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TWO-DIMENSIONAL TRANSITION METAL DICHALCOGENIDES: ADDITIVE-MEDIATED SYNTHESIS, DOPING AND RELATED APPLICATIONS

A Dissertation in

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by

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ABSTRACT

Two-dimensional (2D) semiconducting transition metal dichalcogenides (TMDs) are an emerging family of 2D materials beyond graphene. 2D semiconducting TMDs possess a series of unique structural and functional properties, such as the presence of atomically flat surfaces without dangling bonds, layer-dependent electronic band structure, and pronounced excitonic effects, thus making them very intriguing both fundamentally and technologically. Apart from these excellent properties, another important feature of 2D TMDs is that these materials are extremely "tunable". For example, the physicochemical properties of TMDs can be effectively modulated by lattice defects (*e.g.*, vacancies, dopants, grain boundaries) and external perturbations (*e.g.*, strain, substrate effect, van der Waals heterostacks), providing rich opportunities for materials engineers to tailor TMD properties by means of doping, alloying, coupling TMDs with predesigned substrates, etc.

Therefore, the research presented in my thesis mainly focuses on the synthesis of 2D semiconducting TMDs, the investigation of their intrinsic defects, and the development of effective substitutional doping and material transfer techniques to engineer their properties for functional applications. Chapter 1 provides an introduction to structures, properties, synthesis techniques, and defect engineering of 2D TMDs. In Chapter 2, two different additive-mediated chemical vapor deposition (CVD) approaches, involving sodium bromide and sodium cholate powders as growth promoters, are demonstrated. Pristine TMDs, alloyed Mo_xW_{1-x}S₂, and in-plane Mo_xW_{1-x}S₂-W_xMo_{1-x}S₂ heterostructures are synthesized using our methods with improved grain size, yield, and reproducibility when compared to the conventional solid precursor CVD approach. Chapter 3 studies intrinsic defects and their distributions within CVD-synthesized TMD monolayers utilizing a combination of various microscopic and spectroscopic characterization techniques. The results indicate that 3d- and 4d-transition metal impurities (*e.g.*, Cr, Fe, V, Mo) are often nonuniformly distributed within single-crystalline WS₂ monolayers, leading to the photoluminescence

inhomogeneity that is common in WS_2 . In addition, scanning tunneling microscopy/spectroscopy studies of CVD-grown WS₂ have also unambiguously identified carbon-hydrogen (CH) complex as a common type of intrinsic defects. Chapter 4 reports an effective, convenient, and generalized method for in situ substitutional doping of 2D TMDs. This method is based on spin-coating and high-temperature chalcogenization of a mixture of water-soluble host precursor, dopant precursor, and growth promoter. Using this liquid phase precursor-assisted CVD method, we demonstrate the successful growth of Fe-doped WS₂, Re-doped MoS₂, and more complex structures such as Vdoped in-plane Mo_xW_{1-x}S₂-W_xMo_{1-x}S₂ heterostructures. In Chapter 5, we develop a clean and deterministic transfer method of 2D TMDs. We report a cellulose acetate-assisted method that transfers TMDs onto various substrates with improved micro- and nano-scale cleanliness. A deterministic transfer system is built up for placing a selected monolayer TMD to target locations on the substrate. The development of 2D TMD transfer techniques facilitates the investigation of their functional applications. As an example, the fabrication and ionic transport properties of monolayer MoS₂ nanopore arrays are demonstrated in Chapter 5, and the correlation between ionic conductance and nanopore diameter distributions is carefully analyzed by combined experimental studies and molecular dynamic simulations. Finally, we provide a summary of main findings in this thesis and an outlook of future directions that can be pursued.

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Chapter 1

Introduction to Two-Dimensional Transition Metal Dichalcogenides

Part of this chapter is based on a review paper that will be submitted to *2D Materials* for which I am the first author (Ref. [1]). Parts of reference [1] are reproduced (adapted) with permission from Zhang, T.; Sanchez, D.; Liu, M.; Zhang, N.; Lei, Y.; Yu, Z.; Zhou, D.; Kong, J.; Terrones, M., Chemical Vapor Deposition of 2D Transition Metal Dichalcogenides: Recent Progress, Opportunities and Challenges towards Practical Applications. *In preparation*.

In materials, apart from the composition and atomic arrangement, size can often play an important role in determining their physicochemical properties. Size effects become very significant when at least one of the dimensions of a material is reduced to less than 100 nm, where quantum confinement effect starts to emerge, resulting in substantially different properties in these so called "nanomaterials" compared to their bulk counterpart.² The investigation of nanomaterials has been made possible over the past few decades thanks to the fast development of a series of nanoscale characterization techniques, such as scanning tunneling microscopy (STM)³, atomic force microscopy (AFM)⁴, and advancements in scanning transmission electron microscopy (STEM).⁵⁻⁶ Nowadays, the research field of nanomaterials is rapidly evolving, where the structural design, synthesis, advanced characterization, and applications of novel nanomaterials are reported on a daily basis. In addition, nanomaterials have been applied in various aspects in our daily lives, such as electronics, surface coatings, energy, and healthcare, exhibiting revolutionary impacts. Thus, it is not overly optimistic to claim that we are already at the age of nanotechnology.

Two-dimensional (2D) layered materials, composed of atomically thin layers of atoms with intralayer covalent bonds and interlayer van der Waals (vdW) interactions, are currently one of the most intriguing members in the field of nanotechnology. The investigations of 2D layered materials all started from the successful isolation of graphene monolayers from bulk graphite in 2004 – a groundbreaking advancement that opens up enormous possibilities to prepare and study graphene and other 2D layered materials (e.g., transition metal dichalcogenides (TMDs), hexagonal boron nitride (h-BN), and black phosphorus (BP)).⁷⁻⁸ 2D materials have a series of unique features that make them interesting both fundamentally and technologically, such as atomically flat surfaces without dangling bonds, one- or few-atom thickness, high transparency, high mechanical strength and modulus, layer number-dependent electronic and optical properties, strong Coulombic interaction between charge carriers, to name a few.⁹⁻¹² In addition, 2D materials possess a wide range of electronic properties depending on their compositions and crystal structures, which results in their diverse functionalities and applications. As displayed in Figure 1-1, the family of 2D materials includes wide-bandgap insulators (e.g., h-BN), semiconductors (e.g., TMDs, BP), and metals and semimetals (e.g., graphene). In this thesis, we particularly focus on 2D semiconducting TMDs (marked with the gray dashed rectangle in Figure 1-1), an emerging family of beyondgraphene 2D materials that holds great potential in fields such as electronics, optoelectronics, sensing, and catalysis. The first chapter of the thesis aims at providing a brief introduction to the structure, properties, applications, and preparation methods of 2D TMDs. We will also briefly discuss the routes of further tuning TMD properties through defect engineering. Finally, the research aims of this thesis will be summarized.

1.1 Introduction to 2D TMDs: Structures, properties and applications

TMDs have a common formula of MX_2 , where M represents a transition metal and X represents a chalcogen. Among all types of TMDs, many of them crystalize in layered structures in their bulk form, which offers the capability of thinning down these TMD crystals down to few- and mono-layers. Figure 1-2 (a) illustrates the combinations of M and X elements that can lead to 2D layered TMDs. The highlighted transition metal elements denote that the element can form 2D layered TMDs with all types of chalcogen elements (*i.e.*, S, Se, and Te), while the partially highlighted Co, Rh, Ir, and Ni elements represent that these transition metals only form 2D layered structures with some chalcogen elements. According to these versatile combinations of M and X atoms, a variety of 2D TMDs (~40 types of binary compounds) exist, resulting in a wide range of physicochemical properties within the family of TMD materials. Moreover, while an individual layer of TMDs is always comprised of three atomic layers, with a layer of M atoms sandwiched by two layers of X atoms through covalent bonds, TMDs can exhibit several structural polytypes depending on the atomic configurations (Figure 1-2 (b)). At the monolayer limit, possible polytypes include trigonal prismatic 1H phase, octahedral prismatic 1T phase, and 1T' (distorted 1T) phase. In the case of multilayers, the variation in stacking sequences of individual 1H TMDs can result in additional polytypes, which are 2H phase (D_{3h} (D_{3d}) point group for odd (even) layer numbers) and 3R phase (non-centrosymmetric C_{3v} point group).¹³⁻¹⁴ As a consequence of various M and X combinations and structural polytypes, the electrical properties of 2D TMDs span from semiconducting (2H-MoS₂, 2H-WSe₂) to semimetallic (1T'-WTe₂) and metallic (1T-MoS₂, 2H-NbS₂).⁹ Many exotic properties such as superconductivity (2H-NbSe₂) and room-temperature ferromagnetism (1T-VSe₂) are also observed in some TMDs at their 2D limit.¹⁵⁻¹⁶ The versatile properties of 2D TMDs offer exciting opportunities for them to be studied in fundamental and

technological research fields such as electronics, spintronics, optoelectronics, and energy-related applications.¹⁷



Figure 1-1: The bandgap values of different types of 2D materials. The gray horizontal bars represent the range of bandgap values that can be achieved by changing the number of layers, strain engineering or alloying of the corresponding 2D materials. 2D TMDs, the main type of materials investigated in this thesis, is marked with a gray dashed rectangle. Adapted from Ref. 18.

Among the family of 2D TMDs, group-VIB TMDs (MX₂, where M = Mo, W; X = S, Se, and Te) are arguably one of the most intriguing and actively studied categories. Particularly, 2H phase group-VIB TMDs are semiconductors with optical bandgaps in ~0.7-2 eV range.¹⁹⁻²⁰ More interestingly, the bandgaps of these TMDs can be tuned as a function of layer number, and an indirect-to-direct bandgap transition can occur when TMD crystals are thinned down to monolayer.²¹ Taking 2H-molybdenum disulfide (MoS₂) as an example, according to density

functional theory (DFT) calculated layer-dependent band structures presented in Figure 1-3 (a), the direct bandgap energy at the K point of the Brillouin zone is relatively insensitive to the layer number. However, the indirect transition energy, corresponding to the valence band maximum (VBM) at Γ and the conduction band minimum (CBM) along the K- Γ direction, increases monotonically with the decrease of layer number and becomes even larger than the direct band gap energy in the case of monolayer MoS₂. As a consequence, MoS₂ is a direct bandgap semiconductor when thinned down to monolayer limit, and exhibits more than 10⁴ times stronger photoluminescence (PL) and largely enhanced PL quantum yield (QY) compared to the few-layer or bulk counterpart (Figure 1-3 (b-c)).¹¹



Figure 1-2: Elemental composition and structural polytypes of 2D TMDs. (a) Elemental composition of 2D TMDs. Transition metal atoms and chalcogen atoms that predominantly crystalize into layered TMDs are highlighted. Co, Ni, Rh, and Ir elements are partially highlighted because only some of the corresponding dichalcogenides form layered structures (*e.g.*, NiS₂ crystallizes as a non-layered pyrite structure, but NiTe₂ is layered). Adapted from Ref. 9. (b) Different structural polytypes of layered TMDs. Adapted from Ref. 13.



Figure 1-3: Band structure and photoluminescence (PL) of MoS_2 with different layer numbers. (a) Layerdependent band structure evolution in MoS_2 . Adapted from Ref. 21. (b) PL spectra of mono- and bilayer MoS_2 samples. Inset: PL quantum yield (QY) of 1-6 layered MoS_2 . (c) Normalized PL spectra by the intensity of peak A of thin layers of MoS_2 for layer number N = 1-6. Adapted from Ref. 11.

Tungsten disulfide (WS₂) is another type of actively studied semiconducting TMDs. The structure, schematic of Brillouin zone, and DFT calculated band structures of WS₂ bulk and monolayer are shown in Figure 1-4 as a comparison with MoS₂. Very similarly, WS₂ also possesses direct electronic transitions at the K point of the Brillouin zone, represented as A and B in Figure 1-4 (d), as well as an indirect transition from the VBM at Γ point to the CBM at T point (along the K- Γ direction). At the monolayer limit, the direct bandgap energy is smaller than that of the indirect

bandgap, leading to the direct bandgap and strong light-emitting features of monolayer WS2.22 Despite the similarities between WS_2 and MoS_2 , there are additional characteristics that make WS_2 monolayers perhaps even more interesting. Firstly, monolayer WS₂ can often exhibit greatly enhanced PL emission around edges and corners of the flake, which are uncommonly seen in MoS2 and likely to be associated with sulfur vacancies or surface adsorbates.²³⁻²⁴ This implies the possibility of tailoring and/or patterning optical properties of WS₂ monolayers for nanooptoelectronic devices. Secondly, synthetic WS2 monolayers can have more pronounced shape morphology variation (e.g., triangular- or hexagonal-shaped single crystals) and spatial variation of optical properties (e.g., edge-enhanced PL that we mentioned above, and three-fold PL intensity variation in hexagonal WS₂).²⁵⁻²⁶ These features provide opportunities for studying the structureproperty relationship in TMD monolayers. Thirdly, monolayer TMDs exhibit strong spin-orbit coupling. According to the DFT calculated spin splitting of the conduction band, monolayer WS_2 and WSe₂ have optically dark exciton ground states because their CBM and VBM are calculated to have antiparallel spins, while monolayer MoX₂ have optically bright exciton ground state, which is the opposite of WX₂.²⁷⁻²⁸ The presence of dark exciton states in WS₂ and WSe₂ makes them intriguing for investigations of novel excitonic effects in 2D system.



Figure 1-4: Crystal structure and band structure of WS₂. (a-b) Top view and cross-section view of layered 2H-WS₂. (c) Brillouin zone for WS₂ monolayer. (d-e) Electronic band structure (left) and total density of states (right) of WS₂ bulk and monolayer, respectively. Adapted from Ref. 22.

Due to their ultra-thin nature coupled with fascinating electrical and optical properties that we have summarized above, 2D semiconducting TMDs show great promise for various technological applications, and a few of these applications where TMDs may play revolutionary roles are displayed in Figure 1-5. For electronic applications, since semiconducting TMDs have bandgap in the infrared to visible range compared to the gapless graphene, a large on/off ratio (10^{5} - 10^{8}) with decent mobility (10^{1} - 10^{2} cm²/V·s) can be achieved when TMDs are at their 2D limit (Figure 1-6).²⁹ Thus, field-effect transistors built from semiconducting TMDs are expected to consume less power without compromising performances. In terms of optoelectronics and photonics, because of the layer-dependent photoresponse, strong PL in monolayers, and the ultrathin form-factor, TMDs are suitable for constructing photodetectors and photovoltaics. By integrating TMDs with designed substrates, such as a photonic crystal cavity and patterned nanopillars. TMDs can also demonstrate lasing and single-photon emission.³⁰ Thus, 2D TMDs can be used as active optoelectronic components for the Internet of Things (IoT) platform, and for onchip novel quantum photonic technologies.³⁰⁻³¹ Moreover, different types of 2D materials can be vertically stacked and held together by vdW force just like assembling "atomic-scale Lego blocks", which leads to 2D vdW heterostructures with highly tunable properties depending on the selection of 2D components and their relative twist angles (Figure 1-5 (e)).³²⁻³³ This feature is exciting because there are a plethora of 2D materials and possible stacking sequences, which result in countless types of heterostructures and material properties.³⁴ Based on 2D vdW heterostructures with TMD as a component, electronic and optoelectronic devices, such as tunnel diode and interlayer exciton optoelectronics, have been demonstrated.^{32, 35} It should be noted that although we try to highlight the applications of 2D TMDs in Figure 1-5, this list is far from comprehensive. As an example, TMD-based systems have been demonstrated as an excellent catalyst for energy conversion applications such as hydrogen evolution reaction (HER).³⁶ In addition, recent advancements in twisted TMD homo- and hetero-bilayers enabled the engineering of physical properties of TMDs through moiré periodic potentials. Exotic phenomena such as twist-angle dependent moiré excitons³⁷, moiré flat bands³⁸, and quantum phase transitions³⁹ have been observed in these systems, and more exciting breakthroughs in 2D TMDs and their heterostructures can be anticipated in the near future.



Figure 1-5: Example applications of 2D semiconducting TMDs. (a) Field-effect transistor (FET). Adapted from Ref. 40. (b) Photodetector. Adapted from Ref. 41. (c) Nanocavity laser. Adapted from Ref. 30. (d) Single-photon source. Adapted from Ref. 42. (e) Schematic of constructing 2D van der Waals (vdW) heterostructures, which resembles building up atomic-scale Lego blocks. (f) Tunneling device based on vdW heterostructures. (g) Interlayer exciton optoelectronics based on TMD heterostructures. (e)-(g) adapted from Ref. 32.



Figure 1-6: Mobility/on–off ratio spectrum for three typical 2D materials: graphene, black phosphorus, and TMDs. Scattered points (black square, purple circles, and green triangles) represent literature reported results. The shaded regions are approximate possible ranges of performance for the respective materials. Adapted from Ref. 29.

1.2 The preparation and transfer of 2D TMDs

The routes for preparing TMD materials have been investigated for many decades. Early efforts were mainly focusing on preparing TMD nanostructures (*e.g.*, nanotubes, nanoparticles, nanorods) which were not in the 2D regime⁴³⁻⁴⁴, and until recently, the research advancements in 2D layered materials triggered studies on the preparation of TMDs in their 2D form. In this section, these various synthesis approaches of 2D TMDs will be introduced, with an emphasis on chemical vapor deposition (CVD) method that will be mainly investigated and applied in my thesis. Moreover, the implementation of as-prepared TMD materials for device applications often requires a transfer process, which places TMDs onto desired substrates. As a result, we will also provide a brief introduction of commonly used TMD transfer techniques.

1.2.1 The preparation of 2D TMDs

The effective preparation of 2D TMDs is of great importance for their applications that we highlighted in the section above. In general, the methods for preparing 2D TMDs can be categorized in two types: 1) top-down approaches (*i.e.*, exfoliation of the existing bulk TMD crystals into monoor few-layers), and 2) bottom-up approaches (*i.e.*, the assembly and reaction of precursor molecules that are able to synthesize 2D TMDs).⁴⁵ This section of the thesis will summarize state-of-the-art routes for preparing 2D TMDs.

1.2.1.1 Top-down approaches

In bulk TMD crystals, individual layers are held together only through interlayer vdW interactions that are much weaker than intra-layer covalent bonds, which leads to the capability of

obtaining 2D layers from bulk crystals through top-down exfoliation. In practical, either mechanical force or chemical interactions can be used to overcome the vdW force and isolate mono- or few-layers of TMDs. In the first method, mechanical exfoliation of TMDs can be achieved by a scotch tape-assisted process. As shown in Figure 1-7, bulk crystals of TMDs are first prepared by *chemical vapor transport (CVT)*. Since CVT reaction occurs under near equilibrium conditions and takes days or weeks to take place, this process can yield high-quality large single crystals.⁴⁶ Afterwards, these bulk crystals are used as the starting material for mechanical exfoliation. During a typical mechanical exfoliation process (Figure 1-7 (b)), bulk TMD crystals are attached to a piece of scotch tape, and the tape with TMD crystals is usually folded and separated for several times to enhance the yield of thin TMD layers. Subsequently, the tape is attached to a piece of clean SiO₂/Si wafer and slowly released, leaving exfoliated TMD flakes on the substrate.⁴⁷ Since mechanical exfoliation uses high-quality single crystals without the need of any chemical agents, this method can thus yield high-quality 2D TMDs that are ideal for demonstrating electronic and optoelectronic device applications. However, the main limitation is that mechanical exfoliation usually yields few-layers and thick TMD crystals, and the yield and sizes of exfoliated monolayers are usually small and uncontrollable, making this method to be limited for laboratory-scale research. Recently, several studies have demonstrated gold-mediated mechanical exfoliation of TMDs that can achieve millimeter- and even centimeter-scale uniform MoS₂ monolayers, based on the strong vdW interaction between gold and monolayer MoS₂.⁴⁸⁻⁴⁹ These advancements take one step closer to the large-scale preparation of monolayer TMDs, but the complex experimental procedures and associated costs are still barriers to overcome.



Figure 1-7: Schematic illustrations of the (a) CVT synthesis of bulk crystals (adapted from Ref. 46), and (b) scotch tape-assisted mechanical exfoliation (adapted from Ref. 47).

Liquid-phase exfoliation methods, such as sonication, shear exfoliation and intercalationexfoliation, are also commonly applied for the top-down production of 2D TMDs.⁵⁰⁻⁵¹ During a typical sonication exfoliation process, bulk TMD crystals are sonicated with the assistance of surfactant molecules or solvents with favorable surface tension. For example, Coleman et al. found that solvents with surface tensions around 30-40 mJ/m² tend to yield exfoliated TMD dispersions.⁵⁰ Similar to the case of sonication exfoliation, shear exfoliation also utilizes mechanical force to overcome vdW force among TMD layers, which can typically be achieved using a kitchen blender. Varrla *et al.* demonstrated the sheer exfoliation of MoS_2 nanosheets in aqueous solution with sodium cholate as the surfactant. It was found that size-controlled MoS₂ nanosheets can be produced by this method, and surfactant concentration could be used to tune the thickness and lateral size of exfoliated flakes.⁵² Intercalation-exfoliation is another type of liquid phaseexfoliation method. As an example, lithium (Li) ion can be intercalated between layers of TMDs by immersing TMD crystals into n-butyllithium or through an electrochemical lithiation process, forming the intercalated compound LixMoS₂. This process leads to the expansion of interlayer spacing and weakened vdW interaction, and allows the subsequent exfoliation of 2D layers by simple sonication.⁵³ It should be noted that Li intercalation-exfoliation mainly produces 2D TMDs with metastable 1T phase, due to a large amount of charge transfer during the intercalation process.

Thus, if one needs to obtain chemical exfoliated 2H-TMDs, the exfoliated flakes usually need to be deposited onto a substrate and annealed at high temperature (above 200 °C) to achieve the 1T-2H phase transition.⁵⁴ In all, liquid-phase exfoliation is considered to be a scalable technique when compared to other TMD preparation methods. Another benefit is that the produced TMD dispersions are easily processable in liquid phase, allowing the further fabrication of TMD thin films, networks, and nanocomposites. As an example, inks based on exfoliated TMDs can be used for printing flexible electronic devices.⁵⁵⁻⁵⁶ Nevertheless, the liquid-phase exfoliated flakes usually have small domain sizes (tens of nanometers to a few micrometers), and the controls of layer number and crystal quality remain challenging.

1.2.1.2 Bottom-up approaches

Bottom-up synthesis of TMDs is critical for realizing the scale-up electronic and optoelectronic applications.⁵⁷ To date, much research effort has been made to controllably synthesize 2D TMDs, and <u>chemical vapor deposition (CVD)</u> is arguably the most widely explored method. In a general CVD process for synthesizing 2D TMDs, transition metal and chalcogen precursors are introduced into a quartz tube furnace, and then react at high temperature (usually > 500 °C) in vapor phase, depositing 2D TMD on a substrate placed inside the tube.⁵⁸ Depending on the initial state of precursors used for CVD synthesis, CVD method can be further categorized into three types: <u>solid precursor CVD</u>, <u>liquid phase precursor assisted CVD</u>, and <u>gas-source CVD</u>. As depicted in Figure 1-8 (a), in a typical solid precursor CVD process, solid transition metal precursors (*e.g.*, Mo film, MoO_x) are either deposited onto or placed in the vicinity of a growth substrate (*e.g.*, SiO₂/Si, sapphire, mica). Subsequently, the substrate with transition metal precursors is placed into a tube furnace and chalcogenized by evaporated sulfur or selenium,

forming 2D TMDs on the substrate. A series of synthesis parameters, including temperature, types of precursor, growth promoter, substrate, carrier gas type and flow rate, and pressure, can be rationally tuned to control the growth outcomes.⁵⁷ Focusing on improving the yield and grain size of solid precursor CVD growth, we also developed an alkali metal halides-assisted synthesis method for pristine WS₂ and alloyed $Mo_xW_{1-x}S_2$ monolayers, which will be further discussed in Chapter 2 of this thesis.

In the second method (Figure 1-8 (b)), liquid phase transition metal precursors are spincoated or drop-casted onto the growth substrate, followed by a high-temperature chalcogenization process. This method is relatively newly established, which can also be regarded as a special case of solid precursor CVD, since the liquid phase precursors will solidify prior to chalcogenization reaction. To implement the liquid phase precursor-assisted CVD method, the key is the utilization of soluble precursors. Water-soluble ammonium heptamolybdate (AHM, (NH₄)₆Mo₇O₂₄) and ammonium metatungstate (AMT, $(NH_4)_6H_2W_{12}O_{40}$) are commonly used transition metal precursors.⁵⁹⁻⁶⁰ In a recent study, Ji et al. demonstrated a liquid phase precursor-assisted CVD approach using MoO₃ dissolved in ammonia as a precursor and potassium iodide (KI) as a growth promoter, resulting in millimeter-sized MoS₂ monolayers with growth reaction dynamics matching with Brønsted-Evans-Polanyi (BEP) relation.⁶¹ In brief, liquid phase precursor-assisted CVD method is capable of producing single-crystalline TMD monolayers⁶⁰ and continuous polycrystalline films⁶² with scaling up capabilities. In addition, different soluble transition metal precursors can be mixed homogeneously in the liquid phase prior to the spin-coating process, which offers a great possibility for synthesizing doped TMDs and in-plane heterostructures using this approach. Our related studies will be presented in Chapter 2 and Chapter 4 of the thesis.

The third CVD approach, gas-source CVD, involves the use of volatile transition metal and chalcogen precursors that are both located outside of the reaction chamber (Figure 1-8 (c)). A few

examples of precursors for gas-source CVD include metal carbonyls (e.g., Mo(CO)₆, W(CO)₆), halides (e.g., MoCl₅, WCl₆), and hydrogen chalcogenides (e.g., H₂S, H₂Se).⁶³ Compared to solid precursor and liquid phase precursor-assisted CVD methods, gas-source CVD holds the advantage that the precursor vapor pressures and ratios can be independently tuned, which offers wellcontrolled processes of nucleation, domain ripening, and lateral growth.⁶⁴ Gas-source CVD has been used for growing wafer-scale uniform monolayer TMDs, exhibiting excellent layer number uniformity.⁶⁵⁻⁶⁶ However, gas-source CVD still has several limitations in the current stage. Firstly, gas-source CVD is usually costly among various synthesis method and involves chemicals that may pose high hazard risks. Secondly, TMDs synthesized by gas-source CVD often have small domain sizes (a few micrometers or less), resulting a large density of grain boundaries when TMD domains merge together. Even if epitaxial substrates are used, 60° antiphase grain boundaries are still unavoidable.⁶⁴ The presence of these grain boundaries may lead to unwanted variation and degradation of electrical transport and optical properties.⁶⁷⁻⁶⁸ Thus, aiming at eliminating grain boundaries in CVD-synthesized TMD films and obtaining large-area single crystals, recent research efforts have been focusing on the epitaxy of single-orientation TMD monolayers via substrate symmetry engineering or defect engineering.⁶⁹⁻⁷⁰

Apart from the CVD approach that we have explained in details above, other bottom-up TMD synthesis methods include molecular beam epitaxy⁷¹, pulsed laser deposition⁷², colloidal synthesis⁷³, hydrothermal synthesis⁷⁴, electrochemical deposition⁷⁵, etc. The discussion of these synthesis approaches is beyond the scope of this thesis, but it is worth mentioning that a variety of morphologies (*e.g.*, nanosheets, nanoflowers, monolayer films, multilayer films) of TMDs can be obtained by applying different synthesis approaches, demonstrating diverse functional properties. Thus, the choice of TMD synthesis techniques can be application-driven.


Figure 1-8: Schematics of the bottom-up CVD synthesis of 2D TMDs. (a) Solid precursor CVD method. Adapted from Ref. 76. (b) Liquid phase precursor-assisted CVD method. Adapted from Ref. 77. (c) Gassource CVD method. Adapted from Ref. 65.

1.2.2 The transfer of 2D TMDs on substrates

For practical applications of 2D TMDs, as-prepared materials often require to be integrated onto certain types of substrates. Especially, for CVD-grown TMDs that we will mainly investigate in the thesis, the post-growth transfer process is highly nontrivial because of three major reasons: (1) High temperature (>500 °C) is usually required during CVD reaction, which largely restricts the choice of substrates; (2) CVD-grown TMDs are usually strained because of the thermal expansion coefficient mismatch between TMDs and the growth substrate, and thus a transfer process is desired to release the thermally induced strain; (3) the post-growth transfer process enables the fabrication of sophisticated heterostructures and device configurations that would otherwise be difficult to achieve by bottom-up synthesis, such as twisted moiré heterostructures and suspended monolayer devices.⁷⁸⁻⁸⁰ To date, the most common approach of transferring CVDsynthesized TMDs is polymer-assisted wet-transfer (Figure 1-9 (a)). As an example, in order to transfer TMDs from SiO₂/Si, a widely used growth substrate, a layer of poly(methyl methacrylate) (PMMA) is first spin-coated onto TMDs. Subsequently, SiO_2 layer of the substrate is etched in sodium hydroxide (NaOH) or hydrofluoric acid (HF) solution, lifting off the PMMA/TMDs film. Finally, the PMMA/TMDs film is transferred to the target substrate, and the PMMA layer is removed by acetone and isopropanol (IPA) baths, leaving the transferred TMDs on the target substrate.⁸¹ Although PMMA-assisted wet-transfer has been widely adapted for transferring 2D TMDs, enabling their characterization and application on a variety of substrates, a main drawback is that this process inevitably leaves residues, wrinkles, and cracks on transferred TMDs, leading to the degradation of their optical and electrical properties.⁸² Recently, several improved transfer methods have been developed to tackle this issue, such as water-assisted etchant-free delamination⁸³ and alternative polymer-assisted transfers.⁸⁴ We have also developed a cellulose acetate (CA)-assisted wet-transfer method that largely improves the cleanliness and reduces wrinkles/cracks in as-transferred TMDs, which will be discussed in detail in Chapter 5 of the thesis.

Another category of TMD transfer methods is dry-transfer, which involves the use of a viscoelastic stamp, such as polydimethylsiloxane (PDMS), to carry and release 2D TMDs onto the target substrate (Figure 1-9 (b)).⁸⁵ This dry-transfer technique can often be integrated with a micromanipulator-based deterministic transfer system, which enables the controlled positioning of TMD flakes for building up complex device structures such as artificially-stacked TMD heterostructures.⁸⁶ One of the state-of-the-art dry-transfer methods is the vdW pick-up transfer method. In this method, a layer of polypropylene carbonate (PPC) can be used to capture TMD

flakes from the substrate and release them onto the target substrate, which can be well controlled by temperature.⁸⁷ Compared to wet-transfer techniques, dry-transfer usually yields a better surface and interface cleanliness, which is ideal for investigating novel physics and device functionalities using TMD flakes produced by mechanical exfoliation. Nevertheless, the dry-transfer of CVDsynthesized large-area films remains challenging. In addition, dry-transfer inevitably involves a mechanical peeling process that is not compatible with fragile target substrates, such as transmission electron microscopy (TEM) grids.



Figure 1-9: Schematics of the transfer of 2D TMDs. (a) PMMA-assisted wet-transfer of TMDs. Adapted from Ref. 81. (b) PDMS-assisted dry-transfer of TMDs. Adapted from Ref. 85.

1.3 Defect engineering of 2D TMDs

"Crystals are like people: it is the defects in them which tend to make them interesting!" – C. J. Humphreys.⁸⁸ This quote highlights the importance of defects that tunes the material properties. 2D TMDs are atomically thin materials with ultimately high surface to volume ratio, and thus their physicochemical properties are more sensitive to any created surface defects. Several review articles from our group have previously demonstrated that having defects within TMDs is not necessarily a disappointment, it can indeed lead to interesting phenomena and open up novel applications if one is able to fully characterize and control these defects.^{13,45} Therefore, the ultimate goals of defect engineering may be to understand different types of defects, controllably create defects, and controllably eliminate defects depending on target applications.

By definition, "defect" is any kind of localized disruption to the perfect crystalline order.⁸⁹ As schematically summarized in Figure 1-10, defects in 2D TMDs can be categorized by dimensionality: (1) Zero-dimensional (0D) defects such as vacancies, adatoms, substitutional dopants, and structural defects; (2) one-dimensional (1D) defects such as edges, grain boundaries, and in-plane heterointerfaces; (3) 2D defects such as wrinkles, folds, ripples, and heterostacks.¹³ Because of these diverse types of defects, it is apparent that defect engineering of 2D TMDs is a very broad topic. Thus, this section is not intended to summarize the recent breakthroughs in this field in a comprehensive way. Instead, we aim at mainly introducing three types of defects that are particularly investigated in this thesis: vacancies, substitutional dopants, and heterostructures. A very comprehensive review of defects in 2D TMDs, including their classification, creation methods, characterization, and applications, was provided by Lin *et al.*¹³

<u>Vacancies</u> are always present in the lattice of TMDs as intrinsic defects. Taking monolayer MoS₂ as an example, mono-sulfur vacancies (V_S), di-sulfur vacancies (V_{S2}), and molybdenum vacancies (V_{Mo}) were all observed in MoS₂ regardless of preparation methods (*i.e.*, mechanical exfoliation, physical vapor deposition (PVD), and CVD). In some cases, larger vacancies such as V_{MoS6} , as well as antisite defects such as $S2_{Mo}$ (a column of S atoms occupying a Mo site), were also found.⁹⁰ Among these vacancies, V_S defects are usually most prevalent because of their low formation energy indicated by DFT calculations.⁹⁰⁻⁹¹ For electronic and optoelectronic applications, these vacancy defects have been found to impair the device performances by reducing the carrier mobility and introducing mid-gap states.^{23, 92} On the other hand, these defects can lead to new opportunities and functionalities, such as enhanced catalytic performance⁹³, single photon emission⁹⁴, and nanopore sensing capabilities.⁸⁰ In order to controllably introduce these vacancies into the TMD lattice, various methods including electron irradiation⁸⁰, ion irradiation⁹⁵, plasma treatment⁹⁶, and thermal annealing⁹⁷, have been explored. In this context, we developed a Ga⁺ ion irradiation method that is capable for large-scale creation of vacancies (or 2D voids at higher Ga⁺ ion dose), enabling the studies of ionic transport through monolayer MoS₂ membranes.⁹⁸ The related work will be discussed in detail in Chapter 5.

<u>Substitutional dopant atoms</u> are another category of important defects in 2D TMDs. According to both theoretical and experimental studies, a variety of physicochemical properties can be modified by introducing certain types of dopants that occupy either transition metal or chalcogen sites of TMDs.⁹⁹ The properties that can be modified by dopants include optical emission¹⁰⁰, electrical doping type¹⁰¹⁻¹⁰², magnetic property¹⁰³, and sensing capability⁷⁵, to name a few. By adding dopant compounds into the CVT or CVD reactor, substitutional dopants can be incorporated *in situ* during synthesis, which is one of the most effective and widely used method to obtain doped TMD bulk crystals and atomic-thin layers.¹⁰⁴⁻¹⁰⁵ However, substitutional dopants can sometimes be a bit "annoying" too, because they may also be induced by impurities from precursors and/or reactors, and thus become unintentional dopants within the lattice and lead to undesired variations of the material properties.¹⁰⁶⁻¹⁰⁷ These unintentional dopants are difficult to be experimentally eliminated and characterized. In Chapter 3 of the thesis, we made efforts towards understanding the substitutional dopants in CVD-grown TMD monolayers using a combination of various microscopic and spectroscopic tools. Unintentional dopants, together with vacancies and antisites that are mentioned in the paragraph above, constitute the main types of point defects that present in TMD single crystals. In recent years, STEM and scanning tunneling microscopy (STM) were employed as effective techniques to estimate point defect densities, and several studies found that the density of these point defects are usually on the order of 10^{13} - 10^{14} /cm². Recent efforts have also been made to reduce the defect density in as-grown TMD crystals. For example, Edelberg *et al.* developed a self-flux method that produced WSe₂ single crystals with defect concentration below 10^{11} /cm², which could pave the way to observing novel quantum phenomena or realizing certain device applications of 2D TMDs.¹⁰⁸⁻¹⁰⁹

Finally, we would like to discuss about <u>*TMD heterostructures*</u>, which can be categorized as 2D defects (in the case of vertical heterostructures) or 1D defects (in the case of in-plane heterostructures). TMD heterostructures are not only interesting candidates for 2D p-n junction devices (*e.g.*, FETs and photovoltaics), but also promising for novel device applications, such as twistronics and interlayer exciton optoelectronics that we introduced in Section 1.1.³² The preparation of <u>vertical heterostructures</u> mainly relies on mechanical transfer methods described in Section 1.2.2, because this method is capable for stacking any types of 2D materials together through vdW interaction, with the capability of controlling their twist angles. Bottom-up CVD synthesis has also been reported to grow vertical heterostructures, however the resulting TMD layers are usually epitaxially aligned, and thus the engineering of the rotational degree of freedom remains challenging.¹¹⁰⁻¹¹¹

To prepare *in-plane heterostructures*, CVD is likely to be the only viable approach to date, because mechanical transfer method is unable to seamlessly stitch dissimilar TMDs laterally

through covalent bonds. The CVD synthesis of in-plane heterojunction can be further classified into two types (*i.e.*, single-step and two-step routes). In the first case, in-plane TMD heterojunctions are synthesized within a single CVD reaction. For example, Gong *et al.* achieved the synthesis of MoS₂-WS₂ in-plane heterojunctions, taking advantage of the different vapor pressures of Mo/W precursors and different nucleation and growth rates of MoS₂ and WS₂.¹¹⁰ In the second case, TMD heterostructures are produced by two consecutive CVD processes, including the first synthesis of a layer of pristine TMDs followed by the lateral epitaxy of another TMDs in the second CVD step. Compared to single-step CVD, the two-step route provides a better spatial and size control of TMD components within the heterostructure.¹¹² However, in order to achieve controlled in-plane stitching of TMDs, it remains a challenge to promote the lateral growth of the second TMD components versus undesired vertical growth, and it is likely that growth temperature, precursor selection, and precursor-to-substrate distance are the key parameters to be controlled.



Figure 1-10: An overview of defects with different dimensionalities in 2D TMDs. (a) Typical zerodimensional (0D) defects. (b) Typical one-dimensional (1D) defects. (c) Typical 2D defects. Adapted from Ref. 13.

1.4 Research aims of this thesis

Motivated by the intriguing properties of 2D TMDs that are highly tunable through synthetic and post-synthetic defect engineering, this thesis focuses on the synthesis, defect engineering and related applications of 2D TMDs. Specifically, as the effective synthesis of TMDs is of great importance for their applications, in Chapter 2, we presented growth additive-mediated CVD methods that improved the yield, uniformity, and grain size of synthesized monolayers compared to conventional CVD approaches. The additive-mediated synthesis of ternary alloys $(Mo_xW_{1-x}S_2)$ and TMD in-plane heterostructures $(Mo_xW_{1-x}S_2 - W_xMo_{1-x}S_2)$ were also investigated in Chapter 2. These growth methods developed in Chapter 2 were utilized for preparing all types of TMD materials studied in further Chapters. Since all materials inevitably contain structural defects that affect material properties, CVD-synthesized 2D TMDs are not the exception. Thus, it is of great significance to understand the intrinsic defects and their effects on the properties of "nominally pristine" TMDs, and our related efforts are summarized in Chapter 3. Motivated by the effects of different substitutional dopants on the physicochemical properties of TMDs, in Chapter 4, we developed a liquid phase precursor-assisted approach that is capable for the *in situ* substitutional doping of TMDs to controllably tune their properties. We demonstrated the incorporation of various transition metal atoms, such as iron (Fe), rhenium (Re) and vanadium (V), into the lattice of TMD monolayers, and we expect this method to be extended to other types of doped TMDs and heterostructures that can promote the advancements of materials by design. Finally, in Chapter 5 of the thesis, we developed 2D TMD transfer techniques with improved cleanliness and deterministic transfer capability, enabling the coupling of CVD-synthesized TMDs with desired substrates for various applications, such as water desalination and DNA translocation.

As schematically illustrated in Figure 1-11, the scope of thesis is closely correlated with the materials science tetrahedron, which covers the four crucial aspects of 2D TMD materials:

structure, properties, processing, and performance. Characterization is the core of the material science tetrahedron that makes all the four projects of this thesis possible, because various characterization techniques are performed in order to provide understandings of the structural, optical, and/or electrical properties of TMD materials.



Figure 1-11: An overview of the research aims of this thesis. The research projects are closely associated with the materials science tetrahedron, covering the four crucial aspects of 2D TMDs: structure, properties, processing, and performance.

Chapter 2

Additive-Mediated Synthesis of TMD Monolayers

Parts of Sections 2.2 and 2.3 are based on a manuscript that is under preparation, for which I am an equally-contributing first author (Ref. [113]). Parts of reference [113] are reproduced (adapted) with permission from Ghafouri, Y.¹; Zhang, T.¹; Zhou, D.; Terrones, M.; Abate, Y., Intralayer Excitons of Graded Alloys and Nano-Interfaces of $Mo_xW_{1-x}S_2$ Monolayer Heterostructures. *Under preparation*. Note that ¹ represents equally-contributing authors.

Besides, parts of Section 2.3 are based on previously published work for which I am the first author (Ref. [77]). Parts of reference [77] are reproduced (adapted) with permission from Zhang, T.; Fujisawa, K.; Zhang, F.; Liu, M.; Lucking, M. C.; Gontijo, R. N.; Lei, Y.; Liu, H.; Crust, K.; Granzier-Nakajima, T.; Terrones, H.; Elías, A. L.; Terrones, M., Universal *In Situ* Substitutional Doping of Transition Metal Dichalcogenides by Liquid-Phase Precursor-Assisted Synthesis. *ACS Nano* **2020**, *14*, 4326-4335. Copyright 2020, American Chemical Society. (https://pubs.acs.org/doi/abs/10.1021/acsnano.9b09857)

2.1 The motivation of developing additive-mediated TMD synthesis approaches

As discussed in Chapter 1, CVD has been an effective method for the synthesis of a variety of high-quality 2D TMDs that are suitable for electronic and optoelectronic applications. However, two main drawbacks exist in the conventional powder-based CVD synthesis using metal or metal oxide as precursors: (1) many metal or metal oxide precursors (*e.g.*, Nb-, Ti-, and W-based) have very high melting temperatures and low vapor pressure, which largely limits the precursor vapor flux during the CVD process and results in a low yield; (2) in order to guarantee the formation of large-area uniform TMD monolayers without additional layers or atom clusters on top, a high lateral growth rate is required. It remains a challenge to achieve such preferential lateral growth while suppressing vertical growth during CVD.¹¹⁴ These reasons have triggered the modification of conventional CVD to improve the yield, uniformity, and grain size of synthesized monolayers. One of the most effective and intriguing methods is the addition of rationally selected growth additives during the CVD process, which can assist the growth of TMDs by altering the reaction pathways, serving as seeding promoters, and/or enhance the adsorption of precursors on the growth substrate.¹¹⁵⁻¹¹⁶

Alkali metal halides (MX, where M = Na, K; X = Cl, Br, I) are a group of inorganic compounds that have been shown to be helpful for the CVD synthesis of TMDs. In 2015, Li *et al.* reported the atmospheric-pressure CVD (APCVD) synthesis of TMD monolayers using mixed WO_{2.9} and alkali metal halide powders as the precursor (Figure 2-1). Single-crystalline WS₂ and WSe₂ monolayers with domain sizes larger than 100 μ m were grown at a moderate temperature (optimum temperature at ~825 °C).¹¹⁷ Since then, halide-assisted CVD has been widely used as a powerful method for TMD synthesis. For example, Zhou *et al.* generalized this approach and synthesized a wide variety of TMD-based compounds, including 32 binary TMDs, 13 TMD alloys, and 2 heterostructures, which largely expands the family of monolayer TMDs that can be synthesized by CVD.¹¹⁴ Studies have also focused on elucidating the roles of alkali metal halides in TMD growth. Although a systematic understanding of the mechanisms is still required, recently literatures have shown that both the alkali metal cation and halide anion can assist the synthesis process. Taking NaCl-assisted growth as an example, as shown in Figures 2-2 (a) and (b), density functional theory (DFT) calculations revealed that Na⁺ cations can adsorb at edges of TMDs, which function as a catalyst that reduces the energy barrier for the attachment of S atoms at TMD edges,

and thus increase the growth rate.¹¹⁸ Li *et al.* also investigated the role of during TMD growth, and the results indicated edge-adsorbed Na⁺ works as a surfactant which mediates the layer-by-layer (Frank-van der Merwe) growth.¹¹⁹ Regarding the role of anions, it was found that various metal oxide precursors can react with alkali metal halides to form volatile transition metal oxyhalides *(e.g.*, MoO₂Cl₂), which increases the mass flux of metal precursors and facilitate the growth (Figure 2-2 (c) and (d)). Besides, DFT calculation indicated the sulfurization of MoO₂Cl₂ is energetically favored, compared to that of MoO₃, further confirming that TMD growth can be promoted by oxyhalide formation.¹¹⁴



Figure 2-1: Halide-assisted CVD of WS₂ and WSe₂ monolayers. (a) Schematic illustration of the halideassisted CVD growth setup. (b–e) Optical microscopy images of WSe₂ monolayers grown with (b) KCl, (c) KBr, (d) KI, (e) NaCl as the growth promoters at 825 °C. Insets of (b), (c) and (e) are high-magnification optical images of polygon-shaped crystals with hexagonal symmetry. Inset of (d) is an optical image of WSe₂ monolayers grown at 700 °C. (f) Optical image of triangular WS₂ monolayers grown with NaCl as the growth promoter at 825 °C with ~50 mg S. (g) Optical image of triangular WS₂ monolayers grown by KI-assisted CVD at 750 °C. Inset is an optical image of WS₂ grown at 700 °C. (h) Optical image of WSe₂ monolayers grown at 850 °C. (i) Optical image of hexagonal WS₂ monolayers grown at 825 °C with ~10 mg S. (j) Optical image of WS₂ monolayers grown at 850 °C. Adapted from Ref. 117.



Figure 2-2: The roles of sodium and chlorine from alkali metal halides in promoting the growth of TMD monolayers. (a)-(b) DFT-calculated energy diagrams for MoS_2 growth along the S-terminated edges, (a) without and (b) with Na adsorption. Adapted from Ref. 118. (c) The proposed process of the added salt decreasing the melting point of the precursors. (d) The proposed growth process of the 2D atomic layer with intermediate product, as well as optical images of several 2D TMDs synthesized by salt-assisted CVD. Adapted from Ref. 114.

Another important type of growth additive is the "seeding promoters", and the commonly used ones include reduced graphene oxide (rGO), perylene-3,4,9,10-tetracarboxylic acid tetrapotassium salts (PTAS), perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA), and sodium cholate.^{60, 120-121} Typically, these seeding promoters are dissolved in H₂O or organic solvents, and then coated on either the growth substrate or another substrate in the vicinity (seeding substrate). Afterwards, conventional CVD process is carried out with commonly used metal oxide and

chalcogen precursors. The reasons for applying these promoters during the CVD process include: 1) these molecules can serve as heterogeneous nucleation centers for TMDs and initiate the growth ; 2) these molecules typically possess aromatic structures, which have been reported to increase the surface adhesion strength between TMDs and the growth substrate, and thus result in the enhanced lateral growth of TMD monolayers.¹¹⁶ It is worth noting that the use of seeding promoters not only improves the yield of monolayer TMDs, but also can enable the patterned growth of TMD at selective locations. For example, it was found that PTAS seeding promoters tend to be preferentially deposited on hydrophilic substrates, rather than hydrophobic substrates or the surface of 2D materials.¹²² Therefore, selected-area growth of TMDs can be achieved by patterning the hydrophilicity of the corresponding substrate regions by O_2 plasma treatment (Figure 2-3).¹¹⁶ As demonstrated by Guo et al., PTAS-assisted CVD synthesis was performed on a SiO₂/Si substrate with enhanced hydrophilicity in selected regions that were patterned by photolithography and subsequent O₂ plasma treatment. During the synthesis, PTAS molecules preferentially adsorbed on patterned hydrophilic regions on the substrate, which promoted the growth in those areas and formed patterned MoS₂ monolayers (Figure 2-3 (b-d)). Notably, patterned MoS₂ can be transferred to arbitrary substrates using etchant-free methods, such as PDMS-based dry-transfer and waterassisted transfer, preserving the surface properties of patterned SiO₂/Si substrate. Thus, the patterned substrate can work as a "master template" and be reused for a next cycle of CVD process.¹¹⁶

Based on the previous literature mentioned above, it can be concluded that the use of growth promoters during TMD synthesis can improve the yield and thickness uniformity, increase the grain size, expand the library of CVD-synthesized TMDs, and achieve the patterned growth. In terms of our work, inspired by the pioneering study by Li *et al.* of using alkali metal halides to enhance the synthesis of TMDs¹¹⁷, in 2016, we started working independently on the CVD-

synthesis of WS₂, MoS₂, as well as alloyed Mo_xW_{1-x}S₂ monolayers using NaBr as a growth additive. Our results will be presented in Section 2.2 of the thesis. In addition, aiming at tuning the interface width between MoS₂ and WS₂ (*i.e.*, the formation of sharp interfaces versus Mo_xW_{1-x}S₂ alloys), we explored the additive-mediated growth of Mo_xW_{1-x}S₂-W_xMo_{1-x}S₂ in-plane heterostructures. In this case, a liquid-phase precursor-based synthesis approach was developed, with sodium cholate (C₂₄H₃₉NaO₅) as a growth additive. The rationale and details of the synthesis and characterization of Mo_xW_{1-x}S₂-W_xMo_{1-x}S₂ in-plane heterostructures will be presented in Section 2.3.



Figure 2-3: PTAS-assisted patterned growth of MoS_2 nanostructures. (a) Schematic representation of the process for the direct growth of MoS_2 nanostructures by PTAS-promoted growth and substrate engineering. (b) A typical optical image of a monolayer MoS_2 wave array. (c) An optical image of a monolayer MoS_2 wave film that grows at the opposite locations when a negative photoresist was used for the wave pattern in b. (d) AFM image of a monolayer MoS_2 kirigami structure, showing the flat surface and ordered edge morphology. (e) Schematic illustration of repeated growth procedures for directly grown MoS_2 patterns. Adapted from Ref. 116.

2.2 Alkali metal halides-assisted CVD synthesis of TMDs

2.2.1 Alkali metal halides-assisted CVD of pristine WS₂

As introduced in Section 2.1, alkali metal halides-assisted CVD has recently emerged as a powerful method for the synthesis of a variety of 2D TMDs. In order to synthesize pristine WS₂ monolayers, in this Section we employed an APCVD method using WO₃ and S powders as precursors, and NaBr as a growth promoter. Schematics of the synthesis setup and temperature profiles are depicted in Figure 2-4. Briefly, WO₃ and NaBr powders were mixed in a 10:1 ratio by weight and placed inside a porcelain boat. A piece of SiO₂/Si wafer was placed on top of the boat with the polished side facing down, serving as the growth substrate. During the growth, the furnace was ramped up to 800-950 °C in 30 min, and then held for 10 min. Meanwhile, S powder was heated up to 220 °C separately by a heating belt, and argon (100 sccm) was used as a carrier gas to transport S vapor to the center of furnace. The as-synthesized WS₂ flakes predominantly exhibit triangular or truncated triangular morphologies with large domain sizes (~100 µm or more) (Figures 2-5(a)-(c)). Compared to our previous results on WS₂ monolayer synthesis without applying growth promoters²³, introducing NaBr during the growth significantly increased the yield and grain size of synthesized WS₂ flakes. With the addition of NaBr, possible CVD reaction routes could be¹¹⁴:

$$2WO_{3}(s) + 2NaCl(s) \rightarrow WO_{2}Cl_{2}(g) + Na_{2}WO_{4}(s)$$
(1)
$$WO_{2}Cl_{2}(g) + 3S(g) \rightarrow WS_{2}(s) + SO_{2}(g) + Cl_{2}(g)$$
(2)

It is worth noting that tungsten oxyhalides (such as WO₂Cl₂) have largely increased vapor pressure compared to WO₃, which is likely to contribute to improved lateral growth. In addition, Na⁺ may function as a surfactant that promotes the lateral growth, leading to higher growth rate and increased grain size (up to millimeter scale).^{114, 119}



Figure 2-4: Schematics of the (a) NaBr-assisted synthesis setup and (b) temperature profiles for growing 2D WS₂. The synthesis experiments were typically carried out at 800 - 950 °C for 10 min.

To optimize the TMD synthesis, we carried out CVD reaction at different growth temperatures (*i.e.*, 800 °C, 900 °C, and 950 °C) with other experimental parameters being consistent, and examined the growth outcomes by optical microscopy. Interestingly, a clear and reproducible shape evolution as a function of growth temperature was found. Specifically, the growth at 800 °C mainly yield triangular monolayers (Figure 2-5 (a)); the growth at 900 °C predominantly lead to truncated triangular monolayer (Figure 2-5 (b)); while the growth at 950 °C result in a mixture of monolayer flakes and bilayers flakes with truncated triangular shape (Figure 2-5 (c)). Atomic force microscopy (AFM) was used to confirm the layer number of a typical WS₂ flake synthesized at 950 °C (Figures 2-5 (d) and (e)). The surface height profile along the white line in Figure 2-5 (e) shows step heights of 0.65-1 nm across each step on the flake, indicating that the flake contains monolayer, bilayer, and trilayer regions from edge towards center.¹²³ The preferential formation of WS₂ bilayers and multilayers at higher temperatures is in agreement with the literature, which can be

understood as the nucleation and growth of secondary layers on WS₂ is thermodynamically favorable at elevated temperatures.^{110, 124} In addition, the triangular-to-truncated triangular shape evolution at higher temperatures is an indication that the growth rate of different edges (W-zigzag (W-zz) and S-zigzag (S-zz)) varies as a function of temperature, which may be associated with temperature-dependent variations of W and S chemical potentials.¹²⁵



Figure 2-5: 2D WS₂ synthesized at various temperatures. (a-c) Typical optical images of WS₂ flakes synthesized at (a) 800 °C, (b) 900 °C, and (c) 950 °C. (d-e) Optical image of multilayer WS₂ synthesized at 950 °C, and the corresponding AFM image and surface height profile.

We performed a series of optical characterization, including fluorescence microscopy, Raman, and PL spectroscopy, to evaluate the structural and optical quality of monolayer WS₂ synthesized by NaBr-assisted CVD. Figures 2-6 (a) and (b) show optical and fluorescence microscopy images of a typical monolayer WS₂ grown at 800 °C. Overall, the flake exhibits high fluorescence intensity with edge enhancement, which agrees with previous results and it is likely induced by edge adsorbates or a higher density of sulfur vacancies.²³⁻²⁴ Three narrow lines with reduced fluorescence intensity were also observed in the fluorescence image, and their origin were investigated and will be discussed in Chapter 3 of the thesis. Finally, Raman and PL from assynthesized monolayer WS₂ were measured using 488 nm laser excitation. The Raman spectrum (Figure 2-6 (c)) contains the in-plane E' mode, out-of-plane A₁' mode, and 2LA(M) mode that is overlapped with the E' mode, which match well with Raman peaks of 1H-WS₂ monolayers.¹²⁶ The PL spectrum of monolayer WS₂ (Figure 2-6 (d)) exhibits a sharp PL peak (FWHM ~ 40 meV at room temperature) that originates from the direct bandgap excitonic transition, indicating the assynthesized WS₂ possesses good optical quality.



Figure 2-6: Optical characterization of monolayer WS_2 . (a) An optical image and (b) the corresponding fluorescence image of a triangular WS_2 flake synthesized at 800 °C. (c) Raman and (d) PL spectra of monolayer WS_2 synthesized by NaBr-assisted CVD, matching well with previously reported optical signatures of WS_2 monolayers.

2.2.2 Alkali metal halides-assisted CVD of alloyed MoxW1-xS2 monolayers

To explore the capability of alkali metal halide-assisted APCVD for the synthesis of 2D TMDs beyond binary MX₂ compounds, we used the mixed MoS₂ and WO₃ powders as transition metal precursors and NaBr as a growth promoter, aiming at synthesizing ternary alloys of Mo_xW₁. xS_2 (Figure 2-7(a)). The as-synthesized material (an optical image is shown in Figure 2-7(b)) was characterized by aberration-corrected high-resolution scanning transmission electron microscopy (AC-HRSTEM) for atomic structure analysis. Figures 2-7(c)-(e) show high-angle annular dark field (HAADF)-STEM images obtained from different regions (*i.e.*, center, middle, and edge of a single flake). In this imaging mode, the ADF intensity of atoms and their atomic Z-numbers have a positive correlation, and thus Mo atoms display darker contrast due to their relative lower Z-number and can be differentiated from W atoms.¹²⁷ Therefore, the alloying of Mo and W in the assynthesized materials is confirmed. Additionally, it can be observed that center regions have a higher Mo (darker dots) concentration, whereas the edge regions are dominated by W (brighter dots). By statistical analysis of HAADF-STEM images shown in Figures 2-7(c)-(e), the compositions of these three areas are: Mo_{0.54}W_{0.46}S₂ (center), Mo_{0.24}W_{0.76}S₂ (middle), and Mo_{0.01}W_{0.99}S₂ (edge).



Figure 2-7: Synthesis and STEM characterization of alloyed monolayer $Mo_xW_{1-x}S_2$. (a) Schematic of the powder-based CVD method with the addition of NaBr growth promoter, which yields alloyed monolayer $Mo_xW_{1-x}S_2$. (b) An optical image of alloyed monolayer $Mo_xW_{1-x}S_2$ synthesized on SiO₂/Si. (c)-(e) Typical HAADF-STEM images taken from (c) center, (d) middle, and (e) edge regions of the composition-graded alloy.

In order to further understand the structural and optical properties of as-synthesized $Mo_xW_{1-x}S_2$ alloys, we performed far-field Raman and PL measurements. Figures 2-8(b) and (c) illustrate the Raman and PL spectra acquired from different regions of the $Mo_xW_{1-x}S_2$ alloys, respectively. In the Raman spectra, MoS_2 -like vibrational modes dominate in center regions and WS_2 -like vibrational modes are prominent in edge regions, while the middle regions exhibit a combination of both sets of modes. The PL spectra of $Mo_xW_{1-x}S_2$ alloy constantly displayed a single peak at different locations, and a continuous blue-shift from center (~1.85 eV) to edge (~1.95 eV) was observed (Figure 2-8(c)). Thus, these results suggest that our sample may have a continuous composition gradient from center to edge, similar to graded TMD alloys reported previously.¹²⁸⁻¹²⁹ To verify this hypothesis, Raman and PL line scans were performed on a representative alloyed monolayer $Mo_xW_{1-x}S_2$ flake along the scan direction marked in Figure 2-8(d). Figure 2-8(e) shows

the Raman intensity line scans of WS₂ E' and 2LA(M) modes (black line) as well as MoS₂ E' mode (red line), and both of these modes display a gradual change along the scan direction, which unambiguously indicates a composition gradient from center to edge of the flake. We then analyzed the PL line scan results and plotted the PL peak positions as a function of location (Figure 2-8(f)). As a consequence of the composition gradient confirmed by Raman line scan, the optical band gap of the alloyed Mo_xW_{1-x}S₂ was continuously modulated due to the lateral variation of degree of alloying, indicated by the gradual change in PL peak positions that is consistent with previous results on graded TMD alloys.¹²⁹⁻¹³⁰ This feature makes our graded alloys Mo_xW_{1-x}S₂ intriguing for the investigation of composition-dependent properties, such as excitonic properties, thermal properties, and spin-orbit coupling, within a single flake.¹³¹⁻¹³²



Figure 2-8: Far-field optical characterization of alloyed monolayer $Mo_xW_{1-x}S_2$. (a) Schematic of the structure of alloyed monolayer $Mo_xW_{1-x}S_2$. (b) Raman and (c) PL spectra of various regions in alloyed monolayer $Mo_xW_{1-x}S_2$. (d) Optical image of the $Mo_xW_{1-x}S_2$ flake used for Raman and PL line scans (the scan direction is marked by the black arrow). (e) Raman intensity profiles of WS₂ E' and 2LA(M) modes (black) and MoS₂ E' mode (red line) as a function of distance along the scan direction. Both of the Raman modes display gradual changes with scan direction. (f) The evolution of PL peak positions of alloyed monolayer Mo_xW_1 . xS_2 as a function of distance along the scan direction. The gradual shift in the peak position along the scan direction indicates spatially varying optical band gaps within the material.

2.3 Liquid-phase precursor-assisted synthesis of in-plane Mo_xW_{1-x}S₂-W_xMo_{1-x}S₂ heterostructures

As we highlighted in Chapter 1, liquid phase precursor-assisted CVD has been shown as a powerful method for synthesizing single-crystalline monolayers and continuous films of TMDs. In this context, we further explored the possibility of utilizing liquid-phase precursor-assisted method to synthesize 2D heterostructures. Our developed approach involves the spin-coating of an aqueous solution containing water-soluble Mo and W precursors (ammonium heptamolybdate (AHM, $(NH_4)_6Mo_7O_{24}$ and ammonium metatungstate (AMT, $(NH_4)_6H_2W_{12}O_{40}$), as well as sodium cholate $(C_{24}H_{39}NaO_5)$ onto a SiO₂/Si substrate, followed by a controlled high temperature sulfurization process (Figure 2-9(a)). In our case, Mo and W precursors are well mixed before spin-coating, which decreases the effect of gas-phase diffusion of precursor species, thus reducing the influence of kinetic factors on the growth outcomes. Thus, the control of thermodynamic factors become more significant in order to acquire heterostructures with clearly resolved interfaces. In a previous work by Chen et al., it has been suggested that the synthesis reaction of MoS₂ using AHM initiates at temperatures lower than that of AMT-synthesized WS₂. Thus, in-plane MoS₂-WS₂ heterostructures can be produced using a two-step temperature ramp.¹³³ In our experiment, we used a similar two-step ramp strategy, in which we first ramped the furnace temperature to 700 °C and held for 10 min for the growth of MoS₂, and subsequently increased the temperature to 800 °C and held for another 10 min for achieving the lateral epitaxy of WS₂.⁷⁷

Additionally, it is important to point out the role of the growth additive, sodium cholate, on the synthesis process. We believe that sodium cholate mainly plays three roles: (1) sodium cholate works as surfactant, which has been found to help with the adhesion of precursors onto SiO_2/Si substrates during spin-coating¹³⁴; (2) recent studies have shown that both aromatic molecules and alkali metal-containing compounds can promote the lateral growth of TMDs.^{121, 135}

Sodium cholate possesses aromatic structures with Na⁺ cations, which have been reported as growth promoters for acquiring high-coverage monolayer TMDs.^{112, 136}

An optical image of typical as-grown in-plane heterostructures is displayed in Figure 2-9(b), showing triangular morphologies with distinct optical contrast between center and edge regions. To examine the compositions of different regions within the flake, we performed AC-HRSTEM characterization. Figures 2-9(c)-(e) show HAADF-STEM images obtained from center, interface, and edge regions of a typical flake. It was observed that the center and edge regions are predominantly MoS₂ and WS₂ with a small amount of W and Mo dopants, respectively, and the interface region is alloyed Mo_xW_{1-x}S₂ with intermixed of Mo and W atoms in the lattice. Because of the presence of W and Mo dopants in the Mo-rich and W-rich regions, we choose to name the synthesized heterostructures as "Mo_xW_{1-x}S₂-W_xMo_{1-x}S₂" instead of "MoS₂-WS₂" for accuracy. The sharpness of the interface region was further examined by low-magnification STEM (Figure 2-10), indicating an alloyed 2D interface of approximately 20-100 nm width.



Figure 2-9: Synthesis and STEM Characterization of monolayer $Mo_xW_{1-x}S_2-W_xMo_{1-x}S_2$ in-plane heterostructures. (a) Schematic of the liquid-phase precursor-assisted growth method that yields monolayer $Mo_xW_{1-x}S_2-W_xMo_{1-x}S_2$ in-plane heterostructures. (b) An optical image of monolayer $Mo_xW_{1-x}S_2-W_xMo_{1-x}S_2$ in-plane heterostructures (c) An optical HAADF-STEM images taken from (c) center, (d) interface, and (e) edge regions of the heterostructures.



Figure 2-10: STEM characterization of the interface in monolayer $Mo_xW_{1-x}S_2-W_xMo_{1-x}S_2$ in-plane heterostructures. (a) Low-magnification and (b) zoomed-in STEM images, revealing an approximate interface with of ~20-100 nm.

We then performed far-field Raman and PL at center, interface, and edge regions of the $Mo_xW_{1-x}S_2-W_xMo_{1-x}S_2$ heterostructures. Similar to $Mo_xW_{1-x}S_2$ alloys studied in Section 2.2, $Mo_xW_{1-x}S_2-W_xMo_{1-x}S_2$ heterostructures also exhibit varied Raman signatures depending on probed regions, with MoS_2 -like and WS_2 -like vibrational modes dominating in center and edge regions (Figure 2-11(b)). Nevertheless, the PL of $Mo_xW_{1-x}S_2-W_xMo_{1-x}S_2$ heterostructures appeared distinct from that of $Mo_xW_{1-x}S_2$ alloys (Figure 2-11(c)). Instead of a single exciton peak with continuous varying energy, two separate peaks that correspond to MoS_2 -like PL and WS_2 -like PL were observed at the interface of $Mo_xW_{1-x}S_2-W_xMo_{1-x}S_2$ heterostructures. The PL signature corroborates the existence of in-plane interfaces within the material, which clearly separate Mo-rich center and W-rich edge regions and allow two distinct PL peaks to be observed upon laser excitation.

For a direct comparison of the structural and optical property differences between $Mo_xW_{1-x}S_2-W_xMo_{1-x}S_2$ in-plane heterostructures and the alloyed $Mo_xW_{1-x}S_2$, Raman and PL line scans were performed on a representative flake of $Mo_xW_{1-x}S_2-W_xMo_{1-x}S_2$ along the scan direction marked in Figure 2-11(d), and plotted in Figures 2-11(e) and (f) in similar ways as the case of $Mo_xW_{1-x}S_2$ alloys that we presented in Figure 2-8 (e) and (f) of Section 2.2.2. As expected, it was observed from Figure 2-11(e) that edge regions are dominated by Raman modes of WS₂, while the MoS₂ E'

mode is negligible. On the contrary, the center regions are dominated by Raman modes of MoS₂. The regions with coexisted MoS₂- and WS₂-Raman modes were highlighted in green, which represent interface regions. The PL peak positions as a function of location were plotted in Figure 2-11(f), which showed WS₂-like PL emission energy (~1.94-1.96 eV) at edge regions, and MoS₂-like PL emission energy (~1.82-1.86 eV) at center regions. Similar to the Raman line scan results, there are interface regions with both MoS₂- and WS₂-like PL peaks (highlighted in green). It should be noted that the interface width (~4 μ m) observed in Raman and PL line scans is much larger than TEM-measured result (~20-100 nm), due to the larger laser spot size compared to the interface width that limits the resolution of far-field Raman and PL line scans, and thus the interface cannot be well resolved. Nevertheless, the clear WS₂-to-MoS₂ transition from edge to center regions, observed in both Raman and PL line scans, confirms the existence of interfaces within the sample.

To summarize, this Section demonstrated a one-step synthesis of in-plane TMD heterostructures using a liquid-phase precursor-assisted approach. Compared to previous one-step routes using powder precursors, our approach is based on the spin coating and sulfurization of homogeneously mixed precursor solution, which eliminates the precursor-to-substrate distance variations and is likely to result in a more uniform growth of heterostructures throughout the substrate. Our method may be further applied to the synthesis of in-plane heterostructures based on other members of the 2D TMD family, promising for constructing in-plane p-n junctions for future monolayer electronics and optoelectronics, such as diodes and photovoltaics.¹³⁷



Figure 2-11: Far-field optical characterization of monolayer $Mo_xW_{1-x}S_2-W_xMo_{1-x}S_2$ in-plane heterostructures. (a) Schematic of the structure of monolayer $Mo_xW_{1-x}S_2-W_xMo_{1-x}S_2$ in-plane heterostructures. (b) Raman and (c) PL spectra of various regions in monolayer $Mo_xW_{1-x}S_2-W_xMo_{1-x}S_2$ inplane heterostructures. (d) Optical microscopy image of the $Mo_xW_{1-x}S_2$ - $W_xMo_{1-x}S_2$ flake used for Raman and PL line scans (the scan direction is marked by the black arrow). (e) Raman intensity profiles of WS_2 E' and 2LA(M) modes (black) and MoS_2 E' mode (red line) as a function of distance along the scan direction. (f) The evolution of PL peak positions of monolayer $Mo_xW_{1-x}S_2-W_xMo_{1-x}S_2$ in-plane heterostructures as a function of distance along the scan direction. Note that two separate PL emission peaks can be observed at interface regions, and the peak position of the one with relatively lower intensity is marked as red dots.

2.4 Growth mechanisms of alloyed Mo_xW_{1-x}S₂ and in-plane Mo_xW_{1-x}S₂-W_xMo_{1-x}S₂ heterostructures

It is very interesting that the two approaches investigated in this Chapter result in large differences in the composition of as-synthesized monolayers. Especially, the MoS₂-WS₂ interface sharpness can be tuned from ~20-100 nm width (liquid phase precursor-assisted method) to fully graded (alkali metal halide-assisted CVD method). Thus, it is necessary to discuss about possible growth mechanisms that lead to this difference. In the liquid phase precursor-assisted CVD method, AHM and AMT were applied as precursors, and it has been previously reported that the

sulfurization of AHM can initiate at lower temperatures compared to the sulfurization of AMT.¹³³ Besides, MoS_2 is expected to have a much higher nucleation and growth rate than WS_2 during the CVD growth.¹¹⁰ These reasons may explain the sequential growth of a MoS₂-rich center and a WS₂rich region at the edge, forming in-plane heterostructures. While in the alkali metal halide-assisted CVD method, powders of MoS₂ and WO₃ are used as Mo- and W- precursors and an alkali metal halide salt (NaBr) is employed as a growth promoter. In a previous study, Modtland et al. reported the chemical vapor transport (CVT) growth of high-quality WS_2 monolayers using mixed WS_2 and NaCl powders, and the Cl⁻ in NaCl functioned as a transport agent that can react with WS₂ powder to form gaseous tungsten chloride (WCl_x) and sulfur.¹³⁸ Thus, it is speculated that in our case, Brplays a similar role in promoting the growth of MoS₂ monolayers by serving as a transport agent for MoS₂ powders. On the other hand, it has been suggested that NaBr can react with WO₃ precursor to form volatile oxyhalides (WO_xBr_y), which largely increases the vapor pressure of the W source and enhances the growth of WS₂.^{101, 117} Based on these results highlighting the role of halides in the synthesis of TMDs, we believe that Br ion in our CVD reaction simultaneously promotes the growth of MoS₂ and WS₂ monolayers, leading to the intermixing of Mo and W and the formation of Mo_xW_{1-x}S₂ alloys. Although more detailed studies are desired to elucidate the thermodynamics and kinetics of these growth methods and to understand roles of different growth promoters, our results clearly show the possibility of engineering the composition and interface properties of 2D TMDs by proper combinations of growth setup design, precursors, and growth promoters.

2.5 Conclusions

In summary, two different additive-mediated CVD approaches were developed in Chapter 2 for the synthesis of pristine WS₂, MoS₂, alloyed Mo_xW_{1-x}S₂, and Mo_xW_{1-x}S₂-W_xMo_{1-x}S₂ in-plane

heterostructure monolayers. The use of growth additives was found to significantly enhance the grain size, yield, and reproducibility, without compromising the structural and optical properties of as-synthesized monolayers. The additive-mediated methods developed in this Chapter were further used to prepare different types of pristine/doped TMDs and their heterostructures, which will be studied and discussed in the following Chapters of my thesis. Our developed synthesis methods not only reliably provide the materials of interest throughout my thesis, but also pave the way for growing large-area 2D TMD monolayers and creating 2D in-plane heterointerfaces. Future work will be focused on further optimizing experimental parameters to obtain spatially homogeneous Mo_xW_{1-x}S₂ alloys with tunable composition and/or in-plane heterostructures with atomically sharp interfaces. The control of relative vapor pressures of Mo/W precursors may be the key, since the formation of homogeneous alloys would require steady and comparable vapor pressures of Mo and W precursors is preferred for the formation of sharp heterointerfaces.^{133, 139} Experimentally, it is anticipated that the furnace temperature ramp, as well as the relative positions of Mo precursor, W precursor and growth promoters, can be tuned to achieve this goal.

Chapter 3

Understanding Intrinsic Defects and Their Influences on the Properties of CVD-Grown 2D TMDs

Section 3.2.1 is based on parts of a manuscript that is under preparation, for which I am a co-author and am contributing to this part (Ref. [140]). Parts of reference [140] are reproduced (adapted) with permission from Rosa, B. L. T.; Fujisawa, K.; Santos, J. C. C.; Zhang, T.; Sousa, F. B.; Barbosa, T. C.; Lafetá, L.; Ramos, S. L. L. M.; Carvalho, B. R.; Neves, B. R. A.; Terrones, M.; Malard, L. M., Understanding the Impact of Defects on the Optical Properties of CVD-Grown WS₂. *Under preparation*.

Section 3.2.2 of this chapter is based on parts of previously published work for which I am a co-author and am contributing to this part (Ref. [141]). Parts of reference [141] are reproduced (adapted) with permission from Murray, W.; Lucking, M.; Kahn, E.; Zhang, T.; Fujisawa, K.; Perea-Lopez, N.; Elias, A. L.; Terrones, H.; Terrones, M.; Liu, Z., Second Harmonic Generation in Two-Dimensional Transition Metal Dichalcogenides with Growth and Post-Synthesis Defects. *2D Mater.* **2020**, *7*, 045020. Copyright 2020, IOP Publishing. (https://iopscience.iop.org/article/10.1088/2053-1583/aba564)

In addition, Section 3.3 of this chapter is based on previously published work for which I am a co-author and am contributing to this part (Ref. [142]). Parts of reference [142] are reproduced (adapted) with permission from Cochrane, K. A.; Zhang, T.; Kozhakhmetov, A.; Lee, J. H.; Zhang, F.; Dong, C.; Neaton, J. B.; Robinson, J. A.; Terrones, M.; Bargioni, A. W.; Schuler, B., Intentional Carbon Doping Reveals CH as an Abundant Charged Impurity in Nominally Undoped Synthetic WS₂ and WSe₂. *2D Mater.* **2020**, *7*, 031003. Copyright 2020, IOP Publishing. (https://iopscience.iop.org/article/10.1088/2053-1583/ab8543)

3.1 The motivation of investigating intrinsic defects and inhomogeneity in CVD TMDs

Defects play very important roles in affecting the mechanical, electronic, optical, and chemical properties of 2D TMDs. As we described in Chapter 1.3 of the thesis, in many cases, controllably introduced defects, such as vacancies, grain boundaries, and heterostacks, can lead to enhanced functional device applications and/or novel physicochemical phenomena.¹³ However, unfortunately, defects are often detrimental to the optical and electronic properties of TMDs.^{67,97} Especially, unintentionally introduced defects can present in as-prepared TMDs in various forms (e.g., vacancies, impurity atoms, line defects, grain boundaries, layer number variations, wrinkles), which result in undesired sample-to-sample variations in properties and pose significant challenges for the large-scale integration of TMDs into commercial applications.¹³ For example, McCreary et al. investigated Raman and PL signatures of WS₂ monolayers obtained by three different methods: exfoliated monolayers from CVT-grown single crystals, triangular monolayer islands grown using ambient-pressure CVD, and continuous films grown by low-pressure CVD. The results show that the intensity of defect-activated LA(M) Raman mode, PL intensity, PL peak position, and full width at half maximum (FWHM) noticeably vary among different samples, indicating that different TMD preparation methods and growth parameters lead to variations in defect densities.¹⁴³ In this context, from the material synthesis perspective, it becomes an important task to optimize the synthesis process and minimize unintentional defects with a large-scale uniformity. In terms of material characterization, it is desired to characterize and identify different types of defects in TMDs, which will provide invaluable information for establishing structure-property relationships of these defects and understanding sources that may introduce them, and will be a great step towards reliably controlling defects in synthetic 2D TMDs.

Previous studies as well as Chapter 2 of this thesis have demonstrated that CVD method can controllably synthesize single-crystalline flakes of TMD monolayers by using desirable growth parameters. Nevertheless, although these monolayer single crystals are free of 1D and 2D defects (e.g., grain boundaries, additional layers), inhomogeneity still presents in these CVD-grown flakes, which is likely induced by either 0D defects in TMDs or extrinsic disorders (e.g., charge transfer between TMDs and substrate, strain, etc.).^{23, 144} Recently, fluorescence microscopy and PL spectroscopy have been employed as rapid and non-destructive techniques to visualize inhomogeneity in optical properties of TMDs. As displayed in Figure 3-1, many research groups around the world have reported the spatially inhomogeneous optical properties in CVD-grown TMDs. In single-crystalline triangular TMD flakes, edge-enhanced PL emission (Figure 3-1(a)), concentric fluorescence patterns (Figure 3-1(b)), and irregular center-to-edge PL distributions (Figure 3-1(d)), were observed depending on sample growth conditions. At reduced temperatures (77 K or 4 K), additional exciton species, such as defect-bound exciton and biexciton (Figure 3-1 (c)) emerged at edge regions of some TMD flakes.^{23, 60} In some cases, even more interesting inhomogeneous PL patterns were observed in certain flakes, such as the presence of grain boundaries within a "seemingly single-crystalline" triangular MoS₂ flake (Figure 3-1 (e))¹⁴⁵, and the segmented PL pattern in hexagonal WS₂ monolayers (Figure 3-1 (f)).²⁵⁻²⁶ Although these luminescence patterns seem fascinating, the reality is that the inhomogeneous PL quantum yield and/or exciton species have to be induced by certain types of disorders. The reasons that lead to non-uniform optical properties in CVD-grown TMDs are important to be understood, because it will shed light on the structure-property relationship of certain types of disorder/defects and further trigger the development of TMD defect engineering approaches.



Figure 3-1: Examples of inhomogeneous optical properties in CVD-synthesized TMD monolayers. (a) Edge-enhanced PL in WS₂ monolayers. Adapted from Ref. 22. (b) Concentric fluorescence patterns in WS₂ monolayers. Adapted from Ref. 146. (c) Biexciton emission from WS₂ edges observed at 77 K. Adapted from Ref. 60. (d) Center-to-edge PL variations in WS₂ monolayers. Adapted from Ref. 147. (e) "Wellhidden" grain boundaries in MoS₂ monolayers grown by a two-dimensional core-shell growth mode. Adapted from Ref. 145. (f) Hexagonal WS₂ monolayers with PL segmentation. Adapted from Ref. 26.

In previous work, Kelvin probe force microscopy (KPFM), PL, STEM, AFM, and scanning tunneling microscopy/spectroscopy (STM/STS) have been employed to characterize the inhomogeneity in TMDs. Carozo *et al.* systematically studied the origins and spatial distributions of defect-bound excitons within monolayer WS₂ flakes by a combination of temperature- and power-dependent PL spectroscopy, atomic-resolution STEM, and DFT calculations. It was found that a higher density of V_8 present at WS₂ edges, which is responsible for bound-exciton emission.²³ Wang *et al.* used KPFM and PeakForce tunneling atomic force microscopy (PF-TUNA) to map the work function variations and conductivity variations throughout a single monolayer WS₂ flake, respectively. The KPFM and PF-TUNA mappings were further correlated with PL mapping, and it was found that a lower work function region in the flake correlated to lower electronic conductivity and higher PL intensity. Their further STEM imaging and DFT calculation revealed that the presence of antisites defects S2_w is likely to cause the PL variation.¹⁴⁷ In another study, Rosenberger *et al.* correlated the spatially varied PL intensities within a monolayer WS₂ flake with conductive AFM (CAFM) results. CAFM characterization revealed discrete electronically active defects with nanometer-scale resolution, and a higher density of these defects was associated with a weaker PL emission (Figure 3-2).¹⁴⁸ These pioneering studies demonstrated that correlated microscopic and spectroscopic characterization may be the key to unambiguously understanding intrinsic defects and their spatial distributions.



Figure 3-2: CAFM measurements of the points labeled in (e). These spots exhibit defect densities of (a) $6.1 \times 10^{10} \text{ cm}^{-2}$, (b) $1.2 \times 10^{11} \text{ cm}^{-2}$, (c) $1.6 \times 10^{11} \text{ cm}^{-2}$, and (d) $4.5 \times 10^{11} \text{ cm}^{-2}$. (e) PL intensity mapping across a WS₂ grain. Adapted from Ref. 148.

In light of this, we would like to employ a series of combinatorial characterization techniques to provide a more comprehensive analysis of the types of intrinsic defects, as well as the impact of defects on the properties of 2D TMDs. In this Chapter, through several collaborated projects with Prof. Leandro Malard's group (Universidade Federal de Minas Gerais, Brazil), Prof. Zhiwen Liu's group (Penn State, USA), and Prof. Bruno Schuler's group (Lawrence Berkeley National Laboratory, USA), we investigated our 2D TMDs, particularly WS₂ monolayers, synthesized by solid precursor CVD and liquid phase precursor-assisted CVD methods. A variety of characterization techniques, including optical microscopy, hyperspectral PL imaging, second harmonic generation (SHG), STEM, time-of-flight secondary ion mass spectrometry (ToF-SIMS), STM/STS, and AFM, were carried out to unveil the types of intrinsic defects at cation (W) and anion (S) sites. Through these correlated micro- and nano-scale characterization studies, we also made important links between the inhomogeneous fluorescence/PL patterns with the presence of atomic defects. Our results not only improve the understanding of intrinsic defects in TMDs and their optical and electronic properties, but also pave the way for the controlled elimination and generation of defects through synthesis.

3.2 Unveiling the photoluminescence inhomogeneity in CVD-grown WS₂ monolayers

As we mentioned above, CVD-grown monolayer WS_2 flakes often exhibit inhomogeneous optical properties, and comprehensive characterization and analyses are desired to reveal the types of defects/disorders that lead to such inhomogeneity. In this Section, we reported the CVD synthesis of WS_2 monolayer with two different morphologies and inhomogeneous PL patterns (*i.e.*, triangular WS_2 monolayers with dark PL lines, and hexagonal WS_2 monolayers with PL segmentation). A series of characterization techniques were applied to identify the possible defect types and the impact of these defects on properties of 2D TMDs. It should be noted that these types of inhomogeneous PL patterns were not only consistently reproduced in our experiments, but also observed and reported by multiple research groups.^{25, 106, 147-150} Thus, in the end of this Section, we also discussed possible mechanisms that lead to the inhomogeneous incorporation of defects during synthesis. We expect that our work may provide useful and generalized information for 2D materials synthesis community to achieve a reliable defect engineering (*i.e.*, on-demand elimination or introduction of defects with long-range uniformity).

3.2.1 Understanding the origin of dark PL lines in triangular CVD-grown WS₂ monolayers

In the first case, we focused on unveiling the origin of dark PL lines that were consistently observed in triangular pristine WS₂ monolayers. The synthesis of monolayer WS₂ flakes followed the setup and growth parameters detailed in Section 2.2.1 of the thesis. Briefly, a NaBr-assisted APCVD method was applied, with WO₃ and S powders as precursors. The synthesis was carried out at 800 °C, and the growth time was 15 min. Figures 3-3 (a) and (b) show optical and fluorescence microscope images of an identical triangular-shaped WS₂ flake that is ~100 μ m in lateral size. While the optical image of the flake is homogeneous (Figure 3-3 (a)), the fluorescence emission from this identical flake displays large inhomogeneity (Figure 3-3 (b)). Particularly, it can be noticed that the fluorescence emission is bright at the edges and is gradually decreased from edge to center regions. Moreover, three dark PL lines, connecting the center to vertices of the triangular flake, are clearly observed.

SHG is a nonlinear optical technique that is capable for the characterization of a material's structural properties, such as crystallographic orientations and grain boundaries.¹⁵¹⁻¹⁵² Second harmonic (SH) imaging can be performed based on this technique, which exhibits great advantages
of high sensitivity, noninvasiveness, and fast image rates with diffraction limited resolution (~400 nm).¹⁵² Thus, we performed polarization-resolved SHG and dark-field SHG studies to obtain more insights into the origin of PL inhomogeneity. Figures 3-3 (c)-(f) display polarization-resolved SH images of four different WS₂ monolayers. Since SHG intensity varies as a function of the relative orientations between the crystallographic orientation of the flake and the incident laser polarization, different grain orientations yield different SH intensities in the polarization-resolved SH imaging mode. In Figures 3-3 (c) and (f), distinct SH intensities are observed within the monolayer, indicating the polycrystalline nature of these flakes and the presence of grain boundaries. Figure 3-3 (g) shows SH intensity as a function of input laser polarization angle for the grains marked with blue, green, and red dashed lines in Figure 3-3 (f), which further confirms the variations in their crystallographic orientations. By dark-field SH imaging (Figure 3-3 (h)), a better visualization of grain boundaries in Figure 3-3 (f) was achieved, where the grain boundaries can be clearly observed as bright lines. In the case of the WS_2 monolayer shown in Figure 3-3 (d), although the SH intensity is uniform throughout the monolayer, a suppressed SH response is found at the interface between the two grains, which indicates the presence of an antiphase grain boundary formed by the coalescence of 0° and 60° oriented domains.⁶⁴ In contrast, the triangular monolayer WS₂ exhibits a very uniform SH intensity without any differences at the dark PL line (Figure 3-3 (e)), which rules out the possibility that the PL inhomogeneity is due to grain boundary formation.



Figure 3-3: Optical microscopy, fluorescence microscopy, and second harmonic imaging of CVD-grown WS₂ monolayers. (a) Optical and (b) fluorescence microscopy imaging of an identical WS₂ flake, and dark PL lines can be clearly observed from the fluorescence image. (c)-(f) Polarization-resolved SHG imaging of different WS₂ monolayers. (g) Second harmonic intensity as a function of input laser polarization angle for the three different domains in (f). (h) Dark-field SHG imaging of the flake shown in (f).

Furthermore, hyperspectral PL imaging was performed for a quantitative analysis of the variations in PL emissions between the dark line and "normal" regions (*i.e.*, the regions adjacent to the dark PL line that display a relatively uniform PL intensity), and the results are presented in Figure 3-4. Figure 3-4 (a) shows an optical image of a star-shaped WS₂ flake with an overlaid hyperspectral PL intensity image. The dark lines are clearly distinguished by hyperspectral PL imaging, similar to the lines observed by fluorescence imaging. Figure 3-4 (b) displays the PL spectrum taken at regions 1 and 2 marked in Figure 3-4 (a) and the corresponding normalized PL

spectra plotted in logarithmic scale. It can be noticed that the PL signal at the dark line (region 1) is quenched when compared to region 2. The normalized PL spectra exhibits a low energy shoulder below the X⁰ exciton energy (marked by the gray box) for the case of region 1, while the peak position of the X⁰ exciton remains unchanged. Furthermore, a relative PL intensity image is shown in Figure 3-4 (c) to highlight the PL signal variations at the dark line compared to other regions in the flake, which displays the ratio between the integrated intensity of the gray region and the integrate intensity of the blue region. It is noticed from Figure 3-4 (c) that the regions corresponding to the dark PL line display a higher contrast, indicating a consistently higher PL spectral weight from the lower energy emissions, which implies that the formation of dark PL lines may be associated with the presence of midgap states originated from lattice defects.^{23, 106}



Figure 3-4: Hyperspectral PL imaging of monolayer WS₂. (a) An optical image of a star-shaped WS₂ monolayer with the overlaid hyperspectral PL intensity image. The scale bar is 10 μ m. (b) Top: PL spectrum taken at regions 1 and 2 shown in (a) and (c); Bottom: Normalized PL spectrum at position 1 and 2 shown in logarithmic scale. (c) Relative PL image obtained by dividing the integrated intensity of the gray region by the integrate intensity of blue region plotted in (b). The scale bar is 4 μ m.

The identification of defects in WS_2 monolayers requires the use of nanometer- and atomicscale characterization tools. We performed HAADF-STEM imaging at the "normal" monolayer region (Hole 1, marked with a blue square in Figure 3-5 (a)), and two regions at the dark line (Holes 2 and 3, marked with red and pink squares in Figure 3-5 (a)). The HAADF-STEM images obtained from these three regions are shown in Figures 3-5 (b)-(d). In the ADF imaging mode, the contrast of atoms is positively correlated with the atomic Z number. Thus, the appeared darker atoms (marked by white and yellow arrows) can be identified as substitutionally doped lighter atoms at tungsten (W) sites. Note that white and yellow arrows denote dopant atoms with relatively lower and higher ADF signal, which will be discussed later. By comparing the density of darker spots in Figures 3-5 (b)-(d), it is found that dark line regions contain a larger numbers of substitutional defects, suggesting that these defects are likely to act as non-radiative decay centers and may be associated with PL quenching.

In order to identify the elements that are substituting W, we analyzed the ADF-STEM image intensity and plotted results in Figure 3-5 (e). The total ADF intensity of an atom was obtained by integrating ADF signals over a circular area with 0.2 nm diameter around the atom. The total intensities were then normalized by using W and S₂ signals as 1.00 and 0.75, respectively. Two peaks emerge in the ADF-STEM image intensity profile at the dark line (Hole 2), while only one peak appears in the intensity profiles of Holes 1 and 3. The emergence of two peaks also matches with our observation of two types of darker spots (marked with white and yellow arrows in Figure 3-5 (c)) in Hole 2. Thus, we performed STEM simulation to understand this behavior. STEM simulation indicates that the peak with lower ADF intensity matches with Sc to Ga (first-row transition metals (3d-transition metals)), and the peak with higher ADF intensity matches with Y to Mo (second-row transition metals (4d-transition metals)). Although the exact impurity elements presenting at dark PL lines remain to be further identified, STEM results narrow down the possibility of these impurities to be 3d- and 4d-transition metals, which may originate from trace amount of impurities in the growth system or chemicals used for preparing WS₂ monolayers. A more detailed summary and discussion will be provided in Section 3.4.



Figure 3-5: STEM characterization of monolayer WS₂. (a) Fluorescence image of a triangular WS₂ on TEM grid. The scale bar is 20 μ m. (b-d) HAADF-STEM images at the regions shown by hole 1, 2, and 3. Scale bars are 2 μ m. Insets show magnified fluorescence images, and the pin indicates the location investigated by STEM. (e) Histogram of total ADF intensity of atom. Total ADF intensity from S₂ sites is not shown to prevent overlapping with signals from lighter transition metals. Profiles from holes 2 and 3 are shifted vertically for visibility. The vertical lines correspond to simulated normalized total ADF intensities of substitutional lighter transition atoms incorporated into the W site of WS₂ structure.

Finally, we carried out ToF-SIMS measurements for further chemical information of the impurities (ToF-SIMS experiment carried out by Dr. Sebastiaan Van Nuffel, Penn State). A 30 keV energy Bi^{3+} primary beam, operating at a DC current of 1.5 nA, was used to chemically image the WS₂ triangle in the positive and negative polarity. For negative polarity ions, as expected, we mainly observed the presence of sulfur at triangular WS₂ regions. However, interestingly, two peaks matching with V⁺ and HV⁺ appear in the positive polarity mass spectrum shown in Figure 3-6 (a), which unambiguously indicate the presence of vanadium (V) impurity. The total ion image and ToF-SIMS mappings of V⁺ and HV⁺ are displayed in Figure 3-6 (b-d), and V impurities are found to be homogeneously distributed throughout the flake. Dark PL lines were not identified by ToF-SIMS mapping, which may be due to the very low impurity concentration (<1 at%) and the relatively small concentration differences among regions, as well as the fact that dark PL lines are very narrow (around hundreds of nanometers).

As a brief summary of this Section, we investigated the origin of dark PL lines that commonly present in CVD-grown triangular WS₂ monolayers. A series of characterization techniques were correlated to examine the presence of defects located at the dark PL line region. It was found that a relative larger number of substitutional 3d- and 4d-transition metal impurities were accumulated at the dark line region. Although these impurities are on the order of ppm level, they are likely to introduce midgap states that significantly quench the PL. Based on the ToF-SIMS measurement, V is likely to be a 3d-metal impurity within our monolayer WS₂. For the 4d-transition metal impurities, though we did not obtain experimental evidences, previous literatures suggested molybdenum (Mo) may be a prevalent defect due to the good miscibility of Mo into WS₂.^{129, 153} Further work is desired to use atomic-resolution spectroscopic tools, such as electron energy loss spectroscopy (EELS), to precisely identify types of these substitutional defects.



Figure 3-6: ToF-SIMS characterization of WS₂ monolayers. (a) Positive polarity mass spectrum. The ion at m/z 50.944 can be attributed to V⁺ with a mass accuracy of ~5 ppm. The ion at m/z 51.953 can be attributed to HV⁺ with a mass accuracy of 19 ppm. (b-d) ToF-SIMS ion images. (b) Total ion image, (c) the ion at m/z 50.944 (V⁺) colocalizes with the WS₂ triangle and appears homogeneously distributed, and (d) the ion at m/z 51.953 (HV⁺) colocalizes with the WS₂ triangle and appears homogeneously distributed.

3.2.2 Understanding the origin of PL segmentation in hexagonal CVD-grown WS_2 monolayers

CVD-grown TMD monolayers usually exhibit faceted morphologies, such as triangles, truncated-triangles, or hexagons. Since Metal-zigzag (M-zz) and Sulfur-zigzag (S-zz) edges have lowest formation energies among all types of edge morphologies, TMD monolayers often have M-zz or S-zz edge terminations and their shape morphology can be determined by the ratio of S-zz growth rate (v_S) to M-zz growth rate (v_M).^{125, 154} For example, starting from a hexagonal-shaped nucleus depicted in Figure 3-7 (a), if v_S/v_M is significantly larger than 1, one would expect a much faster propagation of S-zz edges while the M-zz edges remain relatively stable, and this leads to the formation of M-zz terminated triangular TMDs as a final product. In particular cases when $v_S/v_M = 1$, due to the simultaneous growth of M-zz and S-zz edges, hexagonal-shaped TMD monolayers will form.

In order to establish a correlation between the edge growth rates with CVD experimental conditions, Chen *et al.* proposed an approach by considering the formation energy of different edge types as a function of sulfur chemical potential (μ_s).¹²⁵ It should be noted that although MoS₂ system was investigated in this study, the idea can be generalized to WS₂ monolayers too. Figures 3-7 (b) and (c) depict the schematics of the growth process of Mo-zz and S-zz edges. As an example, for S-zz edges to grow (Figure 3-7 (b)), they will first be converted to Mo-antenna edges by the attachment of a row of Mo atoms, and then converted back to S-zz edges by attaching a row of S atoms. Due to the relatively higher formation energy of antenna-type edges, there is always an energy barrier (ΔE_1) to be overcome. Similarly, the energy barrier for W-zz edge growth can be denoted as ΔE_2 . As the growth of S-zz and W-zz edges follows Arrhenius-type kinetics, the edge growth rate ratio can be associated with the energy barriers:

$$v_S/v_M = exp[(\Delta E_2 - \Delta E_1)/(k_B T)]$$

Furthermore, since ΔE_1 and ΔE_2 vary as a function of μ_S and Mo chemical potential (μ_{Mo}) (Figures 3-7 (d) and (e))¹⁵⁵, it is clear that the edge growth rate ratio and the shape morphology can be tuned by CVD reaction conditions (determining μ_S and μ_{Mo}). Specifically, in the case of a relatively higher $\mu_{S,} \Delta E_1$ is larger than ΔE_2 (Figure 3-7 (e)), thus we have $v_S/v_M < 1$ and the formation of S-zz terminated triangles is expected. Similarly, based on this model, it can be deduced that a low μ_S leads to the formation of W-zz terminated triangles, and hexagonal WS₂ can be formed at a certain μ_S that corresponds to $v_S/v_M = 1$. Experimentally, we achieved the controlled growth of hexagonal WS₂ monolayers using the NaBr-assisted CVD method described in Section 2.2.1, and we noticed that a higher growth temperature (e.g., 900 °C) lead to a larger coverage of truncated triangular and hexagonal flakes (Figure 3-8 (a)), while triangular WS₂ flakes were dominate at lower growth temperatures (e.g., 800 °C-850 °C). Based on the model that we have described above, a possible explanation for this shape evolution is that at a lower growth temperature, there is a relatively steady and sufficient W supply, which leads to a higher stability of W-zz edges (lower v_W), forming W-zz terminated triangles. At higher temperatures, W precursors are evaporated and depleted faster, resulting in the favored formation of S-zz edges at later growth stage and leading to the triangle-to-hexagon shape evolution.



Figure 3-7: Mechanisms of the formation of triangular and hexagonal TMDs with different edge terminations. (a) atomic ball model showing a hexagonal MoS₂ with two types of low-index edges (Mo-zz and S-zz edges). (b)-(c) Schematics of the evolution of S-zz and Mo-zz edges during CVD growth, with energy barriers of ΔE_1 and ΔE_2 , respectively. (d) Variation of the edge formation energy with the chemical potential of sulfur μ_S for the different edges. (e) Variation of the energy barrier of the S edges (ΔE_1) and Mo edges (ΔE_2) with μ_S , respectively. Adapted from Ref. 125.

Remarkably, we observed that the fluorescence of hexagonal WS₂ monolayers display an interesting segmented pattern with three-fold symmetry (Figure 3-8 (b)). This fluorescence pattern is experimentally reproducible and consistent with previous reports, ruling out the possibility that such segmented PL pattern is induced by any uncontrolled variation in experimental conditions.^{25-26, 106, 156} Nevertheless, although the origin of PL segmentation effects was investigated to some extent, controversial results exist in previous studies. Specifically, the mechanisms of PL segmentation have been attributed to different W vacancy and S vacancy concentrations in adjacent domains²⁵, the existence of different phases¹⁵⁷, different distributions of unintentional dopants¹⁰⁶, and edge-initiated delamination of monolayers from the substrate during growth.¹⁵⁸ In this context, we then characterized our hexagonal WS₂ flakes to find out possible reasons that lead to this PL variation.

Firstly, Raman and PL measurements were carried out at two different spots in adjacent regions of a typical hexagonal WS₂ flake. The measured spots were marked by red and black dots in Figure 3-8 (c). PL spectra from these two different points were compared and plotted in Figure 3-8 (d). A ~30% difference in PL intensity is observed, which is in agreement with the segmented fluorescence pattern shown in Figure 3-8 (b). Raman spectra from the two different points acquired at a resonant condition (514.5 nm excitation) are shown in Figure 3-8 (e), which remains similar in terms of peak positions and defect-activated LA(M) mode intensity. Additionally, we note that the Raman fingerprints from both regions display large $I_{2LA(M)}/I_{A'1}$ ratios ($I_{2LA(M)}/I_{A'1} > 1$), which is an evidence that the bright and dark regions are both monolayers, excluding the possibility that the fluorescence and PL variations are due to layer number inhomogeneity.¹⁵⁹



Figure 3-8: Optical characterization of hexagonal monolayer WS_2 . (a) An optical image and (b) corresponding fluorescence image of a hexagonal monolayer WS_2 flake. (c) An optical image of monolayer WS_2 flake for Raman and PL measurements. Signals from two different spots in adjacent regions of the flake (marked by red and black dots) were measured. (d) PL and (e) Raman spectra from the two different spots (514.5 nm excitation). A difference in PL intensity can be clearly observed in these two spots, while the Raman signatures remain similar.

The PL segmentation mechanism was then investigated at atomic scale by STEM characterization. Figure 3-9 (a) shows optical and fluorescence images of hexagonal WS₂ transferred onto a Quantifoil TEM grid. The segmented PL pattern is preserved after transfer, evidencing that the pattern formation is unlikely to be associated with strain/wrinkling, because it is expected that strain should be fully released by the transfer process.⁷⁸ We further performed HAADF-STEM imaging at different magnifications to reveal more details of defects within the flake. We specifically focused on understanding two aspects: (1) The observed alternating bright/dark domains imply that it is possible that these domains are corresponding to different edges (S-zz and W-zz). Thus, the edge terminations that correspond to bright and dark PL domains were examined by correlating STEM images with domain orientations observed in fluorescence images. (2) By performing high-magnification STEM imaging at locations that belong to bright and dark PL domains.

We first acquired HAADF-STEM images at relative lower magnifications for the edge termination analysis. We retrieved the exact flake location under TEM, and the edges observed in the STEM image (Figure 3-9 (b)) was aligned and correlated with the optical and fluorescence images. STEM imaging was then performed in a selected region that is close to the center (marked with red squares in Figures 3-9 (a) and (c)), where we knew from fluorescence imaging that the region contained a boundary between bright and dark domains. Strikingly, the STEM image (Figure 3-9 (d)) shows an obvious difference in the density of dark dots across the boundary, indicating a different density of point defects between bright and dark domains. No grain boundaries across the bright/dark domains, demonstrating the single crystalline nature of the flake. On the right side of Figure 3-9 (d), we used a magnified HAADF-STEM image to outline the directions of W-zz and S-zz edges. By matching these atomic-scale edge directions with the actual sample edge directions shown in Figures 3-9 (a) and (b), we unambiguously identify that the regions with higher and lower

PL emissions correspond to W-zz and S-zz edges, which agrees well with a previous report by Jeong *et al.*²⁵ High-magnification STEM images were further acquired from these two domains (Figures 3-9 (e) and (f)). From the density of dark dots, it can be found that the bright and dark regions are associated with lower and higher defect densities, respectively. Similar with the case of dark PL lines, the observed defects here are also occupying W sites, and the dark dots are found to exhibit two types of ADF contrasts (marked with white and yellow circles). The results advocate that the PL segmentation effect is originated from the inhomogeneous distribution of impurity dopants at different domains within hexagonal WS₂ monolayers, which is likely to have a very similar origin with the case of PL dark lines.



Figure 3-9: STEM characterization of hexagonal monolayer WS₂. (a) Optical and fluorescence images of a hexagonal WS₂ on TEM grid. (b-d) Low-magnification HAADF-STEM images at the regions marked by green and red squares and arrows, which were used for the identification of edge terminations corresponding to bright and dark PL regions. (e-f) High-magnification HAADF-STEM images from bright and dark regions of the hexagonal WS₂ flake, respectively.

Associated with distinct defect densities and PL segmentations at regions corresponding to W-zz and S-zz edges, it is interesting to investigate the robustness of nonlinear optical properties within the hexagonal WS₂ flake. Therefore, we quantitively compared the distribution of fluorescence and SHG intensities in hexagonal WS₂ monolayers grown in a single CVD reaction (Figure 3-10). Figure 3-10 (a) shows the fluorescence intensity probability distribution obtained from the fluorescence image in Figure 3-10 (e), displaying a large variability. The normalized fluorescence line scan along the direction marked with the white dotted line in Figure 3-10 (e) also indicates the segmentation of fluorescence intensity (Figure 3-10 (c)). In contrast, the SHG intensity probability distribution shown in Figure 3-10 (b) appears to be more uniformly localized around 0.85-0.9, which is also confirmed by the SHG intensity line scan (Figure 3-10 (d)), displaying uniform SHG signal across the white dotted line in Figure 3-10 (f). Thus, we can deduce that compared to PL, the SHG signal is more robust against structural defects in hexagonal WS_2 monolayers. This effect can be understood as the inertness of the second-order nonlinear susceptibility of monolayer WS₂ against the presence of substitutional defects, which further demonstrates a great potential for these materials to be used as defect-tolerant nonlinear optical components.



Figure 3-10: The comparison of fluorescence and SHG from hexagonal monolayer WS_2 . (a) A histogram showing the relative probability distribution of normalized fluorescence intensity within the flakes shown in (e). (b) A histogram showing the relative probability distribution of normalized SHG intensity within the flakes shown in (f). (c) Normalized fluorescence intensity line scan across a hexagonal WS_2 flake in (e) marked with a white dotted line. (d) Normalized SHG intensity line scan across a hexagonal WS_2 flake in (f) marked with a white dotted line. (e) Fluorescence microscopy image of hexagonal WS_2 monolayers. (f) SHG raster scanned image of hexagonal WS_2 monolayers with a step size of 4 μ m.

In Section 3.2.2, we investigated the origin of segmented PL emission from hexagonal monolayer WS₂, and we found that the inhomogeneous distribution of 3d- and 4d-transition metal impurities could be an important cause. Specifically, domains that associated with W-zz and S-zz edges exhibit relatively lower and higher defect densities, respectively. The growth mechanism of domains with inhomogeneous defect distributions may be understood as a difference in affinities between impurity atoms and different edge terminations.^{106, 160} For example, Cr and Fe atoms have been found to exhibit stronger adsorption at S-zz edges in WS₂.¹⁰⁶ Thus, it is likely that impurity atoms are preferentially adsorbed at S-zz edges during the growth and incorporated into the lattice, forming defective domains with quenched PL emission. In addition, it is hypothesized that the formation of dark PL lines in triangular WS₂ monolayers follows the same mechanism, which may be an extreme case of hexagonal WS₂ where the dark PL domains shrinks into a narrow line. In future work, DFT calculation will be employed to verify our hypothesized growth mechanism, and

we also envisage that atomic-scale spectroscopic characterization techniques can be used to analyze the elemental identity of these dopants.

3.3 Carbon-hydrogen complex as an abundant charged impurity in nominally undoped WS₂

Correlated STM/STS and CO-tip AFM characterization techniques were recently reported as powerful tools to study 2D TMDs.¹⁶¹⁻¹⁶² By examining both topological and electronic properties of defects, these techniques are not only effective for unambiguously identifying point defects and corroborating the results, but also capable to establish the structure-property relationship of those atomic-scale defects. In light of this, in this section, we performed STM/STS and CO-tip AFM characterization to study the atomic structures and properties of intrinsic defects in our CVD-grown WS₂ monolayers (in collaboration with Prof. Bruno Schuler's group (Lawrence Berkeley National Laboratory, USA)).

Prerequisites for investigating 2D TMDs using STM/STS include sample cleanliness, high coverage, and conductive substrates, and thus the challenge in material synthesis is to directly grow monolayer WS₂ on conductive substrates (*e.g.*, epitaxial graphene/silicon carbide (EG/SiC)) instead of conventionally used SiO₂/Si. Experimentally, we observed that the yield of WS₂ monolayers on EG/SiC was greatly suppressed under identical reaction conditions, which may be explained by the lack of dangling bond on graphene surface that make nucleation and growth more difficult.¹⁶³ In addition, in contrast to the synthesis of WS₂ on SiO₂/Si substrate, we found that the use of NaBr provided little help for the growth on EG/SiC, and such substrate-dependent growth mechanisms remain to be explored in the future.

To tackle this problem, we modified our setup by using an inner tube (\sim 1 cm in diameter) to contain both the EG/SiC substrate and WO₃ powders that were placed on top of the substrate

(see schematics in Figure 3-11 (a)). The use of inner tubes has been found to enhance the growth yield by slowing down chalcogenization of WO₃¹⁶⁴ and/or increasing the local vapor pressure of WO₃.¹⁵⁰ The synthesis was carried out at 900 °C for 60 min. Using the modified growth technique, WS₂ monolayers were epitaxially grown on EG/SiC with an improved yield, and the coverage at some regions reached ~50 %. As shown in Figures 3-11 (b)-(c), scanning electron microscopy (SEM) and optical images demonstrate that as-grown WS₂ flakes are usually as David stars and triangles with lateral sizes of ~5-10 μ m, smaller than that of WS₂ grown on SiO₂/Si by the NaBrassisted CVD method.



Figure 3-11: Synthesis of high-coverage monolayer WS_2 flakes on epitaxial graphene (EG). (a) Schematics of the synthesis setup for growing monolayer WS_2 on EG/SiC. The use of an inner tube is found to effectively improve the yield of WS_2 . (b) SEM and (c) optical images of the morphology of WS_2 flakes, and the regions with bright contrast are likely to be thick layers.

The as-grown pristine WS_2 monolayers were examined using STM for possible point defects. In previous studies, a variety of common defects have been observed in CVD-grown WS_2 , such as Cr_W , Mo_W , and O_S top/bottom (oxygen substituting top or bottom sulfur). Apart from these defects, we noticed a negatively charged defect (referred to as nCD) that was imaged as a ~2 nm dark depression at positive biases (marked with orange dashed circles in Figure 3-12 (c)), and also a protrusion at negative biases. This contrast inversion is due to upwards band bending in the

proximity of a negatively charged defect. Besides, atomically-resolved CO-tip noncontact (nc)-AFM images (Figures 3-13 (b) and (e)) show that this negatively charge defect is located at a chalcogen site. This defect also exhibits a small repulsive feature, which indicates that the defect is closer to the middle tungsten plane or smaller than sulfur atoms. Based on previous DFT calculations, the possible identity of this nCD was narrowed down to two candidates: (1) a carbonhydrogen (CH) group at S site (CH_S); (b) a nitrogen atom at S site (N_S).

In a previous study from our group, an Ar/H₂/CH₄ plasma-assisted process was applied to dope carbon atoms into monolayer WS_2 (Figure 3-12 (a)), and CH_S dopants were found in these intentionally C-doped WS₂ samples.¹⁰¹ Thus, in order to verify the hypothesis that the observed nCDs are CH_s dopants, we employed this CH-doping method to prepare intentionally CH-doped WS₂ monolayers for STM measurements, and 1 sccm flow of methane was used during the doping experiment. Figure 3-12 (b) presents resonant Raman spectra of WS₂ monolayers before (blue) and after CH-doping (purple). The spectra were acquired using 532 nm excitation wavelength and were normalized to the intensity of A₁' mode. It is found that the double-resonance 2LA(M) peak is significantly quenched after doping, which agrees with previous results and indicates a modulation in the electronic structure of WS₂.¹⁰¹ Once the successful doping of CH into WS₂ was confirmed, STM analysis of CH-doped WS₂ was performed and the overview STM image is depicted in Figure 3-12 (d). Interestingly, a noticeable increase in nCD defect density is observed, and the nCD defect density is measured to be ~ 0.6 %, which is about two orders of magnitude higher than that of the undoped sample (Figure 3-12 (c)). This result clearly demonstrates that the observed nCD is likely to be CH_s, due to its increased density after intentional CH doping. We further performed CO-tip nc-AFM image simulation by DFT (Figures 3-13 (c) and (f)). The simulated and experimental nc-AFM images exhibit a good match, further corroborating that the observed nCD defects are indeed CH_S.



Figure 3-12: CH-doping of monolayer WS₂. (a) Schematics of the plasma-assisted CH doping process. (b) Raman spectra of pristine and CH-doped WS₂ monolayers (532 nm excitation wavelength). (c) STM topography ($V_B = 0.7V$, $I_t = 100pA$) of pristine CVD-grown WS₂. (d) STM topography ($V_B = 1.4V$, $I_t = 100pA$) of CH-doped CVD-grown WS₂.



Figure 3-13: STM and CO-tip nc-AFM imaging of defects in CH-doped WS₂. (a) STM ($V_b = 1.2V$, $I_t = 100pA$) image of a CH_S defect in CH-doped WS₂. (b) CO-tip nc-AFM image of the same CH_S defect as in (a). Sulfur atoms in the upper S layer are imaged as bright protrusions. (c) Simulated nc-AFM image of CH_S using the calculated DFT geometry and the probe particle method. (d) STM ($V_b = 1.2V$, $I_t = 100 pA$) and (e) nc-AFM images of two CH_S (orange circles), an O_S top (green circle) and O_S bottom (blue circle) defect in CH-doped WS₂. (f) Top and side view of the DFT calculated structural model of CH_S.

In summary, in this Section, we used a combination of targeted CVD synthesis and doping approaches, STM/STS, and nc-AFM imaging to unambiguously identify that carbon-hydrogen (CH) complex at chalcogen sites is a common, charged impurity in CVD-grown WS₂. Similar CH_{Se} defects are also observed in MOCVD-grown WSe₂, which is beyond the scope of this thesis. In addition, we validated our previous work that methane plasma treatment could controllably induce CH dopants into TMD monolayers.

3.4 Conclusions

In summary, Chapter 3 of the thesis investigated intrinsic defects in CVD-grown WS_2 monolayers and their effects on the material's properties. Through a series of collaborated work, we employed correlated microscopic and spectroscopic characterization techniques to reveal that "pristine" WS_2 was not as pristine as we perceived. In fact, different types of point defects can be introduced into the lattice during CVD synthesis, and we have demonstrated that the non-uniform distribution of these defects leads to the formation of inhomogeneous PL patterns. A summary of our findings is listed in Figure 3-14.

Defect Site	Defect Types
Transition metal site (W site)	3d- and 4d-transition metal substitution $(M_W: M = V, Cr, Fe, Mo, etc.)$
Chalcogen site (S site)	CH-substitution (CH _S); oxygen substitution (O _S); S vacancy (V _S)
Note: <i>M_W</i> defect concentration displays a spatial variation at regions corresponding to W-zz and S-zz edges.	

Figure 3-14: A summary of observed intrinsic defects in CVD-grown WS₂ monolayers.

Based on the current understanding of intrinsic defects in TMDs, future work will be focused on developing means to control their densities. The origin of the impurity sources remains elusive, but they are mostly likely from the growth precursors and reactors.¹⁶⁵ For example, Robertson *et al.* observed V and Cr impurities in CVD-grown MoS₂ using ADF-STEM and EELS characterization, and these metal dopants were attributed to the impurity in the MoO₃ precursor.¹⁰⁷ Lin *et al.* also noticed the presence of Fe and Cr in hexagonal WS₂ monolayers, as we mentioned in Section 3.2.2.¹⁰⁶ Thus, the use of high-purity precursors and contamination-free reactors dedicated for the growth of certain TMDs may be the key to minimizing synthetic defects. On the other hand, even if the contamination source is difficult to be identified and/or eliminated, our results on hexagonal WS₂ monolayers open up an alternative defect control route: Since the edge termination is highly related to the defect densities within the corresponding domains (W-zz/S-zz domains contain fewer/more substitutional dopants, respectively), and previous experimental work has demonstrated the possibility of tuning edge terminations by metal-chalcogen precursor ratio.^{25,} ¹⁵⁴, it may be an interesting and viable idea to use edge termination as a control knob to reduce/increase the density of dopants on demand.

Chapter 4

Liquid-Phase Precursor-Assisted *In Situ* Substitutional Doping of 2D TMDs and Their Heterostructures

This chapter is based on previously published work for which I am the first author (Ref. [77]). Parts of reference [77] are reproduced (adapted) with permission from Zhang, T.; Fujisawa, K.; Zhang, F.; Liu, M.; Lucking, M. C.; Gontijo, R. N.; Lei, Y.; Liu, H.; Crust, K.; Granzier-Nakajima, T.; Terrones, H.; Elías, A. L.; Terrones, M., Universal *In Situ* Substitutional Doping of Transition Metal Dichalcogenides by Liquid-Phase Precursor-Assisted Synthesis. *ACS Nano* **2020**, *14*, 4326-4335. Copyright 2020, American Chemical Society. (https://pubs.acs.org/doi/abs/10.1021/acsnano.9b09857)

4.1 The motivation of developing effective TMD doping strategies

Doping of semiconducting TMDs constitutes an efficient approach for tuning their physicochemical characteristics and, ultimately, for adding more functionalities to devices based on complex nanoarchitectures. One of the most effective routes for achieving doped TMDs is by the substitution of transition metal atoms within the TMDs lattice. Because this doping strategy involves the chemical bonding (usually covalent) between dopant atoms and the host lattice, it is considered to be more stable and non-volatile when compared to surface charge transfer doping *via* physisorption, another well-established doping method.⁹⁹⁻¹⁰⁰ Examples of modified properties upon doping include the charge carrier density and electrical doping type. Previous reports have shown that introducing Nb atoms into the MoS₂ lattice leads to a stable *p*-type transport, while the incorporation of Re and Fe dopants results in an *n*-type behavior.^{100, 104, 166-167} Recent theoretical

and experimental studies have also implied that ferromagnetism can be induced by doping TMDs with transition metal elements including Mn, Fe, Co and Zn.^{103, 168-170} In addition, the catalytic performance of semiconducting TMDs has been boosted *via* doping as well as alloying of two different TMDs.^{36, 171-172} Moreover, by constructing heterojunctions either based on doped-undoped TMDs, or involving two pure phases of different TMDs, 2D *p-n* junction FETs and photovoltaic devices have been successfully fabricated.^{104, 173}

Regarding dopant incorporation routes, post-synthesis diffusion and ion implantation methods commonly used for doping 3D semiconductors¹⁷⁴⁻¹⁷⁵ are hardly applicable for atomically thin TMDs, since the required high-temperature processes and/or ion bombardments can lead to quick degradation of TMDs in the one- to few-layer form. In comparison, synthesis techniques that can achieve the incorporation of heteroatoms *in situ* during the TMDs growth, are more suitable for obtaining substitutionally doped atomically thin TMDs. While pioneer studies on doped TMDs are based on chemical vapor transport and subsequent mechanical exfoliation of obtained monocrystals,^{104, 176} a number of single-step routes based on powder precursors for substitutionally incorporating transition metal atoms into TMD monolayers have recently emerged, and Nb, Mn and Re have been introduced into TMDs lattices.^{105, 172, 177}

In Chapter 4 of this thesis, we developed an alternative strategy that involves the usage of liquid phase precursors for synthesizing doped TMDs and their heterostructures. We demonstrated that this method could dope several transition metal elements into monolayers of both WS₂ and MoS₂. For instance, Fe-doped WS₂, Re-doped MoS₂, and V-doped WS₂ have been synthesized. More importantly, we demonstrated the synthesis of doped TMD in-plane heterostructures *via* a single-step process. Various optical and electron microscopy characterization techniques were used to study their properties, verify the incorporation of substitutional dopants, and characterize the hetero-interfaces in the doped heterostructures. This work provides a facile yet powerful doping

method, which may also be generalized as a universal technique to incorporate dopants into various TMD monolayers (*i.e.*, selenides and tellurides), thus paving the way to the discovery of emergent properties and functionalities in TMDs and their heterostructures.

4.2 Liquid phase precursor-assisted doping of TMD monolayers

Figure 4-1 (a) depicts a general flow diagram of the developed liquid phase precursorassisted synthesis method that leads to atomically thin doped TMDs and their heterostructures. This method is built upon the liquid phase precursor-assisted CVD method that we discussed in Section 2.3. Because water-soluble precursors of both the host and dopant are homogeneously mixed at the atomic level before spin-coating and sulfurization, compared to conventional solid precursor-based doping methods, it is expected that our method reduces the spatial variation of precursor supply and guarantees a more uniform growth in terms of doping concentration and shape morphology. In fact, this idea of doping materials has long been implemented in ceramics, (i.e., the sol-gel technique),¹⁷⁸⁻¹⁸¹ where a colloidal suspension, "sol", is used to coat a substrate, and later undergoes a gelation process involving hydrolysis and polycondensation, which leads to the formation of a "gel". Finally, the target solid material can be obtained by thermally processing the gel.¹⁷⁸ In brief, our synthesis approach starts with the spin-coating of an aqueous solution containing the transition metal precursor(s) and sodium cholate onto a SiO₂/Si substrate, followed by a high-temperature sulfurization process. Sodium cholate works as surfactant, which has been found to help with the adhesion of precursors onto SiO₂/Si substrates during spin-coating.¹³⁴ Moreover, recent studies have shown that both aromatic molecules and alkali metal-containing compounds can promote the lateral growth of TMDs.^{121, 135} Sodium cholate possesses aromatic structures with Na⁺ cations, which have been reported as growth promoters for acquiring high-coverage monolayer TMDs.^{112,}

Figure 4-1 (b) displays the doped TMDs systems investigated in this work, including monolayer Fe-doped WS₂, Re-doped MoS₂ and V-doped WS₂,¹⁵⁰ as well as V-doped Mo_xW_{1-x}S₂- $W_xMo_{1-x}S_2$ in-plane heterostructures. It is worth mentioning that the rationale behind choosing these doped TMDs systems consists of three aspects: (1) Due to the requirement of mixing precursors in liquid phase, there should be water-soluble compounds readily available as dopant precursors. (2) The dopant atom should have a large atomic Z-number difference compare to that of Mo and W. For example, we choose WS₂ system to demonstrate Fe and doping, and MoS₂ for Re doping due to the relatively larger Z-number differences, which result in distinguishable atomic contrasts when performing STEM characterization, thus facilitating the identification of these dopants.¹⁸² (3) The dopant should possess similar or slightly smaller atomic radius compared to that of the transition metal atom in the host lattice, thus ensuring a minimal amount of lattice strain when the dopant atom is incorporated into TMDs.^{145, 183} In addition, substitutional doping of the selected V, Fe, and Re elements has been either experimentally reported^{105, 176-177} or theoretically calculated to possess moderate formation energies (among d-block elements)^{103, 184}, ensuring the feasibility of incorporating these dopants.



Figure 4-1: Liquid phase precursor-based approach for doping TMDs. (a) Flow diagram for the substitutional doping of 2D TMDs and their in-plane heterostructures. By appropriately selecting and mixing water-soluble compounds as precursors, doped TMDs and their in-plane heterostructures can be synthesized accordingly. (b) A schematic of the choice of doped TMDs systems, as well as the rationales of dopant selection.

4.3 Fe-doped WS₂ monolayers

Firstly, we synthesized Fe-doped WS₂ using AMT and iron (III) chloride (FeCl₃) as W and Fe precursors. In order to investigate the tunability of doping concentration using our synthesis approach, Fe-doped WS₂ were synthesized using precursor solutions with two different FeCl₃ concentrations (*i.e.*, "low doping" and "high doping"). Briefly, solution 1 (Sol 1, host precursor) was prepared by dissolving AMT ((NH₄)₆H₂W₁₂O₄₀, Sigma-Aldrich, purity of 99.99%; 0.05 g) and sodium cholate hydrate (Sigma-Aldrich, purity of $\geq 99\%$; 0.2 g) into DI water (10 mL). Solution 2 (Sol 2, dopant precursor) was prepared by dissolving iron (III) chloride hexahydrate (FeCl₃ • 6H₂O, Sigma-Aldrich, purity of 98.0-102% (RT); 0.014 g) into DI water (25 mL), resulting in a solution of FeCl₃ 2.07 mM. To synthesize Fe-doped WS₂, a fresh mixture of Sol 1 (2 mL) and Sol 2 (500 μ L (high doping case) or 100 μ L (low doping case)) was spin-coated onto a clean SiO₂ (300 nm)/Si substrate (2500 rpm, 1 min). Subsequently, the precursor-coated substrate was loaded in the center of a quartz tube, and 400 mg of sulfur powders were placed in an alumina boat located upstream. During synthesis, the furnace was ramped up to 800 °C in 30 min and held for 15 min. Simultaneously, the sulfur powders were vaporized at 220 °C, allowing the sulfurization of the spin-coated precursors. 100 sccm of the Ar carrier gas flowed throughout the synthesis.

Figure 4-2 (a) (see inset) displays an optical image of the as-synthesized monolayer Fedoped WS₂ (high doping) with triangular morphology and lateral sizes of ~100 µm. Other morphologies, such as hexagons and irregular shapes, could also be found, indicating local variations in the ratio of sulfur-terminated edge growth rate, v_S and tungsten-terminated edge growth rate, v_W . Since the v_S/v_W growth rate ratio is strongly influenced by the local chemical potential of sulfur (μ_S) and tungsten (μ_W) during synthesis, we believe that the observed morphology variations in Fe-doped WS₂ flakes may either result from the sulfur supply variation at different locations of the substrate or from the Fe dopant addition effect, which are factors that may modify the local μ_S and μ_W .^{125, 154} Atomic force microscopy (AFM) image and the height profile across the edge region of Fe-doped WS₂ (Figure 4-3) confirm its monolayer nature, featured by the measured step height of ~0.7 nm that is in agreement of typical thicknesses of TMD monolayers.¹²³ The Raman spectra of as-synthesized monolayer pristine and Fe-doped WS₂ with two different doping concentrations are obtained at a resonance condition (using a 514.5 nm laser excitation) and shown in Figure 4-2 (a). The Raman spectra were normalized to the intensity of the A'₁(Γ) mode. Pristine WS₂ exhibits the prominent first-order vibrational modes (E'(Γ) and A'₁(Γ)) at 357 cm⁻¹ and 419 cm⁻¹, respectively. In comparison, E'(Γ) and A'₁(Γ) modes are red-shifted with increased Fe doping, and both modes in highly doped Fe-doped WS₂ exhibit a red-shift of 1 cm⁻¹. The observed Raman frequency shifts are believed to originate from both lattice strain and charge doping effects induced by the presence of Fe dopants.^{167, 185} Apart from the first-order modes, all spectra obtained at resonance conditions contain several higher-order Raman modes and combination modes, which were identified and labeled in Figure 4-2 (a). Among the higher-order modes, the second-order 2LA(M) is the most intense mode in pristine WS₂ monolayers, which is generated from a double resonance Raman process.¹⁵⁹ However, the relative intensity between the 2LA(M) and the first-order A'₁(Γ) gradually decreases with increased Fe doping, indicating a suppression of the double resonance process. The intensity reduction of the 2LA(M) mode also constitutes a direct evidence of the alteration of the WS₂ monolayers caused by the incorporation of Fe dopants.¹¹⁵ Furthermore, ZA(M) and LA(M) are strongly enhanced in Fe-doped WS₂, which supports the claim of the defect-induced nature of such bands identified in WS2.186-187 Room temperature PL characterization was also performed to study the change of optical properties of WS_2 monolayers after Fe doping (Figure 4-2 (b)). Our results indicate that the PL spectra of both lightly doped and highly doped Fe-doped WS_2 are noticeably broadened. In addition, their intensities display a gradual decrease with increased doping concentration, where the PL intensities of lightly doped and highly doped Fe-doped WS₂ are suppressed by ~ 20 times and ~ 120 times when compared to pristine WS₂, respectively. PL intensity mappings (Figure 4-4) of pristine and highly doped WS₂ at 1.97 eV (corresponding to the optical band gap of monolayer WS₂) reveal a uniform PL quenching in the entire Fe-doped WS₂ flake, indicating the uniform distribution of Fe dopants. The PL quenching in Fe-doped WS₂ observation matches well with the previous work by Lin et al., which reported the PL quenching of subdomains in hexagonal WS₂ monolayers resulting from Fe

dopants unintentionally introduced in the lattice.¹⁰⁶ Fe dopants can introduce deep-level defect states that lead to the non-radiative recombination of photoexcited carriers and, therefore, they could be responsible for the observed PL quenching.^{106, 167}



Figure 4-2: Monolayer Fe-doped WS₂. (a) A comparison of Raman spectra of Fe-doped WS₂ with two different doping concentrations and pristine WS₂ (normalized to the A'₁(Γ) mode) obtained at resonance, using a 514.5 nm laser. Frequencies of active Raman modes were determined by fitting the spectra with Voigt profiles. Inset: Optical image of monolayer Fe-doped WS₂ flakes, where the scale bar is 50 µm. (b) PL spectra of Fe-doped WS₂ and pristine WS₂ monolayers. (c) Atomic-resolution STEM-ADF images of monolayer Fe-doped WS₂ (high doping level). Two different dopant configurations (Fe_W and 3Fe_W+V_S) are identified with blue- and red-colored circles, respectively. (d)-(e) Experimental and simulated STEM images and line scans of Fe_W and 3Fe_W+V_S dopant configurations. The dots in the line scans represent experimental results, while the solid lines are simulated curves.



Figure 4-3: An AFM image of Fe-doped WS_2 , and the corresponding height profile along the white dashed line in the image.



Figure 4-4: PL intensity mappings of pristine and Fe-doped WS₂ (high doping) at 1.97 eV, which corresponds to the optical band gap of monolayer WS₂. Fe-doped WS₂ exhibits a uniform PL quenching in the entire triangular flake.

In order to confirm the incorporation of Fe dopants, study their atomic configuration, and determine Fe doping concentrations, the as-synthesized Fe-doped WS₂ monolayers were transferred onto Quantifoil TEM grids to conduct STEM characterization. A representative HAADF-STEM image of Fe-doped WS₂ (high doping) is shown in Figure 4-2 (c), where Fe atoms stand out as the darker atoms occupying the W sites, according to their relatively lower atomic Z-number. Two major types of dopant configurations can be found in ADF images, which are the

single Fe substitution in a W site (Fe_w; highlighted with blue-colored circles) and the triple Fe substitutions with a sulfur vacancy in the middle (3Fe_w+V_s; highlighted with red-colored circles), which have also been previously observed by Lin et al.¹⁰⁶ To examine the doping concentrations in Fe-doped WS_2 synthesized with two different FeCl₃ precursor concentrations, we performed statistical analysis of STEM images acquired at three random regions in each sample. The Fe doping concentrations were estimated as ~ 2.8 at % and ~ 0.7 at % in the case of high doping and low doping, respectively (Fe/(W+Fe) at % was used for calculating doping concentration value; see Figure 4-5 for typical STEM images of monolayer Fe-doped WS₂), which demonstrates that tunable doping can be achieved through controlling dopant precursor concentration in the mixed precursor solution. Simulated STEM images and line scan results for Few and 3Few+Vs are presented in Figures 4-2 (d) and (e), respectively. Our experimental and simulated results exhibit a good match for both types of dopant configurations. It is worth noting that for 3Few+Vs, we observed that the atomic positions of Fe dopants deviate from those of W atoms in the pristine WS_2 lattice. The sulfur atom opposite the vacancy moves into the transition metal plane, causing the 3 Fe atoms to move away from the vacancy center and toward the other sulfur pairs they are bound to. Similar defect coupling and lattice distortion have also been observed in Mo-doped WS₂ lattice by Azizi et al.¹⁸⁸ Thus, an optimization of the 3Fe_W+V_S structure was carried out using DFT calculations prior to STEM simulation in order to relax the structure and obtain accurate atomic coordinates. Furthermore, we used TEM-based energy dispersive X-ray spectroscopy (EDS) to analyze the chemical composition of Fe-doped WS₂ (Figure 4-6). The characteristic Fe K α emission was clearly observed, thus confirming the successful incorporation of Fe dopants into the WS_2 lattice.



Figure 4-5: Typical STEM images of monolayer Fe-doped WS₂ for doping concentration analysis. Statistical analysis shows Fe-doping concentrations of ~0.7 atomic % (at %) and ~2.8 at % in the case of low doping and high doping, respectively. Some examples of Fe dopants are marked with red-colored circles. In the low doping case, almost all iron dopants appear in the single Fe_w substitutional configuration, while $3Fe_w+Vs$ becomes another major type of dopant structure in the case of high doping. Similar dopant structures have also been observed in synthetic Co-doped MoS₂ by Zhou *et al.*, indicating the tendency of excessive Fe/Co dopants to aggregate when the doping concentration is increased.¹⁸⁹



Figure 4-6: EDS characterization of monolayer Fe-doped WS₂. (a) The HAADF image of transferred Fedoped WS₂ on Quantifoil TEM grid, as well as the EDS intensity mapping at energies corresponding to the Fe-K α , S-K α and W-L α emission lines. Note that the Fe signals colocalize with the regions where WS₂ present, indicating the incorporation of Fe dopants in WS₂. (b) EDS spectra from the same region as (a), and individual peaks are labeled based on their characteristic energies. The characteristic Fe-K α emission is clearly observed in Fe-doped WS₂ sample (labeled in red). The EDS spectrum from bare Quantifoil grid region is also plotted as a reference (vertically shifted), eliminating the possibility that the Fe signal may originate from the background.

4.4 Re-doped MoS₂ monolayers

Re-doped MoS₂ was synthesized using AHM and ammonium perrhenate (APR) as the Mo and Re precursors, respectively. In this case, Sol 1 was prepared by dissolving AHM ((NH₄)₆Mo₇O₂₄, Alfa Aesar, purity of 99.999%; 0.01 g) and sodium cholate hydrate (0.2 g) into DI water (10 mL). Sol 2 was prepared by dissolving APR (VII) (NH₄ReO₄, Alfa Aesar, purity of 99.999%; 0.01 g (low-doping case) or 0.1 g (high-doping case)) into DI water (10 mL). To synthesize Re-doped MoS₂, freshly mixed Sol 1 (1 mL) and Sol 2 (1 mL) was spin-coated onto a clean SiO₂ (300 nm)/Si substrate (2500 rpm, 1 min). Subsequently, the precursor-coated substrate was loaded in the center of a quartz reaction tube, and 400 mg of sulfur powders were placed in an alumina boat located upstream. During synthesis, the furnace was ramped up to 800 °C in 30 min and held for 15 min. Simultaneously, sulfur powders were vaporized at 220 °C, allowing the sulfurization of the spin-coated precursors. Ar was used as the carrier gas throughout the process, with a flow rate of 100 sccm. It should be noted here that samples synthesized with two different metal concentration ratios were both investigated, which are AHM:APR 1:1 wt. (low doping) and 1:10 wt. (high doping) ratios. The results presented in Figures 4-7 (a)-(e) are all corresponding to the "low doping" case, because we found the increased amount of Re dopant precursors leads to the phase segregation into 1T'-ReS₂ and 1H-MoS₂, which deviates from the case of substitutional doping and will be discussed later in Figure 4-7 (f).

Figure 4-7 (a) depicts an optical image of as-synthesized Re-doped MoS₂ monolayers, exhibiting a triangular morphology with typical lateral sizes of ~20 μ m. The Raman spectra of Redoped and pristine MoS₂ are displayed in Figure 4-7 (b). Both spectra exhibit two prominent first order vibrational modes (E' and A'₁). The frequency of the E' mode in Re-doped MoS₂ does not show prominent changes when compared to that of pristine MoS₂. However, the A'₁ mode is redshifted by 1 cm⁻¹ in Re-doped MoS₂. It has been previously found that the frequency of the E' mode in MoS₂ is relatively insensitive to doping; however, the A'₁ mode tends to soften with higher electron doping concentrations, due to MoS₂'s stronger electron-phonon coupling.¹⁹⁰⁻¹⁹¹ Thus, the A'₁ mode shift in Re-doped MoS₂ monolayers could be attributed to the electron doping caused by Re dopants, as Re has been identified as an *n*-type dopant for monolayer TMDs in previous works.^{100, 177} Room-temperature PL studies revealed that the emission from monolayer Re-doped MoS₂ is red-shifted by 20 meV with an intensity quenching of more than 5x (Figure 4-7 (c)). This also constitutes an evidence of the Re doping, since the *n*-type doping can effectively reduce the spectral weight of exciton, leading to a negative trion-dominated PL emission.¹⁹²



Figure 4-7: Monolayer Re-doped MoS₂. (a) Optical image of monolayer Re-doped MoS₂ flakes. The scale bar is 20 μ m. (b) Raman spectra of pristine and Re-doped MoS₂ obtained using a 488 nm laser (normalized to A'₁ mode). Active Raman modes were determined by fitting the spectra with Voigt profiles. (c) PL spectra of Re-doped MoS₂ and pristine MoS₂ monolayers. (d) Atomic-resolution STEM-HAADF images of monolayer Re-doped MoS₂ synthesized with AHM:APR 1:1 wt. (low doping). Re dopants are marked with red-colored circles. (e) Experimental and simulated STEM images and line scans of a Re_{Mo} dopant. The dots in line scans represent experimental results, while the solid lines represent simulated results. (f) Atomicresolution STEM-HAADF images of monolayer Re-doped MoS₂ synthesized with AHM:APR 1:10 wt. (high doping). Interestingly, the increase of amount of Re dopant precursors leads to the formation of heterointerfaces between 1T'-ReS₂ and 1H-MoS₂ in local regions.



Figure 4-8: An AFM image of Re-doped MoS₂, and the corresponding height profile along the white dashed line in the image.

Atomic resolution STEM-HAADF imaging was performed to confirm the substitutional doping of Re into MoS_2 (see Figure 4-7 (d)). Relying on the Z-contrast, Re atoms stand out as brighter atoms at Mo sites in the MoS_2 lattice (highlighted with red-colored circles in Figure 4-7 (d)). The Re doping concentration was estimated to be ~0.3 at % according to performed statistical analysis on three random regions of low-magnification STEM images. A comparison between experimental and simulated STEM images and intensity line profiles (Figure 4-7 (e)) further confirms the presence of Re dopants at Mo sites.

It is also worth noting that, high magnification STEM-ADF image of the highly doped Re-MoS₂ samples (Figure 4-7 (f)) revealed the aggregation of Re into clusters and embedded islands of 1T'-ReS₂, forming a 1D sharp interface between 1T'-ReS₂ and 1H-MoS₂. The formation of ReS₂ is also evidenced by Raman spectroscopy characterizations (Figure 4-9). We attribute the formation of aggregated 1T'-ReS₂ to the addition of an excess amount of Re dopant precursors. From another perspective, this interesting phase segregation phenomenon implies the possibility of our method in synthesizing in-plane heterostructures of dissimilar phases. Since 1T'-ReS₂ and 1H-MoS₂ construct a type-I semiconducting heterojunction,¹⁹³⁻¹⁹⁴ the synthetic in-plane heterostructure, if controllable, can also serve as an excellent platform for studying fundamental phenomena such as carrier confinement and diffusion across the interface, as well as for constructing 2D optoelectronics such as ultrathin light emitting diodes and nanolasers. Future work will be focused on controlling the formation of 1T'-ReS₂/1H-MoS₂ heterostructures over Re-doped MoS₂, by tuning a series of parameters (*e.g.*, growth temperature and heating/cooling ramps) that influence the growth thermodynamically and/or kinetically.¹⁹⁵⁻¹⁹⁶ Finally, EDS characterization of Re-doped MoS₂ provided chemical composition information of the synthesized samples (Figure 4-10). No obvious characteristic Re-La emission line is observed for the low doping case (red-colored spectrum in Figure 4-10 (b)), indicating the current Re doping concentration is below the EDS detection limit. In comparison, the Re-La emission line is clearly present in the EDS spectra corresponding to highly doped Re-MoS₂ (blue-colored spectrum in Figure 4-10 (b)), which can be attributed to the aggregation effect of Re.



Figure 4-9: Raman spectra of pristine and Re-doped MoS₂ synthesized with high Re precursor concentration (normalized to A'₁ mode). Individual Raman modes are identified and labeled in the figure. Inset: Zoom-in Raman spectra from the black dash square region (120-250 cm⁻¹). In addition to the characteristic Raman modes of MoS₂, several additional peaks are observed in highly doped MoS₂ (see the inset, two most prominent peaks are labeled in red), which matches with the previously reported $A_g^1 \mod (~150 \text{ cm}^{-1})$ and $A_g^7 \mod (~212 \text{ cm}^{-1})$ of 1T'-ReS₂.¹⁹⁷ The Raman spectra corroborate the formation of 1T'-ReS₂ with increased amount of Re dopant precursors.



Figure 4-10: EDS characterization of monolayer Re-doped MoS₂. (a) The HAADF image of transferred highly Re-doped MoS₂ on Quantifoil TEM grid (corresponding to the spectrum in blue in panel (b)), as well as the EDS intensity mapping at energies corresponding to the Re-L α , S-K α and Mo-K α emission lines. (b) EDS spectra of Re-doped MoS₂ synthesized from precursor solutions with two different APR concentrations (labeled low and high). Individual peaks are labeled based on their characteristic energies. The characteristic Re-L α emission is only observed in Re-doped MoS₂ sample synthesized from precursors with high APR concentrations (the spectrum in blue). The EDS spectrum from bare Quantifoil grid region is also plotted as a reference (vertically shifted), eliminating the possibility that the Re signal may originate from the background.

4.5 V-doped in-plane W_xMo_{1-x}S₂-Mo_xW_{1-x}S₂ heterostructures

We further explored the capability of our method for doping in-plane heterostructures based on MoS₂ and WS₂. In Chapter 2, we have achieved a one-step growth of in-plane $W_xMo_{1-x}S_2$ -Mo_x $W_{1-x}S_2$ heterostructures using liquid phase precursors, and here we demonstrate the growth of monolayer V-doped in-plane $W_xMo_{1-x}S_2$ -Mo_x $W_{1-x}S_2$ heterostructures by integrating the heterostructures synthesis route with our doping strategy. For the synthesis of V-doped in-plane $W_xMo_{1-x}S_2$ -Mo_x $W_{1-x}S_2$ heterostructures, Sol 1 (W-precursor solution) was prepared by dissolving
AMT (0.05 g) and sodium cholate hydrate (0.2 g) into DI water (10 mL). In this particular case, two separate Sol 2 were prepared: (a) Mo-precursor solution was prepared by dissolving AHM (0.01 g) into DI water (10 mL); (b) V-precursor solution was prepared by dissolving vanadium (IV) oxide sulfate hydrate (VOSO₄ • xH₂O, 0.005 g) into DI water (100 mL). To synthesize V-doped inplane W_xMo_{1-x}S₂-Mo_xW_{1-x}S₂ heterostructures, the as-prepared Mo- and V-precursor solutions (1 mL each) were consecutively added into Sol 1 (2 mL). Then the fresh mixture was spin-coated onto a clean SiO₂ (300 nm)/Si substrate (2500 rpm, 1 min). Subsequently, the precursor-coated substrate was loaded in the center of a quartz tube, and 400 mg of sulfur powders were placed upstream. During synthesis, the furnace was first ramped up to 700 °C in 20 min, and held for 10 min. After that, the furnace was ramped up to 800 °C in 5 min, and held for 10 min. The sulfur powders were vaporized at 220 °C during the synthesis process, allowing the sulfurization of the spin-coated precursors. A flow rate of 100 sccm of Ar was used during the experiment.

Figure 4-11 shows an optical image of V-doped in-plane $W_xMo_{1-x}S_2$ - $Mo_xW_{1-x}S_2$ heterostructures. An optical contrast difference between the inner (darker blue) outer regions (lighter blue) of the triangular flake can be clearly observed, indicating the composition difference in the corresponding regions. A schematic illustration of the composition of the as-synthesized Vdoped in-plane $W_xMo_{1-x}S_2$ - $Mo_xW_{1-x}S_2$ heterostructures is displayed in Figure 4-11 (b). Due to the growth sequence controlled by the two-step heating ramp, the inner region (red) and outer region (green) are Mo-rich and W-rich, respectively. To verify the formation of heterostructures with the expected compositions, we performed Raman and PL spectroscopy measurements on both regions of the as-synthesized sample. Figures 4-11 (c) and (d) show Raman and PL spectra acquired at center (red), middle (brown) and edge (green) regions of a selected triangular flake, respectively, using a 488 nm laser. From the Raman spectra in Figure 4-11 (c), the center region of the flake shows MoS_2 -like vibrational modes, while the edge exhibits WS_2 -like vibrational modes, consistent with the trend observed in the $W_xMo_{1-x}S_2$ - $Mo_xW_{1-x}S_2$ heterostructures. The PL spectra of V-doped in-plane $W_xMo_{1-x}S_2$ - $Mo_xW_{1-x}S_2$ heterostructures in Figure 4-11 (d) revealed noticeably changes when compared to that of pristine MoS_2 and WS_2 monolayers. The overall significant quenching of the PL intensity, as well as shifts of the PL peak in the V-doped heterostructures are consistent with observations in V-doped WS_2 (see Figure 4-12). Raman intensity mappings from the $W_xMo_{1-x}S_2$ - $Mo_xW_{1-x}S_2$ heterostructures at 380 cm⁻¹ (MoS_2 E' mode) and 353 cm⁻¹ (WS_2 E' mode) are presented in Figures 4-11 (e) and (f), respectively. We can conclude that the MoS_2 -like and WS_2 like in-plane E' modes are only found at the center and edge of the doped heterostructures, respectively.



Figure 4-11: Monolayer V-doped in-plane $W_xMo_{1-x}S_2-Mo_xW_{1-x}S_2$ heterostructures. (a) Optical image of assynthesized V-doped in-plane $W_xMo_{1-x}S_2-Mo_xW_{1-x}S_2$ heterostructures. (b) A schematic illustration of the synthesized in-plane heterostructures. (c) Raman spectra collected from the center (red), middle (brown) and edge (green) regions of the V-doped $W_xMo_{1-x}S_2-Mo_xW_{1-x}S_2$. (d) PL spectra collected from the center (red), middle (brown) and edge (green) regions of the V-doped $W_xMo_{1-x}S_2-Mo_xW_{1-x}S_2$. Typical PL spectra of synthetic pristine MoS_2 (purple) and WS_2 (pink) monolayers are also plotted as references. (e) Raman intensity mapping at 380 cm⁻¹ (MoS_2 E' mode). (f) Raman intensity mapping at 353 cm⁻¹ (WS_2 E' mode).



Figure 4-12: Monolayer V-doped WS₂. (a) Optical image of monolayer V-doped WS₂. (b) PL spectra of V-doped WS₂ and pristine WS₂ monolayers. (c) Atomic-resolution STEM image of monolayer V-doped WS₂. V dopants are marked with red-colored circles.

The interface width and the atomic configuration of V dopants were further examined at the atomic scale by TEM. A low-magnification STEM image in Figure 4-13 exhibits an interface of ~100 nm between the center and edge regions, as featured by the image contrast transition. In V-doped in-plane $W_xMo_{1-x}S_2$ - $Mo_xW_{1-x}S_2$ heterostructures, three different transition metal atoms are expected to occupy metal sites. Due to differences in their atomic Z-numbers, V, Mo, and W atoms should display increasingly brighter contrasts in atomic-resolution STEM-ADF images. Figures 4-14 (a) and (b) show STEM-ADF images of the V-doped W_xMo_{1-x}S₂-Mo_xW_{1-x}S₂ heterostructures at center and edge of a representative island, respectively. We have found the presence of V dopants in both regions, which are highlighted using blue circles. Moreover, we performed a doping concentration analysis of the acquired ADF images in Figures 4-14 (a) and (b). A V concentration of ~ 0.5 at % and a W concentration of ~ 11.1 at % were estimated at the center (Mo-rich region), while the W-rich edge has an estimated V concentration of \sim 1.5 at % and a Mo concentration of ~ 0.7 at %. Figure 4-14 (c) presents simulated and experimental STEM images and intensity line profiles of V and Mo atoms at the W sites of WS₂ monolayers, showing a very good agreement, which further confirms the V-doping in these heterostructures. Since V atom is expected to be a ptype dopant of TMDs,198 and STEM characterization reveals a ~1% difference in V doping concentrations across the interface, we envisage that the synthesized V-doped $W_xMo_{1-x}S_2-Mo_xW_1$

 $_{x}S_{2}$ heterostructures may be utilized to construct atomically thin in-plane *p*-*n* junctions for electronics and optoelectronics.



Figure 4-13: Low-magnification STEM characterization of monolayer V-doped in-plane $W_xMo_{1-x}S_2$ -Mo_x $W_{1-x}S_2$ heterostructures, revealing an interface width of ~100 nm.



Figure 4-14: STEM characterizations of monolayer V-doped in-plane $W_xMo_{1-x}S_2-Mo_xW_{1-x}S_2$ heterostructures. (a)-(b) Atomic-resolution STEM-ADF images of the V-doped $W_xMo_{1-x}S_2-Mo_xW_{1-x}S_2$ heterostructures acquired at center and edge regions. Examples of Mo, W and V atoms are identified and marked with red, green and blue circles, respectively. (c) A comparison between experimental and simulated STEM images and line scans of V_W and Mo_W dopant configurations, indicating the feasibility of distinguishing Mo, W, V atoms by their relative contrasts. The dots in line scans represent experimental results, while the solid lines represent simulated results.

4.6 Conclusions

In Chapter 4 of this thesis, we have developed a liquid phase precursor-assisted technique for the *in situ* substitutional doping of TMD monolayers and in-plane heterostructures. Compared to conventional solid precursor CVD that uses powdered precursor and dopant sources, by homogeneously mixing and spin-coating the precursor solution, our approach minimizes the variation in local vapor pressures of different precursors at different locations of the substrate, and is likely to result in improved homogeneity of morphology and doping concentrations. We have also demonstrated that tunable doping can be easily achieved by controlling dopant precursor concentration in the mixed precursor solution. It is also noteworthy that the precursor film deposition involves spin-coating of minute amounts of an aqueous solution in the absence of high vacuum and/or high temperature techniques previously used for depositing films for sulfurization, thus greatly reducing the energy footprint associated with the growth of doped TMDs. To demonstrate the generalizability of this method, monolayer Fe-doped WS₂ and Re-doped MoS₂ were synthesized. Moreover, the achievement of V-doped in-plane $W_xMo_{1-x}S_2-Mo_xW_{1-x}S_2$ heterostructures by this method showcases the capability of performing simultaneously doping and hetero-interfacing of TMDs using our developed approach.

Our facile and reliable doping method constitutes an effective approach of engineering properties and functionalities in 2D TMDs and their heterostructures. For example, the successful incorporation of Fe, Re and V atoms may result in electron/hole doping and/or spin polarization, which can potentially significantly alter the electrical and magnetic properties of the host TMDs. Thus, future work will be focused on studying electronic transport and magnetic properties in doped TMD monolayers, as well as across the interface of the doped in-plane heterostructures. Moreover, with the development of computational approaches and materials databases of 2D TMDs, different dopants that give rise to optimal properties in fields such as energy conversion, electronics and

spintronics, can be identified and proposed. Furthermore, our synthesized doped atomically thin layers constitute components for vertical heterostructures, so as to form van der Waals solids which can be assembled in electronic and optoelectronic devices with emergent functionalities. In combination with computational predictions, in the future our work may be extended to other types of doped TMDs and heterostructures, boosting the advancements of materials by design.

Chapter 5

Clean and Deterministic Transfer of 2D TMDs for Ionic Transport Applications

This chapter is based on previously published work for which I am the first author (Ref. [79]). Parts of reference [79] are reproduced (adapted) with permission from Zhang, T.; Fujisawa, K.; Granzier-Nakajima, T.; Zhang, F.; Lin, Z.; Kahn, E.; Perea-López, N.; Elías, A. L.; Yeh. Y.; Terrones, M., Clean Transfer of 2D Transition Metal Dichalcogenides Using Cellulose Acetate for Atomic Resolution Characterizations. *ACS Appl. Nano Mater.* **2019**, *2*, 5320-5328. Copyright 2019, American Chemical Society. (https://pubs.acs.org/doi/abs/10.1021/acsanm.9b01257)

Section 5.2 of this chapter is based on parts of previously published work for which I am a co-author and am contributing to this part (Ref. [98]). Parts of reference [98] are reproduced (adapted) with permission from Thiruraman, J. P.; Fujisawa, K.; Danda, G.; Das, P. M.; Zhang, T.; Bolotsky, A.; Perea-López, N.; Nicolaï, A.; Senet, P.; Terrones, M.; *et al.* Angstrom-Size Defect Creation and Ionic Transport through Pores in Single-Layer MoS₂. *Nano Lett.* **2018**, *18*, 1651–1659. Copyright 2018, American Chemical Society. (https://pubs.acs.org/doi/10.1021/acs.nanolett.7b04526)

Atomically thin TMDs can be controllably synthesized on SiO₂/Si substrates by CVD. However, for many practical applications, those 2D crystals usually need to be detached from the growth substrate and placed onto target substrates. Hence, as discussed in Section 1.2.2 of this thesis, a robust and effective transfer of TMDs is often required as a post-synthesis processing step. Currently, the most widely used PMMA-based approach for transferring CVD-grown TMDs often causes substantial accumulation of polymer residues, as well as severe structural damage of TMDs induced during the etching of substrates at elevated temperatures. Chapter 5 of this thesis focuses on developing an alternative approach for the transfer of CVD-grown TMDs that can address the issues mentioned above, *i.e.*, cellulose acetate (CA)-assisted transfer method. The CA-transferred TMDs exhibit well-preserved structural integrity and unaltered optical properties, as well as largely improved micro- and nano-scale cleanliness with reduced wrinkles and cracks. Our work related to CA-assisted transfer of TMDs will be presented in Section 5.1.

Furthermore, driven by the need of controllably transferring TMD flakes to specific locations on the target substrate, especially for building up stacked vdW heterostructures and complex device structures, we have also designed and built a deterministic transfer system that consists of an optical microscope and an XYZ micromanipulator. This system is compatible with both PMMA- and CA-based transfer methods, allowing for the micro-precision transfer of TMD layers. Owing to the deterministic transfer capability, we not only built a WS₂-MoS₂ vertical heterojunction with an electronically coupled and uniform interface, but also fabricated MoS₂ nanopore devices for ionic transport studies. In collaboration with Prof. Marija Drndić's group at University of Pennsylvania, we systematically studied the correlation between ionic conductance of nanopore devices and the diameter of pores, which provided useful fundamental insights towards designing nanopore structures for practical applications involving large-scale ionic transport, such as water desalination. This work will be discussed in Section 5.2.

5.1 Clean transfer of 2D TMDs using cellulose acetate

5.1.1 The motivation of developing an alternative transfer technique with improved cleanliness

As discussed in Chapter 1, semiconducting TMDs have recently attracted considerable research interest due to their electrical and optical properties complementary to gapless graphene.⁸, ^{11, 21, 199} Utilizing the vdW interactions of atomically flat surfaces of TMD monolayers, their physical properties could be further engineered by creating vertically stacked vdW heterostructures³⁴ and by coupling TMDs with pre-designed substrates to form complex devices.^{30, 200} The ability to integrate 2D TMDs with different substrates has enabled numerous novel applications such as ultra-broadband photodetectors, interlayer exciton optoelectronics and portable lasers.^{30, 201-202}

To date, the fast development of CVD synthesis technique has led to the production of monolayer TMDs at relatively large scales.^{120, 203} However, high temperature is usually required during CVD synthesis, thus limiting the choice of suitable substrates. Because of the difference in thermal expansion coefficients between TMDs and the growth substrate, strain is also introduced into the TMD lattice during the growth and cooling processes.²⁰⁴ Thus, post-growth transfer of TMDs from the growth substrate is usually performed for device integration. Insulating SiO₂/Si substrates are among the most widely used substrates for the CVD synthesis of mono- and few-layer TMDs.^{76, 114, 205} Currently, the transfer of TMDs from SiO₂/Si onto arbitrary substrates is usually achieved by PMMA-based wet-transfer (PMMA-transfer), which involves the spin-coating of a PMMA support layer and the subsequent etching of SiO₂ in base solutions such as NaOH at ~90 °C.²⁰⁶⁻²⁰⁸ In 2008, the PMMA-transfer of 2D materials was first reported by Reina *et al.* for transferring exfoliated graphene to various substrates.²⁰⁷ Since then, the PMMA-based transfer

method was further adapted to CVD-synthesized 2D materials, which has been making profound impacts by enabling the investigation and applications of synthetic 2D materials on diverse substrates.^{205, 208} However, PMMA-based transfer process leaves polymer residues, cracks and wrinkles on transferred TMDs, which have been reported to degrade the electrical and optical properties of TMDs and their heterostructures.^{82, 209} Recently, several alternative transfer approaches have been developed,^{83-85, 210-222} such as the water-assisted delamination method^{83, 210-212}, dry transfer using viscoelastic polydimethylsiloxane (PDMS) stamps^{85, 213}, water-soluble polymer-mediated transfer⁸⁴ and double-support layer enabled transfer.²¹⁴ However, many of these existing transfer methods either require TMDs to be grown on substrates with certain properties (*e.g.*, hydrophilic sapphire substrate, conductive gold substrate), or involve a mechanical peeling process during transfer, which may not be suitable for fragile target substrates. In this context, PMMA-based method is still being widely used to transfer TMDs grown on SiO₂/Si considering its universality and handiness.

In this work, and in order to address the issues of TMD transfer-induced residues, surface wrinkles and cracks, we aimed at developing a clean and non-destructive alternative TMDs transfer technique based on the following points: (1) Using an alternative transparent polymer support layer that can be easily dissolved to obtain cleaner TMDs surfaces; (2) Optimizing the SiO₂ etching procedure for minimizing the formation of wrinkles and cracks during transfer. For the alternative polymer support layer, it has recently been reported that natural cellulose-derived compounds, such as cellulose acetate (CA) and cellulose acetate butyrate (CAB), can be easily dissolved in acetone, leaving considerable less residue than the case of PMMA, and thus work as better support layers for the clean and damage-free transfer of large area graphene from copper.²²³⁻²²⁴ In addition, CA is a low cost and low health harmfulness polymer with long shelf life, robust mechanical properties and suitable transparency, which are ideal characteristics for the application in 2D material

transfers.²²⁴⁻²²⁵ However, besides the transfer of graphene, its applications in transferring other 2D materials growing on different substrates have not yet been explored or achieved. In light of this, we employed CA as an alternative support layer during TMDs transfer. For the SiO₂ etching, conventional NaOH etching usually leads to wrinkles and cracks within as-transferred TMDs due to the bubble generation and sample's thermal expansion at elevated temperatures.⁸³ In our work, we substitute hot NaOH etchant with a mixture of NH₄F and HF that works at room temperature. Such mixture is known as buffered oxide etch (BOE) in the silicon microfabrication technology. When compared to NaOH solutions, BOE releases TMDs from the substrate without bubble formation (6HF + SiO₂ \rightarrow H₂SiF₆ + 2H₂O).²²⁶ In addition, the CA film has an increased hydrophilicity when compared to PMMA.²²⁷ This drives the etchant to penetrate through the CA/SiO₂ interface, thus enabling a room-temperature etching process.

A variety of microscopic and spectroscopic techniques, including Raman, PL, AFM, AC-HRSTEM, were employed to investigate the crystal quality and micro-/nano-scale surface morphology of CA-transferred TMDs. A significantly improved surface cleanliness was observed in WS₂ monolayers transferred using CA compared to the ones transferred using PMMA. Remarkably, without any post-transfer treatments, the CA-transfer method yields large clean areas (more than 20 \times 20 nm²) under STEM imaging conditions. Beyond the application for STEM imaging, the CA-transfer technique can potentially be beneficial for other atomic resolution characterization techniques of 2D TMDs, including scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS).

5.1.2 CA-assisted transfer method

The schematic illustration of our CA-assisted transfer process is shown in Figures 5-1 (a)-(e). The method involves four major steps: (1) CA powder (cellulose acetate, product number 419028, Sigma-Aldrich) was dissolved in acetone to obtain a 10 mg/mL solution, which was then spin-coated onto the TMDs at 3000 rpm for 60 s, forming a CA film (Figure 5-1 (b)); (2) The SiO_2 layer was etched in BOE (ammonium fluoride – hydrofluoric acid mixture, product number 40207, Sigma-Aldrich), which released the CA/TMDs films in a few minutes without heating (Figure 5-1 (c)); (3) The CA/TMDs film was triple-washed in deionized water and then scooped out using the target substrate. The transferred assembly was dried on a 50 °C hot plate for \sim 30 min to ensure a conformal contact (Figure 5-1 (d)); (4) The CA layer was then removed by acetone and isopropanol (IPA) baths, leaving the transferred TMD flakes well adhered on the target substrate (Figure 5-1 (e)). Owing to the usage of BOE-based room-temperature and a bubble-free etching process, no observable macroscale cracks/wrinkles were introduced to the delaminated CA film (see Figure 5-2). The 495K PMMA A4 was used in this study for comparison, which has been commonly applied during PMMA-transfer of TMDs²²⁸⁻²²⁹. It is worth noting that the BOE etching process is not directly applicable to the PMMA-transfer method due to the insufficient etchant penetration (the etching reaction could take several hours to complete, see Table 5-1). We attribute this significant etching rate difference to the increased hydrophilicity of the CA film when compared to that of PMMA, as previously reported.²²⁷ For the CA-transfer method, the increased hydrophilicity can effectively drive BOE to penetrate through the CA/SiO₂ interface to initiate etching. While a previous study has suggested that hydrophilicity of the polymer film can lead to weakening of the polymer-TMDs adhesion in aqueous solution,⁸³ we confirmed the intactness of as-transferred flakes by the CA-transfer method. Optical microscopy images reveal that CA-transferred WS₂ flakes have no obvious damage or morphological change (Figure 5-1 (f)), suggesting that the interaction

between CA and TMDs is strong enough during the transfer process, thus preserving the initial configuration of the flakes. Apart from the transfer of WS_2 , we also demonstrated the versatility of the CA-transfer method for transferring other TMDs onto various substrates. For example, the optical images of transferred MoS₂ on Au (100 nm)/Cr (5 nm)/SiO₂, $W_xMo_{1-x}S_2$ on polydimethylsiloxane (PDMS), and WS₂ on graphene/SiO₂/Si substrate, are shown in Figure 5-3.



Figure 5-1: CA-transfer of CVD-grown TMDs. (a-e) Schematic illustration of the CA-transfer process. (a) TMDs flakes are located on SiO_2/Si substrate. (b) A layer of CA film is spin-coated onto TMDs surface. (c) The assembly is placed on the surface of BOE at room temperature. The CA/TMDs film is separated from the Si substrate in a few minutes. (d) The CA/TMDs film is rinsed in deionized water and then fished by the target substrate. (e) The CA layer is removed by acetone and IPA, leaving transferred TMDs on the target substrate. (f) Typical optical images of as-grown WS₂ on 300 nm SiO₂/Si and CA-transferred WS₂ on 100 nm SiO₂/Si, indicating the preserved morphology and configuration after the transfer process.



Figure 5-2: Morphology comparison of CA and PMMA films before and after the etching process. Two $1 \times 1 \text{ cm}^2 \text{ WS}_2$ samples were transferred by two different transfer methods, respectively. (a) Photographs of the spin-coated CA and PMMA film before transfer. (b) Photographs of the CA-WS₂ and PMMA-WS₂ film on new substrates after the etching process.



Figure 5-3: Examples of transferred TMDs on various substrates using CA-transfer method. (a) MoS_2 on an Au (100 nm)/Cr (5 nm)/SiO₂ substrate. (b) $W_xMo_{1-x}S_2$ on a polydimethylsiloxane (PDMS) substrate. (c) WS_2 on a graphene/SiO₂/Si substrate. All scale bars are 20 μ m.

Table 5-1: Etching efficiency comparison between CA-transfer and PMMA-transfer techniques. The tests of etching efficiency are all based on 1×1 cm² WS₂ samples grown on 300 nm SiO₂/Si. The etching efficiency results show that the room-temperature BOE etching is an efficient method for CA-based transfer, but not directly applicable to PMMA-based transfer.

Transfer Method Etching Medium	CA-based Transfer	PMMA-based Transfer
2M NaOH Solution (on 90 °C Hot Plate)	N/A (CA reacts with NaOH)	23 min
BOE (Room Temperature)	7 min	~5 h (Insufficient wetting)

The quality of CA-transferred TMDs was subsequently examined by Raman and PL spectroscopies. CVD-grown monolayer WS₂, a representative semiconducting TMD with direct bandgap, was employed as the test system. Raman spectroscopy is a powerful and non-destructive tool that investigates physical and structural properties of a wide range of 2D materials by probing

their vibrational modes.¹³ Figure 5-4 (a) depicts typical Raman spectra of as-grown and transferred monolayer WS₂. Lorentzian functions were used to determine the frequencies of Raman modes. The acquired Raman spectra contain three main peaks corresponding to the in-plane E' mode, outof-plane A1' mode and 2LA(M) mode that is convoluted with the E' mode. It is noteworthy that, no prominent enhancement of defect-activated LA(M) mode is observed in CA-transferred monolayer WS₂, indicating preserved structural properties after the transfer process. When compared to as-grown WS₂, the in-plane E' mode in CA-transferred WS₂ exhibits a ~2 cm⁻¹ blue shift. However, the out-of-plane A_1 ' mode remains unchanged after the transfer process. The observed phenomena can be understood as a tensile strain release effect, which matches well with previous reports on transferred CVD-grown TMDs.^{149, 230} Additionally, the frequency of the outof-plane A1' mode is sensitive to charge doping effects.¹⁹⁰ The frequency of A1' mode in CAtransferred and as-grown WS₂ remains identical, indicating that no additional doping effects have been introduced by the presence of impurities during the CA-transfer. The optical properties of CAtransferred WS₂ monolayers were then investigated by PL measurements. In order to avoid laser heating effects, all measurements were performed under a low laser power (33.9 μ W). Typical intensity-normalized PL spectra and the corresponding fitting of as-grown and transferred monolayer WS₂, are shown in Figure 5-4 (b). As-grown monolayer WS₂ exhibits a sharp peak centered at 1.97 eV associated with the neutral exciton (X⁰) emission.^{126, 149} In contrast, PL spectra of CA-transferred monolayer WS2 exhibit a blue-shift of ~40 meV, which again confirms the release of strain after the transfer process.²⁰⁴ Further PL spectral fitting indicates that the X⁰ of CAtransferred monolayer WS₂ has an average FWHM of 39 ± 4 meV, which is slightly narrower than that of PMMA-transferred WS₂. The X⁰ FWHM value of CA-transferred WS₂ is also comparable with that of as-grown WS₂ (see Figure 5-5), which suggests that the CA-transfer process preserves the optical quality of CVD-grown TMDs.



Figure 5-4: Optical characterization of CA-transferred monolayer WS₂. (a) Typical Raman spectra of asgrown and CA-transferred monolayer WS₂ under 488 nm excitation. The spectra are normalized to the A_1 ' mode. Three Raman modes: 2LA(M), E' and A_1 ' modes, are used for fitting. (b) Normalized PL spectra of as-grown and CA-transferred monolayer WS₂ under 488 nm excitation. PL spectra are deconvoluted into X⁰ and X⁻ peaks. Both as-grown and CA-transferred WS₂ are on 300 nm SiO₂/Si substrates.



Figure 5-5: The fitted average X^0 linewidth of as-grown, CA-transferred and PMMA-transferred monolayer WS₂. CA-transferred monolayer WS₂ has a X^0 linewidth of 39 ± 4 meV that is comparable with as-grown WS₂. X^0 linewidth of PMMA-transferred WS₂ is slightly broadened to 41 ± 4 meV. The presented average values and error bars were based on measurements of 10 random monolayer WS₂ flakes each. All measured WS₂ flakes were synthesized in one CVD reaction cycle.

5.1.3 Surface morphology and cleanliness of CA-transferred WS₂

The surface morphology and cleanliness of CA-transferred monolayer WS₂ were studied and compared with conventional PMMA-transferred ones using AFM. Figures 5-6 (a)-(b) depict AFM images of CA-transferred monolayer WS₂ with two different magnifications, which exhibit a clean and uniform surface of the transferred monolayer WS₂, with an average root-mean-square (rms) roughness of 0.29 nm. The height profile in Figure 5-6 (c) shows no observable surface protrusions higher than 1 nm, thus indicating an effective dissolution of the CA film without large polymer residues. We also measured intrinsic rms roughness values of bare SiO₂/Si (0.23 nm) and as-grown monolayer WS₂ on SiO₂/Si (0.27 nm), which are comparable with the rms value of CAtransferred WS₂. Thus, it can be deduced that the CA-transfer process can largely preserve the inherent surface flatness and homogeneity of the transferred TMDs flakes. In contrast, the AFM images in Figures 5-6 (d)-(e) reveal the surface morphology of conventional PMMA-transferred monolayer WS₂, showing an increased inhomogeneity caused by the remaining PMMA debris. These PMMA residues induce surface protrusions with typical heights of ~4 nm, as is shown by the height profile in Figure 5-6 (f). Accordingly, the surface rms roughness extracted from Figure 5-6 (e) is also increased to 1.01 nm due to the surface inhomogeneity, which is a consistent value when compared to previous reports on PMMA-transferred 2D materials.^{224, 231} In addition, surface wrinkles are largely reduced in our CA-transferred monolayer WS₂ when compared to the PMMAtransferred counterpart, as shown in Figures 5-6 (b) and (e). A large density of wrinkles in PMMAtransferred WS₂ may originate from the sample's thermal expansion and bubble generation during the NaOH etching process. In comparison, the etching process in the CA-transfer occurs at room temperature without bubble formation, which effectively reduces the mechanical damage of TMDs during transfer.



Figure 5-6: Micro-scale surface morphology of transferred monolayer WS₂ on 300 nm SiO₂/Si using (a-c) CA-transfer and (d-f) PMMA-transfer techniques. (a) AFM image and (b) zoom-in AFM image of the surface of CA-transferred WS₂. (c) The surface height profile of CA-transferred WS₂ corresponding to the black line shown in (b). (d) AFM image and (e) zoom-in AFM image of the surface of PMMA-transferred WS₂. (f) The surface height profile of PMMA-transferred WS₂ corresponding to the black line shown in (e).

Based on the micrometer-scale cleanliness improvement revealed by AFM, we speculated that our CA-transfer technique could potentially yield cleaner TMDs surfaces even at the nanometer-scale. In this context, STEM imaging was carried out to investigate the nanometer-scale cleanliness. A HAADF detector was used for imaging. In the STEM-ADF imaging mode, the ADF intensity changes depending on the atomic Z-number ($\sim Z^{1.6-1.9}$ dependence).¹⁸² Thus, clean regions and contaminated polymer residue regions can be easily distinguished by the intensity and uniformity of the ADF signal. Figure 5-7 (a) shows representative STEM-ADF images acquired from monolayer WS₂ transferred using CA and PMMA, and the regions that contaminated with polymer residues are highlighted in yellow. In the acquired images, uniform ADF intensity is expected in the clean regions due to the absence of layer number variation. It is obvious that the area of each clean region is larger for CA-transferred WS_2 (see Figure 5-7 (a), and other lower magnification STEM-ADF images included in Figure 5-8). It is also worth noting that, no thermal annealing or other post-transfer treatments were performed prior to STEM-ADF imaging. Although it has been reported that air and Ar/H_2 two-step annealing can further improve the nanoscale surface cleanliness of transferred 2D materials, the cost is the generation of defects and nanoscale tears and ripples, which are unwanted problems for TEM characterizations.²⁰⁹ In comparison, the CAtransferred method allows us to access to much larger clean areas (more than 20×20 nm²) under STEM imaging conditions without any post-transfer treatments, which provides significant convenience to atomic resolution characterizations of 2D TMDs. Figure 5-7 (b) shows a magnified STEM-ADF image of CA-transferred WS₂. The bright spheres in the image correspond to tungsten (W) atoms, and the slightly darker spheres correspond to the sulfur columns (S_2) of the WS_2 hexagonal structure. The STEM characterization also further confirms that the CA-transfer process did not induce any structural damage or change to monolayer WS₂. In order to quantitatively compare the nanometer-scale cleanliness of the monolayer WS₂ transferred using the CA-transfer and PMMA-transfer methods, ADF intensity histograms (Figure 5-7 (c)) were acquired from low magnification STEM images (Figure 5-8). The noise in the STEM-ADF images, as well as atomic contrast from the W and S₂ columns, are flattened by a Gaussian blur filter with a large size blurring radius. Subsequently, the ADF intensity histograms were generated from those filtered images. A Gaussian peak was used to fit the component of the ADF histogram corresponding to the clean region, whereas a log-normal peak was used to fit the component of the ADF histogram corresponding to the contaminated region, caused by the thickness variation induced by the contamination layers. Total clean areas were calculated based on the fitting results of the ADF

histograms (Figure 5-7 (d)). We found that the total clean area increased from 12.7 % to 30.7 % when the polymer support layer is changed from PMMA to CA.

To summarize, our CA-transfer method leads to largely improved surface morphology and micro-scale cleanliness compared to the conventional transfer method. In addition, by utilizing STEM imaging as an effective technique to evaluate the nanometer-scale cleanliness, it is revealed that CA-transfer leads to ~3 times higher percentage of uncontaminated area when compared to PMMA-transferred ones. Because of the improved cleanliness and uncompromised simplicity/convenience of this CA-transfer method, it holds promise as an alternative to the widely-used PMMA-method, especially when preparing samples for high-resolution nanometer-scale characterization.



Figure 5-7: STEM-based cleanliness investigation of the transferred WS₂ with different techniques. (a) STEM-ADF image acquired from WS₂ flakes transferred using CA and PMMA. (b) Atomic-resolution STEM-ADF image acquired from the clean region shows the intact crystal structure of monolayer WS₂. (c) Representative ADF intensity histograms of the STEM-ADF images acquired from the CA-transfer and PMMA-transfer methods. The ADF intensity of the histogram was normalized using the FWHM of the WS₂ peaks. (d) Calculated total clean area from STEM-ADF images.



Figure 5-8: Low magnification STEM-ADF images of CA- and PMMA-transferred WS₂. STEM-ADF images obtained from CA- and PMMA-transferred WS₂ at different magnifications (a) and (b).

5.2 Controlled fabrication of monolayer MoS2 nanopore devices for ionic transport

5.2.1 The motivation of investigating ionic transport in 2D membranes

Water is invaluable resource for human life, and the availability of adequate and fresh water has becoming a serious challenge due to the population growth and increasing energy needs. Although water covers more than 70% of the Earth's surface, the vast majority of the water are stored in seas and oceans. As a result, the advancement of water desalination technology is greatly desired. In recent years, membrane-based desalination has been demonstrated as an energy-efficient technique for high-quality water purification²³², which consists of nanopore arrays that can permeate water molecules but reject hydrated ions. The key for this membrane-based desalination technology is to seek for a membrane that has high water permeability through nanopores without losing salt rejection capability. Theoretical modelling shows that the water molecule flux through nanopores can be expressed as $A = \frac{\epsilon r_p^2}{8\mu\delta_m}$, where A is water molecule flux, ϵ is surface porosity, r_p is the radius of a single nanopore, μ is solution viscosity and δ_m is layer thickness. Thus, water flux A scales inversely with membrane thickness δ_m . Because of the ultrathin nature of 2D materials, 2D nanoporous membranes can potentially exhibit orders of magnitude higher water flux compared with commercially available polymer membranes.²³³⁻²³⁵ Especially, based on molecular dynamics simulations, Heiranian *et al.* have reported that monolayer MoS₂-based nanopores with single pore area of 20 - 60 Å² can even exhibit up to 70% higher flux than graphene nanopores as well as reject more than 88% of ions, which demonstrates that monolayer nanoporous MoS₂ can be a very promising candidate as next-generation desalination membrane.²³⁶

Although the high performance of monolayer MoS₂ nanopores for water desalination have been theoretically predicted, the experimental demonstration is still lacking, which is partially due to the challenge of scaling-up synthesis of MoS₂ materials, effectively transferring MoS₂ flakes for the fabrication of MoS₂ nanopore device, determining the optimized nanopore sizes, as well as controllably creating uniformly-sized nanopores on monolayer MoS₂ membrane. In this work, we developed an optical microscope-based deterministic transfer method that is capable for placing TMD flakes onto target locations on the substrate. By Ga⁺ ion irradiation on monolayer MoS₂ membrane with varied doses at 30 kV, MoS₂ nanopore arrays with sub-nanometer to nanometer sizes were fabricated. Correlated Raman, PL, STEM, and ionic transport studies were performed, which not only made a correlation between the irradiation doses and resulted vacancy (nanopore) numbers and size distributions, but also demonstrated how ionic conductance varied as a function of nanopore sizes. Our work lays the foundation for future efforts in designing 2D nanopore membranes for scale-up water desalination applications.

5.2.2 Deterministic transfer of TMD monolayers

To fabricated MoS₂-based nanopore devices, a prerequisite is to transfer the as-grown MoS_2 flake onto a silicon nitride (SiN_x) nanopore device chip dedicated for ionic transport measurements. Basically, in a typical SiN_x nanopore device, a SiN_x membrane (~100 nm thick) is suspended at the center of a Si wafer. A pore with diameter of 100-200 nm is drilled on the SiN_x membrane by focused ion beam (FIB), which is the target location for suspending the transferred MoS_2 . In this case, due to the randomness of depositing flakes using conventional wet-transfer method, an alternative position-controlled manipulation (*i.e.*, deterministic transfer) is desired for reliably fabricating the aforementioned device structures.

For this purpose, we have developed a micromanipulator-based deterministic transfer system that is compatible with both PMMA- and CA-based transfer methods. Our setup consists of an optical microscope, an XYZ micromanipulator and a computer monitor (Figure 5-9), which is similar to the ones in previous reports.^{85, 98} During transfer, XYZ positions of the flake to be transferred (top) and the target substrate (bottom) were controlled independently *via* micromanipulator and microscope stage, respectively. The monitor was used for observing/aligning the flakes during the transfer process. To describe our method in detail, the schematics of deterministic transfer process is depicted in Figures 5-10 (a)-(f), which contains five major steps: (1) A polymer film (either PMMA or CA) was spin-coated onto a substrate covered with as-grown TMDs (Figure 5-10 (b)); (2) The sample region of interest was identified under an optical microscope, and then a piece of polydimethylsiloxane (PDMS) stamp with a pre-opened square window (approximately 2 mm × 2 mm), was attached to the sample. Note that the square window region was placed on top of the region of interest (Figure 5-10 (c)); (3) The assembly was subsequently placed in the etchant (NaOH (for PMMA-transfer) or BOE (for CA-transfer)) to lift off the SiO₂/Si layer. Then, the PDMS/polymer film/TMDs was mounted onto a micromanipulator

for micro-positioning. The deterministic transfer process was carried out under an optical microscope equipped with a long working distance objective lens. The relative position of the sample and target substrate can be well controlled by separately tuning the micromanipulator and stage position. During this step, the pre-opened PDMS window enables a better optical visibility of TMDs (Figure 5-10 (d)); (4) After finishing the positioning of the TMDs, the assembly was heated up to 190 °C either *in situ* on the microscope stage or *ex situ* on a hot plate, in order to ensure a good contact between TMDs and the substrate (Figure 5-10 (e)); (5) The deterministically placed TMDs flake was then cleaned with acetone/IPA (Figure 5-10 (f)).



Figure 5-9: The setup of the deterministic transfer stage for micro-positioning MoS_2 flakes onto SiN_x windows. A micromanipulator consisting of a piezoelectric stage (NanoMax-TS flexure stage, Thorlabs) and a custom-built cantilever was applied to align the MoS_2 sample with SiN_x . An optical microscope (Olympus BH2 Microscope) was used to monitor the deterministic transfer process.



Figure 5-10: Schematic illustration of the deterministic transfer procedure. (a)-(b) A layer of polymer is spincoated onto the TMDs surface. (c) The sample is attached to a PDMS stamp with a square opening. (d) The SiO₂/Si layer is etched in NaOH or BOE. Then, the deterministic positioning is carried out under an optical microscope, equipped with a long working distance (LWD) objective, by aligning PDMS/polymer film/TMDs with the target location of the substrate. (e) The assembly is heated up to enhance the contact between TMDs and the target substrate. (f) The deterministic transfer is finished with acetone/IPA cleaning.

To demonstrate the effectiveness of the deterministic transfer method, a vertically stacked WS₂-MoS₂ heterostructure was first fabricated. In this case, monolayer MoS₂ was first transferred to a bare SiO₂/Si substrate using our CA-assisted wet-transfer method. Then, a WS₂ flake was deterministically placed on top of the transferred MoS₂. The step-by-step optical images during the deterministic transfer process were recorded and are presented in Figure 5-11. The stacked WS₂-MoS₂ was finally annealed at 250 °C in Ar/H₂ to remove trapped residues and enhance interfacial contact. Figure 5-12 (a) shows the optical microscopy image of the final assembly of the WS₂-MoS₂ heterojunction. The bottom flake, top flake and overlapped bilayer regions are marked in the optical image. Raman spectra acquired from the monolayer MoS₂, WS₂ and heterostructure regions (Figure 5-12 (b)) reveal distinct vibrational modes from the WS₂ and MoS₂ regions, respectively, and the Raman signal from the overlapped region comprises vibration modes from both layers. Raman mappings of the MoS₂ A₁' (Figure 5-12 (d)) and WS₂ A₁' modes (Figure 5-12 (e)) confirm

the structural uniformity of both layers after the deterministic transfer process. Importantly, it can be noticed from Figures 5-12 (d) and (e) that the Raman signal in the overlapped WS₂-MoS₂ region is not a simple "addition" of spectra from both layers, but exhibits a Raman intensity quenching, which can be explained as an interlayer coupling-induced Raman quenching effect that has been observed previously.²³⁷ In order to probe the interfacial cleanliness and optical quality of the stacked heterostructures, fluorescence microscope imaging was performed using a band pass filter centered at 673 nm, which is close to the X^0 exciton energy of monolayer MoS₂, as shown in the inset of Figure 5-12 (a). A uniform quenching of fluorescence emission in the WS₂-MoS₂ regions can be clearly observed. Further PL measurements (see Figure 5-12 (c)), confirmed the quenching of the emission from WS₂-MoS₂, as indicated by the large suppression of the PL signals (more than 25 times), from the WS₂-MoS₂ region when compared to individual monolayers of WS₂ and MoS₂. The significant PL quenching results from the charge separation in WS₂-MoS₂ heterostructures with type-II band alignment, which is a direct optical evidence of interlayer electronic coupling.²³⁸⁻ ²³⁹ PL intensity mappings corresponding to the PL peak energies of MoS₂ (Figure 5-12 (f)) and WS_2 (Figure 5-12 (g)) show the uniform quenching of the PL intensity in the overlapped region, which further indicates the created high-quality uniform interface.



Figure 5-11: Step-by-step optical microscope images of stacked WS_2 -MoS₂ heterostructures fabrication by CA-based deterministic transfer. Target flake on substrate (monolayer MoS₂) and CA-covered monolayer WS_2 were brought into focus separately by the optical microscope stage and micromanipulator, respectively. The relative position was carefully aligned under optical microscope. After the alignment process, the assembly was heated up and subsequently cleaned in acetone and IPA to acquire stacked heterostructures. All scale bars are 20 μ m.



Figure 5-12: Manually stacked WS₂-MoS₂ heterostructures. (a) Optical image of WS₂-MoS₂ heterostructures fabricated by position-controlled artificial stacking. Inset: fluorescence microscopy image of the same WS₂-MoS₂ heterostructures. (b) Raman spectra and (c) PL spectra collected from monolayer MoS₂ (blue), monolayer WS₂ (orange) and WS₂-MoS₂ (red) regions, respectively. (d) Raman mapping of the intensity of MoS₂ A₁' mode (404.7 cm⁻¹). (e) Raman mapping of the intensity of WS₂ A₁' mode (418.5 cm⁻¹). (f) PL intensity mapping of MoS₂ PL (1.90 eV). (g) PL intensity mapping of WS₂ PL (2.01 eV). All scale bars are 20 µm.

5.2.3 The fabrication of MoS₂ nanopore devices

Once the deterministic transfer system was successfully developed, MoS_2 monolayers were transferred to the SiN_x chip for fabricating nanopore devices. Figures 5-13 (a) and (b) show typical optical and fluorescence images of as-transferred MoS₂, indicating the intact monolayer MoS₂ flake with retained fluorescence emission on the rectangular SiN_x window after transfer. In order to examine the crystallinity and optical properties of transferred MoS₂, Raman and PL characterizations were performed on both bare SiN_x and MoS₂-SiN_x regions using 488 nm excitation. Two characteristic peaks appear in the Raman spectrum (Figure 5-13 (c)), which represent the in-plane mode E['] (~385.7 cm⁻¹) and out-of-plane mode A₁['] (~404.5 cm⁻¹), respectively. The frequency separation between E['] and A₁['] modes is ~19 cm⁻¹, confirming the transferred sample is indeed monolayer MoS₂.¹²³ For the PL spectra shown in Figure 5-13 (d), though the SiN_x window has a background fluorescence (black line), the transferred MoS₂ still retains strong PL emission with clearly defined A and B exciton peaks.



Figure 5-13: Monolayer MoS_2 transferred onto a SiN_x window. (a) Optical image and (b) fluorescence image of transferred monolayer MoS_2 on the SiN_x nanopore device. (c) Raman and (d) PL spectra of bare SiN_x region and monolayer MoS_2 -SiN_x region, respectively.

Nanopores were then produced on suspended monolayer MoS₂ membranes by rastering Ga⁺ beam with different doses using a FIB. The surface damage created by Ga⁺ ion bombardment can be quantified as $\sigma = it/Ae$, where σ is the defect density, *i* is the measured ion current, *t* is the beam exposure time, *A* is the irradiation area and *e* is the ion charge.²⁴⁰ By varying ion irradiation time *t*, Ga⁺ ion doses were tuned, resulting in different defect densities created in monolayer MoS₂. To evaluate the defect structure and distribution, STEM was performed on MoS₂ membranes irradiated with varied Ga⁺ ion doses. STEM images (Figure 5-14 (a)) shows that defect clusters with good uniformity among the randomly chosen imaging area are produced by ion irradiation, forming sub-nanometer to nanometer sized nanopore arrays. It should also be noted that, with increased irradiation dose in the investigated range (0 - 2.5 × 10¹³ ions/cm²), the nanopore density increases without obvious mean nanopore size expansion. The details related to statistical analysis of pore size/density distributions are beyond the scope of this thesis, but they can be found in this reference.⁹⁸



Figure 5-14: STEM, Raman, and PL characterization of Ga^+ irradiated monolayer MoS₂. (a) AC-STEM images of pristine and Ga^+ irradiated MoS₂ with different ion doses. Increased density of nanopores can be observed with the increase of Ga^+ dose. (b) Raman spectra of pristine and Ga^+ irradiated MoS₂. Inset shows increased LA modes intensity with the increase of Ga^+ dose. (c) PL spectra of pristine and Ga^+ irradiated MoS₂. Significant PL quenching and emergence of defect-induced D peak are observed with the increase of Ga^+ dose.

Degree of disorder in irradiated MoS_2 was then investigated by Raman and PL spectroscopy. The overlapped LA(M) and LA(K) Raman modes both originate from double resonance processes involving a phonon and a defect. As a result, the intensity of defect-induced LA(M) + LA(K) modes can be used to qualitatively determine the disorderness of monolayer MoS_2 .

Raman spectra of MoS₂ irradiated with different doses (Figure 5-14 (b)) show a noticeable uplifting of LA(M) + LA(K) modes (Figure 5-14 (b) inset), indicating the increased defect density with irradiation dose. Also, a broadening of E' with increased defect density can also be identified. This effect can be interpreted according to Mignuzzi *et al.* as the emergence of an additional Raman mode LO(M) at ~377 cm⁻¹, overlapping with E', which is a defect-activated mode as well.²⁴⁰ Furthermore, PL spectra normalized to A₁' Raman mode (relatively inert to defects) shows a drastic quenching with increased defect density, as is shown in Figure 5-14 (c). The decrease of exciton peak can be related to defect-induced charge trapping and mid-gap states, inducing the emergence of bound exciton (X^B) as well as non-radiative recombination pathways.²³ In all, through a combination of STEM, Raman, and PL characterization techniques, Ga⁺ ion irradiation was identified as a controllable route for producing sub-nanometer to nanometer pore arrays in monolayer MoS₂.

5.2.4 Ionic transport measurements of nanopores in MoS₂ monolayers

The ionic transport property of nanopore arrays created by varied doses of Ga⁺ irradiation was further investigated using the experimental setup shown in Figure 5-15 (a). The measurements were carried out and the data were analyzed by Prof. Marija Drndić's research group. Basically, an electrochemical cell was used to measure the I-V curve across the MoS₂ nanopore device in 1 M KCl solution, and the flow of hydrated ions (K⁺ and Cl⁻, and K⁺ is the smaller ion compared to Cl⁻) would contribute to the measured ionic current. Figure 5-15 (b) demonstrates the I-V curve of a MoS₂ membrane irradiated with Ga⁺ dose of 1.6×10^{13} ions/cm², and the top inset shows a STEM image of the irradiated MoS₂ membrane. For comparison, the bottom inset plots the I-V characteristics of pristine MoS₂ membrane, and it can be clearly seen that the irradiated membrane exhibits an ionic flow with nonlinear I-V curve, while the ionic conductance across pristine membrane is negligible (ionic conductance G = dI/dV). The difference in conductance values indicates that the pristine MoS₂ is impermeable to ionic transport, and Ga⁺ irradiation opens up nanopores that serve as channels for hydrated ions to flow through. The nonlinear I-V response has been demonstrated in sub-nanometer 2D nanopores, which can be understood by the stripping of the ionic solvation shell at a higher voltage.²⁴¹



Figure 5-15: Experimental setup and current-voltage (I-V) plot of irradiated MoS₂ device. (a) Experimental setup to measure the conductance of MoS₂ nanopore devices. (b) The I-V curve of MoS₂ irradiated with a dose of 1.60×10^{13} ions/cm², showing a nonlinear trend in the voltage range of V_B = ± 0.8 V. (bottom inset) I-V curves for a pristine MoS₂ membrane (black) and the same irradiated MoS₂ device (orange) for V_B = ± 0.1 V. (top inset) STEM image of a Ga⁺ irradiated suspended MoS₂ membrane.

Utilizing this experimental setup, the ionic transport properties as a function of Ga^+ ion doses were studied. Since we have performed a statistical analysis of pore size distributions in MoS_2 membranes irradiated with different doses, it is expected that the measured ionic conductance can be correlated with pore diameters. Figure 5-16 shows the pore diameter distributions in pristine and defective MoS_2 monolayers irradiated with different doses, which were extracted from STEM images (performed by Dr. Kazunori Fujisawa). Interestingly, it is found that within the applied Ga^+ doses, although the density of nanopores significantly increases with irradiation dose (featured by the uplifting of the bar graphs), the created nanopores are mainly smaller pores (V_{1Mo} , V_{1Mo+3S} , and V_{2Mo+2S}) with diameters < 0.6 nm. In contrast, the density of large pores (marked with the green box in Figure 5-16) exhibits a much smaller change with Ga⁺ doses, indicating the applied irradiation doses are relatively small for creating large-sized pores or inducing the merge of small pores.



Figure 5-16: Distribution of the pore diameters for pristine MoS_2 and defective MoS_2 membranes produced by Ga⁺ ion irradiation with different doses. The red (blue)-colored box corresponds to diameter ranges for V_{1Mo+yS} (V_{2Mo+yS}) pores which is calculated from simulated STEM-HAADF images (inset, scale bar is 500 pm).

Figure 5-17 plots experimentally obtained conductance G values (MoS₂ pores created by Ga⁺ doses 1-3), as well as various literature results and simulated ionic conductance by molecular dynamics (MD), as a function of effective defect diameters (D). The effective D is defined as D of a circle with the same area as the pore. It should be noted that the dose 1 (6.25×10^{12} ions/cm²), dose 2 (1.11×10^{13} ions/cm²), and dose 3 (2.5×10^{13} ions/cm²) used here exactly match with the doses of irradiated MoS₂ samples for pore diameter distribution analysis, which we have discussed

in Figure 5-16. Based on the measurement results, the average G of dose 1 is \sim 1.4 nS (marked by the red four-pointed star), which is slightly higher than the average G of dose 2 (\sim 0.9 nS, marked by the green four-pointed star). In comparison, dose 3 yields the largest average G, which is \sim 10 nS (marked by the blue four-pointed star). While a gradual increase of G is expected in devices irradiated with dose 1-3, the experimentally observed smallest G in dose 2 can be explained as two reasons: (1) although the pore density in samples irradiated with dose 2 is larger compared to that of dose 1, their mean pore sizes and effective D are very similar. (2) The variations in the measured G values for devices irradiated at each dose are larger than the difference between the average G values of doses 1 and 2. In order to further evaluate the conductance of pores with different diameters, MD simulation was applied. The simulated G values of pores with different effective D (the blue line, and six-pointed stars in Figure 5-17) qualitatively coincide with the experimental results, demonstrating a negligible conductance (<20 pS) when pore diameters are smaller than 0.6 nm and a gradual increase in conductance for larger pores.



Figure 5-17: Conductance G as a function of the pore diameter. G is shown as a function of pore diameter for the continuum (black, yellow, orange, and pink) and MD simulated (blue) models. Plotted are also G values from the MD model and the experimentally obtained G values for MoS₂ nanoporous membranes and single nanopores, as well as reported values from previous works on SiN, a-Si, and MoS₂ nanopores.

5.3 Conclusions

In this Chapter, we reported a novel CA-assisted technique enabling the clean transfer of CVD-grown TMDs on SiO₂/Si onto arbitrary substrates. Various characterization techniques were performed in order to confirm the well-preserved crystalline quality of CA-transferred flakes, as well as the largely improved surface morphologies when compared with those that were transferred using the conventional PMMA-based technique. Our developed TMDs transfer technique shows great potential as a cleaner alternative when compared to the currently and widely used PMMAtransfer method, providing convenience to high-resolution nanometer-scale characterization and further facilitating novel applications based on CVD-grown TMDs. Furthermore, since CA has been reported as an effective electron-beam resist that has a high resolution comparable to PMMA,²²⁵ in future work we will explore the usage of CA as an alternative resist for 2D TMDs device fabrication. It is envisioned that, with the utilization of PMMA contamination-free TMDs transfer and device fabrication techniques, improved electrical properties can also be achieved in CVD-grown TMDs. In addition, it should be noted that although the observed total clean area was improved to 30.7 % by applying CA-assisted transfer method, there is still much room for improvement. Recently, by a combined DFT calculation and experimental study, Leong et al. identified paraffin as an alternative support layer for large-area graphene transfer, exhibiting superior cleanliness and electrical performance in transferred graphene. DFT calculation was applied for evaluating the chemical reactivity of the paraffin molecule and their non-covalent interaction strength with graphene.²¹⁹ Inspired by this work, a theory-guided approach may be applied in the future to identify most favorable molecules as the polymer support layer for TMD transfer.

Moreover, in the second part of this Chapter, we developed a deterministic transfer system that is compatible with both CA- and PMMA-based transfer methods. This transfer system enabled the fabrication of electronically coupled high-quality vdW heterostructures, as well as MoS₂ nanopore devices for ionic transport studies. Collaborating with Prof. Marija Drndić's group at University of Pennsylvania, we developed a Ga⁺ ion irradiation method for reliably creating subnanometer to nanometer nanopore arrays on suspended monolayer MoS₂. Ionic conductivity measurements were performed on nanopore devices with different Ga⁺ irradiation doses, revealing the correlation between ionic conductance and the diameter of pores. By a combination of experimental and MD simulated results, it was demonstrated that the defects with diameters less than ~0.6 nm are impermeable to ions, and only large nanopores contribute to the ionic conductance. Since the statistical analysis of pore distributions shows that Ga⁺ ion irradiation within our dose range mainly creates pores with diameters < 0.6 nm, our nanopore arrays may hold promise for desalination applications (*i.e.*, rejecting ions but allowing water molecules to pass).²³⁶ Future work will be focusing on investigating the ionic transport behavior of individual types of atomic defects (*e.g.*, V_{2M0+6S}, V_{3M0+5S}). It is also desired to evaluate the water desalination efficiency and ion selectivity in large-scale MoS₂ nanopore membranes.
Chapter 6

Conclusion and Future Directions

The work in this dissertation focused on the synthesis, defect characterization, property tuning, and related applications of 2D TMD materials. Our efforts covered the four important aspects of 2D TMDs: structure, properties, processing, and performance.

6.1 Summary of contributions

First, two different additive-mediated CVD methods were developed to synthesize TMD monolayers with improved grain size (single crystals with lateral sizes on the order of ~100 μ m), yield, and reproducibility. The first method involves the addition of NaBr powders during a conventional solid precursor CVD process, while the second method is based on the spin-coating and high-temperature sulfurization of mixed liquid phase precursors and the growth additive (sodium cholate). These approaches are capable of producing pristine MoS₂ and WS₂ monolayers, alloyed Mo_xW_{1-x}S₂, and in-plane heterostructures of Mo_xW_{1-x}S₂-W_xMo_{1-x}S₂. Our developed additive-mediated CVD approaches not only pave the way for synthesizing large-area uniform monolayer TMDs, but also serve as the foundation of this thesis by reliably producing the materials of interest.

In Chapter 3 of this thesis, we investigated inhomogeneity and intrinsic defects in CVDgrown TMDs, particularly in monolayer WS₂. A variety of characterization methods, including optical microscopy, Raman, PL spectroscopy, AC-HRSTEM imaging, ToF-SIMS, STM, and STS, were employed to identify the types of defects and probe associated optical/electronic properties. We characterized WS₂ monolayers that exhibited two types of inhomogeneous PL patterns (*i.e.*, triangular WS₂ with dark PL lines, and hexagonal WS₂ with segmented bright/dark PL domains), and clearly observed an inhomogeneous distribution of 3d- and 4d-transition metal impurities at regions corresponding to W-zz and S-zz edges, which was likely to be responsible for quenching the luminescence signal. In addition, we synthesized WS₂ monolayers on EG/SiC for atomic resolution STM/STS measurements and observed negatively charged defects located at chalcogen sites in pristine WS₂. By performing careful STM, STS, and nc-AFM analysis and comparison of both pristine and controllably CH-doped WS₂ monolayers, these charged defects were unambiguously identified as CH₅. Our results provide a detailed analysis of the defect types and possible ways to control defects in synthetic 2D TMDs, and also contribute to the establishment of structure-property relationships of these intrinsic defects.

Once the intrinsic defects in 2D TMDs were studied, we then aimed at developing synthesis methods to introduce defects intentionally and controllably into TMDs. Specifically, in Chapter 4, we reported a liquid phase precursor-assisted CVD method for *in situ* substitutional doping of TMD monolayers. Using this method, we synthesized Fe-doped WS₂, Re-doped MoS₂ and V-doped WS₂ monolayers, and demonstrated the modified structural and optical properties by a combination of Raman, PL, and STEM characterization methods. Moreover, we demonstrated that this method could be used to synthesize doped TMD in-plane heterostructures *via* a single-step process. Our method is facile and effective and may also be generalized as a universal method to dope different elements into various types of TMDs, fostering the advancements of materials by design.

Finally, Chapter 5 focused on the processing of TMDs for functional applications. We developed clean and deterministic TMD transfer approaches that are suitable for building up vdW heterostructures and nanopore devices for ionic transport measurements. Using CA as an alternative polymer support layer, we demonstrated well-preserved crystallinity and improved cleanliness in

transferred TMDs compared to the ones transferred using conventional PMMA-based method. Our developed CA-transfer method can thus be applied as a cleaner transfer technique, facilitating highresolution atomic-scale characterization of 2D TMDs. In addition, we built up a deterministic transfer system that is compatible with both CA- and PMMA-based transfer methods. Based on the deterministic transfer of MoS₂ and subsequent Ga⁺ ion irradiation with different doses, we created sub-nanometer to nanometer sized nanopore arrays on suspended MoS₂ monolayers. We systematically studied the pore diameter distributions in nanoporous MoS₂ membranes as a function of Ga⁺ doses using STEM analysis and investigated the correlation between ionic conductance and pore diameters by a combination of ionic transport measurements and MD simulations. Our results provide fundamental understanding of the ionic transport behavior in 2D membranes with a large distribution of sub-nanometer sized pores, which is crucial for designing nanoporous membranes for water desalination applications.

6.2 Future work and perspectives

Although the work presented in this thesis significantly contributed to the 2D community by investigating the synthesis, characterization, doping, transfer, and related applications of semiconducting TMDs, these studies are certainly just the tip of the iceberg, and much more followup studies need to be carried out. Specifically, we envisage that future work can be done in the following aspects:

First, regarding the additive-mediated synthesis of TMD alloys and heterostructures that we presented in Chapter 2, although we have demonstrated the tunability of MoS_2-WS_2 interfaces from ~20-100 nm sharp interface to fully graded alloys, our growth outcomes are still not ideal and there is room for improvement. For example, for optoelectronic applications, it is often desired to have homogeneous alloys with tunable compositions, or in-plane heterostructures with atomically sharp interfaces. Future efforts can be made towards fine tuning a series of growth parameters (*e.g.*, furnace temperature ramp, carrier gas flow, the ratio of precursor/growth promoter, etc.) to control thermodynamic and kinetic factors, which may lead to the growth of uniform alloys and in-plane heterostructures with sharp interfaces. In addition, apart from semiconducting MoS₂ and WS₂ systems, our CVD method can be extended to other newly developed 2D materials. For example, it is anticipated that 1T'-ReS₂, 1T-VS₂ and 2H-NbSe₂ can be synthesized by additive-mediated CVD and be used as heterostructure components.

Concerning the study of intrinsic defects in TMDs that we presented in Chapter 3, although the observed point defects were attributed as 3d- and 4d-transition metal substitutions (M_w : M =V, Cr, Fe, Mo, etc), further studies are needed to unambiguously identify the types of defects, which may be achieved by high-resolution STEM-EELS line scan/mapping. Theoretical studies are also needed to shed light on the formation energy of each type of defects and the influence of different defects on optical and electronic properties of 2D TMDs. From another perspective, for practical applications of large-area TMDs, future work can be focused on developing low-cost, highthroughput and non-destructive characterization techniques for defect analysis. For example, Carozo *et al.* used low-temperature PL spectroscopy to observe S vacancy-induced bound exciton formation at edges of WS₂, and this technique could be applied in future work for large-scale defect evaluation in a rapid way.²³

Considering the substitutional doping of 2D TMDs, our work in Chapter 4 provided a proof-of-concept that liquid phase precursor-assisted CVD method could introduce different transition metal atoms into the TMD lattice. Future studies can be conducted to evaluate and control the long-range uniformity of dopant distributions. For example, detailed analysis is required to examine the possible doping concentration variation among flakes and/or from center to edge of a

single TMD flake. Since our liquid phase precursor-assisted approach has been demonstrated for the large-scale roll-to-roll synthesis of pristine TMDs^{205, 242}, it is anticipated that large-area doped TMD films can be similarly synthesized by optimizing precursor concentration and the spin-coating process, which will be beneficial for applications such as electronics, sensing, and catalysis. Moreover, it will be very interesting to use DFT calculation to predict doped TMD systems with desired physicochemical properties, so that our doping approach can promote the "on demand" engineering of 2D TMDs.

Finally, in Chapter 5, our work of CA-assisted clean transfer was mainly applied to CVDgrown micrometer-sized TMD flakes, but the capability of transferring large-area continuous films was not tested. Future efforts can be made towards developing approaches (not limited to our CAtransfer approach) for transferring of large-area TMD films, such as wafer-scale TMDs synthesized by MOCVD. The damage-free handling of CVD-grown wafer-scale TMDs would be impactful for practical applications. Although we demonstrated artificially stacked MoS₂-WS₂ heterostructures created using our deterministic transfer system, the related optical and electronic properties were not investigated in detail. In recent years, by vertically stacking 2D layered materials with optimum twist angles, novel electronic and optical phenomena have emerged, such as fractal quantum Hall effect²⁴³, superconductivity²⁴⁴, tunable ferroelectricity²⁴⁵, and moiré exciton³⁷. For example, interlayer exciton emission in twisted MoSe₂/WSe₂ bilayer heterostructures can be significantly modified by the periodic potential induced by the moiré pattern, and exhibit ultranarrow emission lines (~100 meV) at low temperatures.²⁴⁶ Such twist angle-dependent moiré exciton is intriguing for creating programmable quantum emitter arrays and excitonic superlattices.²⁴⁷ Thus, follow-up studies that build up TMD moiré heterostructures with different twist angles and characterize their physical properties using a combination of far- and near-field techniques, would be desired. A variety of 2D TMDs (e.g., pristine TMDs, alloys, and doped TMDs synthesized by CVD) can be utilized as material components, which may lead to exciting properties in the engineered Moiré heterostructures.

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- iMatSE Graduate Student Travel Award, The Pennsylvania State University, 2019
- iMatSE Graduate Student Travel Award, The Pennsylvania State University, 2018
- Yuzhi Qu Scholarship of Academic Excellence, Tsinghua University, 2013
- Scholarship of Volunteer Activity, Tsinghua University, 2012

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- 1. Zhang, T.; Fujisawa, K.; Zhang, F.; Liu, M.; Lucking, M. C. *et al.*, Universal *In Situ* Substitutional Doping of Transition Metal Dichalcogenides by Liquid-Phase Precursor-Assisted Synthesis. *ACS Nano* 2020, *14*, 4326-4335.
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- 5. Gontijo, R. N.; Zhang, T.; Fujisawa, K.; Elías, A. L.; Pimenta, M. A. *et al.*, Multiple excitations and temperature study of the disorder-induced Raman bands in MoS₂. 2D Mater. **2021**, *8*, 035042.
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- 11. Fogg, J. L.; Putman, K. J.; Zhang, T.; Lei, Y.; Terrones, Met al., Catalysis-Free Transformation of Non-Graphitising Carbons into Highly Crystalline Graphite. Commun. Mater. 2020, 1, 47.
- 12. Kahn, E.; Liu, M.; Zhang, T.; Liu, H.; Fujisawa, K. *et al.*, Functional Hetero-Interfaces in Atomically Thin Materials. *Mater. Today* 2020, *37*, 74-92.
- 13. Wang, M.; Krasnok, A.; Zhang, T.; Scarabelli, L.; Liu, H. *et al.*, Tunable Fano Resonance and Plasmon-Exciton Coupling in Single Au Nanotriangles on Monolayer WS₂ at Room Temperature. *Adv. Mater.* **2018**, 1705779.
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