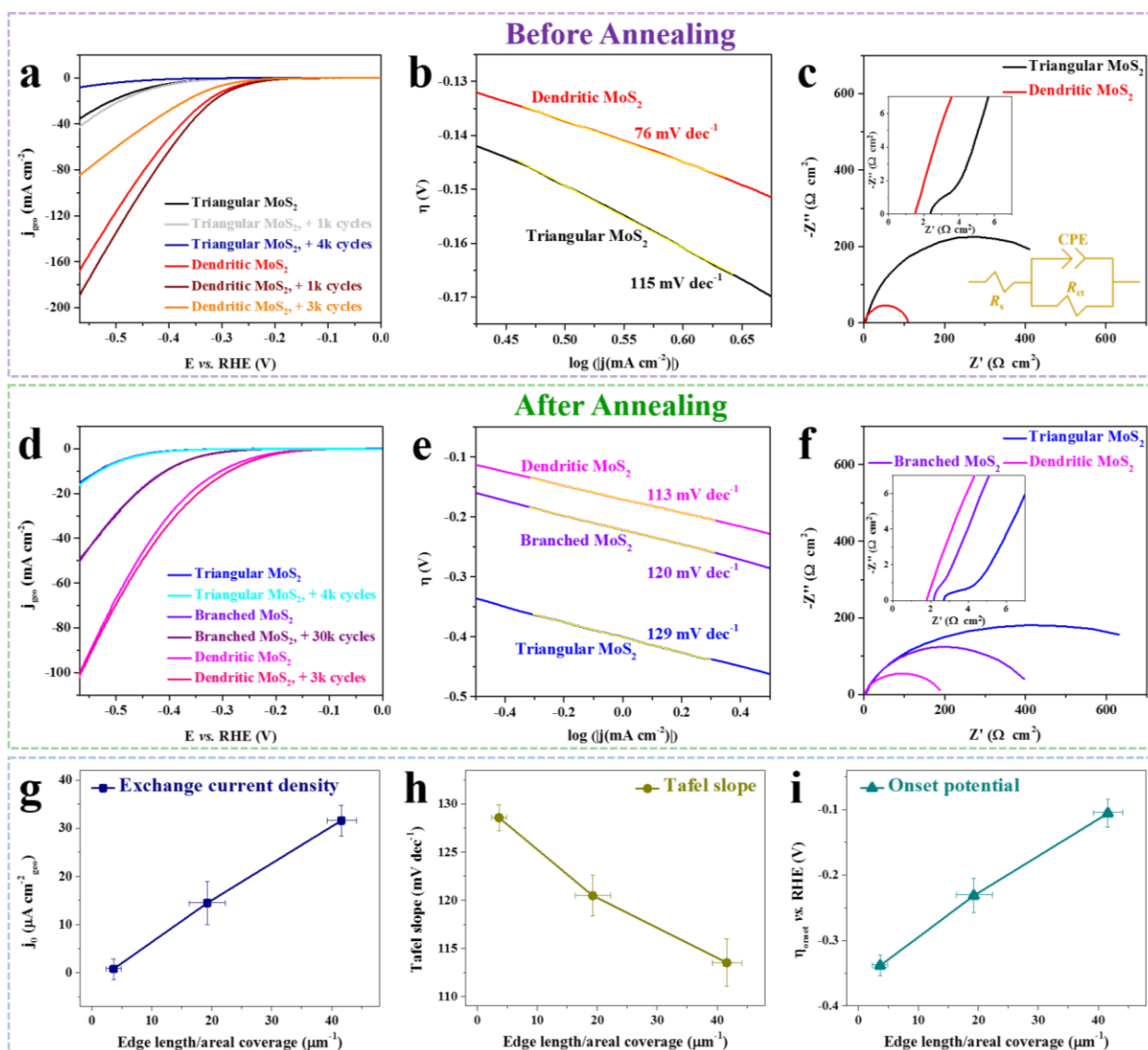


Figure 4.7. HER activities of the triangular and highly dendritic MoS_2 on glassy carbon plates (a–c) before annealing and (d–f) after annealing. (a,d) Cathodic polarisation curves with cycling procedures applied. (b,e) Tafel plots with the slopes obtained *via* linear fits. (c,f) Nyquist plots at 10 mV, indicating the impedance of the electrochemical system, with the insets zoomed in at the high frequency region and an equivalent circuit in panel (c). Correlations of edge length density (E_D = edge length/areal coverage) with the (g) exchange current density, (h) Tafel slope, and (i) onset potential. The HER activities are normalized to the geometric area of the working electrode (glassy carbon plates), denoted by the subscript of ‘geo’, and the edge length densities are calculated with respect to the domain area to exclude the influences of coverage variations.

4.3 Conclusion

In summary, our results show the large-area synthesis of uniform MoS₂ monolayer dendrites on amorphous SiO₂/Si substrates by a three-stage APCVD growth. The domain shape is controllable *via* a precise design of the substrates. The highly dendritic MoS₂ possesses a low fractal dimension of 1.54 associated with its rough edges. The MoS₂ dendrites are derived from a DLA-like process, while their backbones have a six-fold symmetry and the side branches are well-aligned ~60° to the arms because of the preferential growth along certain low-energy directions. Direct gap PL emission is observed in the monolayer MoS₂ both before and after the transfer onto the glassy carbon. Annealing MoS₂ in sulphur atmosphere contributes to high crystallinity by reducing the defect level as well as n-type doping. The large density of catalytically reactive sites enables the dendritic MoS₂ to deliver outstanding HER performance and long-term electrochemical stability after defect restoration.

Chapter 5 Epitaxial Growth and Thermal Degradation of Monolayer MoS₂ on SrTiO₃ Single Crystals for Applications in Nanoelectronics

Monolayer molybdenum disulphide (MoS₂) crystals grown on amorphous substrates such as SiO₂ are randomly oriented. However, when MoS₂ is grown on crystalline substrates, the crystal shapes and orientations are also influenced by their epitaxial interaction with the substrate. In this chapter we present the results from chemical vapour deposition growth and thermal degradation along with properties recovery of monolayer MoS₂ on strontium titanate (SrTiO₃). The crystal structure and physical properties of SrTiO₃ are introduced in Section 2.7.2. The insights into the minimization of grain boundaries, the high-temperature behaviour, and the revival of monolayer MoS₂ would contribute to its scalable application in nanoelectronic devices.

The epitaxial growth was carried out on three different terminations of the single crystal SrTiO₃ substrates. The monolayer MoS₂ crystals on SrTiO₃(111) form equilateral triangles with two main orientations, in which they align their $\langle 2\bar{1}\bar{1}0 \rangle$ -type directions (*i.e.*, the sulphur-terminated edge directions) with the $\langle 1\bar{1}0 \rangle$ -type directions on SrTiO₃. This arrangement allows near perfect coincidence epitaxy between seven MoS₂ unit cells and four SrTiO₃ unit cells. On SrTiO₃(110) the MoS₂ crystals tend to align their edges with both $\langle 1\bar{1}0 \rangle$ and $\langle 1\bar{1}\bar{2} \rangle$ directions on SrTiO₃ as these

both provide favourable coincidence lattice registry. This distorts the crystal shapes and introduces an additional strain detectable by photoluminescence (PL). The triangular MoS₂ crystals grown on SrTiO₃(001), again, show a preference to align the edges with the $\langle 1\bar{1}0 \rangle$ directions on SrTiO₃. The observations can be explained if the interfacial van der Waals bonding between MoS₂ monolayers and SrTiO₃ is greatest when the maximum commensuration between the lattices is achieved.

Considering that the wide-gap MoS₂ semiconductor is a suitable candidate for high-temperature electronics, the thermal degradation process of monolayer MoS₂ supported on strontium titanate (SrTiO₃) substrates in vacuum was also investigated. The monolayer MoS₂ crystals maintained their smoothness until 700 °C when triangular etches showed up parallel to $\langle 2\bar{1}\bar{1}0 \rangle$ lattice directions (*i.e.*, edge directions) of the MoS₂ crystal. They were activated by the preferential loss of sulphur, leaving molybdenum to be oxidized by the SrTiO₃ substrate. Photoluminescence (PL) and Raman signals greatly reduced in intensity at this temperature. The film continued degrading at higher annealing temperatures until it decomposed into MoO_x ($x = 2-3$) particles at 900 °C, and optical properties characteristic of MoS₂ were completely gone in PL and Raman. The macroscopic shapes of MoS₂ crystals were maintained very well until the residual particles evaporated at above 1000 °C. This has the implication that intact crystal shapes do not necessarily mean pristine MoS₂. This work also establishes a detailed pathway of thermal degradation of SrTiO₃-supported monolayer MoS₂ in vacuum, which is envisioned to help future high-temperature studies of monolayer MoS₂ on oxide substrates.

5.1 Epitaxial Growth of Monolayer MoS₂ on SrTiO₃ Substrates

5.1.1 Introduction

Monolayer MoS₂ has been extensively studied as the prototypical material of the family of transition metal dichalcogenides (TMDCs).²⁵⁴ It was discovered that the electronic properties of

TMDCs are drastically affected by dimensionality: MoS₂ in its bulk form is a semiconductor with an indirect bandgap of 1.2–1.3 eV, which transforms into a direct bandgap of 1.8–1.9 eV when the material is as thin as a monolayer.^{1,2} These bandgap energies span the visible and near-infrared range of the electromagnetic spectrum, and therefore MoS₂ is a promising candidate for optoelectronic applications.²⁵⁵ Monolayer MoS₂ is also viewed as a two-dimensional (2D) semiconductor with great potential because of its high charge mobility of more than 200 cm² V⁻¹ s⁻¹ and an on/off current ratio up to $\approx 10^8$.¹⁴⁹ These properties make it competitive with graphene for use in novel low-power digital electronics.¹⁴⁹

For a 2D material like MoS₂, the growth technique of chemical vapour deposition (CVD) has the advantage over exfoliation that it allows the substrate to influence the chemistry and properties of the MoS₂ monolayers. This is important from a technological point of view because the properties of a 2D material can be highly sensitive to its interfaces.²⁵⁴ CVD growth on a well-prepared substrate results in a collection of large MoS₂ domains that have controllable morphology.^{166,184} In particular, epitaxy has been shown to effectively control MoS₂ crystal orientations, which is required to minimize the concentration of grain boundaries in the MoS₂ layer.^{184,185} This is especially important in large-area synthesis of MoS₂ because grain boundaries are detrimental to the electrical properties (*e.g.*, charge mobility) of polycrystalline films.^{85,171,256} By its nature, epitaxial growth cannot occur on amorphous substrates like SiO₂.¹⁷⁸ On crystalline substrates, the main mechanism that allows epitaxy to occur is generally believed to be due to van der Waals (vdW) forces for both metallic and non-metallic substrates,^{183–185,257,258} *e.g.*, *c*-plane sapphire^{184,185} and Au(111)¹⁸³. Although the vdW interaction is relatively weak when compared to in-plane covalent bonding, it still provides a significant force between two 2D sheets. It has been confirmed to powerfully control the interlayer epitaxy of MoS₂ bilayers, where the AA and AB stacking configurations (0° and 60° relative layer rotation) are overwhelmingly favoured compared to others.²⁵⁹ Furthermore, the indirect-to-direct transition of the MoS₂ bandgap in the monolayer limit is a direct consequence of the absence of

neighbouring layers, which only interact *via* vdW forces. This means that the interlayer forces perturb each other's electronic band structures. Therefore, the importance of vdW bonding should not be overlooked with respect to interfacial bonding between MoS₂ and its substrate. Nevertheless, other possible interfacial bonding mechanisms have also been reported, including electrostatic attraction between MoS₂ and sapphire¹⁸⁴ and chemical bonding between S and various metals^{260–263}. The nature of the Au-S bond is particularly controversial; it is claimed to perturb the electronic structure very little in some studies^{183,261} and have a covalent nature in others²⁶².

Finding suitable substrate materials is an important step towards epitaxy or orientation control in the synthesis of MoS₂ films. The substrates used in our work are electrically conducting Nb-doped (0.5 wt%) SrTiO₃ crystals. SrTiO₃ has attracted substantial interest since the 1970s owing mostly to its versatile crystal surfaces.²⁶⁴ It was chosen for our study because several surface terminations with different symmetries can be readily prepared. MoS₂ was grown on the three well-studied SrTiO₃ terminations, (111), (110), and (001). The crystallinity of SrTiO₃ encourages MoS₂ monolayer crystals to grow epitaxially, and the different symmetries of the three terminations lead to distinct epitaxial behaviour. Overall, the interaction between MoS₂ and SrTiO₃ is found to influence the orientations, shapes, and optical properties of MoS₂ monolayers.

5.1.2 Results and discussion

In this project, I conducted the CVD growth, SEM imaging, Raman and PL spectroscopy, while the collaborators provided the SrTiO₃ substrates which had been treated using the techniques specified in S3 (Appendix) and performed scanning tunnelling microscopy (STM). The outermost surfaces of SrTiO₃ are atomically smooth and crystalline with well-defined reconstructions for all the three terminations, as demonstrated by the STM images in Figure S3b,f,h (Appendix). Below the focus is on my work.

For purposes of comparison, data from an amorphous substrate is presented first. Figure 5.1.1 is an SEM image of MoS₂ monolayer crystals grown on SiO₂/Si. As one would expect from S-rich growth conditions, the MoS₂ monolayers preferentially adopt triangular geometries.¹⁷⁸ Figure S3a (Appendix) displays the statistical study regarding the epitaxy of these MoS₂ crystals. The orientation of any crystal was measured as the angle it makes with the horizontal line below it, whichever side is smaller. The corresponding histogram shows their randomly distributed orientations, proving that the vdW interaction between the amorphous substrate and the MoS₂ induces no orientation preferences for the growth.

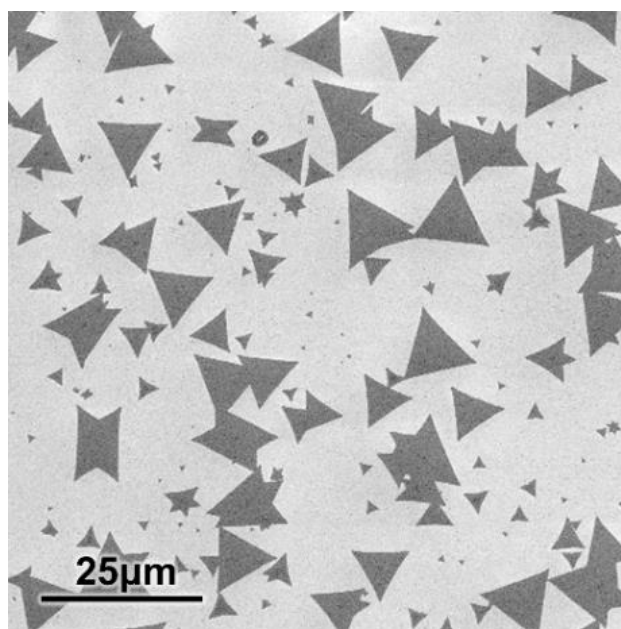


Figure 5.1.1. SEM image of monolayer MoS₂ crystals grown on SiO₂/Si substrate.

Figure 5.1.2a shows a typical SEM image of MoS₂ crystals on SrTiO₃(111). The larger crystals (those with lateral sizes over 5 μm) with S-terminated edges^{178,265,266} appear to be randomly oriented, but in the close-up image of smaller crystals (Figure 5.1.2b), the crystals show more regular alignment. The lattice directions of the SrTiO₃(111) substrate are also drawn at the top-left corner for reference: one can see that the small triangles mostly have their three sides parallel to the three $\langle 1\bar{1}0 \rangle$ -type directions on SrTiO₃(111), resulting in two main orientations as represented by the two blue

schematic triangles. Another observation is that one of the two preferred orientations is more abundant (the darker blue triangle pointing up). These are further supported by the STM image of even smaller crystals (Figure S3c, Appendix), which also shows that the thickness of the MoS₂ is 0.63 ± 0.06 nm, in agreement with the previously reported value of 0.65 nm for monolayer MoS₂.^{149,267} The epitaxy on SrTiO₃(111) was statistically investigated by the orientation histograms shown in Figure S3e. The MoS₂ crystals were grouped into large (15–30 μ m), medium (5–15 μ m), small (1–5 μ m), XS (0.5–1 μ m), and XXS (100–500 nm), according to their lateral sizes. In all cases, the two highest peaks are at 0° and 60°, indicating the two dominant orientations of MoS₂ crystals: ‘(0001)_{MoS₂} || (111)_{SrTiO₃}, [01 $\bar{1}$ 0]_{MoS₂} || [11 $\bar{2}$]_{SrTiO₃}’ and ‘(0001)_{MoS₂} || (111)_{SrTiO₃}, [0 $\bar{1}$ 10]_{MoS₂} || [11 $\bar{2}$]_{SrTiO₃}’. In the preferred orientations, MoS₂ and SrTiO₃(111) are both symmetry coincident and lattice commensurate: the length of 7 MoS₂ unit cells (7×0.316 nm = 2.212 nm) equals the length of 4 SrTiO₃ unit cells (4×0.552 nm = 2.208 nm) with a small difference of <0.2%, as illustrated in Figure 5.1.2c. The histograms in Figure S3e show that the preferred angular orientations are better defined for smaller crystals, and this can be explained by kinetics. The large crystals undergo a rapid growth process with only little time to optimise their orientations relative to the substrate. However, the smaller crystals grow slowly and are able to rotate into orientations that optimize the vdW interaction with the substrate. It is likely that one of the two preferred orientations is thermodynamically more stable. Particularly in the histograms for small and XXS crystals, there is a statistically significant difference between the heights of the two peaks.

Figure 5.1.2b is a typical SEM image of the MoS₂ on SrTiO₃(110), from which it is noticeable that instead of an equilateral triangle, some MoS₂ crystals appear to be distorted along the directions indicated by the red arrows. There are two most commonly observed orientations, which have their three edges parallel to [1 $\bar{1}$ 0], [1 $\bar{1}$ $\bar{2}$], and [1 $\bar{1}$ 2] of the SrTiO₃(110) substrate, with the internal angles of 70°, 55°, and 55° (Figure 5.1.2e). The epitaxy study is presented in Figure S3g (Appendix). The

$[1\bar{1}0]$ direction is favoured because of the 7:4 coincidence epitaxy, similar to the case on $\text{SrTiO}_3(111)$. However, on $\text{SrTiO}_3(110)$ only one edge of any MoS_2 triangle can align with such a direction. Nevertheless, among those low-index (*i.e.*, relatively close-packed) lattice directions which are at $\approx 60^\circ$ to $\langle 1\bar{1}0 \rangle$, the $\langle 1\bar{1}\bar{2} \rangle$ directions are favored for two reasons. The first one is again lattice commensuration: the unit length along $\langle 1\bar{1}\bar{2} \rangle$ is 0.9564 nm, which is three times the in-plane S-S distance in MoS_2 (0.316 nm) with a 0.9% difference. Secondly, $[1\bar{1}0]$, $[1\bar{1}\bar{2}]$, and $[1\bar{1}2]$ on $\text{SrTiO}_3(110)$ form a set of directions arranged in a nearly-regular-hexagonal way, with included angles of 70° , 55° , and 55° (Figure 5.1.2e). However, an equilateral triangle of MoS_2 cannot be distorted to a $70^\circ/55^\circ/55^\circ$ triangle in practice whilst maintaining a perfect crystal structure; this would require an unphysical compressive strain of 18%. Figure 5.1.2f shows an atomic model of MoS_2 that follows the shape in the inset, which is a close-up SEM image of a crystal with an overall shape of a $70^\circ/55^\circ/55^\circ$ triangle. Some internal angles are still 60° , which point to a perfect MoS_2 lattice, while some angles are closer to 55° , meaning that the lattice may have been partially rotated and/or distorted to align one edge with $\langle 1\bar{1}\bar{2} \rangle$. The bottom edge of the crystal is parallel to $[1\bar{1}0]$ on the substrate, along ‘ d_1 ’ labelled, which is a distance corresponding to 7 unit lengths in MoS_2 and 4 unit lengths along $\text{SrTiO}_3[1\bar{1}0]$. The MoS_2 crystal also has some parts of its lattice rotated to align one edge with $\langle 1\bar{1}\bar{2} \rangle$ of SrTiO_3 , highlighted in yellow. ‘ d_2 ’ is labelled along the $[1\bar{1}2]$ direction, and its length represents 1 unit length along $[1\bar{1}2]$ and 3 unit lengths in MoS_2 . The MoS_2 crystal tries to align with both $\langle 1\bar{1}0 \rangle$ and $\langle 1\bar{1}\bar{2} \rangle$, so that defects (*e.g.*, around the rotated areas) are inevitably induced plus a small degree of lattice distortion. The associated strain will be confirmed later by PL spectroscopy. On $\text{SrTiO}_3(110)$, the interfacial crystallographic relationship is ‘ $(0001)_{\text{MoS}_2} \parallel (110)_{\text{SrTiO}_3}$, $[2\bar{1}\bar{1}0]_{\text{MoS}_2} \parallel [1\bar{1}0]_{\text{SrTiO}_3}$ ’, and partially ‘ $(0001)_{\text{MoS}_2} \parallel (110)_{\text{SrTiO}_3}$, $[2\bar{1}\bar{1}0]_{\text{MoS}_2} \parallel [1\bar{1}\bar{2}]_{\text{SrTiO}_3}$ ’.

On the final surface in this study, $\text{SrTiO}_3(001)$, the as-grown MoS_2 crystals clearly show a distinct morphology compared with the other SrTiO_3 terminations (Figure 5.1.2g). The dendritic

growth of MoS₂ on SrTiO₃(001) has been believed to result from a diffusion-limited aggregation (DLA) process.^{127,237} For comparison, an amorphous SiO₂/Si substrate was placed side by side with the SrTiO₃, on which the MoS₂ crystals produced by the same CVD growth are perfectly sharp and triangular (Figure 5.1.1). Therefore, the dendritic growth can be safely attributed to the substrate effect of SrTiO₃(001). To consistently study the epitaxy of crystals with the same morphology, compact triangular crystals were deliberately grown in lieu of dendrites by placing the precursors closer to the substrate in the CVD furnace.¹²⁷ Due to the increased precursor feedstock, the resulting compact crystals are much larger than the dendrites (Figure 5.1.2h vs. g), but few-layer (to bulk) MoS₂ structures are inevitably formed in the meanwhile. The crystal orientations in Figure 5.1.2h were examined, giving the histogram shown in Figure S3i (Appendix). Two peaks are identified at 15° and 45°, relative to the substrate [100] direction. They are two crystallographically equivalent orientations because of the four-fold symmetry of SrTiO₃(001). The interfacial crystallographic relationship can be described as ‘(0001)_{MoS₂} || (001)_{SrTiO₃}, [2 $\bar{1}$ 10]_{MoS₂} || [1 $\bar{1}$ 0]_{SrTiO₃}’. Again, one edge of the triangular MoS₂ crystal preferentially aligns with the <1 $\bar{1}$ 0> directions on SrTiO₃(001) because of the 7:4 coincidence epitaxy. A selection of such edges are highlighted by black dashed lines in Figure 5.1.2h. An atomic model is drawn in Figure 5.1.2i to show an example MoS₂ monolayer crystal and the SrTiO₃(001) lattice commensuration. It should be noted that the histogram peaks at 15° and 45° are not sharp, because the crystals measured are mostly large (15–30 μ m), and their growth is more kinetically controlled than that of the smaller ones, as discussed for the MoS₂ grown on SrTiO₃(111).

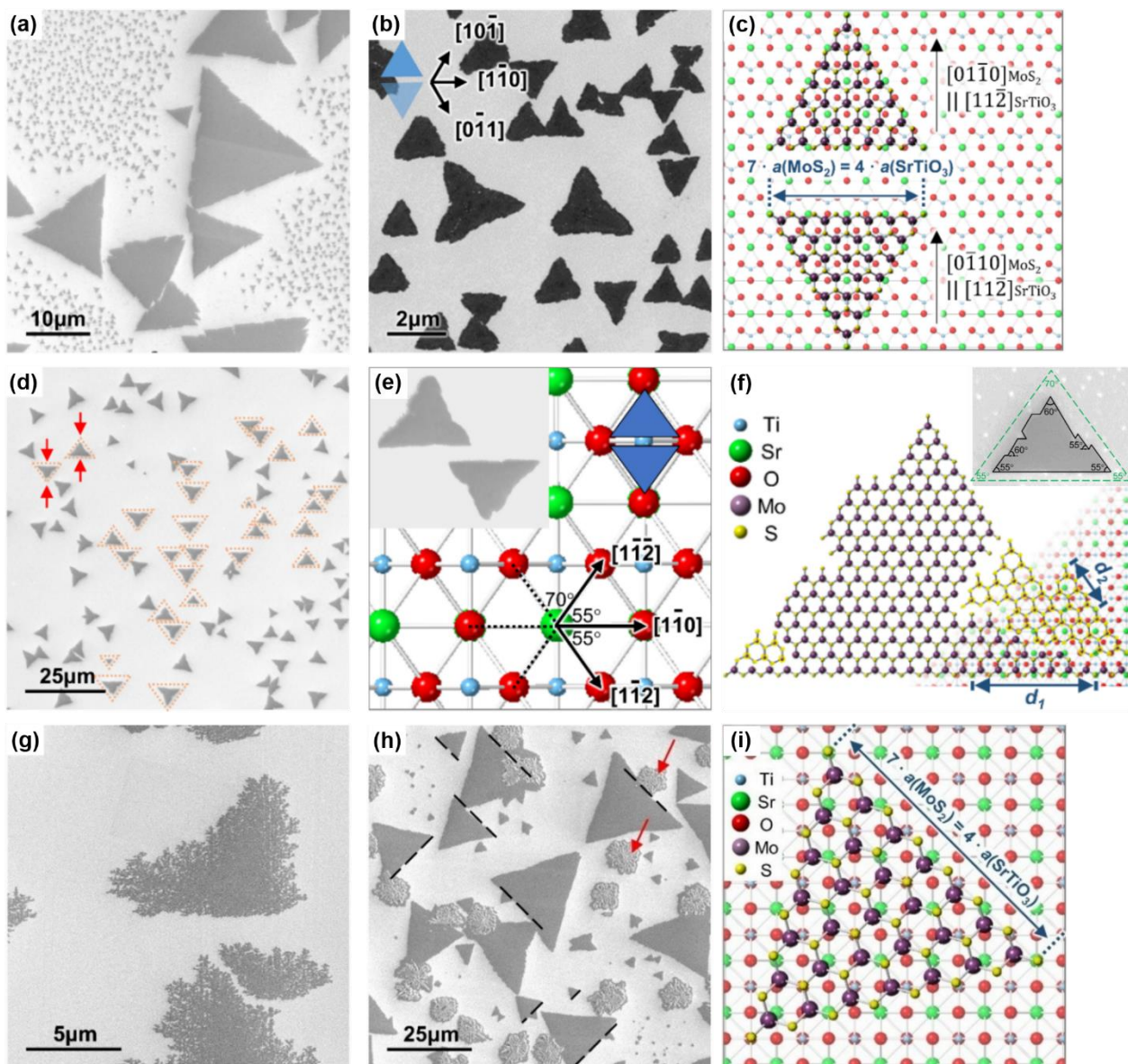


Figure 5.1.2. SEM images and atomic models of MoS₂ grown on (a–c) SrTiO₃(111), (d–f) SrTiO₃(110), and (g–i) SrTiO₃(001). (a) SEM image showing MoS₂ crystals with a large range of sizes (laterally 0.5–30 μm). (b) SEM image of small crystals (laterally 1–3 μm). The preferential crystal orientations are drawn as schematics, between which the darker blue triangle is more preferred. (c) Atomic models showing the two preferred orientations of MoS₂ crystals on SrTiO₃(111). The interface crystallography is written next to each orientation. $7 \text{ MoS}_2 \text{ unit cell lengths (S-S spacings)} = 4 \text{ SrTiO}_3 \langle 1\bar{1}0 \rangle \text{ unit lengths (Sr-Sr spacings)}$. The two orientations of the MoS₂ crystals on SrTiO₃(111) are physically distinct, and their respective interface crystallography is labelled next to them. (d) SEM image of MoS₂ on SrTiO₃(110). Some crystal shapes are ‘compressed’ along the [001] direction relative to equilateral triangles, as outlined by the orange dashed lines and red arrows. (e) SEM image of the most commonly observed crystal orientations of MoS₂ and atomic model of SrTiO₃(110), on which the blue schematic triangles indicate the preferred crystal orientations. (f) Atomic model of a MoS₂ crystal on SrTiO₃(110). The rotated lattice parts are highlighted in yellow. ‘ d_1 ’ = 7 MoS₂ unit

cell lengths (S-S spacings) = 4 SrTiO₃[1 $\bar{1}$ 0] unit lengths (Sr-Sr spacings); ‘d₂’ = 3 MoS₂ unit cell lengths (S-S spacings) = 1 SrTiO₃[1 $\bar{1}$ 2] unit length (Sr-Sr spacing). Inset: SEM image of a MoS₂ crystal with the typical shape, and its rough edges are highlighted in black. (g) SEM image of MoS₂ crystals on SrTiO₃(001) with dendritic shape. (h) SEM image of the MoS₂ crystals on SrTiO₃(001) grown derived from a shorter source–substrate distance. The few-layer (to bulk) MoS₂ formed is indicated by red arrows. (i) Atomic model of MoS₂ monolayer crystal on SrTiO₃(001). 7 MoS₂ unit cell lengths (S-S spacings) = 4 SrTiO₃[1 $\bar{1}$ 0] unit lengths (Sr-Sr spacings). The substrate lattice direction is consistent for each surface termination.

Raman and PL spectroscopy were performed to investigate some of the structural properties of the MoS₂ grown on different substrates (Figure 5.1.3). The Raman and PL spectra are known to be influenced by the layer thickness,¹⁰² lattice strain,^{59,108,109,243,268,269} doping level,^{106,270} and lattice defects²⁴⁴ of MoS₂. These depend on the substrate surface (Figure 6a,b), the MoS₂ crystal morphology (Figure 6c,d), and the MoS₂ layer number (Figure 6e,f). Detailed information can be extracted through Lorentzian fitting for the PL spectra of monolayer MoS₂ on different substrates (Figure 6g–j). In addition to the samples mentioned previously, we also studied MoS₂ monolayers transferred onto a SrTiO₃ substrate. This sample serves as a reference for strain calculations as the crystals have released their strain during the transfer process. Please note that the transferred sample is also Nb-doped (0.5 wt%) and was annealed after the transfer to remove the trapped contaminants and improve the MoS₂–SrTiO₃ interface adhesion. Therefore its doping level can be considered nearly the same as that in the MoS₂ directly grown on SrTiO₃.

Figure 6a,c,e shows the two characteristic Raman modes of MoS₂, E_{2g}^1 (382.0–384.3 cm^{−1}) and A_{1g} (403.0–407.5 cm^{−1}).¹⁰² The E_{2g}^1 and A_{1g} modes are preferentially excited for terrace and edge terminations, respectively.¹²⁸ Therefore, the relative integrated intensities of A_{1g} and E_{2g}^1 can provide information on the texture of MoS₂.^{126,128,271} Regardless of the substrate, all the MoS₂ monolayers predominant with terrace sites exhibit similar integrated intensity ratios of $A_{1g}/E_{2g}^1 \approx 1.05$, whereas the few-layer MoS₂ terminated more by edges shows an increased ratio of $A_{1g}/E_{2g}^1 \approx 1.82$ (Figure

5.1.3a,c,e), conforming well to those reported previously.^{102,271} Also, the frequency difference between A_{1g} and E_{2g}^1 modes can be used to precisely determine the layer number of MoS₂. The obtained values are $\leq 19.5 \text{ cm}^{-1}$ for all the monolayer MoS₂ and $\geq 23.1 \text{ cm}^{-1}$ for the few-layer MoS₂ (Figure 5.1.3a,c,e), in good agreement with the literature.¹⁰² An example of the few-layer structures was shown in Figure 5d. Figure 6f presents the PL of monolayer and few-layer MoS₂ on the same substrate termination, SrTiO₃(001). In addition to the direct transitions (K→K) involving two split valence bands for the emissions of A and B excitons, few-layer MoS₂ shows an additional peak (I) originating from the indirect transition ($\Lambda \rightarrow \Gamma$).^{1,2,99} Compared to the monolayer MoS₂, the few-layer MoS₂ exhibits much weaker PL with lower emission energies (monolayer: 1.85 eV for A excitons and 2.02 eV for B excitons; few-layer: 1.81 eV for A excitons, 1.98 eV for B excitons, and 2.04 eV for indirect excitons).

The lattice strain in MoS₂ develops *via* two processes, which are the epitaxial growth associated with the lattice mismatch between MoS₂ and the substrate, and the fast cooling where strains develop owing to the different thermal expansion coefficients (TEC) of MoS₂ and the substrate.²⁴¹ The TEC of the as-prepared 2H-phase MoS₂ is approximately one order of magnitude larger than that of SiO₂,^{272,273} while it is about one order of magnitude smaller than that of SrTiO₃.²⁷⁴ As a result, in the fast cooling stage following MoS₂ growth, tensile strain develops in the SiO₂-supported MoS₂ whereas compressive strain is introduced in MoS₂ on SrTiO₃.²⁴¹ The tensile and compressive strains respectively lead to red and blue shifts of the E_{2g}^1 and A_{1g} Raman peaks and the A-exciton PL peak, relative to the transferred sample (Figure 5.1.3a,b).^{59,108,109,243,268,269} However, these three peaks are all red-shifted for the monolayer MoS₂ crystals grown on SrTiO₃(110) and (001), which is attributed to epitaxial growth. As manifested in Figure 4 and 5, the MoS₂ monolayer crystals show large lattice mismatch with the SrTiO₃(110) and (001) terminations, leading to the tensile strain. The E_{2g}^1 Raman peak shifts with respect to that on SrTiO₃(111) were used to estimate the growth-

induced tensile strains in the MoS₂ monolayers grown on SrTiO₃(110) and (001).⁵⁴ As stated for SrTiO₃(111), the small difference of <0.2% in the lattice parameters between the monolayer MoS₂ and the substrate should give rise to a compressive strain of ≈0.18% in the MoS₂ adlayer. Taking this into account, the growth-induced tensile strain is ≈0.58% on SrTiO₃(110), caused by the attempt of MoS₂ crystal edges to align with both $\langle 1\bar{1}0 \rangle$ and $\langle 1\bar{1}\bar{2} \rangle$ crystallographic directions, and ≈0.34% on SrTiO₃(001), ascribed to the lattice mismatch along the two non-epitaxial edges of the MoS₂ crystal. Finally, the growth-induced strain can be considered negligible in the monolayer MoS₂ grown on SiO₂/Si because of its amorphous surface, which leads to the random orientation of the MoS₂ crystals (Figure 5.1.1).

Figure 5.1.3b also shows that the tensile strains in the monolayer MoS₂ supported on SrTiO₃(110), (001), and SiO₂/Si substrates commonly lead to decreased PL intensities compared to the transferred sample.⁵⁹ In particular, significant PL quenching is observed on SrTiO₃(110), stemming from the epitaxy-induced lattice defects in the crystals previously shown in Figure 5.1.3f, which will be discussed later. However, on SrTiO₃(111), the PL intensity is enhanced by 58% with a slightly narrower peak width (decrease in the full-width at half-maximum $\Delta\text{FWHM} = 7.05$ meV) compared to the transferred sample, due to the compressive strain,²⁶⁹ which agrees with the Raman results. Moreover, the crystal morphology also impacts the strain level in MoS₂. As shown in Figure 5.1.3c,d, the dendritic MoS₂ crystals on SrTiO₃(001) display small blue shifts of the PL and Raman peaks relative to the compact triangular crystals. (Note that the E_{2g}^1 Raman mode corresponding to the in-plane Mo–S phonon is more sensitive to strain than the A_{1g} mode corresponding to out-of-plane Mo–S phonon.^{53,103,104,299,300}) This is because the dendrites could partially release the growth-induced tensile strain by generating numerous fragmental edges, which suppresses the deterioration of the MoS₂ lattice and results in a stronger PL intensity.

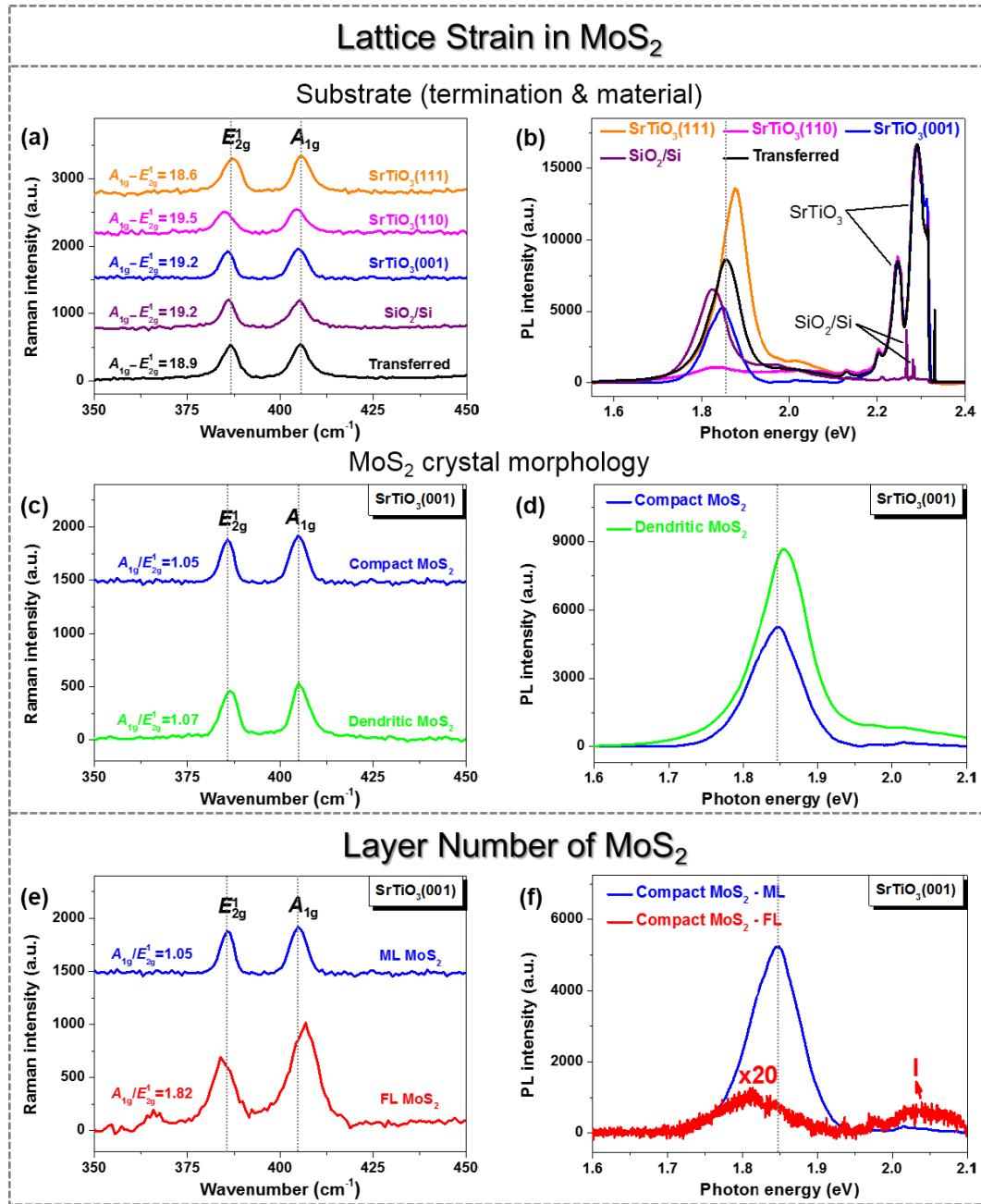


Figure 5.1.3. Raman and PL measurements. (a,c,e) Raman and (b,d,f) PL spectra of the MoS₂ single crystals (a,b) on different substrate surfaces, *i.e.*, SrTiO₃(111), (110), (001), SiO₂/Si, and the MoS₂ transferred onto SrTiO₃, (c,d) with different morphologies, *i.e.*, compact- and dendritic-shaped MoS₂, and (e,f) with different layer numbers, *i.e.*, monolayer (ML) and few-layer (FL) MoS₂. 'I' indicates the indirect optical transition.

The PL spectra are fitted with A and A⁻ peaks for the A-exciton emission, B peak for the B-exciton emission, and localized states (LS) correlated with the structural disorders of MoS₂ (Figure 5.1.4).²⁴⁴ The LS peaks reveal the defect level in the as-grown MoS₂ crystals:

$\text{SrTiO}_3(110) > \text{SrTiO}_3(001) > \text{SrTiO}_3(111)$, associated with the degree of lattice mismatch between the MoS_2 and the SrTiO_3 surface termination. Apart from the neutral A exciton, the negatively charged exciton (trion, A^-) suggests n-type doping in the monolayer MoS_2 on all substrates. The larger $A:A^-$ intensity ratio for SiO_2/Si substrate proves that heavier n-doping has been induced by the surface charge impurities into the MoS_2 adlayer than the Nb (0.5 wt%) on SrTiO_3 substrates.²⁴² Nonetheless, the $A:A^-$ intensity ratio also indicates that the doping level of MoS_2 is very similar despite the SrTiO_3 termination, confirming that the Raman and the A-exciton PL peak shifts are only related to growth-induced strains of the MoS_2 on different SrTiO_3 substrates.

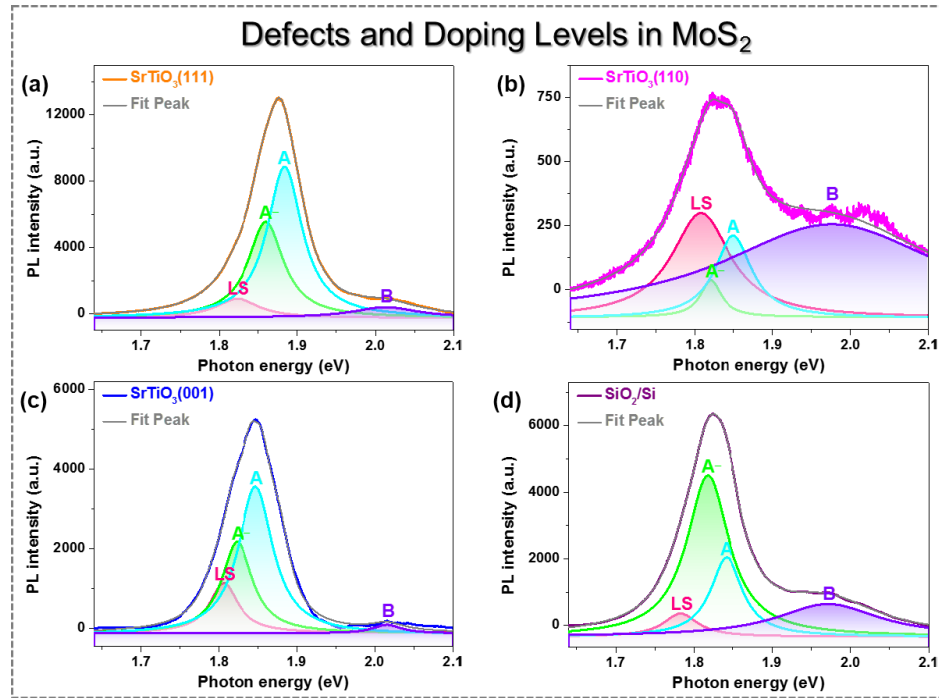


Figure 5.1.4. Lorentzian fitted PL spectra of the monolayer MoS_2 grown on (a) $\text{SrTiO}_3(111)$, (b) $\text{SrTiO}_3(110)$, (c) $\text{SrTiO}_3(001)$, and (d) SiO_2/Si substrates, revealing the presence of A excitons (A), B excitons (B), negatively charged A excitons (trions, A^-), and localized states (LS).

It has been shown that on three different crystal terminations of SrTiO_3 , MoS_2 crystals tend to adopt the orientations that allow its lattice to match that of the substrate *via* coincidence epitaxy. The equilibrium orientations and crystal shapes maximize the number of directions along which this is achieved. The interfacial vdW bonding is strengthened in the epitaxial orientations through lattice

registry, giving rise to a greater number of bonding sites and closer proximity between the two layers. Therefore, when a MoS₂ nucleus is free to rotate in the initial stage, it gets ‘locked’ into the lowest-energy orientation,¹⁸⁵ *i.e.*, in the epitaxial configurations we observed. Other bonding types, *e.g.*, electrostatic attraction¹⁸⁴ and chemical bonds,²⁷⁵ are less likely to exist between MoS₂ and SrTiO₃. This is because they are stronger than vdW bonding by orders of magnitude and would lock the MoS₂ monolayers exclusively into certain orientations, *e.g.*, as observed on Au(111).²⁸⁹ Gold, an electronegative metal, is a very different substrate to SrTiO₃, an oxide ceramic, and can interact with MoS₂ *via* a stronger bonding type. The Nb doping (0.5 wt%) which makes SrTiO₃ conductive may also have played a role in its bonding with MoS₂ monolayers, but we expect any effects to be minimal.

On SrTiO₃(111), it is advantageous to align the $\langle 2\bar{1}\bar{1}0 \rangle$ directions of MoS₂ with $\langle 1\bar{1}0 \rangle$ on SrTiO₃ with favourable coincidence lattice registry. In previous studies of MoS₂ grown on ceramic substrates, SiO₂ does not induce epitaxy as it is amorphous;¹⁷⁸ *c*-plane sapphire, another three-fold symmetric substrate, reveals similar preferred orientations to MoS₂ on SrTiO₃(111) (0° and 60°).^{184,185} In these orientations, either interfacial electrostatic attraction (as a result of charge transfer)¹⁸⁴ or greatly enhanced vdW bonding¹⁸⁵ were proposed. It was not explicitly mentioned why the interfacial bonding prefers particular orientations, but this is likely to be the good lattice registry between MoS₂ and sapphire. Their in-plane periodicities, 0.316 nm for MoS₂ and 0.476 nm for sapphire, have a 2:3 ratio with a 0.4% difference.¹⁸⁴ Therefore we speculate that both SrTiO₃(111) and *c*-plane sapphire show similar low-energy coincidence epitaxial relationships because of lattice commensuration with negligible strain.

Also, one of the two lattice-coincident orientations on SrTiO₃(111) is more strongly preferred, and a similar situation is found in the MoS₂-on-Au(111) system. A single Au(111) layer is six-fold symmetric, while a second layer reduces it to three-fold because of the differentiated fcc and hcp sites. Theoretical studies by Bruix *et al.* reveal a very slim energy difference (16 meV per unit cell) between the ‘MoS₂-on-hcp’ and ‘MoS₂-on-fcc’ configurations,²⁶² but the crystals turn out to exclusively orient

in only one way.²⁸⁹ The termination of Au(111) alternates between hcp and fcc across a ridge of the herringbone structure, so that the MoS₂ triangles ‘flipping’ their directions across each ridge means the same stacking. This exclusivity is also assisted by a much slower growth method adopted than CVD, which results in nanometre-sized crystals (all <8 nm).²⁸⁹ On the other hand, SrTiO₃(111) shows a uniform termination with surface step heights always equivalent to the d_{111} lattice parameter.^{276,277} Hence, the 0° and 60° orientations of MoS₂ are indeed distinct, possibly with a very small but noticeable energy difference like on Au(111).

On SrTiO₃(110), the strong tendency to maximize coincidence epitaxial directions (*i.e.*, $\langle 1\bar{1}0 \rangle$ and $\langle 1\bar{1}\bar{2} \rangle$) competes with the equilibrium shape of MoS₂ crystals. To accommodate the shape distortions, there is an increased defect density and an additional element of strain energy. These both increase the lattice energy of MoS₂ but must have been overcome by the reduction in the interfacial energy because of the improved bonding. Even on SrTiO₃(001), where it is only possible to satisfy one direction of good coincidence epitaxy along $\langle 1\bar{1}0 \rangle$, the MoS₂ crystals still show a preference to orient in such a way.

Based on the above, our understanding of what drives the epitaxy is the interfacial lattice commensuration between $\langle 2\bar{1}\bar{1}0 \rangle$ (*i.e.*, the sulphur edge directions) of MoS₂ and $\langle 1\bar{1}0 \rangle$ on SrTiO₃. We would like to stress the strength of this vdW interaction that can powerfully control the growth of MoS₂ crystals. This would allow highly uniform MoS₂ monolayer to be grown over a large scale even when there are multiple nucleation sites. Furthermore, developing a deeper understanding of MoS₂ epitaxy is an important step towards integrating MoS₂ in future novel electronic devices, owing to the elimination of grain boundaries when the MoS₂ is grown in perfect lattice registry with its crystalline substrate.

5.1.3 Conclusion

To conclude, the orientations and shapes of MoS₂ crystals are strongly influenced by the interactions with SrTiO₃ substrates. The equilibrium orientations maximize the interfacial vdW bonding *via* coincidence epitaxy and hence enhanced bonding, which is assisted by lattice defects and crystal shape distortions when possible. This offers a broader interpretation of epitaxy, which involves minimizing the total energy of the system in a more complex way. It is the sum of the lattice energy of MoS₂ (to maintain its equilateral triangular shape) and the interfacial energy associated with the MoS₂–substrate interactions. The results also confirm that the vdW interaction is sufficiently strong to regulate epitaxy in a powerful way. The strain levels in MoS₂ are found to be adjusted by the different epitaxial relations with the substrate. This allows us more rigorous control in the synthesis of large-scale uniform MoS₂ layers for optimal electronic properties and enables the manipulation of inbuilt strains to fine tune the bandgap.

5.2 Thermal Degradation of Monolayer MoS₂ on SrTiO₃ Supports

5.2.1 Introduction

Many transistors, circuits, and sensors are calling for electronics that can operate at high temperatures.²⁶⁷ This has been fulfilled by semiconducting materials that possess wide bandgaps such as SiC and GaN,^{278,279} but their large-scale applications are still limited due to the expensive fabrication.²⁶⁷ Atomically thin MoS₂ with a direct bandgap of 1.8–1.9 eV² gains intense interest because of its relatively high charge mobility,²⁸⁰ optical transparency, and extreme mechanical flexibility.²⁸¹ It has shown great potential in future electronic devices beyond the conventional silicon-based electronics,²⁸² and even competitive to graphene in field-effect transistors (FETs).^{11,21,149,150,196,198} Therefore it is of great potential to thoroughly investigate the high-temperature processing of monolayer MoS₂, which is another promising candidate benefiting from recent advances in their low-cost synthesis.^{154,156,161,164,166,283,284} Previous works in this respect were mostly carried out as part of the synthesis process of MoS₂ or immediately after its growth. They

were used to enhance the crystallinity,^{190,271,285–287} optical^{190,271,286,287} or electronic properties^{288,289} of the MoS₂ grown. A few studies also explored the thermally-accelerated oxidation of MoS₂ into MoO₃ under ambient conditions, starting from 100 °C until complete transformation at up to 550 °C.^{187,188,290–292} In these studies, the MoS₂ samples adopted are either monolayer/few-layered (supported on SiO₂) or powdered. In the absence of oxygen, MoS₂ is found to be much more stable: the atomic structure of monolayer MoS₂ on Au(111) was seen to be unperturbed up to 630 °C.¹⁸⁹ On few-layer MoS₂ on oxide or nitride substrates, thermal decomposition did not occur until 850 °C in the absence of oxygen.¹⁹⁰ On bulk MoS₂, S is not completely removed until above 1203 °C in vacuum.¹⁹¹ The oxidation of monolayer MoS₂ was seen to start with triangular pits by atomic force microscopy (AFM) in air,^{187,188} while the morphology of the thermally degraded monolayer MoS₂ in vacuum has not been systematically reported. Additionally, any methods to recover the properties of degraded MoS₂ would be of great interest for extending its lifetime and ensuring its working efficiency in practical applications. However, this has rarely been studied so far.

Distinct from most previous studies, monolayer MoS₂ islands were studied herein instead of few-layer or bulk MoS₂. By examining the thermal decomposition of the MoS₂ in vacuum supported on a single crystal strontium titanate (SrTiO₃) substrate, we exclude the effects of oxygen in air, so that all changes upon annealing are attributed to MoS₂ itself and the oxide ceramic substrate which is commonly used to support monolayer MoS₂ in devices. This set-up allows us to assess how MoS₂ would behave in practical devices which require high-temperature processing. In this work, the step-by-step changes in MoS₂ were tracked from its initial degradation at 700 °C to the complete evaporation of MoO_x (x = 2–3) residues at temperatures above 1000 °C. Although the optical properties of MoS₂ deteriorated to a large extent after the annealing in vacuum, they were partially recovered *via* a follow-up annealing treatment while in vaporous sulphur environment.

5.2.2 Results and discussion

In this project, I did the CVD growth and sulphur annealing of monolayer MoS₂ and conducted optical microscopy (OM), scanning electron microscopy (SEM), Raman and photoluminescence (PL) spectroscopy, and X-ray photoemission spectroscopy (XPS). To explore the atomic evolution of MoS₂ during thermal degradation in vacuum, the collaborators performed *in situ* scanning tunnelling microscopy (STM), and the results are shown in Figure S4 (Appendix).

The annealing was carried out in ultrahigh vacuum (UHV, base pressure 10^{-8} Pa), with the temperature for each case specified in the following text, and sequentially, in vaporous S, for which the detailed conditions are elaborated in Section 3.2.6. Upon the UHV heat treatments, the crystals shapes of MoS₂ were observed to remain intact under OM and SEM before they evaporated (at above 1000 °C). In Figure 5.2.1a are some MoS₂ crystals imaged by OM before (Figure 5.2.1a.i) and after (Figure 5.2.1a.ii) annealing at 1000 °C for 5.5 h. They do not show any noticeable difference. Figure 5.2.1b.i,ii are the SEM images of MoS₂ crystals on the same sample at two ends, which was annealed for 2 h with a temperature gradient across the sample. During annealing, the temperature was 700 °C at the colder end and 800 °C at the hotter end. The sample showed a stronger red glow at the hotter end during annealing. After cooling down, the crystals at the colder end are clear and black (Figure 5.2.1b.i); they look no different to the as-grown crystals. Towards the hotter end, the crystals appear fainter and fainter (Figure 5.2.1b.ii). The imaging conditions were exactly the same. Although more detailed internal structure cannot be resolved by SEM, the MoS₂ crystals are expected to have partially lost their mass, which will be further discussed later. Figure 5.2.1c.i,ii are another pair of images demonstrating the effect of annealing at 1150 °C for 3 h. This treatment further lowered the visibility of the crystals, in which they are clearly decomposed with some residues remaining in the triangular shapes. Similar survivor traces have been observed after a lift-off process of WS₂.²⁹³

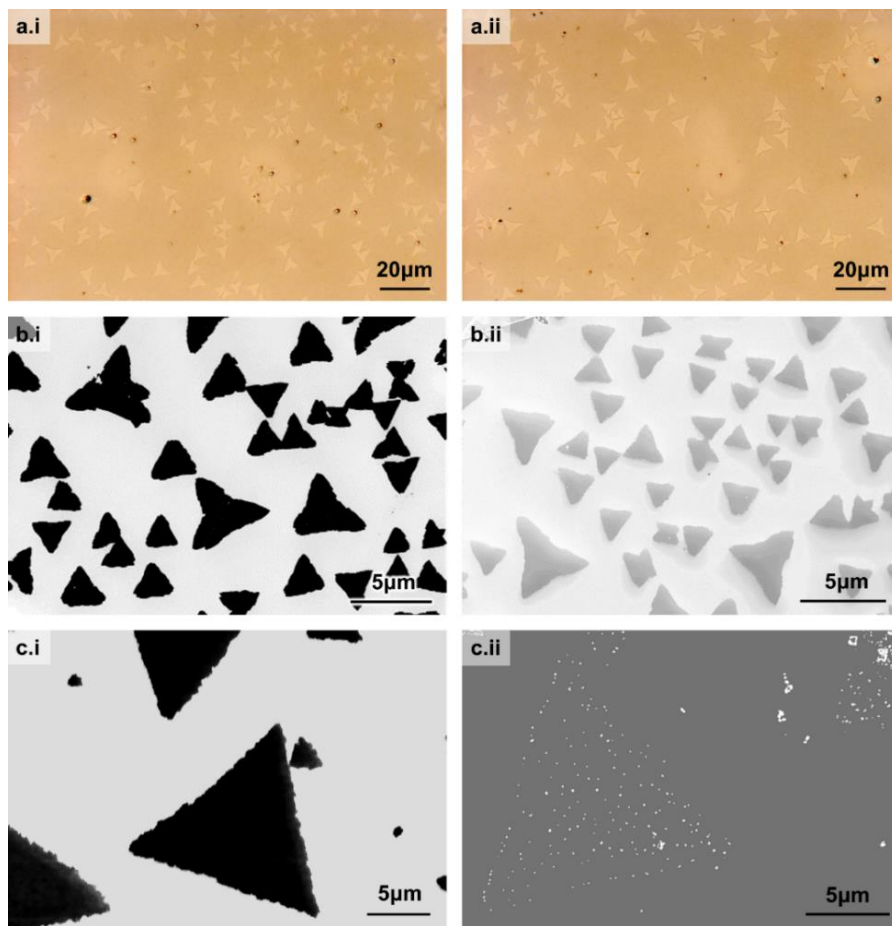


Figure 5.2.1. (a) Optical microscopic and (b,c) SEM images of MoS₂ crystals on SrTiO₃ (i) before and (ii) after annealing: (a) at 1000 °C for 5.5 h, (b) at 800 °C for 2 h, and (c) at 1150 °C for 3 h. The contrast of (c.ii) is enhanced to show the residues clearly.

The MoO₃ particles started to evaporate when sufficient thermal energy was absorbed, generally at temperatures above 1000 °C. Three examples are listed below in Table 5.2.1. Notably, samples 1 and 2 were annealed at the same temperature, but the residues on sample 1 all evaporated after 2 h, while they survived on sample 2 after a 5 h treatment. This is because the temperature was ramped up and down at a much lower rate for sample 1, and the additional temperature ramping time (a few hours) inputs a greater amount of thermal energy. Sample 3, which was heated up at a rate in between and annealed at 1150 °C for 3 h, still has some residues left (Figure 5.2.1c.ii). For comparison, the oxidation products of monolayer MoS₂ in air (MoO₃ and SO₂) quickly vanish at a much lower temperature, 400 °C.¹⁸⁸

Table 5.2.1. Summary of the thermal treatments on three MoS₂-on-SrTiO₃ samples.

Sample No.	Temperature ramp rate/°C min ⁻¹	Annealing temp./°C	Annealing time/h	Residues survived?
1	2.5	1000	2.0	No
2	5.5	1000	5.5	Yes – Figure 5.2.1a.ii
3	3.9	1150	3.0	Partially – Figure 5.2.1c.ii

The thermally decomposed products of MoS₂ were investigated by XPS. Figure 5.2.2 indicates the core level spectra of Mo 3*d* and S 2*p* of the samples. In each column from top to bottom, the spectra compare the compositions of differently treated samples, as labelled in their top-right corners: as-grown few-layer (FL) MoS₂, as-grown monolayer (ML) MoS₂, monolayer MoS₂ annealed to 700, 800, 900, and 1000 °C. The XPS spectra for Mo in Figure 5.2.2a show that the Mo exists as both Mo⁶⁺ and Mo⁴⁺. Both these oxidation states have a doublet peak in their 3*d* spectra: 235.2 eV and 232.3 eV correspond to Mo⁶⁺ (3*d*_{3/2}) and Mo⁶⁺ (3*d*_{5/2}), typical of MoO₃;²⁹⁴ 232.1 eV and 229.2 eV correspond to Mo⁴⁺ 3*d*_{3/2} and Mo⁴⁺ 3*d*_{5/2}, typical of MoS₂.^{295,296} One can note that the Mo⁶⁺ 3*d*_{5/2} and Mo⁴⁺ 3*d*_{3/2} peaks are almost coincident, giving rise to the characteristic three-peak shape of Mo⁶⁺ and Mo⁴⁺.²⁹⁷ Along with the Mo peaks, another peak observed at 226.3 eV belongs to S 2*s*.²⁹⁶ In the spectra for S (Figure 3b), S 2*p* peaks are observed at 163.2 eV and 162.0 eV, which represent the 2*p*_{1/2} and 2*p*_{3/2} orbital splitting.²⁹⁸

Integrating the above observations from XPS results, it can be inferred that the as-grown samples were MoS₂ mixed with a small amount of unreacted MoO₃ precursor. At increasingly higher temperatures, the amount of Mo⁶⁺ increased because more MoO₃ was formed as MoS₂ was oxidized by the SrTiO₃ substrate. The loss of sulphur should account for the reduced mass indicated by the

SEM image in Figure 5.2.1b.ii. The complete desulphuration occurred at a temperature between 700 and 800 °C, Afterwards, the molybdenum oxides all evaporated at $T > 1000$ °C.

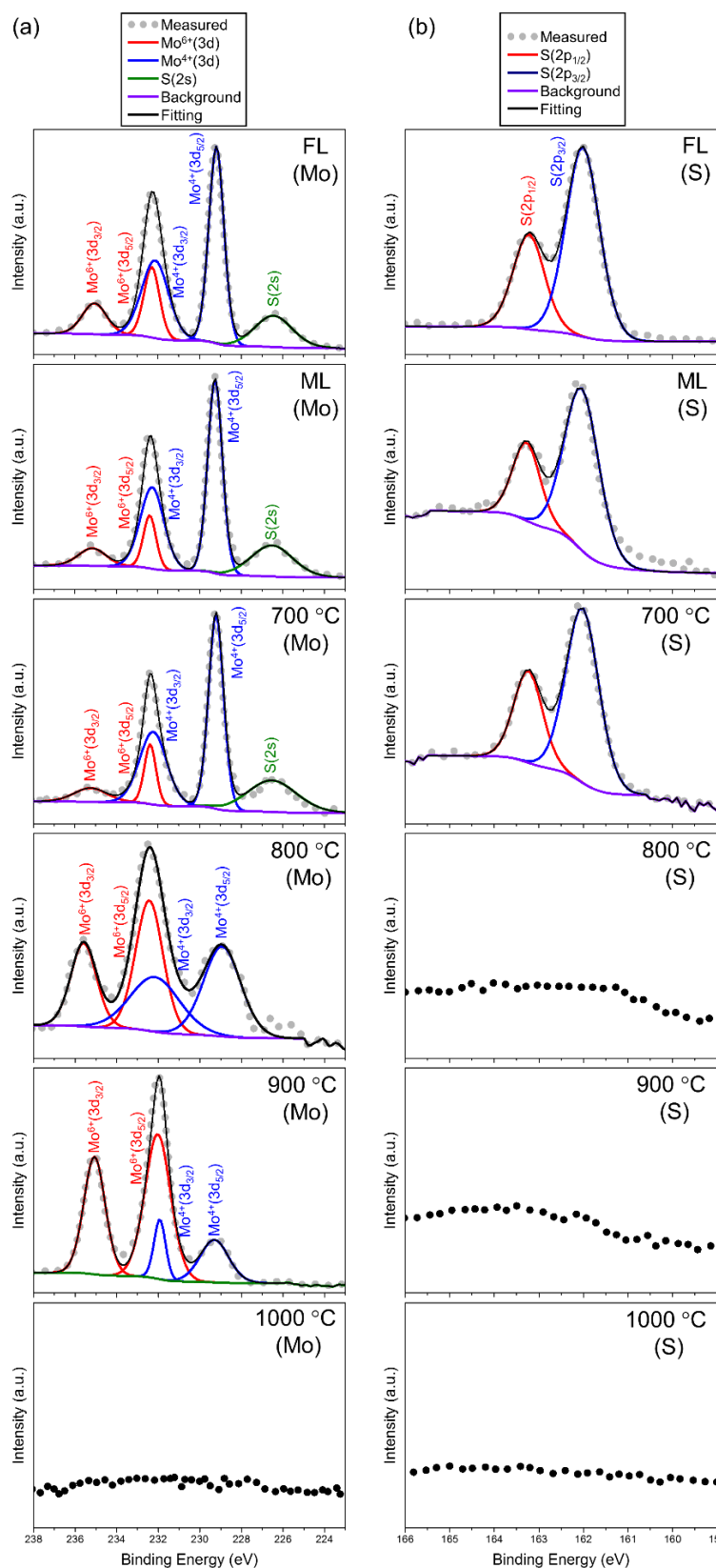


Figure 5.2.2. XPS spectra of the (a) Mo 3d and (b) S 2p core-level peaks for the MoS₂ crystals on SrTiO₃. From top to bottom: as-grown few-layer (FL) and monolayer (ML) MoS₂, and the ML MoS₂ annealed at 700, 800, 900, and 1000 °C.

The relative amounts of MoO₃, MoO₂, and MoS₂ in various samples are estimated from the areas of the Gaussian curves of Mo⁶⁺, Mo⁴⁺, and S²⁻ and by using the relative sensitivity values of these elements. The results are plotted in Figure 5.2.3, with the errors estimated from the uncertainties during peak fitting. The FL, ML, and 700 °C-UHV annealed samples have similar amounts of MoO₃, MoO₂, and MoS₂, where the oxides are the unreacted / incompletely reacted precursor. The FL sample has slightly more MoO₃ than the ML sample, because it had a larger amount of precursors deposited. At 700 °C there is a slightly increased amount of MoO₂ and a virtually unchanged amount of MoO₃ when compared with the ML pristine sample. This means that at 700 °C a small but noticeable amount of MoS₂ has been converted into MoO₂ (but not MoO₃ yet). At 800 °C the %MoS₂ value rapidly decreases to a negligibly small percentage, and similar amounts of MoO₂ and MoO₃ are present. At 900 °C, over 75% of the residue is MoO₃. Therefore the compositional change is likely to follow the route MoS₂ → MoO₂ → MoO₃.

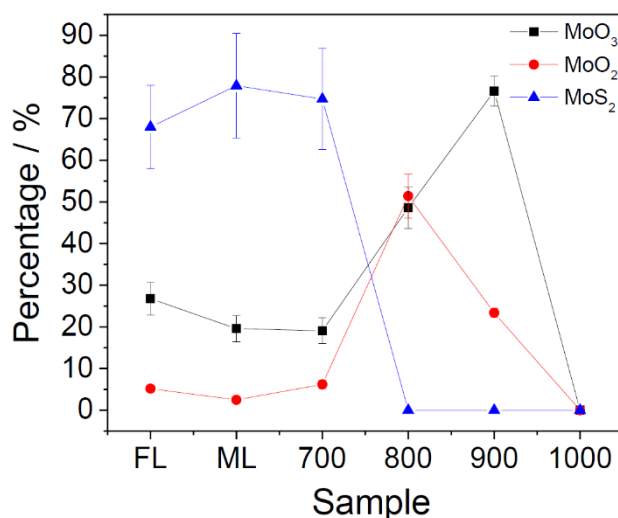


Figure 5.2.3. Atomic percentage of substances in the as-grown MoS₂ crystals (few-layer and monolayer) and MoS₂ monolayers UHV annealed to 700 °C, 800 °C, 900 °C, and 1000 °C.

To validate the thermal degradation of MoS₂, PL and Raman spectroscopy were carried out for different annealing conditions (Figure 5.2.4). Upon laser excitation, the as-grown sample exhibits a strong PL peak at the phonon energy of 1.88 eV (black curve in Figure 5.2.4a), characteristic of monolayer MoS₂.^{1,2,168,299,300} In the Raman spectra (black curve in Figure 5.2.4b) there are two peaks centred at 382.2 cm⁻¹ and 403.0 cm⁻¹, corresponding to the in-plane E_{2g}^1 and out-of-plane A_{1g} vibrational modes of MoS₂, respectively.^{102,301} The frequency difference of ≈ 20 cm⁻¹ is signature of MoS₂ monolayers.^{27,102,168,173,178,301} Then annealing at 700 °C results in greatly decreased intensities of the PL and Raman peaks (red curves in Figure 5.2.4), as clear evidence of the deteriorated crystallinity of the MoS₂. When we further increased the temperature to 800 °C, no PL or Raman signals could be observed. This is consistent with the XPS results in Figure 5.2.2, which show that the MoS₂ were completely oxidised by the SrTiO₃ substrate and transformed into MoO₃ at 800 °C under UHV (purple lines in Figure 5.2.4).

There are a few other interesting observations regarding the as-grown and 700 °C-annealed signals. Firstly, we found that after the thermal annealing the PL peak position is shifted to a lower photon energy (red shift), as shown in Figure 5.2.4a. It could be caused by damage to the crystallinity of MoS₂ and an increase in the localized states,²⁷¹ which are associated with structural defects.²⁴⁴ The generation of defects during the thermal annealing is demonstrated by the etch dots and lines in the STM images (Figure S4b, Appendix). In another regard, the red shift of the PL peak position can also be explained by the fact that the interfacial electron transfer was facilitated between the MoS₂ layer and the Nb-doped SrTiO₃ substrate as their contact would be improved by the thermal annealing,³⁰² resulting in a larger population of negatively charged trions versus neutral exciton emitted upon laser excitation. It is worth mentioning that strains are unlikely to be produced during the thermal annealing process, because the heating and cooling were both applied at very slow rates (down to 2 °C min⁻¹).

Secondly, the relative integrated intensities between A_{1g} and E_{2g}^1 Raman peaks can be used to evaluate the roughness of MoS₂.^{128,271} The A_{1g}/E_{2g}^1 ratio of the as-grown MoS₂ is 1.14 (black curve

in Figure 5.2.4b), and the MoS₂ annealed at 700 °C shows a reduced value of 1.02 (red curve in Figure 5.2.4b). Since the A_{1g} mode is preferentially excited for edge terminations, whereas the E_{2g}^1 mode is preferentially excited for terrace terminations,³⁰³ the smaller ratio suggests a smoother surface of the annealed sample, which could be attributed to the thinning effects,¹⁸⁷ though triangular etches started to form under this condition (Figure S4b, Appendix).

Finally, after being annealed at 700 °C, the Raman peaks are both shifted to higher wavenumbers (“stiffening” or blue shifts), accompanied by peak broadening. It is well known that strains form in the MoS₂ during the cooling process in CVD methods due to the different thermal expansion coefficients between MoS₂ and the SrTiO₃ substrate.²⁴¹ The degradation of MoS₂ could initiate from generating vacancies/holes in the MoS₂ monolayer, which leads to a release of strain. This is similar to a nanopatterning process of monolayer MoS₂, as supported by the stiffening of the two Raman modes.³⁰⁴

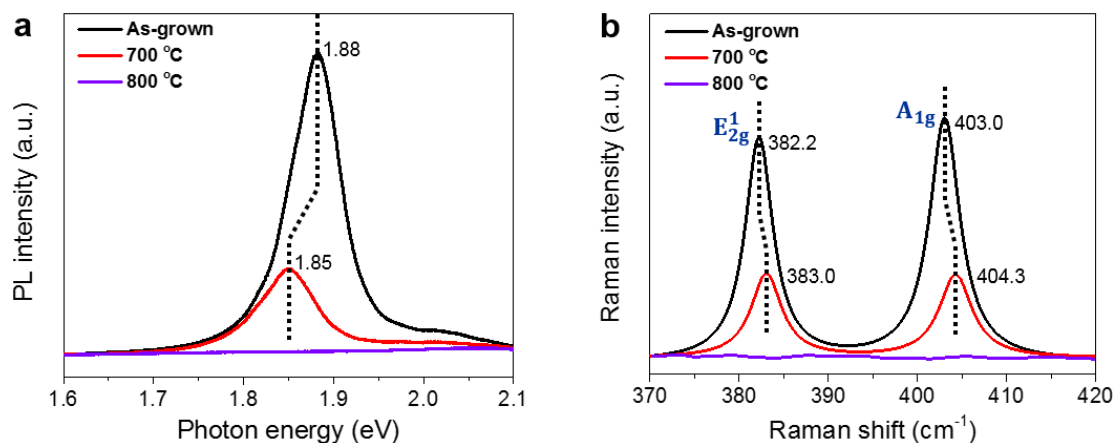


Figure 5.2.4. (a) PL and (b) Raman spectra of monolayer MoS₂ grown on SrTiO₃: as-grown (black), annealed to 700 °C (red) and annealed to 800 °C (blue).

To revive the optical properties of the degraded MoS₂ monolayers due to the thermal annealing in vacuum, we created sulphur atmosphere at elevated temperature, and the sulphur vapour was transported to the MoS₂ surface by argon flow. It is indicated by the SEM images that the 700 °C-annealed MoS₂ crystals look very similar before (Figure 5.2.1b.i) and after (Figure 5.2.5a.i) sulphur

annealing. Although the SEM images reveal a fully recovered morphology of the 800 °C-annealed crystals (Figure 5.2.5a.ii), compared to the non-annealed samples (Figure 5.2.1b.i), their optical properties were partially recovered via the S annealing. Figure 5.2.6a shows that the PL intensity of the 700 °C-annealed MoS₂ crystals is improved and the PL peak position is blue-shifted back to higher photon energy, both of which are very close to those of the newly grown MoS₂ crystals. In addition, the Raman signals are also largely restored (Figure 5.2.6c), in terms of both the peak intensity and the peak position. This could be attributed to two processes. Firstly, as aforementioned, S vacancies exist in the MoS₂ monolayer while being annealed at 700 °C. These vacancies could be filled in the S atmosphere, leading to enhanced PL intensity together with a blue shift of the PL peak position.²⁷¹ Secondly, there was likely a direct sulphurisation process of the molybdenum oxide that had formed on the SrTiO₃ substrate, *i.e.*, MoO₂ in this case. This can be considered as an *in situ* re-growth of MoS₂, with the precursors of MoO₂ and S, while the reactive molybdenum oxide could be in solid and/or vapour phase(s). However, for the 800 °C-annealed MoS₂ crystals, a weak PL signal was detected. Since the XPS data above demonstrated that no MoS₂ had been left prior to the sulphur annealing, the PL signal is only attributed to the sulphurisation of MoO₂ and MoO₃ left on the SrTiO₃ substrate, giving birth to a small amount of MoS₂. Weak Raman signals for MoS₂ are also observed in Figure 5.2.6d, with the A_{1g} and E_{2g}^1 peaks blue-shifted relative to the as-grown MoS₂ monolayer. Besides, the frequency difference of 21.4 cm⁻¹ between the A_{1g} and E_{2g}^1 Raman modes proves that a mixture of monolayer and few-layer MoS₂ was produced.¹⁰² As the PL signal is negligible of few-layer MoS₂, especially for tiny islands, the PL observed in Figure 5.2.6b should result from MoS₂ monolayer.² The PL peak position of 1.87 eV for both the S-annealed samples correspond to direct excitonic transitions.¹

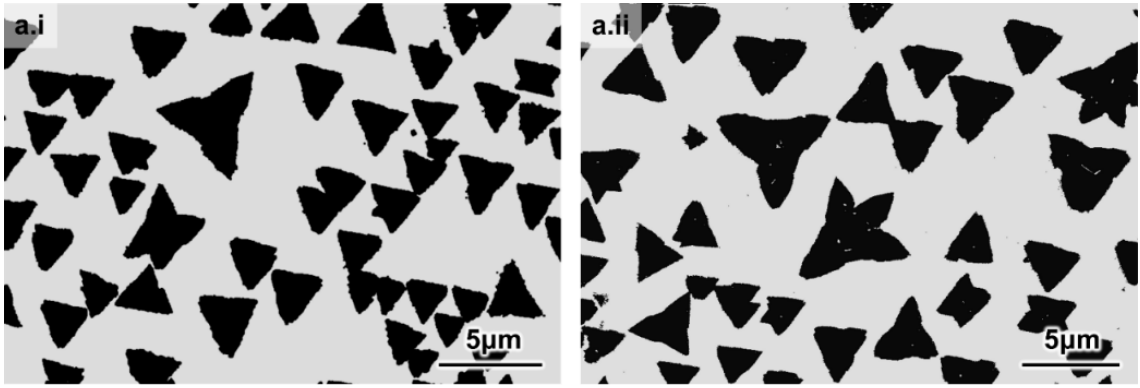


Figure 5.2.5. (a) SEM images of (i) 700 °C- and (ii) 800 °C-annealed MoS₂ crystals on SrTiO₃ after sulphur annealing.

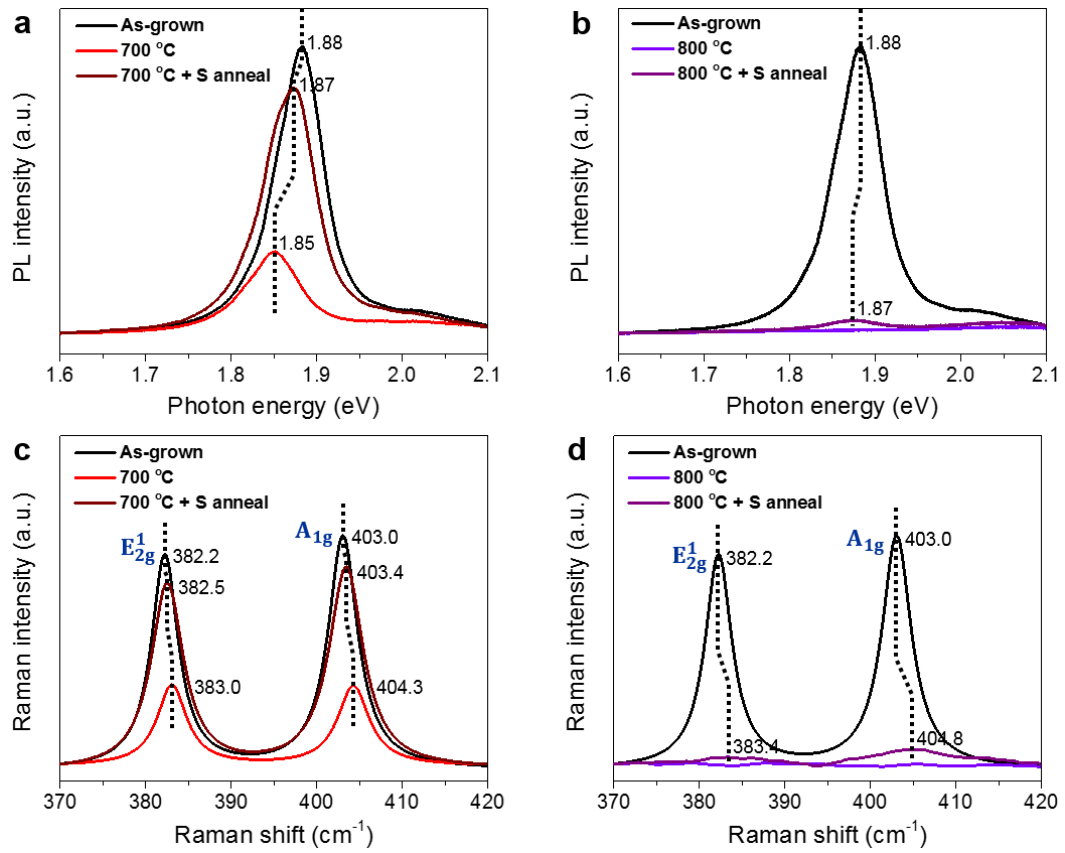


Figure 5.2.6. (a,b) PL spectra and (c,d) Raman spectra of the sulphur-annealed MoS₂ crystals compared with those before (*i.e.*, as-grown) and after the vacuum annealing at (a,c) 700 °C and (b,d) 800 °C.

5.2.3 Conclusion

As summarised in Table 5.2.2, this project established the thermal degradation of monolayer MoS₂ in vacuum induced by the oxidising SrTiO₃ substrate. The MoS₂ evolved from a smooth-

surfaced intact crystal (<700 °C) to a domain with triangular etches because of sulphur loss (at 700 °C), and finally to MoO₃ particles (at 900 °C). The evaporation of the residual MoO₃ particles happens at above 1000 °C. It prominently depends on the total thermal energy absorbed, *i.e.*, the combination of annealing temperature, annealing time, and the temperature ramp rate. The preferential loss of sulphur and oxidation of molybdenum were revealed by XPS, and the decaying of optical properties of MoS₂ was featured by PL and Raman spectroscopy from 700 °C. The crystal shapes of MoS₂ are very stable upon annealing until complete evaporation. This infers that any triangular crystals that look intact under OM and SEM may not be pristine MoS₂, and should be used with care. For retaining the properties of MoS₂ it is important to avoid desulphuration and its exposure to oxygen. This study provides insight into the thermal behaviour of monolayer MoS₂ supported on an oxide substrate in vacuum, to help future studies enabling their extreme-temperature applications in electronics and sensors.

Table 5.2.2. Summary of thermal degradation of MoS₂ on SrTiO₃ in vacuum.

Sample	Annealing time/h	Morphology	Substances (excluding excess
			MoO ₃ precursor)
FL	N/A	Smooth crystal	MoS ₂
ML	N/A	Smooth crystal	MoS ₂
700 °C	0.5–1.0	Crystal + Etches	MoS ₂ (mainly) + MoO ₂
800 °C	0.5–1.0	Crystal + Particles	MoO ₂ + MoO ₃ (similar amounts)
900 °C	0.5–1.0	Particles	MoO ₂ + MoO ₃ (mainly)
1000 °C	2.0–5.5	Particles / Evaporated	N/A

Chapter 6 Vertical Stacked 2D WS₂:hBN:MoS₂

Heterostructures

To study the interactions between 2D semiconductor monolayer transition metal dichalcogenides, herein, WS₂ and MoS₂ both grown by chemical vapour deposition (CVD) were employed and assembled by sequential transfer into vertical layered heterostructures (VLHs). Insulating hBN, also produced by CVD, is utilized to control the separation between WS₂ and MoS₂ by adjusting the layer number, leading to fine-scale tuning of the interlayer interactions within the VLHs. The interlayer interactions are studied by photoluminescence (PL) spectroscopy and are demonstrated to be highly sensitive to the input excitation power. For thin hBN separators (one to two layers), the total PL emission switches from quenching to enhancement by increasing the laser power. Femtosecond broadband transient absorption measurements demonstrate that the increase in PL quantum yield (QY) results from Förster energy transfer from MoS₂ to WS₂. The PL signal is further enhanced at cryogenic temperatures due to the suppressed nonradiative decay channels. It is shown that (4 ± 1) layers of hBN are optimum for obtaining PL enhancement in the VLHs. Increasing thickness beyond this causes the enhancement factor to diminish, with the WS₂ and MoS₂ then behaving as isolated noninteracting monolayers. These results indicate how controlling the exciton generation rate influences energy transfer and plays an important role in the properties of VLHs.

6.1 Introduction

The availability of more 2D materials than just graphene has allowed the expansion of application and science of 2D electronics and optoelectronics.^{281,305–312} In particular, monolayer transition metal dichalcogenides, such as WS₂ and MoS₂, have found widespread interest due to the direct band gap in the visible spectrum that emerges when they are monolayer.^{1,2,30,100,175,313} In bulk, these transition metal dichalcogenides (TMDs) are indirect band gap materials and thus have quite different properties.^{2,30,100,314} Combining the metallic-like properties of graphene, the insulating behaviour of hBN with the semiconducting properties of monolayer TMDs enables all 2D electronics and optoelectronics to be realized.^{68,281,311} These can be with either lateral geometry³¹¹² or vertical stacked structures^{68,281}. The layer-by-layer assembly of 2D materials on top of each other builds complex vertical layered heterostructures (VLHs) that have unique properties through the strong interlayer interactions.^{37,38,317,318,40,41,43,44,50,112,315,316}

The VLHs have been used to produce new types of tunnelling transistors, photodetectors, and light-emitting devices.^{281,307–310,315} In most of these cases, graphene is used as the metal electrode and monolayer TMDs as the active semiconductor material.^{281,309,310} The insertion of insulating hBN between the graphene and TMDs provides the tunnel barrier and tuning its thickness by layer number has shown to result in optimized field-effect mobility in VLHs.²⁸¹ A type II heterojunction is formed when there is no insulator between two distinct TMDs.^{37,40,316} In these systems, the exciton is rapidly separated into the two layers, leading to quenched photoluminescence (PL) emission.^{41,43,44,317,318} Insights into the behaviour of photoexcited excitons can be gained by PL spectroscopy and transient absorption (TA) spectroscopy.

It has been shown that the indirect recombination in WSe₂:MoS₂ heterobilayers could be suppressed by inserting dielectric hBN films in between.⁴³ However, a systematic study on the number of hBN layers has yet to be performed and is important for determining the optimized

separation distance between two TMD layers for maximized energy transfer. For small separation distances, Dexter transfer is expected to dominate, which is associated with charge transfer and PL quenching. As the separation distance increases, Förster energy transfer can then arise, whereby dipole–dipole interactions lead to exciton transfer from one semiconductor to another.⁴⁹ Finally as the separation distance further increases, interlayer interactions should diminish and the two semiconductors behave as isolated materials.³¹⁹ Controlling the interlayer distance across this range of interactions in VLHs has yet to be investigated in detail.

The large exciton binding energy in WS₂ and MoS₂ promotes the study of many-body effects.^{73,95} Increasing the exciton generation rate with higher excitation power causes varied exciton density and in turn the relative population of excitons and trions in the material.^{73,320} The interlayer interactions between TMDs in VLHs should also be influenced by the excitation power, but to date there has been little investigation into this.

In this project, chemical vapour deposition (CVD)-grown WS₂, MoS₂, and hBN were used to create VLHs of WS₂:hBN:MoS₂ and MoS₂:hBN:WS₂ with tunable separation distance by adjusting the total number of hBN layers in between. The effects of input laser power as well as temperature on the PL properties of the VLHs were studied. The WS₂ and MoS₂ are grown as isolated domains that enable their heterostructures to be easily identified by optical microscopy and also the measurement of PL from each monolayer and the heterostacked region can be conducted separately for a direct comparison of the PL signal magnitude. Similar to prior reports, the PL emission from WS₂ is significantly larger than MoS₂ and dominates the VLH emission.^{41,317} PL quenching or enhancement in VLHs can be evaluated by comparing the total integrated PL signal from the WS₂:hBN:MoS₂ region with that of the WS₂ monolayer. The influence of strain on the VLH interlayer interactions is probed by comparing two configurations, one where the WS₂ is as-grown with inbuilt strain and the MoS₂ is transferred on top, and the other where the MoS₂ is as-grown with inbuilt strain and then the WS₂ is transferred on top. The presence of strain induces shifts in the band gap of TMDs

and alters the relative offsets in the band structure that generates the type II heterostructure interface.^{62,68,321} The CVD-grown materials permit large numbers of VLHs to be formed on a single 1 cm × 1 cm chip. Therefore, multiple measurements can be provided to ensure the findings are consistent throughout the sample.

6.2 Results and Discussion

The constituent materials of the heterostructures, *i.e.*, isolated WS₂ and MoS₂ domains and hBN continuous films, are synthesised *via* atmospheric pressure CVD. Sliding transfer method with isopropanol (IPA) was utilised for the layer-by-layer stacking while preserving the TMD materials underneath. The use of highly volatile solvent ensures no residues to be remained so that cleaner interfaces between the 2D layers can be generated compared to the conventional methods based on water.²⁹³ The characterisation of the monolayer WS₂ and MoS₂, and the vertical heterostructures involves optical microscopy (OM), scanning electron microscopy (SEM), and annular dark-field scanning transmission electron microscopy (ADF-STEM). As shown in Figure 6.1a–d, highly uniform, large-area WS₂ and MoS₂ monolayers have been produced. Figure 6.1e,f prove the covering of continuous hBN films on top of MoS₂ and WS₂ domains, respectively. The film boundaries can be visualised through the high contrast. Figure 6.1g–i shows the WS₂:MoS₂ stacks built up by either smooth- or sawtooth-edged MoS₂. The ADF-STEM images in Figure 6.1j–l verify the high crystallinity of the MoS₂ monolayer crystal, and it was found that the optical properties of both the MoS₂ and the as-built VLHs are little affected by the domain morphology. Nevertheless, the analysis in this work is only performed on the basal plane of nanosheets with the edges and grain boundaries excluded, considering that defects could be present in these regions due to the CVD process.²⁴¹ Additionally, the hBN interlayer separator was characterised by Raman spectroscopy and atomic force microscopy (AFM) as presented in Figure S6a and S7 (Appendix), respectively. It is noteworthy that the analysis in this work was performed on the basal planes of the nanosheets, considering that

the defects and atypical properties are possibly present at the crystal edges and grain boundaries.^{28,85,86} Considering the transfer process often introduces defects in the WS₂ and leaves solvent residues between the layers of the as-prepared VLHs, the samples were annealed in vaporous sulphur before the PL measurements both to fill the sulphur vacancies and to eliminate the interlayer contaminants for high-quality stacks.

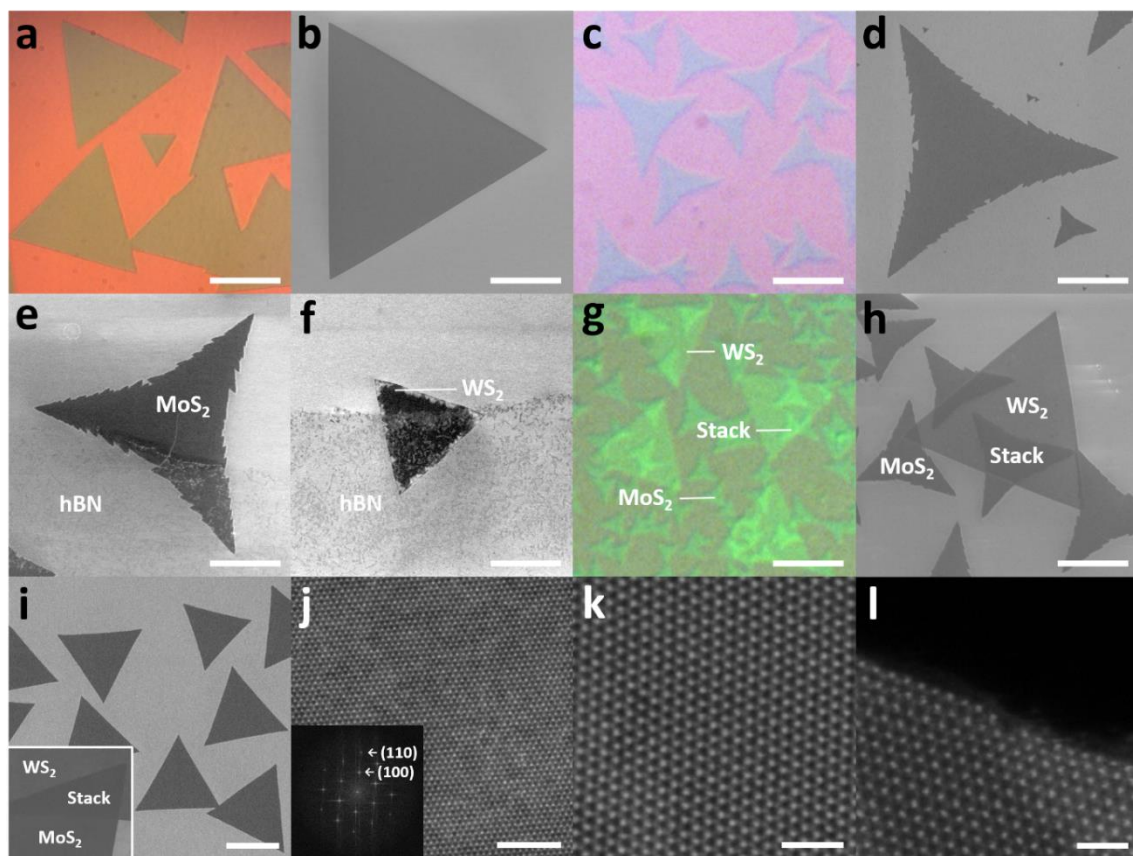


Figure 6.1. (a) Optical microscopic and (b) SEM images of the CVD-grown monolayer WS₂. (c) Optical microscopic and (d) SEM images of the CVD-grown monolayer MoS₂. SEM images of the (e) hBN:MoS₂ and (f) hBN:WS₂ vertical stacks. (g) Optical microscopic and (h) SEM images of the WS₂:MoS₂ VLHs. (i) Equilateral triangular MoS₂ domains with smooth edges, where the inset is a constituted WS₂:hBN:MoS₂ VLH. ADF-STEM images of the MoS₂ monolayer with (j) lower magnification and the corresponding FFT image as an inset and (k) higher magnification. (l) ADF-STEM image of the sawtooth edge of a star triangular MoS₂ domain. Scale bar: (a,c,g) – 100 μ m; (b,d,e,f,h,i) – 40 μ m; (j) – 5 nm; (k,l) – 1 nm.

Quenched PL has been previously observed in semiconducting stacks, for instance, the TMD heterobilayers comprising a variety of materials, because the charge transfer process in the type II

heterojunction can efficiently hinder the intrinsic excitonic recombination from either of the monolayers.^{41,43,44,317,318} Reverse bilayers of WS₂:MoS₂ and MoS₂:WS₂ were made, and the results are displayed in Figure 6.3 and Table 6.1. The MoS₂ and WS₂ are respectively identified by their Raman peaks of (2LA(M) + E') and A'_1 .^{102,110} The Raman spectrum of the WS₂:MoS₂ stack comprises the vibrational modes of both the TMD materials (Figure 6.3d), consistent with the previously reported observation for one-step CVD-grown MoS₂:WS₂ heterostructures.¹¹² As expected, the PL intensity is significantly decreased by 82% compared to the WS₂ monolayer (Figure 6.3e). This reflects the strong interlayer coupling, which can also prove the interface cleanliness of the as-transferred VLHs. The similar degrees of PL quenching in Table 6.1 indicate that the interlayer charge transfer across the type II heterojunction is nearly independent of the excitation power. With the increase in the input laser power, overall red shifts occur across the whole sample area (Figure 6.3j and Figure 6.4e). The reason is related to and the laser-induced heating effects,⁷³ and the decay of the coupled excitons through indirect emissions.⁴⁴ Since the PL signal is extremely weak under very low input laser power, the PL peak position of the VLHs can hardly be distinguished from the background noise.

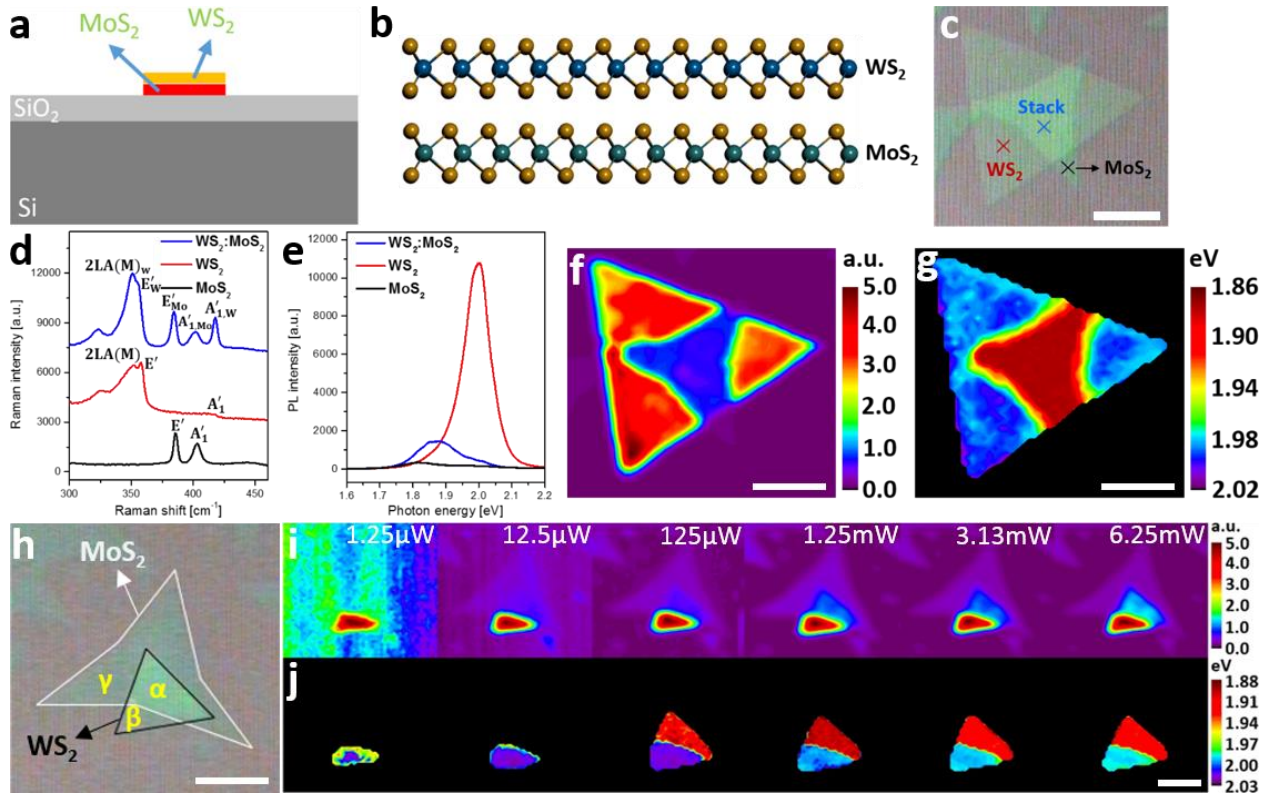


Figure 6.3. (a) Schematic diagram, (b) atomic model, and (c) optical microscopic image of a WS₂:MoS₂ VLH. (d) Raman (12.5 mW laser power) and (e) PL (1.25 mW laser power) spectra taken from the three positions marked in (c), which correspond to the VLH, the WS₂, and the MoS₂ monolayers, respectively. Subscript W represents WS₂, and Mo represents MoS₂. 2D maps of (f) normalized total integrated PL intensity of the VLH vs. the WS₂ monolayer and (g) overall PL peak position across the region shown in (c). (h) Optical microscopic image of another WS₂:MoS₂ VLH. Position α – WS₂:MoS₂, β – WS₂, and γ – MoS₂. Please note that positions α and β are used for the following calculation of the PL ratio in Table S1. 2D maps of (i) normalized total integrated PL intensity of the VLH vs. the WS₂ monolayer and (j) overall PL peak position with increasing excitation powers (1.25 μ W, 12.5 μ W, 125 μ W, 1.25 mW, 3.13 mW, and 6.25 mW) across the region shown in (h). Scale bar: 20 μ m. Conditions for Raman and PL spectroscopy: 532 nm (2.33 eV) laser beam focused down to a $\approx$ 1 μ m spot; acquisition time: Raman spectrum – 3 s, PL spectrum – 1 s, PL mapping – 0.1 s for each point, similarly hereinafter.

Table 6.1. Total integrated PL intensity ratio of α/β in the WS₂:MoS₂ VLH.

Excitation power [μ W]	1.25	12.5	125	1250	3125	6250	Average
PL ratio (α/β)	0.18	0.12	0.11	0.16	0.16	0.14	0.15

To change the interlayer coupling behaviour, an insulating hBN barrier was inserted between the WS₂ and MoS₂ monolayers, shown schematically in Figure 6.5a,b. Figure 6.5c shows the optical microscopic image of a VLH area where WS₂ and MoS₂ contain both regions that overlap and regions that do not. This allows the comparison between the isolated individual TMD layers and their stacks within the same domain. Figure 6.5d,e shows the PL variations when utilising monolayer hBN films, in terms of the integrated intensity and overall peak position, respectively, as a function of laser power. The quenching degree of the heterostacked regions gradually decreases with a red shift of the peak position as the input excitation power increases, indicative of suppressed interlayer charge transfer.^{41,43,44,112} For both the WS₂ and MoS₂ monolayers, higher excitation power produces more electrons and holes in the conduction bands and valance bands, respectively. The larger populations lead to increased Coulomb interactions between the WS₂ and MoS₂ monolayers through the electrons in the conduction bands and holes in the valence bands. Therefore, the possibility is decreased of the electron transition from the conduction band of WS₂ to the conduction band of MoS₂, simultaneous with the reduced hole transition from the valence band of MoS₂ to the valence band of WS₂. The suppression of charge transfer results in decreased PL quenching under higher excitation power.

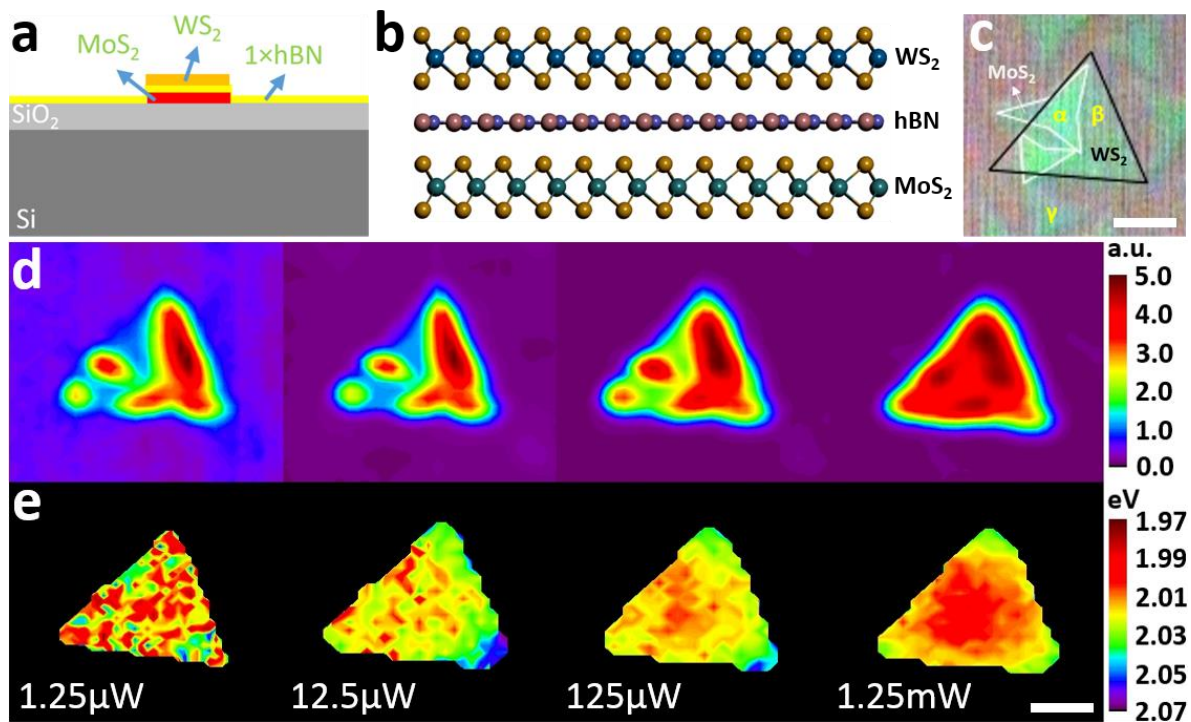


Figure 6.5. (a) Schematic diagram, (b) atomic model, and (c) optical microscopic image of the $\text{WS}_2:1 \times \text{hBN}:\text{MoS}_2$ VLH. Position α – $\text{WS}_2:1 \times \text{hBN}:\text{MoS}_2$, β – WS_2 , and γ – MoS_2 . 2D maps of (d) normalized total integrated PL intensity of the VLH vs. the WS_2 monolayer and (e) overall PL peak position as a function of increasing excitation power (1.25 μW , 12.5 μW , 125 μW , and 1.25 mW) across the region shown in panel (c). Scale bar: 10 μm .

To understand the PL spectra from the $\text{WS}_2:1 \times \text{hBN}:\text{MoS}_2$ regions presented in Figure 6.5 in more detail, we used Gaussian fits to extract the relative contributions of excitons (A), trions (A^-), and localized states (LS) to the total PL emission, as shown in Figure 6.6. Two different excitation powers of 125 μW and 1.25 mW were compared for each TMD layer and their stacked configuration, as these represent the two cases where the changes in charge/energy transfer are observed. For both the monolayers, the A peak arises from neutral exciton emission due to the direct transition at the K point, and the A^- peak is associated with the recombination of negatively charged excitons. In addition, the B peak of monolayer MoS_2 is located at a higher energy, which originates from another direct transition between the conduction and valence bands. The LS peak is normally related to structural disorders and/or impurities.^{73,88,322} The ratio of exciton/trion decreases for both the “pristine” TMDs and the heterostructure. Figure 6.6a,d shows that the total PL of the $\text{WS}_2:1 \times \text{hBN}:\text{MoS}_2$ stack is primarily made up of the emission from WS_2 , which is substantially stronger than that from MoS_2 .

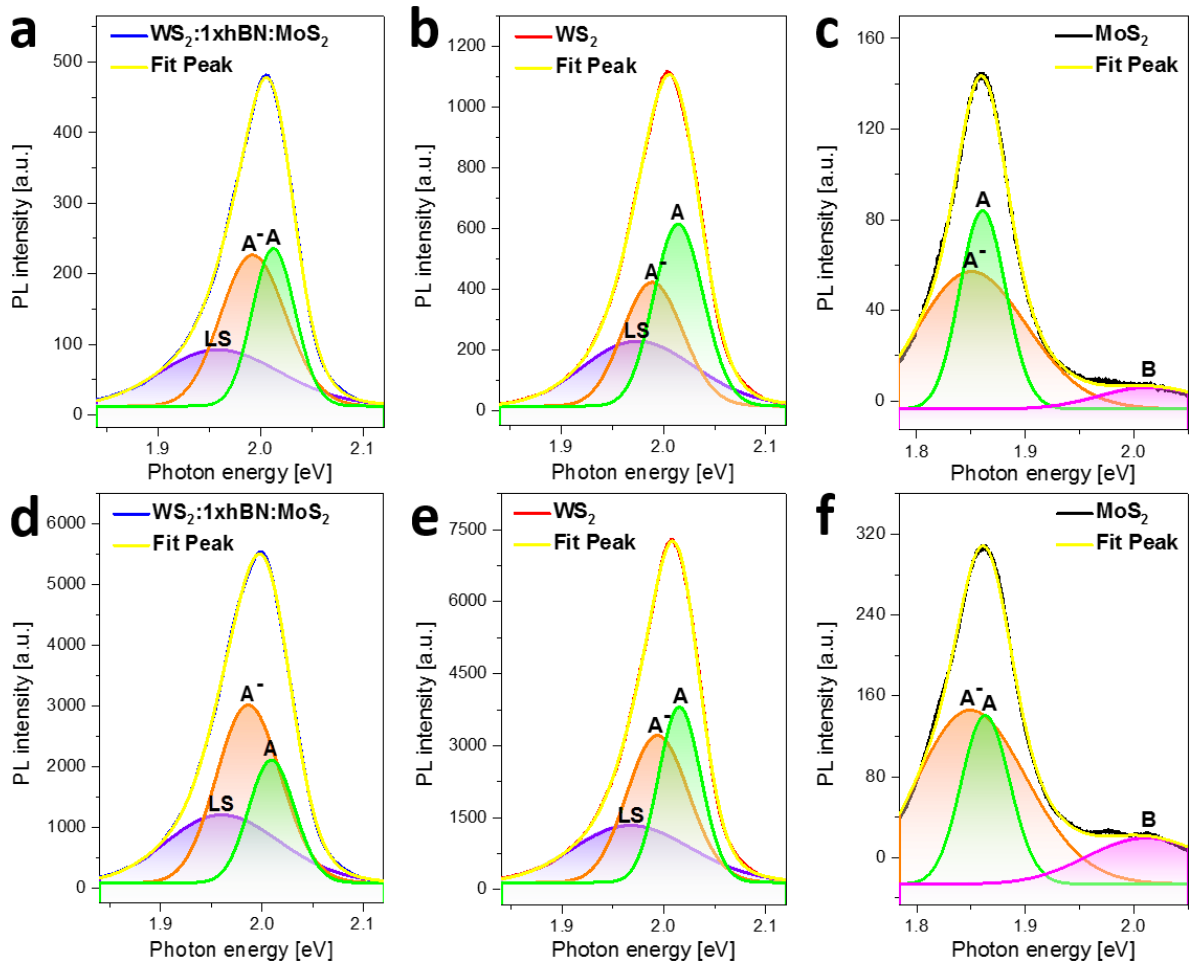


Figure 6.6. PL spectra of the positions marked as α , β , and γ in Figure 1c, with (a–c) 125 μ W and (d–f) 1.25 mW excitation powers. The total PL peaks are deconvoluted using Gaussian functions to extract exciton (A), trion (A⁻), and LS emissions.

Figure 6.7 shows the results when doubling the thickness of hBN to bilayer. Figure 6.7d shows that the (2LA(M) + E') and A₁' Raman modes from both the TMD layers are superpositioned in the heteroregions.^{102,110} This indicates the combination of vibrational modes, which is also observed in the stacks without hBN spacer (Figure 6.3d). The WS₂:2 $\times$ hBN:MoS₂ region does not show quenching at higher excitation powers, but instead an enhanced PL intensity by a factor of 2.11 (Figure 6.7e). The total integrated PL intensity map in Figure 6.7f shows that the enhancement corresponds to the overlapping regions of WS₂ and MoS₂, and the PL peak position map in Figure 6.7g indicates a blue shift in this VLH. Another example is presented in Figure 6.7h and used to probe the PL dependence on the incident laser power. The PL maps in Figure 6.7i show that the PL signal

of the stacked region switches from quenching at low excitation power ($1.25 \mu\text{W}$) to enhancement at high excitation powers ($12.5 \mu\text{W}$ and above); furthermore, the enhancement degree increases with the excitation power. Similarly, the blue shift of the PL peak position becomes more evident at the increased laser power of 1.25 mW (Figure 6.7j). In order to rule out the laser processing effects and prove the reversibility, the samples were excited by different laser powers alternatively. The consistent PL after cyclic excitations proves that the observations result only from the interactions within the heterostacks.

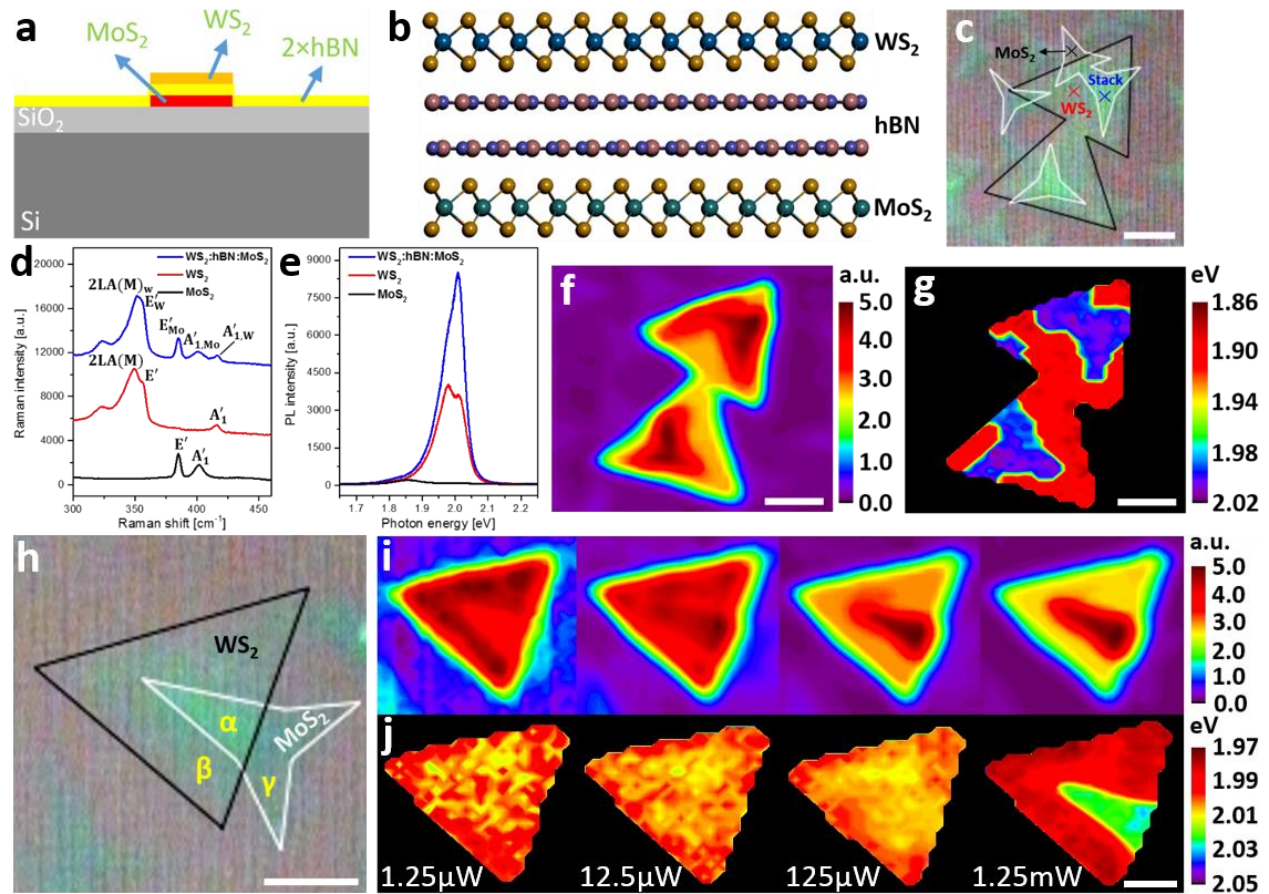


Figure 6.7. (a) Schematic diagram, (b) atomic model, and (c) optical microscopic image of a $\text{WS}_2/2 \times \text{hBN}/\text{MoS}_2$ VLH. (d) Raman and (e) PL spectra taken from the positions marked in panel (c). Raman – 12.5 mW excitation power and 3 s acquisition time; PL – $125 \mu\text{W}$ excitation power and 1 s acquisition time. The subscript W represents WS_2 and Mo represents MoS_2 . 2D maps of (f) normalized total integrated PL intensity of the VLH vs. the WS_2 monolayer and (g) overall PL peak position across the region shown in panel (c). (h) Optical microscopic image of another $\text{WS}_2/2 \times \text{hBN}/\text{MoS}_2$ VLH (position α – $\text{WS}_2/2 \times \text{hBN}/\text{MoS}_2$, β – WS_2 , and γ – MoS_2), for which the 2D maps of normalized total integrated PL intensity of the VLH vs. the WS_2

monolayer and overall PL peak position as a function of increasing excitation powers (1.25 μ W, 12.5 μ W, 125 μ W, and 1.25 mW) are shown in panel (i) and (j), respectively. Scale bar: 10 μ m.

Figure 6.8a–f shows the Gaussian-fitted PL spectra for the VLH and the TMD monolayers at excitation powers of 125 μ W and 1.25 mW. The increase in laser power causes a more pronounced trion emission (*i.e.*, a smaller exciton/trion ratio) for all the three regions. But the heterostack shows larger exciton/trion ratios relative to the WS₂ monolayer, especially under the higher excitation power of 1.25 mW (Figure 6.8a vs. b and d vs. e). This could be attributed to the injection of excitons from the MoS₂ to WS₂ monolayer *via* Förster energy transfer. Since the PL quantum efficiency of the system is increased by the change in excitonic states,^{30,323} the increment in the PL signal of the VLH is even larger than the total intensity of the MoS₂ monolayer. However, the charge transfer is negligible in this VLH as the emission of interlayer exciton is highly suppressed by the hBN separator and the low yield has little contribution to the total PL signal. The varied exciton/trion ratios indicate a difference in the PL behaviour of these two systems and shed light on the origins of the PL enhancement that occurs under high input laser power. 2D maps of the exciton and trion peak positions at these two excitation powers, Figure 6.8g–j, show an increased blue shift for the trion emission with laser power, whereas little change is observed for the exciton emission.

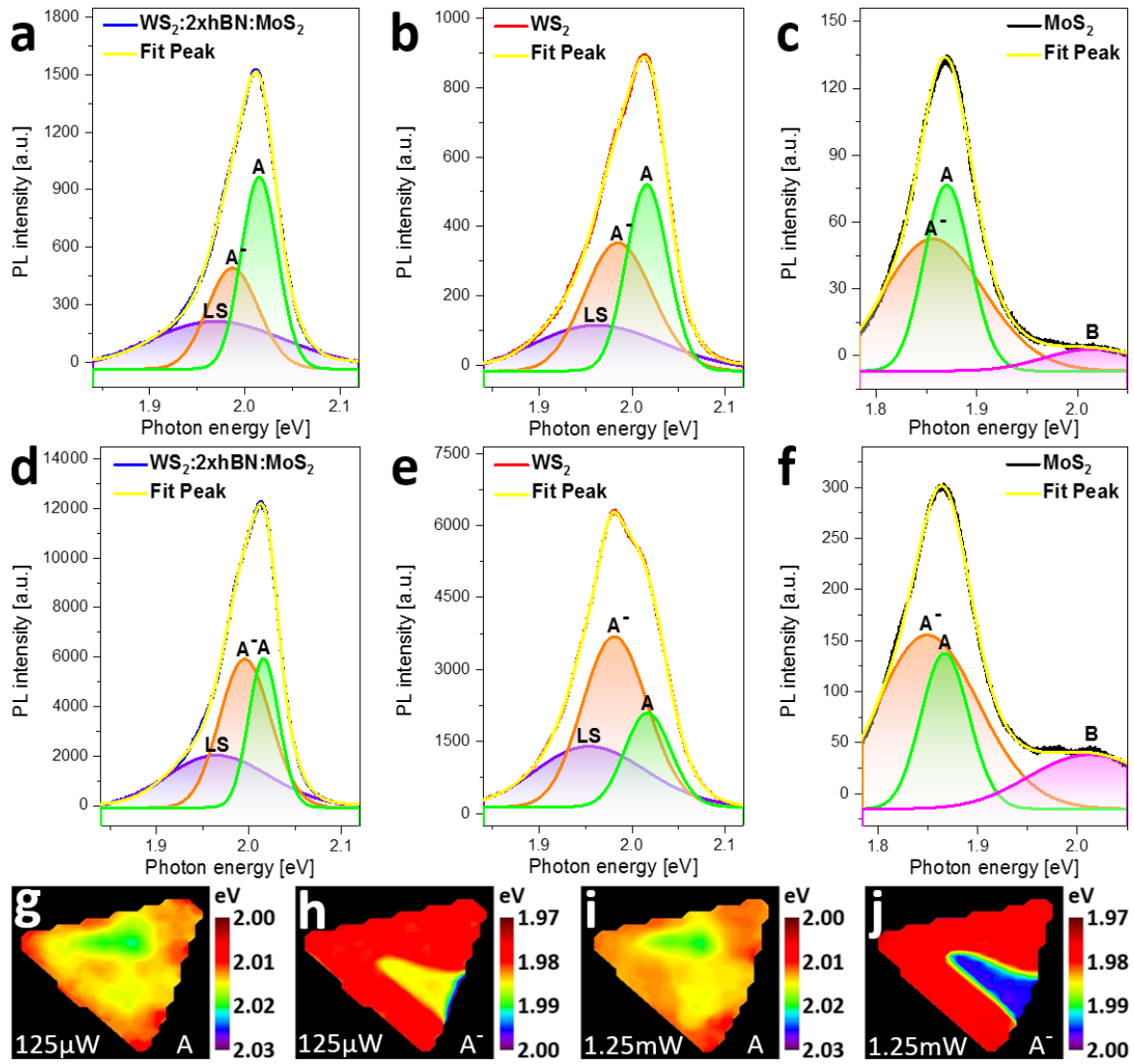


Figure 6.8. Gaussian-fitted PL spectra acquired by using (a–c) 125 μ W and (d–f) 1.25 mW excitation powers for (a,d) position α (WS₂:2 $\times$ hBN:MoS₂), (b,e) position β (WS₂), and (c,f) position γ (MoS₂), as marked in Figure 6.7h. (g,i) Exciton and (h,j) trion peak position maps for the sample region in Figure 3h under 125 μ W and 1.25 mW excitation powers, respectively.

Further insights can be gained by reversing the stacking order and having WS₂ on the bottom and MoS₂ on the top, shown in Figure 6.9. In both cases, the bottom material was as-grown and this typically contains strain in the crystal lattice, induced during the fast cooling stage in CVD.²⁴¹ The amount of strain is evaluated by carefully examining the photon energy in the PL spectra under similar excitation conditions, which is 0.6% for the WS₂ in MoS₂:hBN:WS₂ VLHs and 0.12% for the MoS₂ in WS₂:hBN:MoS₂ VLHs.^{59,62} The monolayer WS₂ is more strained than the MoS₂ due to the higher

growth temperature of WS₂ and their similar calculated linear thermal expansion coefficients relative to the SiO₂/Si substrate,³²⁴ while the cooling procedures in CVD and characterisation parameters are kept identical. The presence of strain causes bandgap modification, which will change the relative band offsets between WS₂ and MoS₂ monolayers and in turn the details of the type II heterostructure.^{62,68,321} The direct bandgap shrinks for strained TMDs, with the conduction band valley downshifting at the K point.^{57,59,95} Inbuilt strain can therefore lead to substantial PL red shift for monolayer WS₂ (Figure 6.2).⁶² The decrease in the energy level of MoS₂ B exciton or WS₂ A exciton could disturb their resonant states and impede their interactions through Förster energy transfer. On the other hand, the charge transfer still occurs because the type of heterojunction is unchanged. Therefore, the involvement of strained WS₂ monolayer in the reversed stack of MoS₂:2 × hBN:WS₂ shows more quenching under low excitation powers (1.25, 12.5, and 125 μW in Figure 6.9d–f), compared to the WS₂:2 × hBN:MoS₂ VLH with unstrained WS₂ (Figures 6.7 and 6.8). Nevertheless, the dipole–dipole interactions are encouraged at higher density of the excitons generated per second. The large population of excitons increases the possibility of energy transfer, based on the small shift of the conduction band, which gives rise to PL enhancement at higher excitation powers (1.25 and 3.13 mW in Figure 6.9g,h). Additionally, the increased LS emissions reveal more structural disorders caused by the strain (Figure 6.9i,j,l,m vs. Figure 6.8a,b,d,e, respectively).³²² The influences of strain can be minimized with high laser input, where the activity of dipoles across the WS₂ and MoS₂ layers is increased and closer to saturation. This explains the observation of the same PL enhancement level for both stack configurations at 1.25 mW excitation power (Figure 6.9o). It is notable that although strains can modulate the QY of TMDs,³²⁵ we study the effects of excitation power and layer number of hBN consistently on WS₂:hBN:MoS₂ to draw safe conclusions. The observation of this switching from PL quenching to enhancement in both VLHs indicates that it is not related to the local dielectric environment or exposure to air or damage, but is an intrinsic property that arises by overlapping WS₂ and MoS₂ with 2 × hBN in between. Utilising

excitation power above 1.25 mW causes material degradation and this is the origin of the downturn in the PL ratio in Figure 6.9o.

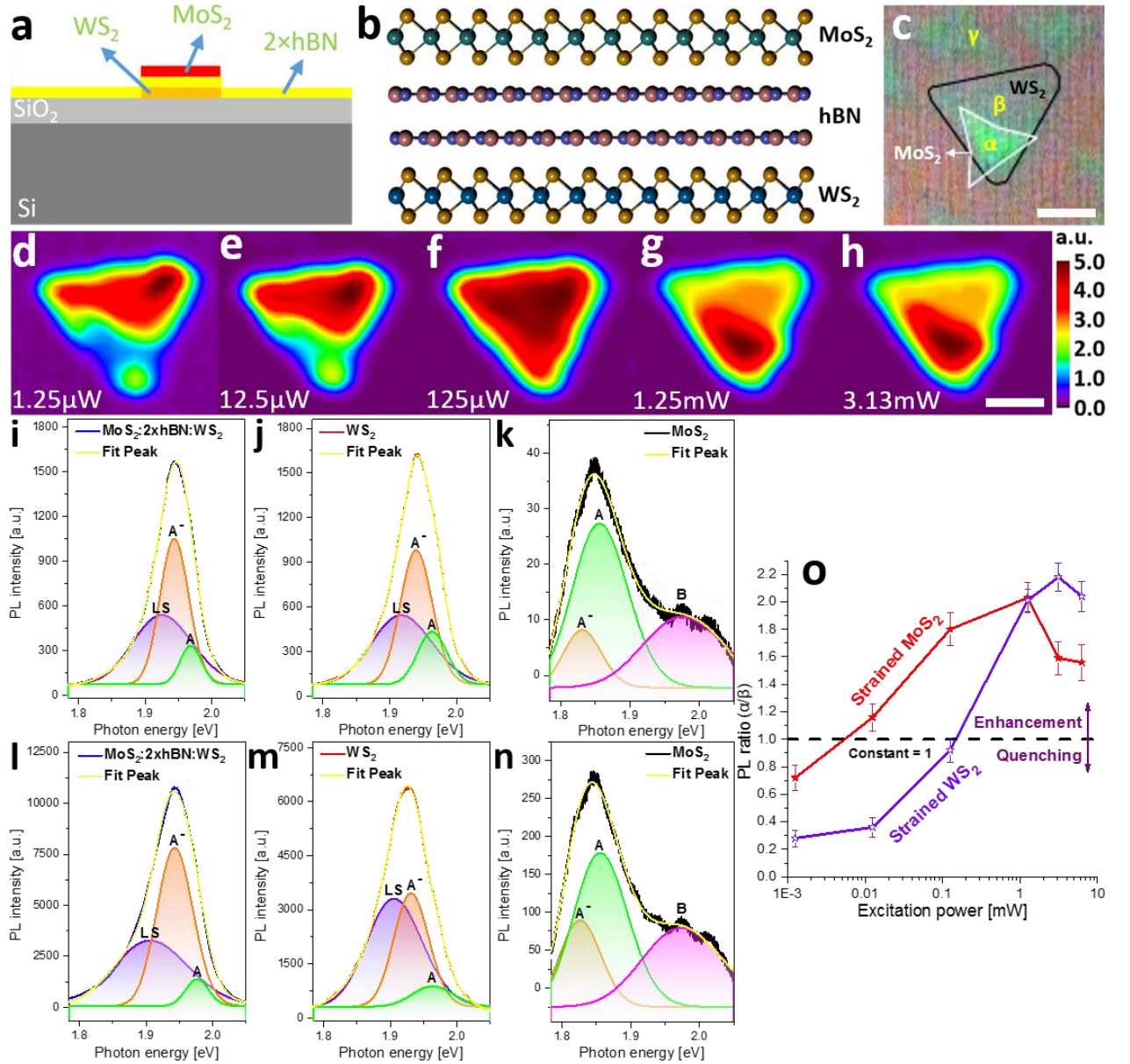


Figure 6.9. (a) Schematic diagram, (b) atomic model, and (c) optical microscopic image of the MoS₂:2 × hBN:WS₂ VLH. (d–h) 2D maps of normalized total integrated PL intensity of the VLH vs. the WS₂ monolayer with increasing excitation powers (1.25 μW, 12.5 μW, 125 μW, 1.25 mW, and 3.13 mW) across the region shown in panel (c). Scale bar: 10 μm. Gaussian-fitted PL spectra acquired by using (i–k) 125 μW and (l–n) 1.25 mW excitation powers for (i,l) position α (MoS₂:2 × hBN:WS₂), (j,m) position β (WS₂), and (k,n) position γ (MoS₂), as marked in panel (c). (o) Plot of the PL ratio (total integrated PL intensity of position α divided by that of position β in the corresponding optical microscopic image) as a function of input excitation power. Dashed line at PL ratio = 1 indicates the cross-over between PL quenching and enhancement. Each PL ratio in panel (o) is an averaged value with the error bar obtained on a statistical basis of 10 measurements.

The observation of PL quenching at low excitation powers in Figures 6.7–9 for bilayer hBN spacers between WS₂ and MoS₂ indicates that charge transfer is still occurring and excitons are efficiently dissociated across the two TMD layers.^{37,40,41} However, the shift at high excitation powers to PL enhancement reveals that energy transfer becomes the dominant mechanism in the VLH regions. Interlayer energy transfer is highly sensitive to distance and rapidly falls off as the separation increases. To explore this in more detail, Figure 6.10 shows how the PL of the VLHs changes with increasing the hBN separator layer from 2, to 4 (Figure 6.10a–f), 6 (Figure 6.10g–l), 8 (Figure 6.10m–r), and 16 (Figure 6.10s–x), as a function of the input laser power. All these VLHs show PL enhancement under excitation powers of 125 μ W and above. However, increasing the hBN separator layers beyond four requires higher excitation power for observing enhanced PL signals due to the reduced strength of the interlayer interactions.

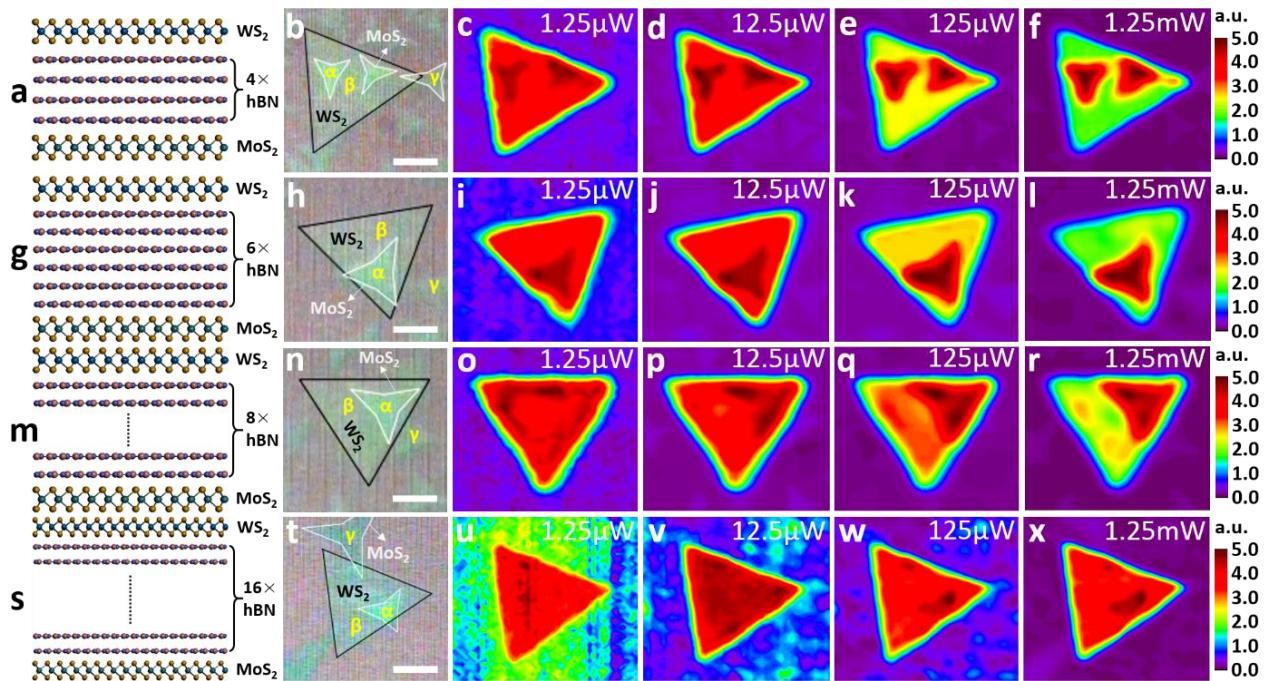


Figure 6.10. PL measurements on VLHs with increasing hBN separator of (a–f) 4, (g–l) 6, (m–r) 8, and (s–x) 16 layers. (a,g,m,s) Atomic models of the VLH stack configurations. (b,h,n,t) Optical microscopic images of the respective heterostacks used in the mapping of normalized total integrated PL intensity with increasing laser power for (c–f) 4, (i–l) 6, (o–r) 8, and (u–x) 16 layers of hBN.

Figure 6.11a plots the PL ratio as a function of excitation power for all the hBN separator layers used in this study, including zero (no hBN involved). Figure 6.11b plots the PL ratio as a function of hBN layer number and suggests that (4 ± 1) layers are the optimal hBN thickness for PL enhancement. The dependence of separation distance allows the extrapolation to show that at a spacing of $\times 24$ hBN layers the two TMD layers are expected to act as isolated materials with negligible interactions. Since the degree of PL enhancement depends on the incident excitation power, it is possible that ultrahigh input laser powers could be used to observe some effects even with $\times 24$ hBN layers, but it is more likely that the high-power laser would destroy the sample first. Considering both charge transfer and Förster energy transfer models enabled a fit to the experimental data for each excitation power (Figure 6.11b), using Equation (1). The fitting done by my collaborator is elaborated and interpreted in the Supporting Information of the corresponding publication. The different distance dependences of charge transfer and Förster energy transfer lead to a peak in the PL ratio, similar to the experimental data. For short distances, energy transfer from WS₂ to MoS₂ dominates with a moderate fraction of charge transfer so that quenching occurs. As the distance then increases between the WS₂ and MoS₂ by adding more hBN layers, Förster energy transfer from MoS₂ to WS₂ overtakes charge transfer and the opposite energy transfer as the main interlayer interaction. The interesting aspect of this Förster energy transfer process is that the direction appears to be from the B exciton in MoS₂ to the A exciton state in WS₂, given the PL enhancement observed in WS₂ but not in MoS₂.

$$\frac{I}{I_0} = \left(1 + a_1 \frac{1}{1 + \left(\frac{R}{R_0} \right)^n} \right) \left(1 - a_2 - a_3 \exp\left(-\frac{2R}{a_B} \right) + a_4 \frac{1}{1 + \left(\frac{R}{R_0} \right)^n} \right) \quad (1)$$

, where R is the separation distance, $R_0 = 4.9$ nm is the Förster distance, $a_B = 1.53$ nm is the exciton Bohr radius referred to the previously reported value,³²⁶ a_1 and a_4 are the Förster energy transfer coefficients, a_2 is the nonradiative decay efficiency of excitons, and a_3 is the charge transfer coefficient.

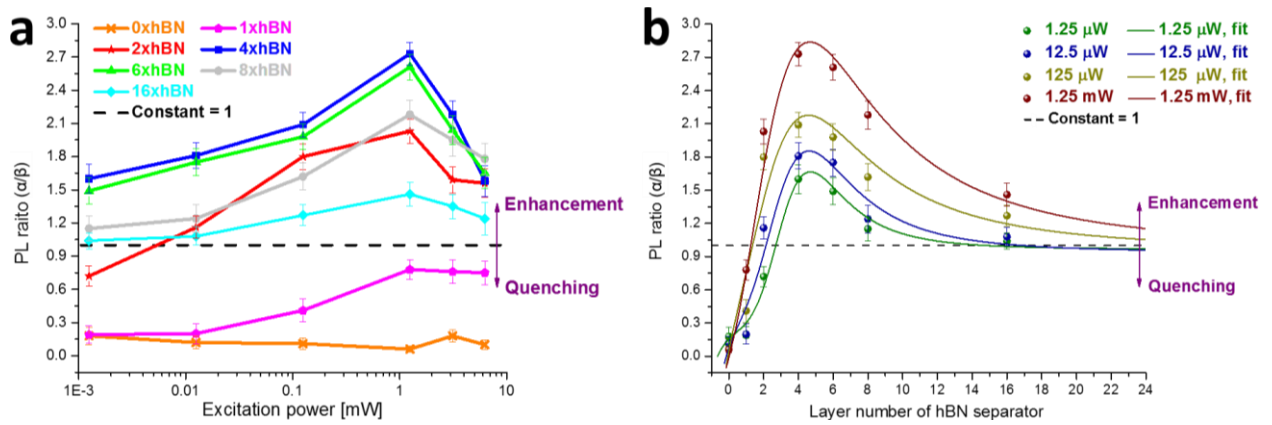


Figure 6.11. (a) Plot of the PL ratio (total integrated PL intensity of position α divided by that of position β in the corresponding optical microscopic image) vs. input excitation power for different hBN layer numbers. (b) Plot of the PL ratio vs. hBN layer number at different excitation powers (solid lines – fit curves using Equation (1); dots – experimental data from panel (a)). Fitting parameters are listed in Supporting Information of the corresponding publication. Dashed line at PL ratio = 1 indicates the cross-over between PL quenching and enhancement. Each PL ratio is an averaged value with the error bar obtained on a statistical basis of 10 measurements.

The excitation power dependence of excitons (A), trions (A^-), and localized states (LS) for different hBN separation layers is investigated in Figure 6.12. The emission from excitons increases almost linearly with excitation power in the log-scaled plots, indicated by the slope of ≈ 0.9 – 1.0 , while the trion emission shows a slightly superlinear dependence with the slope of up to ≈ 1.2 , which can be attributed to the loss of trion population to localized states at low excitation densities.^{95,96} These values, as well as the slope for localized states, are consistent with earlier studies on WS_2 , and are far below the power law exponent of biexcitons (≈ 1.9 for monolayer WS_2).^{73,95} Hence the biexciton emission is absent in our VLHs.

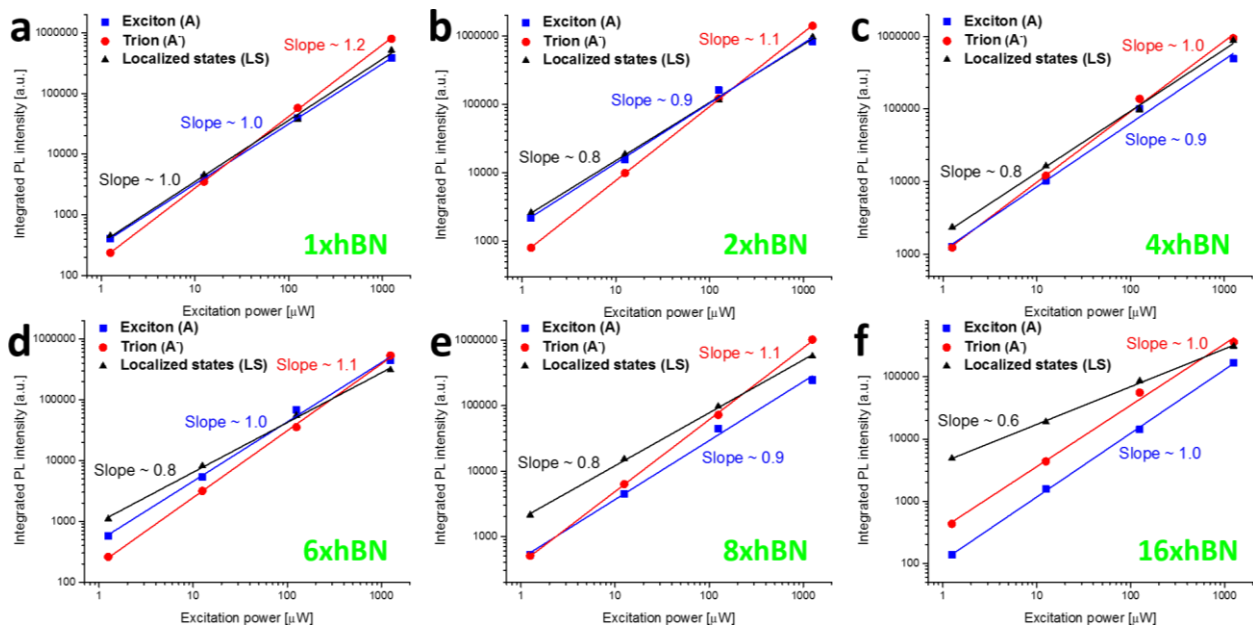


Figure 6.12. Total integrated PL intensity of exciton (A), trion (A^-), and localized states (LS) peaks vs. laser excitation power for the VLHs with increasing thickness of the hBN separator on log-log scales. Solid lines are the linear fit curves, and the slope is indicated in each plot correspondingly.

Femtosecond transient absorption spectroscopy was conducted to investigate the kinetics of the ultrafast photophysical interactions (Figure 6.13 and Table 6.3). The bleaching features correlate well with the photoinduced excitons, and the peak intensity reflects the density of the corresponding excitons. It is found that the bleaching signal caused by the emission of B excitons in MoS_2 monolayer is decreased (by $\approx 50\%$) in the stacked region, while those by WS_2 A and A^- are increased (by $\approx 78\%$ and 75% , respectively) compared to the WS_2 monolayer. These changes in light absorptions offer direct proof of the Förster energy transfer occurring from MoS_2 (B excitonic state) to WS_2 (A excitonic states) in the VLHs, which leads to the increase in QY of the system and thus the observation of PL enhancement. The PL measured at cryogenic temperatures is presented in Figures S8 (Appendix). The increase in PL enhancement at lower temperatures results from the improved efficiency of Förster energy transfer, which is due to the suppression of the non-radiative decay channels.

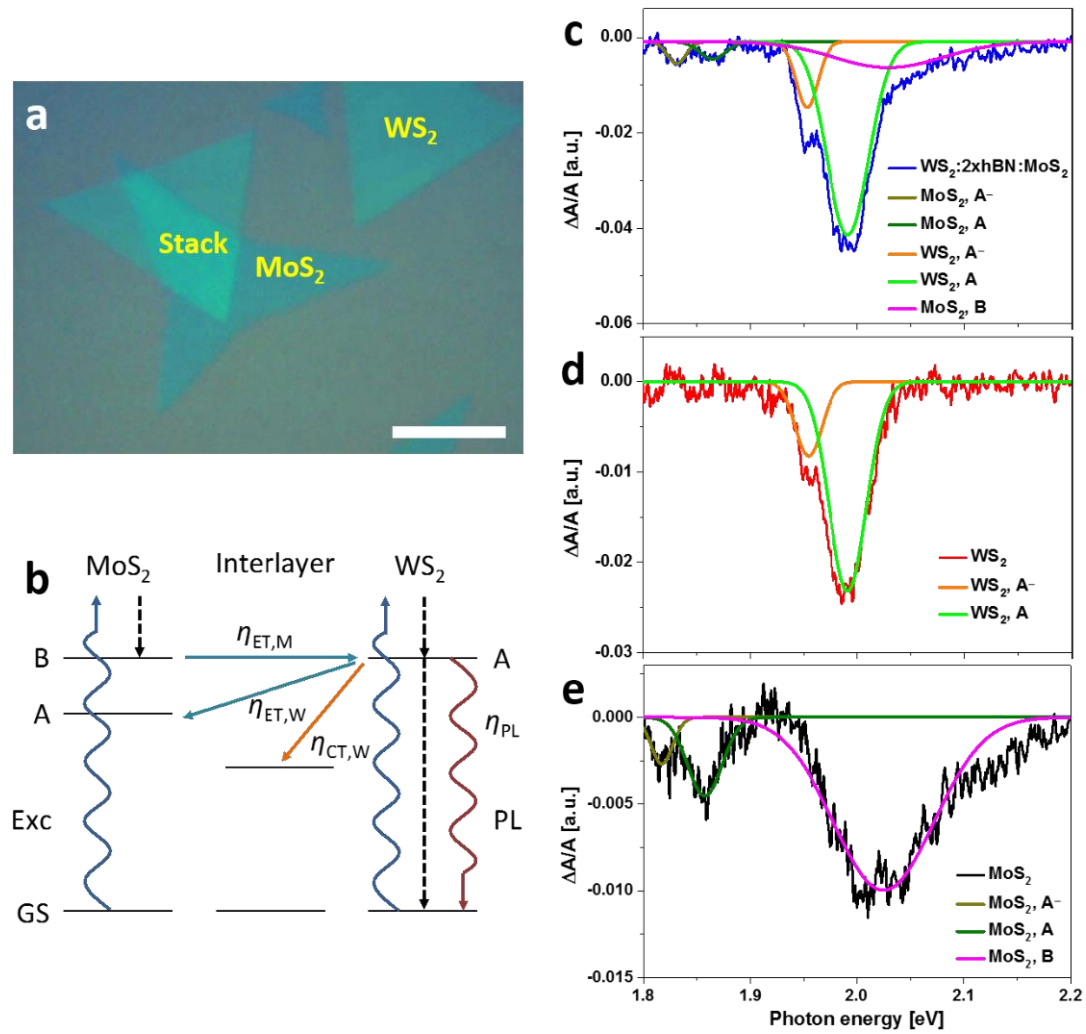


Figure 6.13. (a) Optical microscopic image of a WS₂:hBN:MoS₂ VLH with the regions marked for measurements. Scale bar: 50 μm . (b) Energy diagram of exciton energy decay for WS₂:hBN:MoS₂ VLH. Horizontal lines represent energy level of MoS₂ B and A, WS₂ A and ground state (GS). Blue wavy arrows show excitation process. Red wavy and black broken arrows show radiative and non-radiative decay process. η_{ET} and η_{CT} represent the efficiency of energy and charge transfer, respectively. Blue and orange straight arrows represent energy and charge transfer process. Subscripts M and W indicate the direction of transfer from MoS₂ to WS₂ and vice versa. Radiative and non-radiative decay from MoS₂ and interlayer states, and charge transfer from MoS₂ are not shown for simplicity. (c–e) Gaussian-fitted TA spectra of (c) WS₂:2 $\times$ hBN:MoS₂ VLH, (d) WS₂ monolayer, and (e) MoS₂ monolayer, recorded at 1.5 ps pump-probe delay under a femtosecond pulse laser (≈ 120 fs, 300 nW, 1 kHz) at 400 nm (3.10 eV) with a fluence of $\approx 1500 \mu\text{J cm}^{-2}$.

Table 6.3. Peak intensity with photon energy based on the Gaussian-fitted spectra in Figure 6.8.

Material	Peak intensity [a.u.] (Photon energy [eV])				
	MoS ₂ A ⁻	MoS ₂ A	WS ₂ A ⁻	WS ₂ A	MoS ₂ B

Stack	−0.005 (1.83)	−0.004 (1.86)	−0.014 (1.95)	−0.041 (1.99)	−0.005 (2.03)
WS₂			−0.008 (1.95)	−0.023 (1.99)	
MoS₂	−0.003 (1.82)	−0.005 (1.86)			−0.010 (2.03)

6.3 Conclusion

In summary, the results presented show that the dipole–dipole interactions between WS₂ and MoS₂ in vertically stacked heterostructures are highly dependent upon both the input excitation power and the separation distance. When no hBN spacer is used, only strong PL quenching is observed and for one and two layers of hBN, we see that increasing laser power can switch the PL response from quenching to enhancement. Increasing excitation power has a direct positive effect on the exciton generation rate, and it is found that larger density of the excitons leads to stronger interlayer interactions. Femtosecond transient absorption measurements verify the transfer of B exciton from MoS₂ to the A exciton state in WS₂, giving an increase in the PL QY of the system and enhanced PL signals. The spectral overlap between the MoS₂ B exciton and WS₂ A exciton position makes it difficult to separate these from one another, but confirms their resonant condition required for the Förster excitonic energy transfer. The efficiency of Förster energy transfer can also be improved by suppressing the non-radiative decay channels, and the PL enhancement is much larger at lower temperatures.

Chapter 7 Vertical Stacked 2D WS₂:hBN:WS₂

Heterostructures

Aiming at exploring the interactions across the same type of monolayer transition metal dichalcogenide (TMD) with a controllable interlayer separation, vertical layered heterostructures (VLHs) of WS₂:hBN:WS₂ are fabricated layer-by-layer all utilising CVD-grown materials, and the optical performance is evaluated mainly by PL spectroscopy. It is found that the indirect optical transition across the WS₂ bilayer is greatly suppressed by inserting hBN separators in between. Moreover, different doping levels of the two WS₂ monolayers are realised by applying different dielectric environments. This allows the occurrence of Förster energy transfer from the one with lower quantum yield (QY) to the other one with higher QY, as proved by femtosecond transient absorption spectroscopy. In this way the total PL in the stacked region is increased, and is even higher than the sum of the two WS₂ monolayers. Further increase in the separation distance leads to reduced interlayer interactions, till the stack finally behaves as two individual WS₂ monolayers. Insights are provided into these VLHs made up of the TMD monolayers possessing identical composition yet different doping levels due to the distinct dielectric environments, and the ability to tune their PL would permit a development of photonic applications.

7.1 Introduction

Van der Waals heterostructures built from diverse 2D materials have opened up new possibilities in device manufacturing due to their high functionality.^{204,205,281,309,310,327–331} Exceptional physical properties can be gained through the combination of atomically thin layers of, for instance, graphene, boron nitride (BN), and transition metal dichalcogenides (TMDs).^{281,307,311,332–335} The fabrication methods of vertical layered heterostructures (VLHs) include direct CVD growth,^{112,242,336} and sequential transfer.^{43,281,311,335} The vertical geometry enables the constituting materials to either behave individually, or couple with each other.^{44,47,50,337} Different photoluminescence (PL) properties can be gained by tailoring the structure of the stacks.^{44,317,332,335,337,338}

It has been widely explored that monolayer TMDs are direct bandgap semiconductors.^{1,2,24,57,339} The large exciton binding energies allow many-body effects,^{336,340} which in turn, influence their optical properties.³⁴¹ In bi-/few-layer states, however, indirect transitions are energetically favorable.^{1,24,57,342,343} PL spectroscopy is an effective tool to examine the optical performance of these 2D materials. Multilayer TMDs show significantly reduced PL quantum yield (QY) with a red-shifted peak position relative to their single-layer counterparts.^{2,30,344}

The vertical stacking of TMD materials with unequal bandgaps can form a type II heterojunction at their interface.^{41,43,49,338} Previous studies have demonstrated ultrafast charge transfer in the VLHs composed of two different TMD monolayers, where the electron-hole pairs are spatially separated across the junction and results in PL quenching.^{41,44,317} In contrast, a homojunction is formed when the layers have equal bandgaps but different doping. This could be induced by the varied environment due to dielectric screening effects.³⁴⁵ Given that trions are defined as charged excitons, the intensity ratio of exciton:trion is typically used to reflect the doping level of monolayer TMDs.^{242,345} Intercalating an hBN spacer into the TMD layers could suppress the electron-hole indirect recombination and enable distinct interlayer interactions, such as Förster energy transfer from

one monolayer to the other, which gives rise to PL enhancement in the stacked region.³³⁸ Tuning the thickness of the insulation barrier is expected to change the mechanism and strength of the interlayer interactions.⁴³ Additionally, in-plane tensile strains would shrink the bandgap of TMD monolayers,^{57,59,243,346} and thereby altering the optical transitions in the VLHs.⁶⁸ However, the behaviour of VLHs consisting of identical TMD material has remained unravelled.

In this study, we studied the PL and interlayer interactions in WS₂:hBN:WS₂ vertical stacks with varying hBN thicknesses. The magnitude of the PL signals is compared between the overlapping region and the sum of the WS₂ monolayer constituents. PL quenching was observed with 0 and 1 layer of hBN, while the enhancement arises and shows optimum at 2 layers of hBN. The interlayer interactions then tend to vanish as the separation increases toward 8 layers of hBN. The PL of the VLHs can be further enhanced at cryogenic temperatures due to the suppression of thermally activated non-radiative recombination.

7.2 Results and discussion

The monolayer WS₂ domains and the few-layer hBN films were grown separately *via* atmospheric pressure CVD techniques. Layer-by-layer transfer was employed to build up the vertical stacks, whereby the CVD-induced lattice strain was excluded, proved by the blue-shifted PL peak of the monolayer WS₂ (Figure S5, Appendix). Besides, different substrates for the two WS₂ monolayers in the WS₂:hBN:WS₂ heterostack, *i.e.*, SiO₂/Si and hBN, would tune their doping levels due to the dielectric screening effect of the Coulomb potential.³⁴⁵ The bottom-layer WS₂ contacts the SiO₂/p++ Si substrate containing a large amount of charge impurities on the surface, whereas the top-layer WS₂ is supported by insulating hBN films that acts as a charge screener.³⁴⁵ Therefore, as demonstrated in Figure S6b,c (Appendix), a heavier n-type doping was incurred by the SiO₂/Si substrate compared to the hBN, and is expected to affect the PL properties of the WS₂ adlayer. Considering the transfer process often introduces defects in the WS₂ and leaves solvent residues between the layers of the as-

prepared VLHs, the samples were annealed in vaporous sulphur before the PL measurements to obtain high-quality stacks through the procedures and conditions described in Section 3.2.6,²⁷¹ whereby the sulphur vacancies can be filled and the interlayer contaminants can be eliminated. The as-fabricated WS₂:WS₂ and WS₂:hBN:WS₂ vertical structures are shown in Figure 7.1. Notably, we can achieve more stacking layers by repeating this transfer procedure, however, the coverage of the heteroregions would be decreased due to the lower possibility of overlapping.

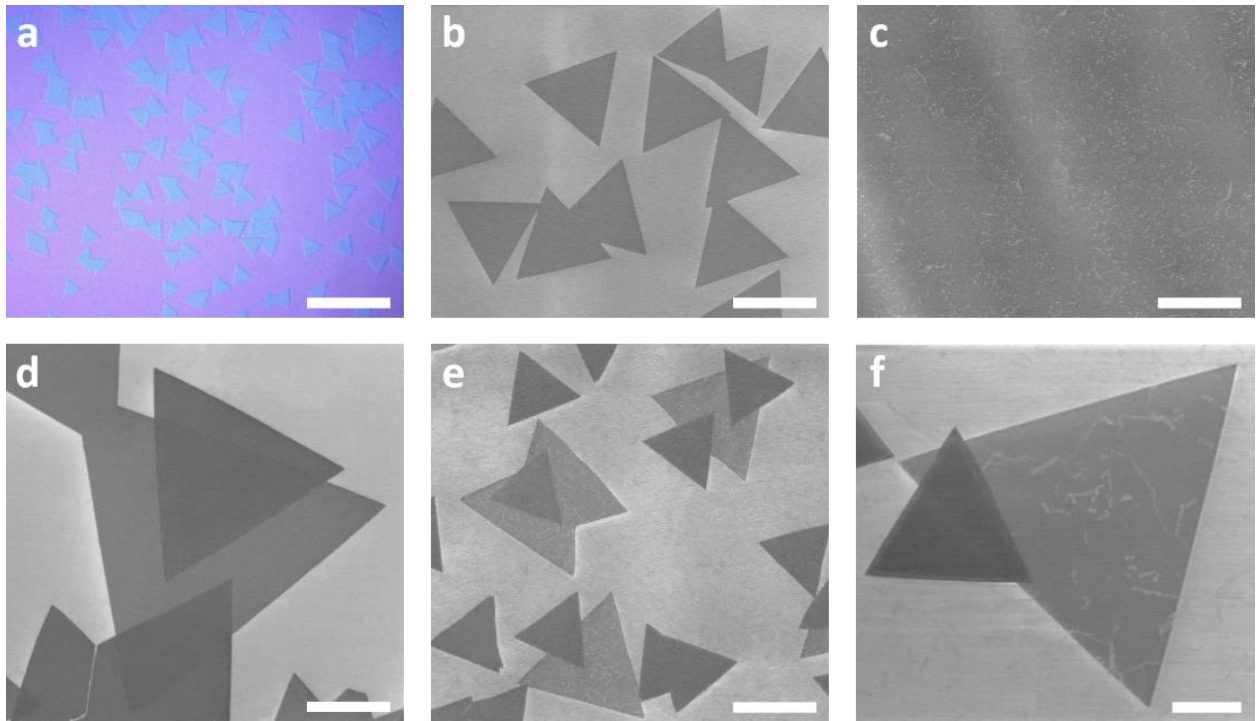


Figure 7.1. (a) Optical microscopic image and (b,c) SEM images of the CVD-grown WS₂ monolayer domains (b) and hBN films (c). (d–f) SEM images of WS₂:WS₂ (d) and WS₂:hBN:WS₂ stacks (e,f) under lower (e) and higher (f) magnifications. The bright tracks in panel (c,e,f) feature the grain boundaries in hBN. Scale bar: (a) 200 μm , (b,c,e) 40 μm , (d,f) 10 μm .

The 2D maps of normalized total integrated PL intensity and PL peak position in Figure 7.2e,f indicate that the annealed stack of WS₂:WS₂ bilayer exhibit uniformly quenched PL along with a red shift because of the indirect optical transition. When an insulating hBN spacer is inserted into the bilayer stack, the total PL signal in the stacked region (WS₂:hBN:WS₂) is found higher than the sum of the PL in the two WS₂ monolayers, *i.e.*, showing PL enhancement, and the PL peak position is

located between those of the WS₂ monolayers (Figure 7.2g,h). Here, we define a modulation factor η to evaluate the PL quenching and enhancement. It can be calculated *via* the equation:

$$\eta = \frac{I_S}{T \cdot I_B + I_T} \quad (1)$$

, where I_S , I_B , and I_T represent the normalized total integrated PL intensities of the stack, the bottom-layer WS₂, and the top-layer WS₂, respectively. T is the laser transmittance through the top-layer WS₂. $T = 1 - A$ (absorbance) ≈ 0.93 at 2.0 eV for monolayer WS₂.³⁴⁷ Figure 7.2i–l shows the PL spectra of the bottom-layer WS₂, top-layer WS₂, and the WS₂:(hBN:)WS₂ vertical stacks. The observation of negatively charged excitons indicates that both the WS₂ monolayers are doped with electrons. However, the Gaussian fitting reveals that the two WS₂ layers have different intensity ratios of exciton:trion (*i.e.*, A/A^-). This suggests their different doping levels, which are correlated with their dielectric environments and agree with the electrical measurements in Figure S6b,c. While an indirect PL emission peak (I) and significant PL quenching was observed in the WS₂:WS₂ stacks (Figure 7.2k), the WS₂:hBN:WS₂ VLH exhibits direct PL emissions, verifying that the two WS₂ layers are decoupled by the hBN separator. Moreover, the PL intensity of the WS₂:hBN:WS₂ VLH is even higher than the additive PL of the WS₂ monolayers. It can be inferred that both the direct PL emissions in the monolayer WS₂ contribute to the PL emission in the stacked region of WS₂:hBN:WS₂ VLH, yet the origin for such enhanced PL will be discussed later.

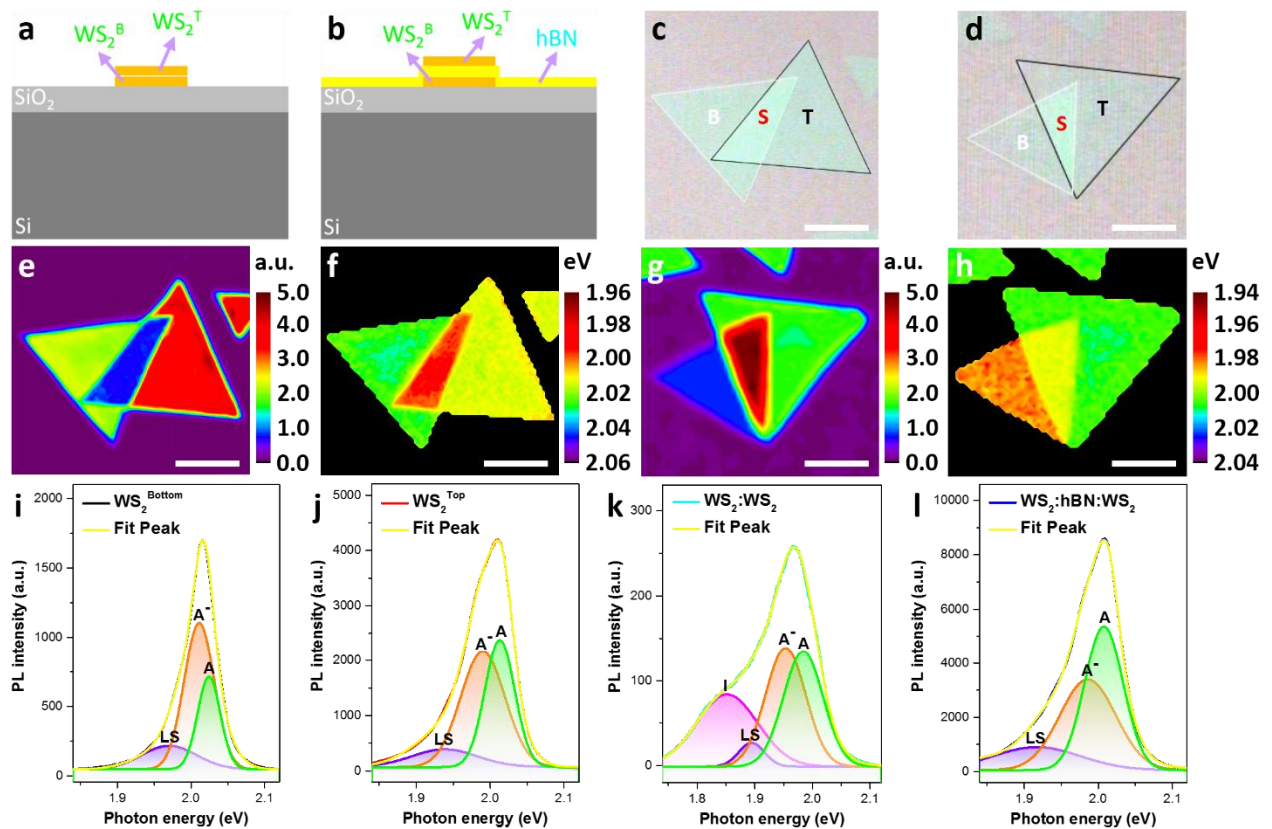


Figure 7.2. (a,b) Atomic models, (c,d) optical microscopic images, and the corresponding 2D maps of (e,f) normalized total integrated PL intensities and (g,h) PL peak positions of stacked (a,c,e,g) WS₂:WS₂ and (b,d,f,h) WS₂:hBN:WS₂. Gaussian fitted PL spectra of (i) bottom-layer WS₂, (j) top-layer WS₂, (k) WS₂:WS₂, and (l) WS₂:hBN:WS₂, acquired from the corresponding positions marked in panel (c,d). Please note the extended scale in panel (k) to show the indirect transition peak (I). The PL peaks are deconvoluted into exciton (A), trion (A⁻), and localized states (LS). Scale bar: 10 μ m.

I further studied the dependence of PL enhancement on the interlayer distance by adjusting the layer number of the hBN separator. To precisely determine the thickness of hBN, AFM measurements were carried out, and the results are displayed in Figure S7 (Appendix). Figure 7.3 presents the PL of the annealed heterostacks with the hBN layer increasing from 1 (Figure 7.3a–e), to 2 (Figure 7.3f–j), 4 (Figure 7.3k–o), and 8 (Figure 7.3p–t). For all these VLHs, the top-layer WS₂ exhibits a stronger PL intensity with a higher emission energy than the bottom-layer WS₂. The histograms in Figure 7.3e,j,o,t illustrate that though the PL intensity is slightly quenched for monolayer hBN, suggesting that the indirect PL emission still occurs in this stack, the PL intensity is enhanced and optimised at

2 layers of hBN. Nevertheless, the PL enhancement decreases for larger hBN layer numbers and vanishes at ≈ 8 , where the two WS₂ monolayers should behave independently. In terms of the PL peak position, a red shift is observed when using monolayer hBN separator (Figure 7.3d) due to the indirect PL emission. For two and more hBN layers, however, the PL peak shifts into the range between those of the WS₂ monolayers, and it is more blue-shifted with the increasing layer of hBN. This can be explained by the relatively higher PL intensity with a higher photon energy of the top WS₂ vs. that of the bottom WS₂ (Figure 7.3h,m,r and j,o,t), given that they both contribute to the overall PL emission in the stack as aforementioned.

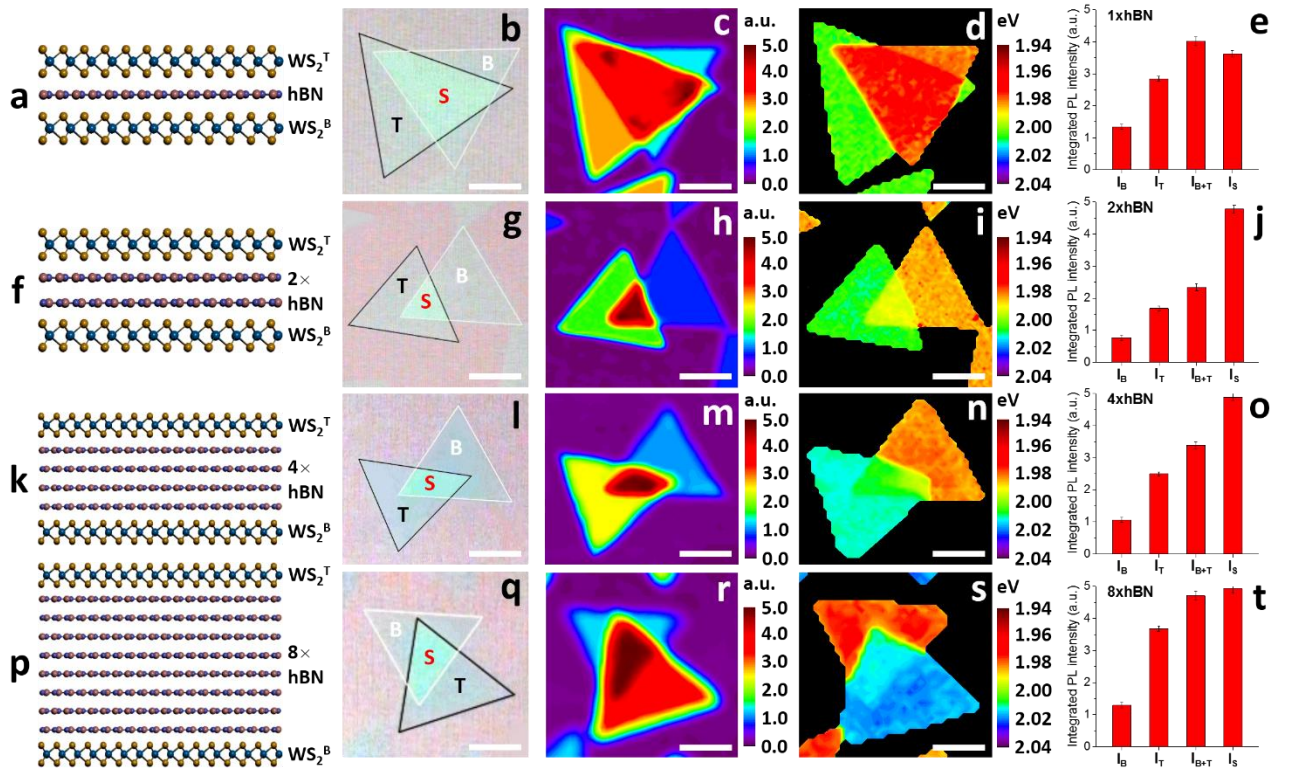


Figure 7.3. Dependence of separation distance between the WS₂ monolayers. (a,f,k,p) Atomic models, (b,g,l,q) optical microscopic images, where the bottom-layer WS₂ (B), top-layer WS₂ (T), and stacked region (S) are marked, (c,h,m,r) normalized total integrated PL intensity maps, (d,i,n,s) PL peak position maps, and (e,j,o,t) histograms with error bars, extracted from panels (c,h,m,r), respectively, for the WS₂:hBN:WS₂ VLHs with (a–e) 1 layer, (f–j) 2 layers, (k–o) 4 layers, and (p–t) 8 layers of hBN. Scale bar: 20 μ m.

Figure 7.4a plots the PL modulation factor η of the WS₂:hBN:WS₂ VLHs and the PL ratio σ between the two constituent WS₂ monolayers as a function of hBN layer number. The optimal PL

enhancement at 2 layers of hBN shows an average modulation factor $\eta = 2.03$. In addition, the PL ratio σ of the top WS₂ to the bottom WS₂ increases with the layer number of hBN. This can be attributed to the greater separation of the top WS₂ from the SiO₂/Si substrate that accommodates much charge impurities when thicker hBN film is used, enabling it to show an increased PL intensity.

Apart from the indirect optical recombination, which would not allow noticeable PL yield, several emission mechanisms are possible to give enhanced PL signals in the WS₂:hBN:WS₂ VLHs: (1) multiple reflections. My collaborators investigated this by conducting simulations for the stacks (Figure S9, Appendix), based on the thicknesses of hBN pre-determined by the AFM measurements (Figure S7, Appendix). Since the multiple reflection leads to a negligible increase in the absorption, and is almost independent of the separation distance across a wide range including what we study herein, especially at ≈ 2.0 eV where the enhanced PL signals are observed. Hence multiple reflections can only be a very minor influence factor for the PL enhancement; (2) interlayer excitons. Interlayer excitons normally have longer lifetime than intralayer excitons.^{348,349} To probe this, my collaborators performed time-resolved PL spectroscopy on the WS₂:2 $\times$ hBN:WS₂ VLHs exhibiting optimal PL enhancement (Figure S10, Appendix). It is found that the decay time of the stack is nearly the same with those of the two WS₂ monolayers, and thereby ruling out this possibility; (3) Förster-type energy transfer. The femtosecond broadband transient absorption (TA) spectra in Figure 7.4b show that the absorption of the VLH is stronger than the monolayer WS₂. Moreover, the peak position of the stacked region aligns well with that of the top-layer WS₂, with a shoulder at lower energy corresponding to the bottom-layer WS₂. The absorption peak positions help to verify that the PL of the stack mainly derives from the excitons in the top-layer WS₂. It is noteworthy that although interlayer excitons could cause improved absorption, they should have lower binding energy and quantum efficiency compared to intralayer excitons and result in PL quenching rather than enhancement.^{47,348,349} Additionally, the absorption of the WS₂ monolayers also varies between each other due to their different doping levels. The heavier doping in the bottom-layer WS₂ is demonstrated

by the relative red shift of the PL peak (Figure 7.2h) along with a lower A/A^- intensity ratio (Figure 7.2i vs. j). For the bottom-layer WS_2 , the n-type doping would induce a down shift of both the conduction and the valence bands while not changing the bandgap. This will then permit energy transfer across the homojunction formed by the two differently doped monolayer WS_2 , which means a migration of excitons from the bottom-layer WS_2 with lower QY to the top-layer with higher QY. Consequently, the total PL efficiency of the heterosystem is increased so that an enhancement of the PL is observed.³³⁷ Such excitonic behaviour is also inferred by the enhanced emission of exciton versus trions in $WS_2:hBN:WS_2$ stack (Figure 7.2l), compared to that in either the constituent monolayer WS_2 (Figure 7.2i,j). Even if the n-doping of the top-layer WS_2 reduces with the increase in separation distance, which can lead to a larger difference in the dielectric environment and thus the QY of the two WS_2 layers, the interlayer interactions are suppressed at the same time. It accounts for the result evidenced previously in Figure 7.3 that the optimal PL enhancement is achieved at 2 layers of hBN.

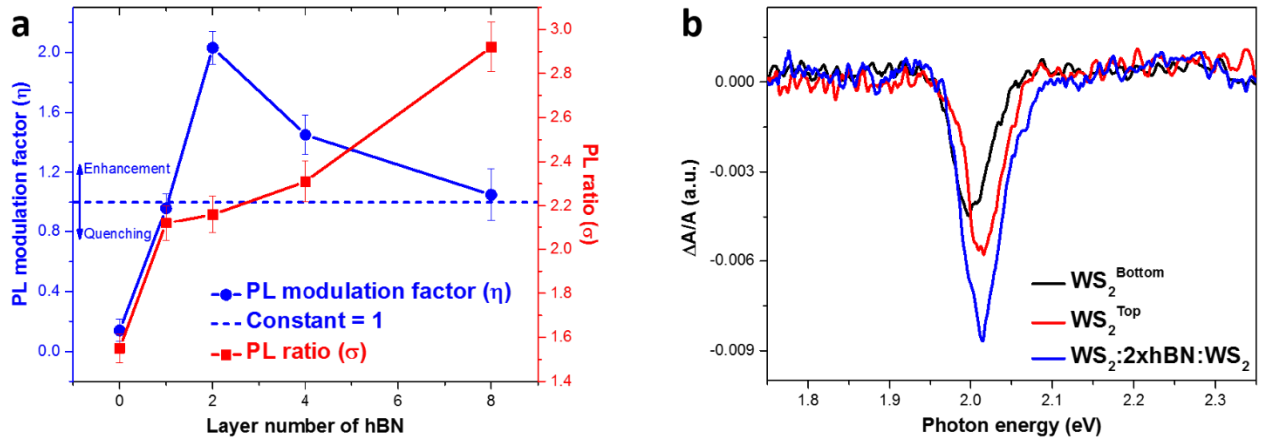


Figure 7.4. (a) Dependence of the PL modulation factor η (red) and PL ratio (σ) of the two WS_2 monolayers (blue) on the layer number of hBN, which were calculated based on the normalized total integrated PL intensities of the stacks (I_S), bottom-layer WS_2 (I_B), and top-layer WS_2 (I_T). PL modulation factor $\eta = \frac{I_S}{(I_B + I_T)}$; PL ratio $\sigma = \frac{I_T}{I_B}$. Each point is an averaged value with the error bar obtained on a statistical basis of 6 measurements. (b) Femtosecond transient absorption (TA) spectra of the different regions in $WS_2:2 \times hBN:WS_2$ VLHs, which were recorded under the same conditions with those for Figure 6.13c–e.

The temperature dependence of the PL was also studied on WS₂:2 × hBN:WS₂ VLHs together with the constituent WS₂ monolayer (Figure 7.5). On one hand, the PL intensities of both the stack and the monolayer WS₂ increase as the temperature drops, ascribed to the suppression of thermally activated non-radiative decay channels. PL enhancement ($\eta > 1$) is obtained in the heterostacks at all temperatures up to 273 K (Figure 7.5d). Unlike the WS₂ monolayer, of which the normalized total integrated PL intensity presents a sublinear relationship with the decrease in temperature (Figure 7.5c), the PL modulation factor η displays a superlinear increase (Figure 7.5d). This is likely to result from the longer lifetime of the WS₂ A state at lower temperatures, so that the possibility of the exciton transfer is increased, giving rise to more enhanced PL QY of the whole VLH.³³⁷ On the other hand, the PL peaks are blue-shifted with the reducing temperature for both the stack and the monolayer WS₂. This could be associated with the increase in exciton emissions over trion owing to the energy transfer. It is noteworthy that biexcitons do not exist in our WS₂:hBN:WS₂ VLHs under the current conditions, because no corresponding shoulder or splitted peak is observed at around 1.99 eV.⁹⁵

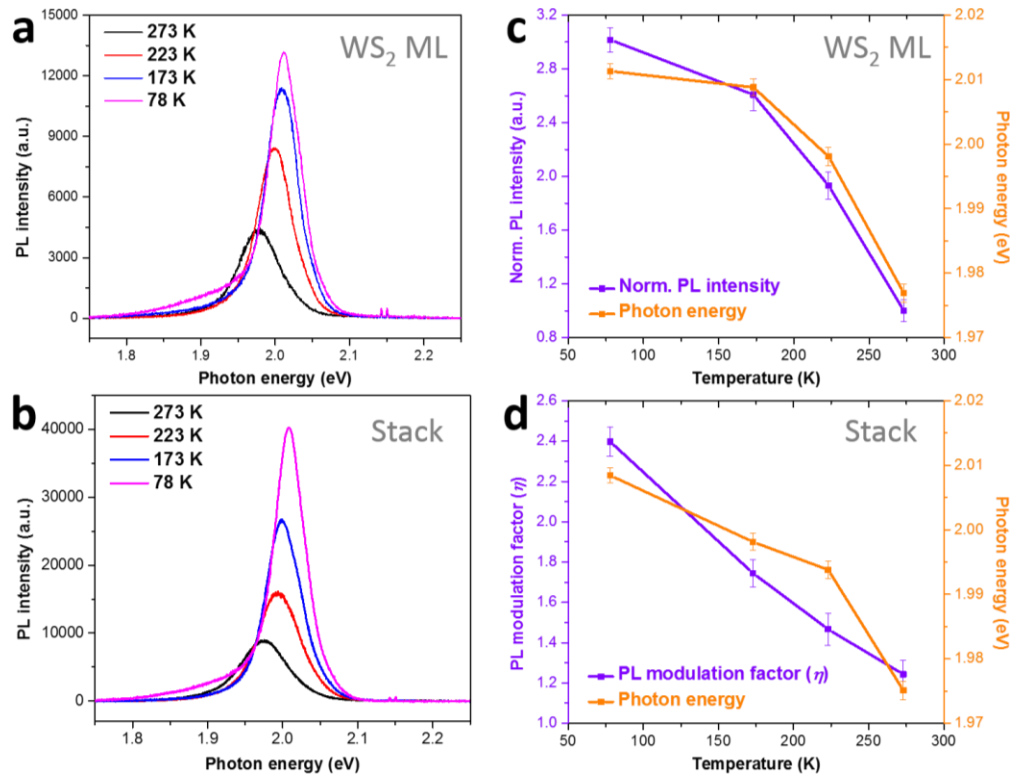


Figure 7.5. Dependence of the PL on temperature. PL spectra of the (a) WS₂ monolayer and (b) heteroregion of WS₂:2 × hBN:WS₂, with decreasing temperatures of 273, 223, 173, and 78 K. The data were normalized by the Raman peaks at 2.14 eV (E_{2g}^1 mode) and 2.15 eV (A_{1g} mode). (c) PL intensity of the monolayer WS₂, normalized to that under 273 K, and (d) PL modulation factor η as a function of temperature.

7.3 Conclusion

To summarise, in this project I assembled WS₂:WS₂ and WS₂:hBN:WS₂ vertical stacks, investigated their optical properties, and explored the interlayer interactions. The PL was studied in the annealed samples with strong interlayer adhesion and low defect density. The excitonic behaviour in the stack is found highly sensitive to the interlayer distance and temperature. It has been shown that the PL intensity of the stack is controllable through altering the layer number of the hBN spacer, yet large separation (≥ 8 layers of hBN) would cause the WS₂ monolayers to act independently. The different dielectric environments vary the doping levels of the WS₂ monolayers and enable them to compile a homojunction, where the excitons are injected from the WS₂ layer contacting charged SiO₂/Si substrate with lower QY to the one supported by insulating hBN with higher QY. This Förster energy transfer is combined with indirect optical transition and multiple reflections, which have minor impacts though, giving optimal PL enhancement at 2 layers of hBN. Our work provides insights into the interactions between identical TMD monolayers but are separated and differently doped. The resulting PL enhancement shows potential in light amplifiers.

Chapter 8 Conclusion and Outlook

8.1 Conclusion

In the past few years, 2D nanomaterials have been predicted to revolutionize future technology in the areas of flexible electronics, displays, energy generation and storage and information processing. A crucial area that underpins this possible success is the ability to manufacture synthetic 2D materials on the large scale. My DPhil research is motivated by developing the methods that will unlock controllable synthesis of 2D materials and fabrication of all-2D layered heterostructures, investigating and offering insights into their unique properties as well as potential applications.

This doctorate thesis focus on the APCVD growth and characterisation of three types of 2D materials, MoS₂, WS₂, and hBN. The project in Chapter 4 aims to obtain monolayer MoS₂ with a range of domain shapes on amorphous SiO₂/Si substrate by employing well-designed growth procedures and conditions, which also have large domain size *via* optimization of the experimental parameters. The as-derived morphology is explained by the balance between kinetic and thermodynamic growth, resulting in sharply dendritic, branched, and triangular MoS₂ crystals. Besides, the high uniformity is demonstrated by SEM, AFM, and Raman and PL spectroscopy. Thermal annealing in sulphur vapour is also applied, not only to improve the quality of the CVD-grown MoS₂ by filling the sulphur vacancies, but also to directly link the edge site density of the

monolayer MoS₂ islands with their HER activities. The large MoS₂ dendrites exhibit improved electrochemical performance, and is promising as a catalyst in HER.

Considering the monolayer MoS₂ crystals grown on amorphous substrates such as SiO₂/Si are randomly-oriented, the next project, as shown in the first part of Chapter 5, centres on the CVD synthesis of monolayer MoS₂ on crystalline substrates, SrTiO₃, with three different terminations, where the crystal shapes and orientations are strongly influenced by their epitaxial interaction with the substrate. The observations give rise to an understanding that the interfacial van der Waals bonding between MoS₂ monolayers and SrTiO₃ is greatest when the maximum commensuration between the lattices is achieved. The second part of Chapter 5 investigates the thermal behaviour of SrTiO₃-supported MoS₂ monolayer. It was revealed that the morphologies of the products after annealing are dependent on the total thermal energy absorbed, *i.e.*, the combination of annealing temperature, annealing time, and the temperature ramp rate. Additionally, the atmosphere also plays an important role. Annealing in vacuum causes material degradation; by contrast, annealing in sulphur atmosphere leads to the filling of sulphur vacancies and an improvement in the quality of MoS₂. The preferential loss of sulphur and oxidation of molybdenum was revealed by XPS, and the optical properties of MoS₂ were featured by PL and Raman spectroscopy. This study explores the thermal behaviour of monolayer MoS₂ on an oxide substrate under different conditions, and lays foundation for their potential use in high temperature applications.

Chapter 6 shows the study on fabricating the WS₂:MoS₂ and WS₂:hBN:MoS₂ VLHs and probing the dipole–dipole interactions between the constituent WS₂ and MoS₂ monolayers. The charge transfer across the spatially separated layers leads to the recombination of excitons and the observation of PL quenching, whereas the Förster energy transfer of the B exciton from MoS₂ to the A exciton state in WS₂ leads to an increase in the PL quantum yield (QY) of the total system and the observation of PL enhancement. These are confirmed both theoretically by data simulations and experimentally by PL spectroscopy and femtosecond transient absorption measurements. The factors

affecting the interlayer interactions include the separation distance, the excitation power, the strain, and the temperature.

Finally, in pursuit of unravelling how separated monolayers of identical TMD would interact with each other, I turned my research attention into $\text{WS}_2\text{:hBN:WS}_2$ VLHs (Chapter 7). It is indicated by the PL study that the QYs are different of the two WS_2 monolayers, so that the exciton transfer from one layer to the other can increase the QY of the heterostack, giving enhanced PL signals which is even larger than the sum of those from the two WS_2 layers. Therefore like the $\text{WS}_2\text{:hBN:MoS}_2$ VLHs, the interlayer interactions in $\text{WS}_2\text{:hBN:WS}_2$ VLHs are also influenced by the separation distance, the excitation power, the strain, and the temperature. For both $\text{WS}_2\text{:hBN:MoS}_2$ and $\text{WS}_2\text{:hBN:WS}_2$ VLHs, the thickness of the hBN separator was respectively optimized to achieve maximum PL enhancement, which renders them promising as a building block in future optoelectronics.

8.2 Future Outlook

The projects I have conducted during my DPhil course have prospects along four directions.

Firstly, the CVD-grown MoS_2 dendrites could be engineered for better HER performance. To this end, two ways are suggested. (1) Decorating the dendritic MoS_2 monolayers with noble metal atoms that are also active for electrocatalysis, such as platinum and cobalt. It would also be of interest to image the atomic dopant within the MoS_2 nanosheets using state-of-the-art STEM. Would they cause single atom substitutions and form chemical bonds? Would they aggregate and form dopant clusters on top of the MoS_2 nanosheets, activating the basal plane, or migrate to the edges as preferential sites? How does the dopant concentration correlate with the improvement in the HER activities? How would the physical properties of MoS_2 be altered after the doping? But as a precondition, approaches need to be developed to successfully dope the MoS_2 dendrites, and knowable dopant concentration is desired. (2) Hybridising the dendritic MoS_2 with conductive

nanomaterials, such as reduced graphite and graphene, by using a feasible method. This could increase the electron transfer rate of the as-prepared composites and hence the working efficiency in the HER.

Secondly, there remained some questions about the relationship between the CVD growth process of monolayer MoS₂ and its substrate. It has been found that the control over domain shape is not applicable on glassy carbon plates, which is a descent counter electrode in the HER. Therefore, the MoS₂ is required to be transferred when practically utilizing the CVD-grown MoS₂ in electrochemical applications. Although the transfer manipulation has one advantage, *i.e.*, releasing the strain in MoS₂, which permits a direct link between the edge site density of MoS₂ domains and their HER activities, it will complicate the sample preparation procedure and inevitably cause material degradation that cannot be fully recovered. To achieve precise control over the domain morphology of MoS₂ in more general cases, deeply understanding the CVD synthesis of monolayer MoS₂ on specific substrates is necessary, based on the knowledge of the substrate surface characteristics.

Thirdly, the commercial viability of 2D materials calls for the production of large area and high quality films. Based on the project in Chapter 5, the orientation of the monolayer MoS₂ domains can be well defined. Under equilibrium conditions, a certain orientation is very likely to be shown by the majority of MoS₂ domains. Continual supply of reactive precursors could enable a seamless coalescence of the adjacent MoS₂ domains with the same orientation into a continuous film when the domain size is large enough. The film is supposed to have high uniformity due to the low density of the grain boundaries, especially when the nucleation density is small. For this goal, the CVD parameters need further adjustment to promote the growth of MoS₂ along lateral directions, while vertical growth would result in few-layer MoS₂ products.

Fourthly, regarding the WS₂:hBN:MoS₂ and WS₂:hBN:WS₂ VLHs, attempts can be made of repeatedly stacking more layers to produce sandwiched heterostructures. More exactly, the

configurations of $(\text{WS}_2:\text{hBN}:\text{MoS}_2)_n$ and $(\text{WS}_2:\text{hBN}:\text{WS}_2)_n$ are supposed to exhibit a larger degree of PL enhancement, so that will be more appealing for applications in nanodevices. Besides, the interlayer interactions between 2D materials are still lack of deep comprehension. Thus it would be meaningful to stack other 2D materials using the fabrication technique established in the current and study the light matter dynamics across the heterojunction. In particular, the incorporation of bilayer WS_2 in TMD heterostructures may lead to additional biexciton emission at low temperatures upon laser excitation, and this would play a role in the many-body effects that are worth being investigated.

Appendix

S1. Annular dark-field scanning transmission electron microscopy (ADF-STEM) imaging of dendritic MoS₂

The low-magnification ADF-STEM images in Figure S1a,b show a small dendritic-shaped domain of MoS₂. The atomic-resolution ADF-STEM images in Figure S1c,d are from typical dendritic MoS₂ samples and show the high crystallinity of the material. The hole in the inset of Figure S1d was induced *in situ* by focused electron beam irradiation (>5 min),³⁵⁰ which reveals that MoS₂ is a monolayer. The dendrite edges in Figure S1e–h indicate that the domain has zigzag edge terminations in both S and Mo directions, which is expected because of the presence of six arm branches from the core of the dendrite. For both the basal plane and the edge of the dendritic MoS₂ monolayer, the hexagonal atomic arrangements are the same as that of the triangular- and truncated triangular-shaped MoS₂,^{118,351} demonstrating an identical crystal lattice at the nanoscale despite the change in crystal morphologies.

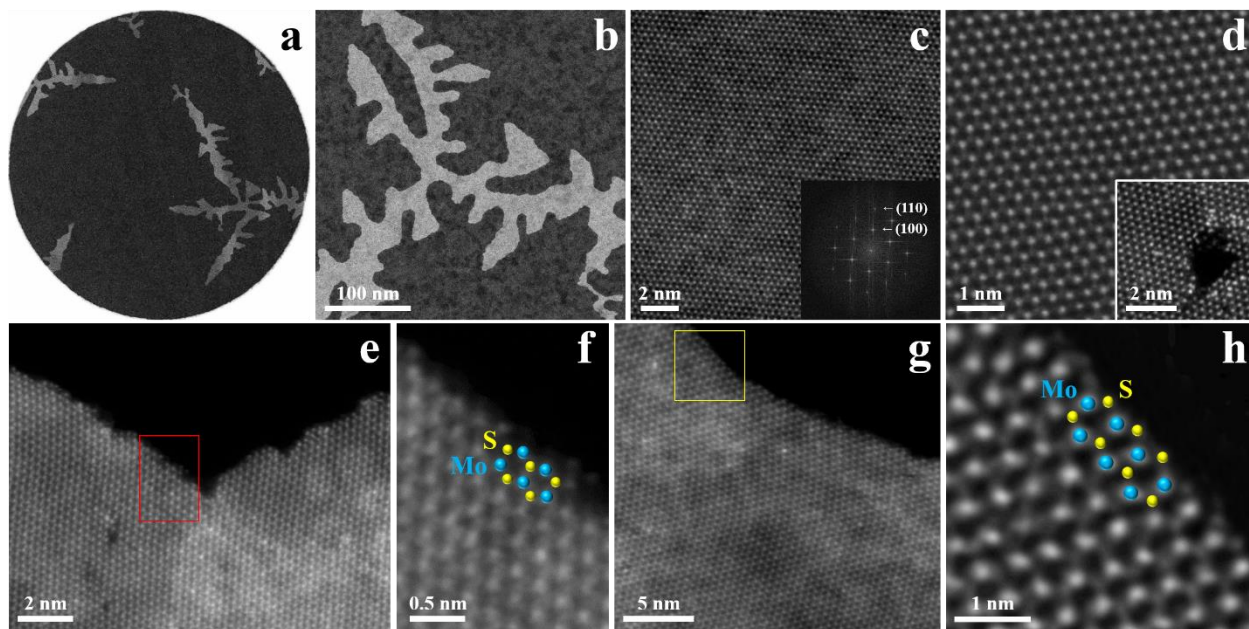


Figure S1. (a,b) ADF-STEM images of the MoS₂ dendrites under lower magnification. (c) Atomic resolution ADF-STEM image of a dendritic MoS₂ monolayer with the corresponding FFT pattern as an inset and (d) higher magnified image with the result after prolonged irradiation as an inset. The dendrite edges under (e,g) lower magnification and (f,h) higher magnification of the red and yellow boxed regions in panel (e,g), respectively, showing that the edge termination is either a Mo (e,f) or an S (g,h) zigzag direction.

S2. Atomic force microscopy (AFM) measurements

Figure S2 shows the thicknesses of triangular MoS₂ and dendritic MoS₂ grown on SiO₂/Si substrates, which are both $\approx 0.7 \mu\text{m}$, indicating that they are monolayer nanosheets.¹ The large-area scan for the MoS₂ dendrite verifies the monolayer thickness with high uniformity, confirmed by taking the height profile at any specific position, exemplified by Figure S2e,f, though the unevenness of the substrate caused long range variations across the regions. It is also observed that the region near the boundary of the dendritic MoS₂ is depleted of tiny MoS₂ domains. This is because the CVD growth for 2D dendrites is typically a diffusion-limited process.^{237,238,352,353} Competition occurs between the nucleation and growth of MoS₂.³⁵⁴ In the proximity of the MoS₂ dendrites, growth is favourable as the edges sites have lower surface energy for the MoO₃ and S precursors than the SiO₂ substrate.¹⁷⁸ Therefore, if given a chance, the dendritic MoS₂ will continuously grow by consuming the precursor feedstocks. However, this process is limited by the diffusion rate,²³⁷ and hence there is

always a space around the MoS₂ dendrites where the precursor atoms cannot reach the domain edges and increase the lateral size but have to nucleate and form small crystals.

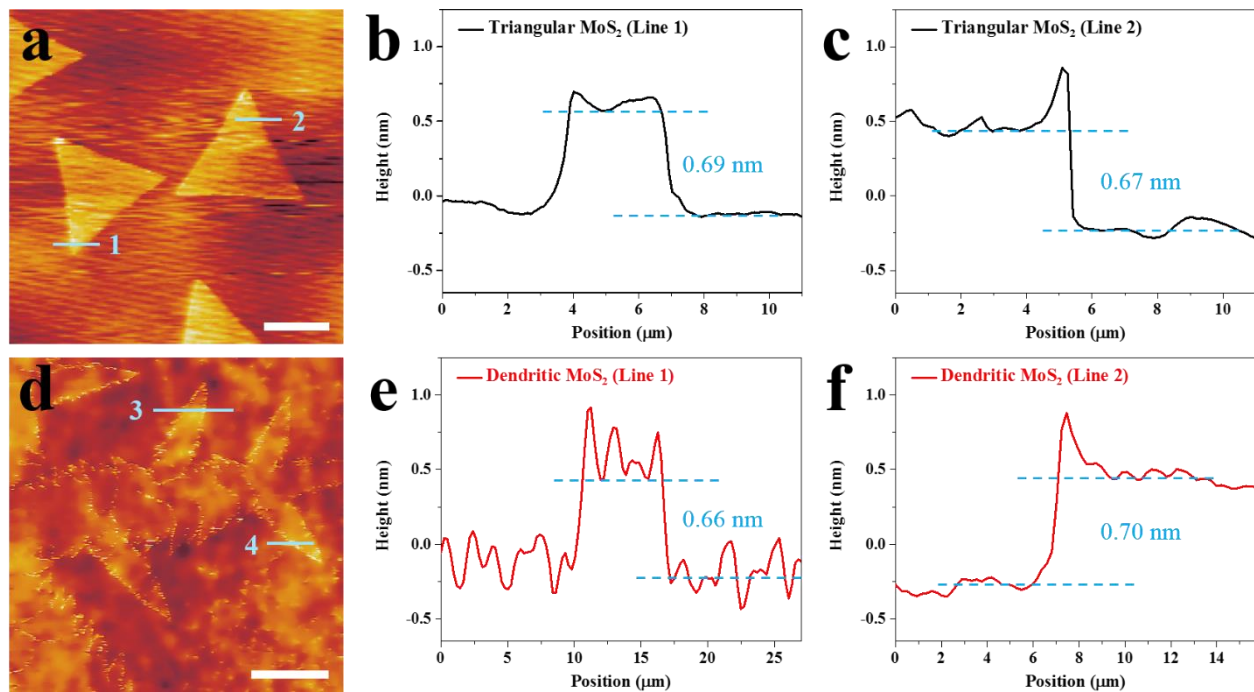


Figure S2. AFM measurements of the CVD-grown MoS₂. (a) AFM image of triangular MoS₂, and (b,c) the corresponding height profiles scanned along the solid lines marked as ‘1’ and ‘2’ in panel (a), respectively. (d) AFM image of dendritic MoS₂ and (e,f) the corresponding height profiles scanned along the solid lines marked as ‘3’ and ‘4’ in panel (d), respectively. Scale bar: (a) 15 μm ; (d) 25 μm .

S3. Scanning tunnelling microscopy (STM) images and/or orientations of the monolayer MoS₂ crystals grown on different substrate surfaces

To statistically investigate the epitaxy of MoS₂ monolayer crystals on SiO₂/Si substrate, an orientation histogram was drawn in Figure S3a based on the corresponding SEM image in Figure 5.1.1 (Chapter 5), with the measurement standard of the angle defined above it. The histogram indicates the random distribution of the as-grown MoS₂ crystals; in other words, the amorphous SiO₂ surface causes no orientation preference for the growth.

Figure S3b is an STM image of the SrTiO₃(111) surface composed of domains of (3 × 3) and (4 × 4) reconstructions,^{277,355} on which the average terrace step height was measured as 0.23 ± 0.03 nm (d_{111} lattice spacing = 0.225 nm). This surface is generated through Ar⁺ ion sputtering at

500 eV for 8 min, followed by annealing at 1140 °C for 3 h in 4.5×10^{-4} Pa O₂. It demonstrates that the outermost surface of this substrate is crystalline. The atomically-resolved STM image in Figure S3d shows a triangular pattern of bright dots with a periodicity of 3.16 ± 0.09 Å, which agrees with the literature value of 3.16 Å.³⁵⁶ Because the MoS₂ monolayer crystal terminates with an outer plane of S atoms, from the topographical point of view the bright protrusions in the STM images are generally thought to be S atoms.^{189,357} As for SiO₂/Si, the orientations of the monolayer MoS₂ crystals on SrTiO₃ substrates were studied in Figure S3e,g,i according to the SEM images for each surface termination (Figure 5.1.2, Chapter 5) and the specified measurement standard of the angle. It is notable that some MoS₂ triangles have saw-toothed/tortuous and/or concave edges in the SEM images. When an edge is not completely flat, its direction is regarded as that of the straight line connecting its two ends. This is a good estimate of the S-termination direction because the MoS₂ crystals were grown in S-rich environment.¹⁷⁸ The SrTiO₃(110) substrate mainly comprising (6×1) reconstruction was prepared through sequential annealing at 890 °C for 2 h and then at 910 °C for 3 h, both in UHV. An STM image of the terraces is displayed in Figure S3f. Figure S3g shows the orientation histogram for SrTiO₃(110), where the grey peaks correspond to the three directions identified above, as expected. For example, $[1\bar{1}\bar{2}]$ is at 55° anticlockwise relative to $[1\bar{1}0]$, which is also shown in Figure 5.1.3e. On the final surface in this study, SrTiO₃(001), $c(4 \times 2)$ reconstruction was generated *via* Ar⁺ ion sputtering at 500 eV for 10 min and post-annealing at 1100 °C for 30 min in UHV (Figure 5.1.4a).

It is worth noting that as the substrate surface reconstructions prepared in vacuum do not usually survive in atmosphere, we do not know what the exact interface is at the time of CVD growth of MoS₂. It cannot be the bulk termination of SrTiO₃ because the surface bonds tend to rearrange themselves to stabilize the polarity. However, there are certain ways in which SrTiO₃ reconstructs. For example, SrTiO₃(111)- (4×4) is one of the lowest-energy reconstruction of the (111) termination, which forms most easily in partial pressures of oxygen.^{277,355} If MoS₂ grows on SrTiO₃(111)- (4×4) , the substrate periodicity (*i.e.*, the unit length along $\langle 1\bar{1}0 \rangle$) becomes four times that of the bulk. The

coincidence epitaxy then turns into a 7:1 ratio, which is an attractive epitaxial relationship. On $\text{SrTiO}_3(110)$, (1×4) , (3×4) , (4×4) , and (6×4) reconstructions have been reported previously,^{358,359} making the periodicity along $\langle 1\bar{1}0 \rangle$ four times that in the bulk as well. Similarly, the (4×4) reconstruction exists on $\text{SrTiO}_3(001)$; there is also a $c(4 \times 4)$ reconstruction, which makes the periodicity along $\langle 1\bar{1}0 \rangle$ $2\sqrt{2}$ times that of the bulk, and this turns the coincidence epitaxy into a 5:1 ratio with a mismatch of 1.2%.

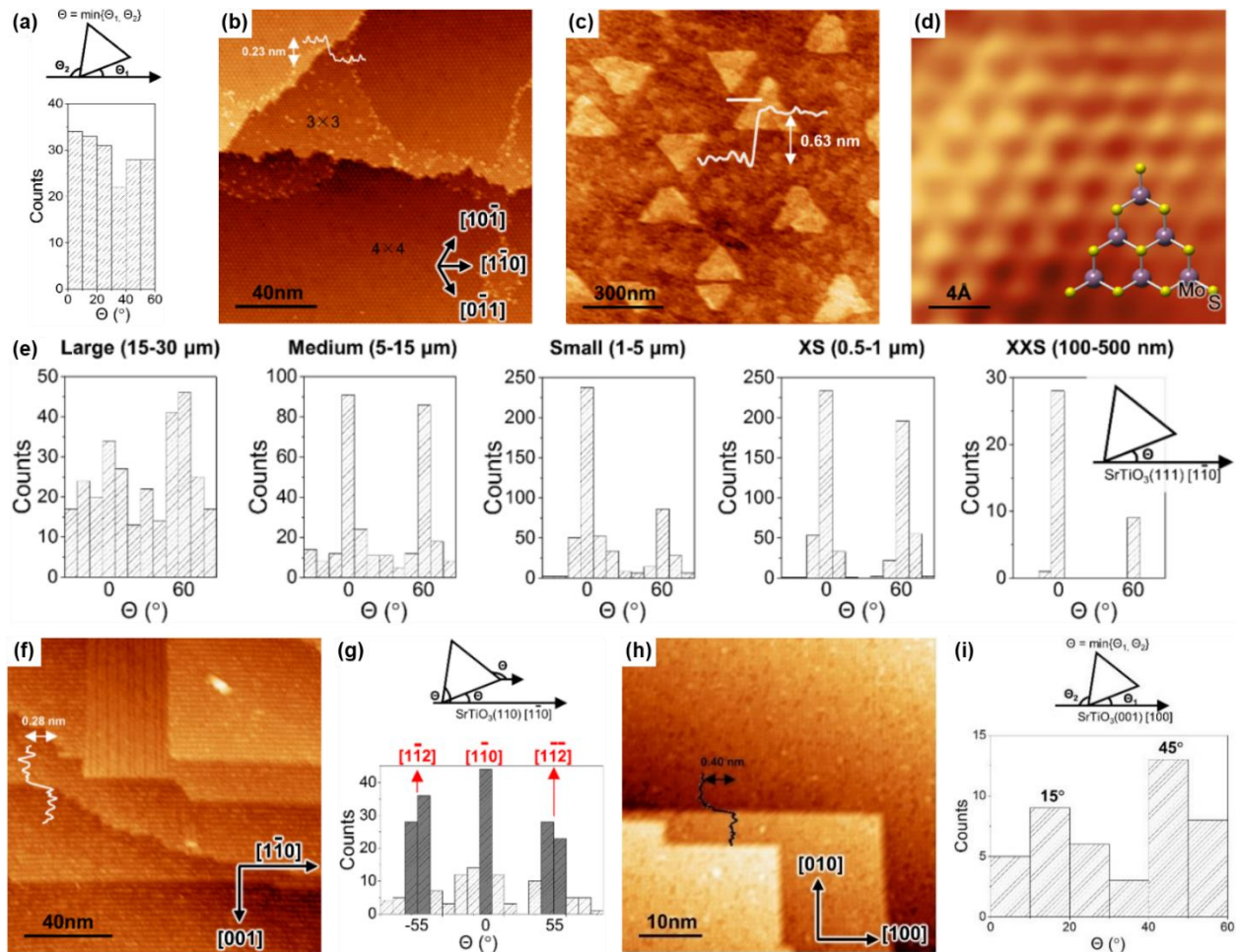


Figure S3. STM images and/or orientation of the monolayer MoS₂ crystals on different substrates. (a) Orientation histogram of the MoS₂ crystals on SiO₂/Si, measured according to the standard above it. (b) STM image of reconstructed SrTiO₃(111), showing terraces with (3×3) and (4×4) reconstructed domains. Two example domains are labelled. Each step height is 0.23 ± 0.03 nm and corresponds to the d_{111} lattice spacing. (c) STM image of very small MoS₂ crystals (200–400 nm), with a line profile showing monolayer thickness. (d) Atomically resolved STM image of monolayer MoS₂ showing triangular atomic lattice with a periodicity of 3.16 ± 0.09 Å, corresponding to the in-plane S-S distance. An atomic model of monolayer MoS₂ is overlaid assuming that S atoms are visualised. (e) Orientation histograms for MoS₂ crystals of different sizes, measured

according to the standard on the far right. (f) STM image of SrTiO₃(110) showing terraces mainly made of the (6×1) reconstruction. Each step height is 0.28 ± 0.04 nm, corresponding to the d_{110} lattice spacing. (g) Edge orientation histogram of MoS₂ crystals on SrTiO₃(110), measured according to the standard above. (h) STM image of SrTiO₃(001) showing terraces consisting of the $c(4 \times 2)$ reconstruction. The step height is 0.40 ± 0.04 nm, corresponding to the d_{001} lattice spacing. (i) Orientation histogram of monolayer MoS₂ crystals, measured according to the standard above.

S4. STM images of the SrTiO₃-supported MoS₂ monolayer upon thermal degradation in vacuum

STM studies better elucidate the structural transformations. The samples were only degassed at 700 °C, *i.e.*, adsorbates and contaminants were removed. Not very much difference was spotted after these gentle anneals in STM either. The monolayer MoS₂ was uniform and conformed to the substrate terraces very well with a thickness of 0.83 ± 0.06 nm, typical of a monolayer (Figure S4a).^{258,360} Figure S4a.i,ii are two close-up images showing the typical morphologies off and on top of the MoS₂ monolayer, respectively. Clusters of tiny triangles were observed on the substrate. The formation of these clusters is believed to be an intermediate step during the high-temperature surface reconstruction of the SrTiO₃(111) substrate.

After being annealed at 700 °C, MoS₂ crystals started to degrade and formed triangular etches (Figure S4b). The etch lines, which are also the edges of the triangular MoS₂ crystal, show three directions along the $\langle 2\bar{1}\bar{1}0 \rangle$ crystallographic directions of MoS₂, as indicated by the overlaid atomic model of MoS₂ illustrating the crystal orientation. The close-up image in Figure S4b.ii shows that the etch lines may have started with points (dark points). Figure S4b.i is an area similar to that in Figure S4a.ii, but annealed at 700 °C. It is an interesting morphology where the clusters protruding from the substrate are still visible, while the triangular etches coexist with them. The etch sites are attributed to the preferential evaporation of sulphur, as confirmed by the XPS results in Figure 5.2.2, because it is lighter and more reactive than molybdenum. Sulphur may leave as SO₂ *via* the reaction with oxygen

given off by the substrate at above 600 °C, leaving oxidised Mo remaining on the surface. This is also observed in the thermally-assisted oxidation of monolayer MoS₂ in air.^{187,188,290–292} In contrast, when MoS₂ is etched in air at lower temperature of 300–340 °C in previous studies,^{187,188} triangular surface pits rather than etch lines are the first sign of degradation, suggesting the simultaneous evaporation of the oxidative products of Mo and S.

At higher temperatures above 800 °C, the MoS₂ crystals ceased to be intact and rather decomposed into particles. Figure S4c manifests a partially degraded MoS₂ layer on top of SrTiO₃(001) substrate terraces, which is half film and half particles. Further, when the annealing temperature exceeded 900 °C, MoS₂ no longer existed and solely granular residues are observed in the place of the original triangular crystal (Figure S4d), performed on a well-reconstructed SrTiO₃(110) substrate. The residual particles are typically 2–5 nm thick and 5–10 nm in diameter.

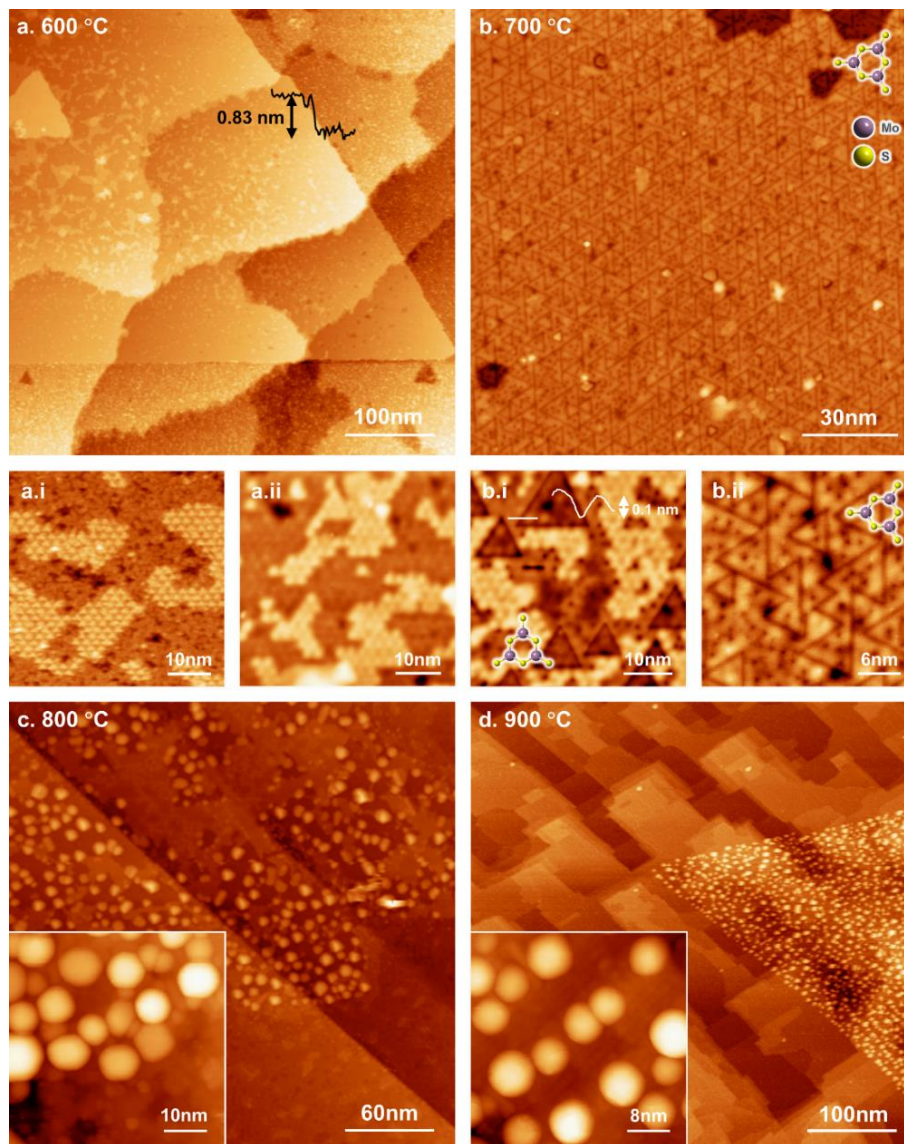


Figure S4. STM images of the thermal degradation process of monolayer MoS₂ in vacuum. (a) MoS₂ smooth surface at up to 600 °C, conforming well to the substrate terraces having a typical height of 0.83 nm. (a.i, a.ii) Zoomed-in images of the SrTiO₃(111) substrate and the MoS₂ monolayer, respectively. (b) Triangular etches on the MoS₂ monolayer at 700 °C. (b.i) An area similar to that in (a.ii), but annealed at a higher temperature. The line profile shows that the depth of etch is ≈ 0.1 nm. (b.ii) Details of the etched features. (c) Degradation of MoS₂ into particles at 800 °C while the film is partially retained. The substrate is SrTiO₃(001) with straight terraces. (d) Decomposition of MoS₂ crystals into particles at 900 °C, which display the original triangular shape. Insets in panel (c,d): close-up images showing the residual particles.

S5. Transfer effects on monolayer WS₂

Due to the different thermal expansion coefficients between WS₂ and the SiO₂/Si substrate, tensile strain develops in the WS₂ at the fast cooling stage of CVD, leading to shrinkage of the WS₂ bandgap and a red shift of the PL peak (Figure S5).⁶² The strain, however, can be released *via* transfer approach, when the WS₂ layer supported by a PMMA coating detaches the substrate and floats on DI water. This enables the WS₂ to behave its intrinsic properties, and the PL peak shifts from ≈ 1.94 eV back to ≈ 2.02 eV.

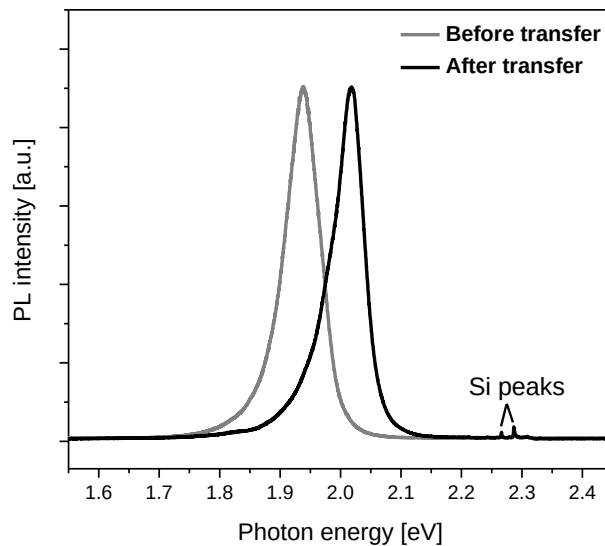


Figure S5. Normalized PL spectra of a WS₂ monolayer before and after transfer.

S6. Substrate doping effects on monolayer WS₂

The CVD-grown hBN used in the heterostructures was identified by Raman spectroscopy. Figure S6a shows the characteristic peak at 1370.9 cm^{-1} . Source-drain bias was applied to a WS₂ monolayer to compare its doping level on SiO₂/Si and hBN substrates (Figure S6b,c, respectively). The threshold voltage (V_{th}) is obtained *via* linear fitting for both the WS₂ on SiO₂/Si and that on hBN. It reveals that the V_{th} of the SiO₂-supported WS₂ (≈ 60 V) is much smaller than the hBN-supported WS₂ (≈ 76 V), indicative of the relatively heavier n-type doping by SiO₂/Si due to the large number of charge impurities.

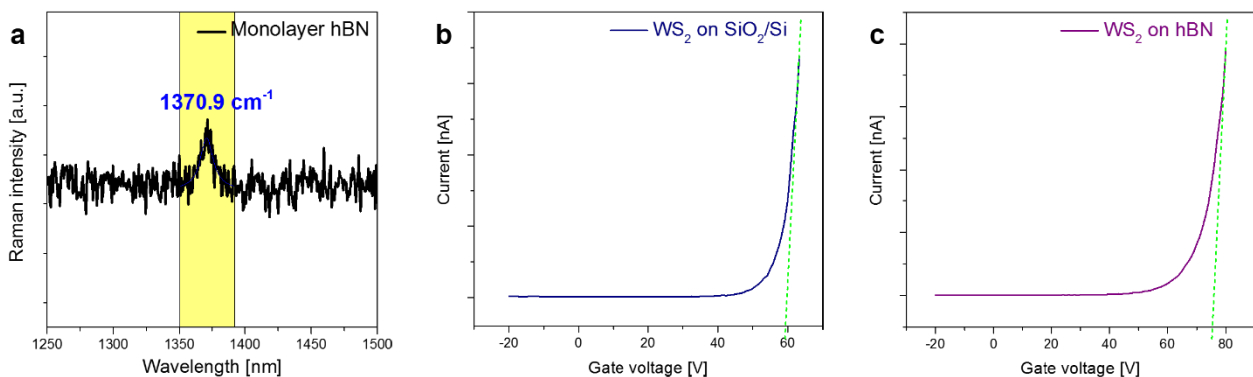


Figure S6. (a) Raman spectra of monolayer hBN. (b,c) I - V curves of monolayer WS₂ supported by SiO₂/Si chip (b) and hBN film (c).

S7. AFM measurements of the hBN separation layers

To examine the film thickness of hBN, we performed AFM measurements on the CVD-synthesised hBN by transferring it onto a SiO₂/Si substrate. The height profiles in Figure S7d,e demonstrate that controlled growth of monolayer and bilayer hBN, respectively. Figure S7f shows a minority of double-folded regions inside the film. The film roughness is evaluated by the root mean square (RMS) value, which is ≈ 0.24 nm for the square region in Figure S7c.

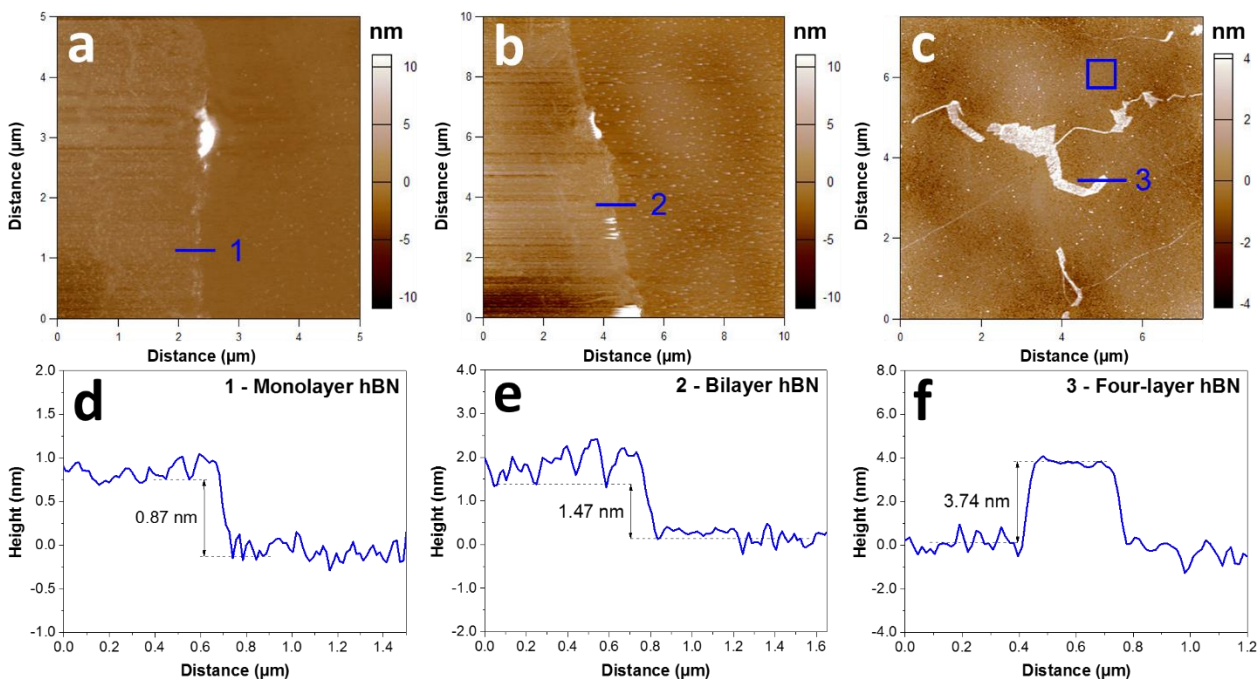


Figure S7. (a–c) AFM images and (d–f) height profiles of (a,d) monolayer, (b,e) bilayer, and (c,f) four-layer hBN. The blue lines 1 and 2 in (a) and (b) indicate the film edges that were scanned. Line 3 in (c), a double-

folded region inside the film, was measured to confirm the film thickness. The RMS value of the square region in (c) is computed from height variance.

S8. Low-temperature PL spectroscopy for WS₂:2 × hBN:MoS₂ VLHs and the WS₂ monolayer

Figure S8a shows the cryogenic PL of a WS₂:2 × hBN:MoS₂ VLH and the WS₂ constituent. At room temperature (293 K), the PL ratio of ≈ 1.20 under 405 nm (3.06 eV) laser excitation is close to that using 532 nm (2.33 eV) laser excitation with similar powers. However, the PL enhancement increases greatly with decreasing temperatures due to the suppression of thermally activated non-radiative decay channels. The lifetime of the MoS₂ B state could be prolonged at lower temperatures, and thereby increasing the possibility of Förster energy transfer between WS₂ and MoS₂.⁴⁹ As the temperature decreases, blue shift of the PL peak together with a narrowing of the full width at half maximum (FWHM) is observed for both the stacked region and the WS₂ monolayer (Figure S8b,c). It is notable that there is no evidence (*e.g.*, a lower-energy shoulder relative to the trion A⁻ peak) for emission of biexcitons under current conditions. Figure S8l reveals that the total integrated PL intensity of the VLH is enhanced more dramatically compared to the WS₂ monolayer, leading to a sharp increase in the PL ratio. Figure S8m,n presents the temperature dependence of exciton and trion emission energies. By adopting the standard expression for semiconductor bandgaps,⁹⁸ this temperature dependence can be written as

$$E(T) = E_0 - S\langle\hbar\omega\rangle \left[\coth\left(\frac{\langle\hbar\omega\rangle}{2k_B T}\right) - 1 \right] \quad (\text{E1})$$

, where E_0 is the emission energy at zero temperature, S is a dimensionless coupling constant, and $\langle\hbar\omega\rangle$ is the average phonon energy. The parameters to obtain best fits are listed in Table S1, which line well with those suggested in an earlier study.³⁶¹ The photon energy of the heterostack is found to be affected by the excitation wavelength (or energy), as the blue shift of the PL peak relative to the monolayer WS₂ under 532 nm (2.33 eV), 12.5 μW excitation (Figure 6.3j) is smaller than that under 400 nm (3.10 eV) excitation at a similar laser power of 20 μW .

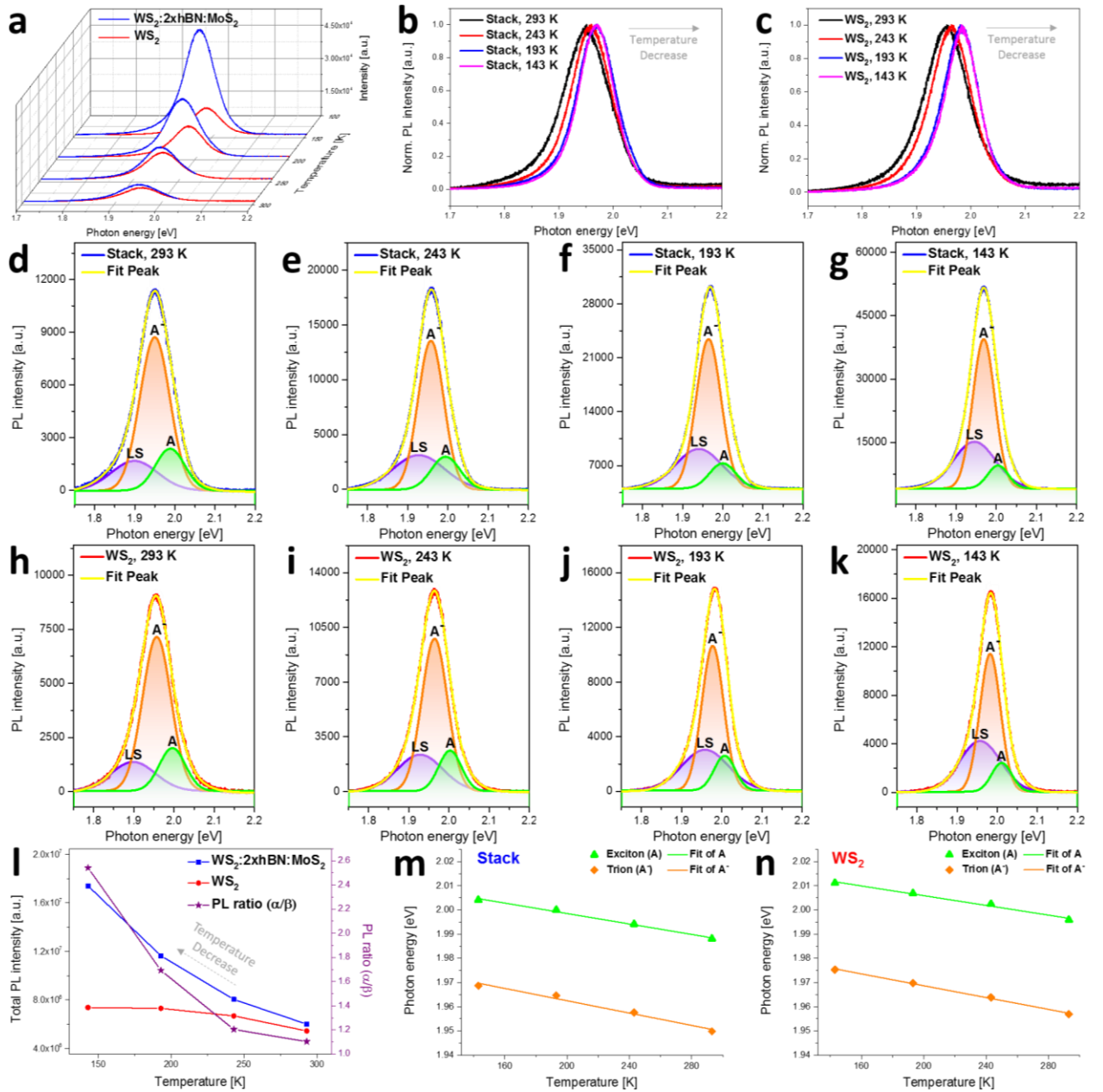


Figure S8. Low-temperature PL with 20 μ W laser excitation at 400 nm (3.10 eV). Absolute (a) and normalized (b,c) PL spectra of $\text{WS}_2/2 \times \text{hBN}/\text{MoS}_2$ VLH (b) and the WS_2 monolayer (c) at different temperatures. (d–k) Gaussian-fitted PL spectra of the stack (d–g) and the WS_2 monolayer (h–k) with decreasing temperatures of 293, 243, 193, and 143 K, respectively. (l) Temperature dependence of total integrated PL intensities of the VLH (α) and WS_2 monolayer (β) (left axis) and the PL ratio (α/β) (right axis). (m,n) Photon energy of exciton (A) and trion (A^-) vs. temperature for the stack (m) and WS_2 monolayer (n). Solid lines are the fits using E1.

Table S1. Fitting parameters for the temperature-dependent photon energy.

Excitonic species	Exciton (A)	Trion (A^-)
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Parameters	E_0 [eV]	S	$\langle \hbar\omega \rangle$ [meV]	E_0 [eV]	S	$\langle \hbar\omega \rangle$ [meV]
Stack	2.015	0.64	9.83	1.982	0.76	9.83
WS ₂	2.021	0.60	10.57	1.987	0.73	10.57

S9. Multiple reflection in WS₂:hBN:WS₂ VLHs with different hBN thicknesses

Transfer Matrix method was used to simulate the multiple reflections in WS₂:hBN:WS₂ VLHs with different hBN thicknesses, with the as-derived modelling results presented in Figure S9. It is indicated that the influence of multiple reflection on absorption (absorbance $A < 1.2$ for all the separation distances under investigation) is minor compared to the obtained enhancement level (*e.g.*, average modulation factor $\eta = 2.03$ for 1.47 nm). Additionally, Figure S9d,h show that the absorbance is not dependent on the interlayer spacing within 10 nm at ≈ 2.0 eV, where the PL signal is enhanced over the sum of the WS₂ monolayers. Therefore multiple reflections in our heterosystems, though could be involved, are at least not dominant for the interlayer interactions leading to PL enhancement.

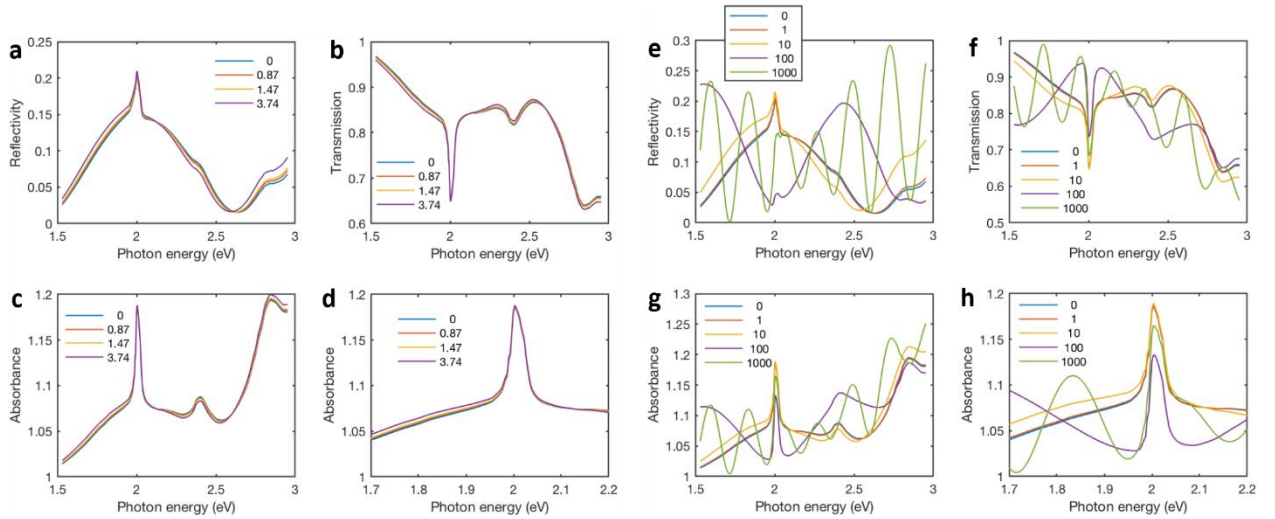


Figure S9. Calculations of WS₂:hBN:WS₂ VLHs, (a–d) with the hBN thickness corresponding to the layer number as determined by the AFM measurements in Figure S7, and (e–h) with the hBN thickness varying from 0 to 1000 nm. (a,e) Reflectivity spectra, (b,f) transmission spectra, and (c,d,g,h) absorption spectra.

S10. Time-resolved PL spectroscopy

The indistinguishable exciton lifetime between $\text{WS}_2:2 \times \text{hBN}:\text{WS}_2$ VLH and the constituent WS_2 monolayers proves that the emission of interlayer excitons is negligible in the stack.

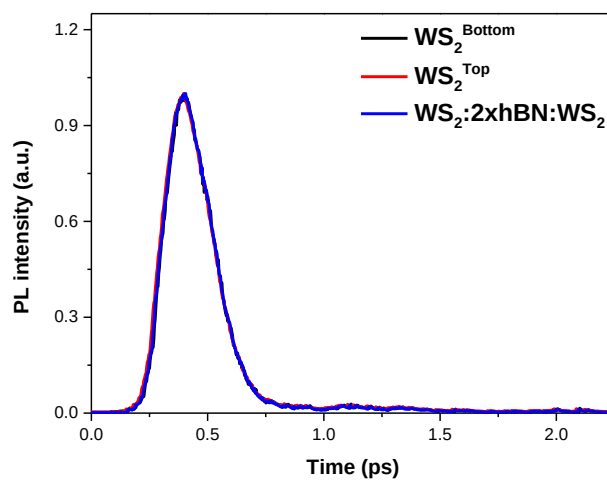


Figure S10. Time-resolved PL spectra of the different regions in $\text{WS}_2:2 \times \text{hBN}:\text{WS}_2$ VLHs, which were recorded under the same conditions with those for Figure 6.13c–e.

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