Synthesis, assembly and applications of novel two-dimensional metal chalcogenide nanomaterials

Tan, Chaoliang

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NANYANG
TECHNOLOGICAL
UNIVERSITY

**SYNTHESIS, ASSEMBLY AND APPLICATIONS OF NOVEL
TWO-DIMENSIONAL METAL CHALCOGENIDE
NANOMATERIALS**

TAN CHAOLIANG

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Abstract

The ability to prepare novel two-dimensional (2D) metal chalcogenide nanosheets and heteronanostructures or construct novel nanostructures via self-assembly by using 2D metal chalcogenides as basic building blocks is of great importance for the further exploration of their properties and varying potential applications. In the light of this, my aim in this thesis is to synthesize novel 2D metal chalcogenide nanosheets and heteronanostructures or assemble 2D metal chalcogenide nanosheets into new nanostructures and then explore their potential applications in fluorescent biosensors, dye-sensitized solar cells, Li-ion batteries and digital data storage devices.

First, I prepared two solution-dispersed ultrathin 2D ternary metal chalcogenide nanosheets, i.e. Ta_2NiS_5 and Ta_2NiSe_5 , in high-yield and large scale in liquid phase by exfoliating their layered bulk crystals via the electrochemical Li-intercalation and exfoliation method. The sizes of the Ta_2NiS_5 and Ta_2NiS_5 nanosheets are 0.05-2 μm . Significantly, the yield for the single-layer Ta_2NiS_5 nanosheet reached up to ca. 86%. The single-layer Ta_2NiS_5 nanosheet was used as a novel sensing platform to construct fluorescent biosensor for DNA detection.

Second, I achieved the high-yield and scalable production of single-layer alloyed $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ and $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ nanosheets with high concentration (~66%) of metallic 1T phase by exfoliation of their micro-sized 2H-phase layered bulk crystals using the electrochemical Li-intercalation and exfoliation method. The $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheet thin film casted on a fluorine-doped tin oxide (FTO) substrate by the drop-casting method was directly used as an efficient electrocatalyst for the tri-iodide reduction at counter electrode in a dye-sensitized solar cell without any post-treatments. A power conversion efficiency of 6.5% was achieved on the $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheet thin film electrode, which is higher than that of 2H-phase $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ (5.4%).

Third, I prepared three kinds of 2D metal chalcogenide heteronanostructures in liquid phase by an electrochemical method by using metal foils and bulk TiS_2 crystal as precursors, in which metal sulphide nanoplates, including CuS , ZnS and Ni_3S_2 , were epitaxially grown on ultrathin TiS_2 nanosheet. TEM analyses revealed that these metal sulphide nanoplates were aligned on the TiS_2 with perfect epitaxial alignment effect to vertical 2D epitaxial heteronanostructures. Moreover, when used as the anode in a Li ion battery, the CuS-TiS_2 heteronanostructure-based electrode exhibited good performance.

Last, I developed a facile and universal approach for the high-yield and scalable preparation of chiral nanofibers by the self-assembly of various ultrathin 2D nanomaterials, including single-layer graphene oxide (GO), MoS_2 , TaS_2 , TiS_2 , few-layer TaSe_2 , WSe_2 and Pt nanoparticle-decorated reduced graphene oxide (Pt-rGO) or MoS_2 (Pt- MoS_2), in vigorously stirred polymeric solutions. These chiral nanofibers can be further transformed into same-handed helical nanorings with a diameter of 400-800 nm via a second assembly process. Chiral MoS_2 nanofiber with P123 was integrated into a resistive memory device as the active layer. Impressively, the fabricated memory device presented a non-volatile flash memory behavior with excellent reproducibility and good stability.

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Abbreviations

0D	Zero-Dimensional
1D	One-Dimensional
2D	Two-Dimensional
3D	Three-Dimensional
AFM	Atomic Force Microscopy
APTES	(3-Aminopropyl)triethoxysilane
BSA	Bovine Serum Albumin
CD	Circular Dichroism
CEs	Counter Electrodes
CV	Cyclic Voltammetry
CVD	Chemical Vapor Deposition
DSSCs	Dye-Sensitized Solar Cells
EDS	Energy Dispersive X-ray Spectroscopy
EIS	Electrochemical Impedance Spectroscopy
FET	Field-Effect Transistor
FFT	Fast Fourier Transformation
FTO	Fluorine-Doped Tin Oxide
GO	Graphene Oxide
HAADF	High-Angle Annual Dark-Field
HRTEM	High Resolution Transmission Electron Microscopy
HRS	High Resistance State
LIBs	Li Ion Batteries
LRS	Low-Resistance State
NMP	N-methyl-pyrrolidone
NPs	Nanoparticles
N-rGO	Nitrogen Doped rGO
PBS	Phosphate Buffer Saline
PCEs	Power Conversion Efficiencies
PET	Polyethylene Terephthalate Film

PL	Photoluminescence
PVDF	Poly(vinylidene fluoride)
PVP	Polyvinylpyrrolidone
rGO	reduced graphene oxide
SAED	Selected Area Electron Diffraction
SAMs	Self-Assembled Monolayers
SCLC	Space-Charge Limited Current
SEM	Scanning Electron Microscopy
STEM	Scanning Transmission Electron Microscopy
TEM	Transmission Electron Microscopy
THF	Tetrahydrofuran
VdW	Van der Waals
XRD	X-Ray Diffraction
XPS	X-Ray photoelectron spectroscopy

Chapter 1

Introduction

This chapter gives the brief introduction on this thesis. The hypotheses of this thesis are introduced first. Based on the hypotheses, the objectives and scope of this thesis are then described. After that, the dissertation overview for each chapter in the whole thesis is also presented. Finally, based on the whole content, the findings and outcomes of this thesis are summarized.

1.1 Hypothesis/Problem Statement

Ultrathin two-dimensional (2D) metal chalcogenide nanosheets, including MoS_2 , TiS_2 , TaS_2 , WS_2 , MoSe_2 , etc., have attracted considerable attention in the past few years. Driven by their unique properties and wide potential applications, various types of effective preparation methods have been identified or developed for preparation of single- and few-layer metal chalcogenide nanosheets. Previously, our group developed an electrochemical Li-intercalation and exfoliation method for the preparation of a number of single- or few-layer metal chalcogenide nanosheets. The hypothesis here is that the well-developed electrochemical Li-intercalation and exfoliation method might be able to exfoliate new layered bulk metal chalcogenide crystals into ultrathin 2D nanosheets, which may have potential in applications like electrocatalysis, electronics, energy storage and sensors.

Layered bulk crystals (for example, MoS_2 , WS_2 , MoSe_2 and WSe_2) normally crystallize into a 2H crystal phase and thus exhibit semiconducting properties with large bandgaps of 1-2 eV. The semiconducting properties render them with low intrinsic electrical conductivity and thus limit their potential in those applications requiring high conductivity. Promisingly, recent studies have shown that the phase engineering from semiconducting 2H phase to metallic 1T phase can remarkably promote the conductivity of metal chalcogenides. Moreover, ultrathin 2D alloyed metal chalcogenide nanosheets, including $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ and $\text{Mo}_x\text{W}_{1-x}\text{S}_2$, have also been the subject of intensive studies over the past few years. The hypothesis here is that the electrochemically-driven Li-intercalation into layered bulk crystals of alloyed metal chalcogenides might be able to induce phase transformation from 2H to 1T and thus to prepare single-layer alloyed nanosheets with high concentration of metallic 1T phase, which are expected to exhibit enhanced electrocatalytic activity in some electrocatalytic reactions.

Engineering 2D lateral or vertical epitaxial metal chalcogenide heteronanostructures, such as MoS_2 - MoSe_2 , WS_2 - WSe_2 , MoSe_2 - WSe_2 and WS_2 - MoS_2 , is fundamentally and technologically intriguing. The epitaxial growth nature of these 2D heteronanostructures renders them with well-defined structure/interface and selectively-exposed facets, thus

making them promising candidates for a wide range of applications. Currently, all the reported 2D lateral and vertical epitaxial metal chalcogenide heteronanostructures were prepared by the gas-phase epitaxy techniques. However, high temperature/vacuum is required in the gas-phase epitaxy method and certain substrate is needed to support the growth of heteronanostructures, leading to high cost and relatively low output. In contrast, liquid-phase epitaxial growth approaches are relatively low cost, which allows for high yield and large amount preparation of heteronanostructures in solution phase. The hypothesis here is that 2D metal chalcogenide epitaxial heteronanostructures might be able to be prepared via a liquid-phase epitaxial growth method, allowing us to prepare 2D epitaxial metal chalcogenide heteronanostructures in large amount at low cost.

The large lateral size and ultrathin thickness of single- or few-layer metal chalcogenide nanosheets enable them with excellent flexibility, making them promising candidates for construction of novel nanostructures via morphology/topology transformative self-assembly with reduced dimensionality. However, there are almost no reports on the assembly of ultrathin 2D metal chalcogenide nanosheets into other kinds of nanostructures. The hypothesis here is that ultrathin 2D metal chalcogenide nanomaterials might be able to be assembled into novel nanostructures via solution-based assembly strategies, which may have potential in applications like electronic devices, catalysis and sensors.

1.2 Objectives and Scope

Based on the hypotheses proposed above, my objectives and scope are listed below.

First, micro-sized layered bulk crystals of two ternary metal chalcogenides, including Ta_2NiS_5 and Ta_2NiSe_5 , will be prepared by the chemical vapor deposition technique from their elementary powders. The obtained micro-sized crystals will be then used as the sources to produce ultrathin 2D nanosheets in high yield and large scale by using the electrochemical Li-intercalation and exfoliation method. The exfoliated nanosheets will be characterized by SEM, AFM, TEM, XPS and Raman spectroscopy. The potential

application of the single-layer Ta_2NiS_5 nanosheet as the sensing platform to construct fluorescent sensors for detection of DNA will be also explored.

Second, micro-sized layered bulk crystals of two alloyed metal chalcogenides, including $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ and $\text{Mo}_x\text{W}_{1-x}\text{S}_2$, will be prepared by the chemical vapor deposition technique by using the elementary powders as precursors. Both of obtained crystals will be used as starting materials to prepare single-layer alloyed nanosheets with high concentration of metallic 1T phase by using the electrochemical Li-intercalation and exfoliation method. The exfoliated nanosheets will be characterized by SEM, AFM, TEM, STEM, XPS and Raman spectroscopy. The crystal phase-dependent electrocatalytic activity of $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheet toward the tri-iodide reduction at the counter electrode in a dye-sensitized solar cell (DSSC) will be explored.

Third, an electrochemical method will be used for epitaxial growth of 2D metal chalcogenide heteronanostructures in solution phase by using the bulk TiS_2 crystal and metal foils as precursors. The effect of reaction time after the discharge process on the morphology of deposited metal chalcogenides (e.g. CuS) on TiS_2 nanosheet will be explored. The as-prepared 2D heteronanostructures will be characterized by TEM, EDS and XPS. The potential application of the obtained CuS-TiS_2 heteronanostructure as the anode material in the Li ion battery (LIB) will be explored.

Last, single-layer graphene oxide (GO), MoS_2 , TaS_2 , TiS_2 , few-layer TaSe_2 , WSe_2 and Pt nanoparticle-decorated reduced GO and MoS_2 (Pt-rGO and Pt- MoS_2), will be used as the building blocks to create assembled chiral nanofibers via the assembly of them in vigorously stirred polymeric P123 solutions. These chiral nanofibers will be further transformed into same-handed helical nanorings via a controlled re-assembling process. The resultant chiral nanostructures will be characterized by SEM and AFM. The potential application of the MoS_2 chiral nanofiber with P123 as the active material in a non-volatile resistive data storage device will be explored.

1.3 Dissertation Overview

The thesis addresses how to synthesize novel ultrathin 2D metal chalcogenide nanosheets and heteronanostructures, and how to assemble ultrathin 2D metal chalcogenide nanomaterials into chiral nanofibers, and how to use useful techniques to characterize the as-prepared novel 2D metal chalcogenide-based nanomaterials and finally demonstrates the potential of these 2D metal chalcogenide nanomaterials in a number of applications like fluorescent biosensors, DSSCs, LIBs and non-resistive memory devices.

Chapter 1 provides a rationale for the research and outlines the goals and scope.

Chapter 2 reviews the literature concerning the current research progress on the liquid exfoliation of 2D metal chalcogenide nanosheets, epitaxial growth of 2D metal chalcogenide heteronanostructures, preparation of 2D metal chalcogenide nanosheets with metallic 1T phase and assembly of ultrathin 2D metal chalcogenide nanomaterials into one-dimensional (1D) nanostructures.

Chapter 3 discusses the rational for methods/materials selection, the synthesis and characterization techniques employed and the potential applications for 2D metal chalcogenide nanomaterials.

Chapter 4 elaborates the synthesis and characterization ultrathin 2D ternary metal chalcogenide nanosheets, including Ta_2NiS_5 and Ta_2NiSe_5 , and the utilization of single-layer Ta_2NiS_5 as a sensing platform to construct fluorescent sensor for DNA detection.

Chapter 5 elaborates the synthesis and characterization of single-layer alloyed metal chalcogenide nanosheets, including $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ and $\text{Mo}_x\text{W}_{1-x}\text{S}_2$, with high concentration of metallic 1T phase, and demonstrates the enhanced electrocatalytic activity of exfoliated $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheet toward tri-iodide reaction at the counter electrode in a DSSC.

Chapter 6 elaborates the electrochemical synthesis of 2D metal chalcogenide epitaxial

heteronanostructures, including CuS-TiS₂, ZnS-TiS₂ and Ni₃S₂-TiS₂, and the utilization of the CuS-TiS₂ heteronanostructure as the anode in a LIB.

Chapter 7 elaborates preparation and characterization of chiral nanofibers assembled from ultrathin 2D nanomaterials, the further assembly of chiral nanofibers into nanorings and the utilization of chiral MoS₂ nanofiber with P123 for non-resistive memory diodes.

Chapter 8 concludes the whole thesis and elaborates the reconnaissance studies which could be conducted in the near future.

1.4 Findings and Outcomes/Originality

This research led to several novel outcomes:

1. The electrochemical Li-intercalation and exfoliation method has been proved to be very effective for the exfoliation of novel layered ternary metal chalcogenide bulk crystals of Ta₂NiS₅ and Ta₂NiSe₅ into ultrathin 2D nanosheets. High yield of single-layer Ta₂NiS₅ nanosheet (86%) can be obtained. The single-layer Ta₂NiS₅ nanosheet exhibits excellent fluorescence quenching ability toward dye-labeled ssDNA, thus it can be used as a novel sensing platform to develop fluorescent sensor for the detection of DNA. The resultant fluorescent sensor exhibits excellent sensitivity and good selectivity.
2. The electrochemical Li-intercalation into layered bulk crystals of alloyed MoS_{2x}Se_{2(1-x)} and Mo_xW_{1-x}S₂ can induce the phase transformation of them from semiconducting 2H phase to metallic 1T phase. Single-layer alloyed MoS_{2x}Se_{2(1-x)} and Mo_xW_{1-x}S₂ nanosheets with high concentration of metallic 1T phase can be prepared in high yield and large amount after the exfoliation process. The exfoliated single-layer MoS_{2x}Se_{2(1-x)} nanosheet exhibits enhanced electrocatalytic activity towards the tri-iodide reduction compared with the annealed 2H-phase one when coated as a thin film on FTO electrode, thus resulting in a higher power conversion efficiency after assembling in a DSSC as the counter electrode.

3. The preparation of 2D metal chalcogenide heteronanostructures, including CuS-TiS₂, ZnS-TiS₂ and Ni₃S₂-TiS₂, can be achieved by epitaxial growth of metal chalcogenide nanoplates on TiS₂ nanosheet via an electrochemical method from the bulk TiS₂ crystal and different metal foils. The metal chalcogenide nanoplates can be well aligned on the TiS₂ nanosheet with epitaxial growth effect. When used as the anode material in a LIB, the CuS-TiS₂ heteronanostructure presents large capacity and good cycling stability.

4. A facile and universal approach is developed for the high-yield and scalable assembly of various ultrathin 2D nanomaterials, including single-layer GO, MoS₂, TaS₂, TiS₂, few-layer TaSe₂, WSe₂ and Pt nanoparticle-decorated rGO and MoS₂ (Pt-rGO, Pt-MoS₂), into chiral nanofibers in vigorously stirred polymeric solutions. These chiral nanofibers could be further assembled into chiral nanorings via a second assembly process. The chiral MoS₂ nanofiber with P123 could be a promising active material for the construction of non-volatile resistive memory devices. The as-fabricated memory device shows a non-volatile rewritable memory character with excellent reproducibility and good stability.

Chapter 2

Literature Review

This chapter gives the literature review on the recent progress of synthesis of 2D metal chalcogenide nanomaterials. The liquid-phase exfoliation methods for preparation of 2D metal chalcogenide nanosheets are introduced first. The synthesis and advances of 2D metal chalcogenide nanosheets with metallic 1T phase are then summarized. After that, the synthesis of 2D metal chalcogenide epitaxial heteronanostructures is described. The assembly of ultrathin 2D nanomaterials into 1D nanostructures is also presented. Finally, the questions and the thesis in context based on literature are also discussed.

2.1 Overview

The rise of graphene,^[1] an atomic-layer thickness carbon sheet, has stimulated the increasing research interest on the exploration of other graphene-like ultrathin 2D nanomaterials, especially single- or few-layer metal chalcogenide nanosheets.^[2-4] Owing to the outstanding properties arising from their 2D structure and ultrathin thickness, single- and few-layer nanosheets of layered metal chalcogenides, such as MoS₂, TiS₂, TaS₂, WS₂, and MoSe₂, have shown much potential in a variety of applications including electronic devices, sensors, energy storage and conversion devices, and catalysis.^[5] Versatile approaches including mechanical cleavage exfoliation, chemical ion-intercalation and exfoliation, electrochemical Li-intercalation and exfoliation, sonication-assisted liquid exfoliation, chemical vapor deposition (CVD) and wet-chemical syntheses, have been developed to prepare single- and few-layer metal chalcogenides.^[6-15]

Bulk layered metal chalcogenide compounds are one of the most interesting classes of materials that possess diversified striking properties, such as semiconductivity, half-metallic magnetism, superconductivity, or charge density wave.^[16-19] The interesting properties make them attractive candidates for various applications, including lubrication, catalysis, photovoltaics, supercapacitors, and LIB systems.^[16-19] As shown in Figure 2.1, layered metal chalcogenide crystals are consisting of stacked planes that have two hexagonal lattices of MS₂ sandwiches and the layered sandwiches stacked together by van der Waals interactions, which is very similar to the graphite.^[3]

Figure 2.1 (a) The crystal structure of bulk MoS₂ crystal. (b) The top view of a single-layer MoS₂.

2.1.1 Liquid-phase exfoliation of layered metal chalcogenides

Driven by their compelling properties and promising potential applications, a wide spectrum of synthetic methods have been developed or identified for the preparation of single- or few-layer metal chalcogenide nanosheets. Generally, the most widely used methods are the mechanical exfoliation,^[6] CVD,^[7-8] sonication-assisted exfoliation,^[9-11] chemical ion-intercalation and exfoliation,^[12-13] electrochemical Li-intercalation and exfoliation,^[14-15] and wet-chemical syntheses.^[20-22] Specifically, the layered nature of bulk metal chalcogenide crystals allows them to be exfoliated into ultrathin 2D nanosheets by means of exfoliation strategies, including mechanical exfoliation, sonication-assisted exfoliation, chemical ion-intercalation and exfoliation and electrochemical Li-intercalation and exfoliation.^[23] The mechanical cleavage method is a traditional strategy to fabricate atomically pristine 2D metal chalcogenide nanosheets with large size, few defect, and high crystallinity from their parent layered compounds.^[1,6] Therefore, the mechanically exfoliated 2D metal chalcogenide nanosheets are ideal for the investigation of their intrinsic physical and electronic properties and demonstration of high-performance electronic and optoelectronic devices. Although the mechanical cleavage method can exfoliate high quality 2D nanosheets, its low yield makes it difficult for practical applications that require the large-scale 2D metal chalcogenides with solution processability. Bearing this in mind, it is believed that exfoliation of metal chalcogenides in liquid phase might be a promising way to overcome the disadvantages of the mechanical exfoliation, thereby achieving the high-yield and large scale production of 2D metal chalcogenide nanosheets at low cost. In this section, the typical liquid exfoliation methods for the production of ultrathin 2D metal chalcogenide nanosheets will be introduced in detail.

Sonication-assisted liquid exfoliation. In 2011, Coleman and coworkers reported the direct sonication of layered materials in certain solvent for preparation of single- or few-layer metal chalcogenide nanosheets, including MoS₂, WS₂, MoSe₂, NbSe₂, TaSe₂, NiTe₂, MoTe₂, and Bi₂Te₃ (Figure 2.2).^[9] It was found that the used solvent is the key factor in the sonication-assisted exfoliation process. Several kinds of solvents have been explored

for the exfoliation of bulk crystals of layered metal chalcogenides. It was suggested that the enthalpy of exfoliation is minimized when the layered bulk crystal has the surface energy close to that of the solvent. Take MoS_2 as a typical example, solvent like *N*-methyl-pyrrolidone (NMP) with a surface energy of $\sim 70 \text{ mJ/m}^2$ is the best solvent for its exfoliation. In this case, MoS_2 sheet can be produced in large quantities. Later on, some other metal chalcogenide nanosheets, including TiS_2 , TaS_2 , MoSe_2 , *etc.*, were also prepared by this method.^[23] By tuning the experimental parameters, such as starting mass, sonication power, sonication time and centrifugation conditions, the concentration and lateral size of exfoliated nanosheets can be tuned. For example, by increasing the sonication time up to 200 h, MoS_2 nanosheet with a high concentration up to 40 mg/ml was obtained.^[23] Although NMP is effective for the exfoliation, the most commonly used solvents such as water and ethanol were proved to be inefficient for the exfoliation of metal chalcogenides. Importantly, it has demonstrated that the mixture of water and ethanol was effective for exfoliating layered metal chalcogenide bulk crystals into nanosheets.^[10] It is believed that the change of solubility parameters in mixed solvents is the main reason the effective exfoliation. Significantly, the non-toxic water and ethanol are both commonly used solvents that can be easily removed.

Figure 2.2 (a) Photographs of dispersions of MoS_2 , WS_2 and BN. (b) TEM, HRTEM and STEM images of exfoliated BN, MoS_2 and WS_2 nanosheets.^[9]

Alternatively, sonication of layered metal chalcogenide bulk crystals in aqueous solution containing polymers or surfactants has also been proved to be effective for the exfoliation of them into ultrathin 2D nanosheets.^[23] For instance, Coleman and coworkers

demonstrated the preparation of MoS₂ nanosheet by sonication of bulk MoS₂ crystal in aqueous solution containing sodium cholate.^[11] In this case, the sodium cholate surfactant not only can minimize the exfoliation energy to achieve the efficient exfoliation, but also can stabilize the exfoliated nanosheet to form a stable colloidal suspension. Inspired by this work, many other polymers or surfactants, such as long chain amines (e.g. butylamine, octylamine and dodecylamine), non-ionic surfactants (e.g. P123 and polyvinylpyrrolidone (PVP)) and biomolecules (e.g. bovine serum albumin (BSA)) (Figure 2.3), have also been explored for the exfoliation of layered metal chalcogenides bulk crystals into ultrathin 2D nanosheets and thus a wide range of 2D metal chalcogenide nanosheets have been successfully prepared.^[23,24] However, there are several disadvantages on the sonication-assisted exfoliation method. For example, the yield of produced single-layer nanosheets is low. The lateral size of produced nanosheets is relative small. Moreover, the residual solvent (e.g. NMP) or polymer (e.g. PVP and P123) on the exfoliated nanosheets is not favorable for further applications in some areas, such as electronics, electrocatalysis and supercapacitors.

Figure 2.3 Schematic illustration of the BSA-assisted sonication exfoliation of bulk MoS₂ crystal into single-layer nanosheets.^[24]

Chemical ion-intercalation and exfoliation. Chemical Li-intercalation and exfoliation method is a typical method used for high yield and massive production of single-layer metal chalcogenide nanosheets. Note that this method was developed in 1980s for preparation of single-layer MoS₂ nanosheet from the bulk MoS₂ crystal.^[12,13] The basic idea is to intercalate Li ions into the layered spacing of bulk metal chalcogenide crystals to form Li-intercalated compounds. The Li-intercalation can enlarge the interlayer distance of metal chalcogenide layers in bulk crystals and weaken the van der Waals

intercalation between layers. Therefore, single-layer nanosheet suspension can be easily obtained with subsequent sonication of Li-intercalated compounds in water for short time. The most commonly used intercalating agent is n-butyllithium. In a typical process, the bulk crystals of layered metal chalcogenides were refluxed in hexane containing n-butyllithium at high temperature (e.g. 100°C) for long time (e.g. 3 days), in which Li ions reacted with bulk crystals to form intercalated compounds. Then, the Li-intercalated compounds were sonicated in water for short time (e.g. 1 h) to obtain nanosheet suspensions. Finally, high yield single-layer nanosheets can be obtained after purification via centrifugation. Till now, a number of metal chalcogenide nanosheets, such as MoS₂, TiS₂, WS₂, *etc.* have been prepared by this method.^[23] Although high yield of single-layer metal chalcogenide nanosheets can be obtained, the lateral size of the produced nanosheets is relatively small. Interestingly, Loh and coworkers recently developed a two-step expansion and intercalation process in order to produce large size metal chalcogenide nanosheets (Figure 2.4).^[25] For example, the bulk MoS₂ crystal was first reacted with hydrazine (N₂H₄) by a hydrothermal method, in which the N₂H₄ intercalation can significantly expand the volume of bulk MoS₂ crystal after the decomposition of the N₂H₄ molecule. The expanded MoS₂ crystal was then intercalated by metal naphthalenide (metal = Li, Na or K) to form intercalated compound. After sonication and purification, the high-yield production of single-layer MoS₂ nanosheet was up to 90% and the lateral size was up to 400 μm². However, the additional step makes it more complicated compared to the chemical Li-intercalation and exfoliation method. It is worth pointing out that the chemical Li-intercalation process needs long time and high temperature, making this method very time-consuming and inefficient. Very recently, Wang and coworkers demonstrated that with the assistance of sonication, the chemical Li-intercalation process can be finished at room temperature within 1 h.^[26] In this case, the whole exfoliation process can be finished within several hours, which is much more efficient than the original one. Note that one of the major disadvantages is that the chemical Li-intercalation process is hard to be controlled. Therefore, the insufficient Li-intercalation or too much Li-insertion normally occurs, leading to the inefficient exfoliation or decomposition of the metal chalcogenide nanosheets.

Figure 2.4 Schematic illustration of two-step expansion and intercalation process for preparation single-layer metal chalcogenide nanosheets by using the N_2H_4 and metal naphthalenide (metal = Li, Na or K) as the intercalators.^[25]

Electrochemical Li-intercalation and exfoliation. In order to precisely control the Li-intercalation, in 2011, our group developed an electrochemical Li-intercalation and exfoliation method to produce various single-layer metal chalcogenide (e.g. MoS_2 , WS_2 , TiS_2 , TaS_2 and ZrS_2) and few-layer metal chalcogenide (e.g. $NbSe_2$, WSe_2 , Sb_2Se_3 , and Bi_2Te_3) nanosheets.^[14,15] The basic idea is same to the chemical Li-intercalation and exfoliation method using n-butyllithium, which is to weaken the van der Waals intercalation between layers to facilitate the efficient exfoliation. The set-up for the exfoliation was inspired by the LIB system. Generally, the layered metal chalcogenide bulk crystal was coated on a copper foil as a cathode and a lithium foil was used as an anode in a LIB cell (Figure 2.5). The lithium ions were intercalated into the layered metal chalcogenide compounds during the discharge process, which is similar to the intercalation by using the n-butyllithium. Of particular important is that the amount of intercalated lithium ions can be controlled by setting the cut-off voltage at different stages. The Li-intercalated compounds were subsequently sonicated in water or ethanol to get well-dispersed nanosheets. Importantly, the H_2 gas that generated during the sonication process between the reaction of lithium and water (or ethanol) is beneficial to push the adjacent MoS_2 layers further apart. Importantly, this method is able to produce high-yield

of single-layer MoS_2 at room temperature within short time (e.g. 6 h). After purification, the yield of single-layer MoS_2 could reach up to $\sim 92\%$. Importantly, the amount of Li ions can be monitored by the discharge curve in this method, avoiding the insufficient Li-intercalation, or over Li-insertion.

Figure 2.5 Schematic illustration of the electrochemical Li-intercalation and exfoliation method for preparation of ultrathin 2D metal chalcogenide nanosheets from the layered bulk materials.^[14]

2.1.2 2D metal chalcogenide nanosheets with metallic 1T phase

Most of the bulk crystals of metal chalcogenides have a layered structure similar to the graphite. However, unlike graphene, single-layer metal chalcogenides are composed of three atomic layers with a general formula of MX_2 . In each layer, the metal (M) atom is sandwiched between two chalcogen atoms (X). It is worth pointing out that for most studied metal chalcogenides, such as MoS_2 , WS_2 , MoSe_2 , WSe_2 and MoTe_2 , a single-layer metal chalcogenide can crystallize in a trigonal prismatic phase (2H), an octahedral phase (1T) or disordered octahedral phase (disordered 1T or 1T') based on different coordination modes between the metal and chalcogen atoms (Figure 2.6).^[27] It was found that the d orbital electron density of the metal is the key factor in determining the crystal phase in single-layer metal chalcogenides. Therefore, it is possible for us to engineer the crystal phase of metal chalcogenide nanosheets by tuning the filling of the d orbital of the metal.

Figure 2.6 Crystal structure modes of three typical type polymorphs of single- or few-layer metal chalcogenides.^[27]

Till now, a number of strategies, such as Li intercalation, electron beam irradiation and laser irradiation, have been developed or identified for engineering the phase of metal chalcogenides to prepare 2D metal chalcogenide nanosheets with metallic 1T phase. The chemical Li-intercalation and exfoliation method using n-butyllithium discussed in section 2.1.2 is the most widely used method for the preparation of metallic metal chalcogenide nanosheets from the bulk 2H phase crystals.^[28] Early attempt conducted by Py and coworkers in 1983 indicated that the Li intercalation can induce the phase transformation of MoS₂ from 2H to 1T phase,^[13] because the increase of the electron density in the d orbital of Mo atoms due to the electron transfer from the reducing agent to the metal chalcogenide. Therefore, after exfoliation, single-layer MoS₂ nanosheet with metallic 1T phase was obtained, which are negatively charged. Recent theoretical calculation proved that the excess charge on the exfoliated MoS₂ nanosheet make the 1T phase more stable than the 2H phase. Of note, the phase transformation induced by the Li-intercalation is not 100%, thus there are always the coexistence of 2H and 1T phase fractions in the exfoliated metal chalcogenide nanosheets. Not only limited to MoS₂, some other metal chalcogenide nanosheets (e.g. WS₂ and MoSe₂) with metal 1T phase have been also prepared by a similar way. Similarly, it also have been demonstrated that the electrochemically driven Li-intercalation can also induce the phase transformation of metal chalcogenides from 2H to 1T phase.^[29] Therefore, after exfoliation, metal chalcogenide nanosheets (e.g. MoS₂) with metallic 1T phase can be obtained. However,

the mechanism underlying the electrochemical Li-intercalation induced phase transformation is still not clear.

Interestingly, it was demonstrated that electron beam irradiation can also induce the phase transformation of single-layer MoS_2 from 2H to 1T phase to prepare metallic MoS_2 nanosheet.^[30] It was found that the 2H phase was transformed into a new phase to form two atomic stripes under the irradiation of electron beam. The strip is composing of three to four constricted MoS_2 zig-zag chains, in which the Mo-Mo has a reduced distance. Therefore, the 1T phase was formed to release the strain induced by the packed atoms. Along with the continuous electron beam irradiation, the area of the 1T phase became larger and larger to form a triangular shape forming single-layer MoS_2 nanosheet with metal 1T phase. Very recently, it was demonstrated that laser irradiation also can induce the phase transformation of MoTe_2 nanosheet from 2H to 1T' phase to form MoTe_2 nanosheet with patterned 1T' phase (Figure 2.7).^[31] One of the major advantages of this method is that the area of patterned 1T' phase on the MoTe_2 nanosheet can be easily controlled by tuning the location of laser irradiation area. It was suggested that the laser irradiation can induce the generation of Te vacancy on the 2H phase MoTe_2 . When the Te vacancy concentration exceeds 3%, the 2H phase becomes less stable than the 1T' phase. Therefore, a phase transformation from 2H to 1T' phase occurs due to the continuous laser irradiation.

Figure 2.7 Schematic illustration of the laser irradiation induced phase transformation of MoTe_2 from 2H phase into 1T' phase.^[31]

Besides the phase engineering, 2D metal chalcogenide nanosheets with metallic 1T phase could be also directly synthesized via wet-chemical methods. Recently, several wet-chemical synthesis approaches have been developed for synthesis of 2D metallic metal chalcogenide nanosheets. For example, Ozin and coworkers reported the preparation of 1T' WS₂ nanosheet by using the WCl₆ and carbon disulfide (CS₂) as precursors in an oleylamine solution (Figure 2.8).^[32] The reason why the synthesized WS₂ nanosheet has a 1T' phase is still not clear. Interestingly, by introducing a small amount of hexamethyldisilazane in the reaction system, flower-like WS₂ nanosheet with a normal 2H phase can be obtained (Figure 2.8). In another example, a simple hydrothermal method was also developed for the synthesis of ammonia-ion 1T' WS₂ nanoribbon.^[33] The ammonium tungstate hydrate and thiourea precursors dissolved in water were sealed in an autoclave and reacted at 220°C for 48 h to get the final product. It was found that the intercalated ammonia-ion is highly stable, which might be the key factor for the formation of 1T' phase in the obtained WS₂ nanoribbon. Later on, the same group further extended this method to synthesize MoS₂ nanosheet with metallic 1T phase by replacing the ammonium tungstate hydrate with ammonium molybdenum hydrate.^[34]

Figure 2.8 Schematic illustration of the colloidal synthesis of 2H and 1T' WS₂.^[32]

Recent studies have shown that 2D metal chalcogenide nanosheets with metallic 1T phase exhibited much enhanced performance in applications like electrocatalysis, electrochemical supercapacitors and low-resistance contact transistors due to the metallic 1T phase enabled much enhanced intrinsic conductivity compared to the 2H phase ones.

For example, Chhawalla and coworkers first demonstrated that the exfoliated single-layer WS₂ nanosheet with high concentration of metallic 1T' phase exhibited much enhanced electrocatalytic activity toward hydrogen evolution reaction (Figure 2.9).^[35] It presented ultralow overpotentials of 80-100 mV and a Tafel slope of 60 mV/dec. Note that both of the values are much better than that of the 2H phase WS₂ nanosheet and bulk WS₂ crystal. It was suggested that the high proportion of strain and enhanced conductivity enabled by the metallic 1T' phase are the main reason for the much enhanced electrocatalytic performance. Later on, similarly, the enhanced electrocatalytic activity of MoS₂ nanosheets with high concentration of metallic 1T phase was also proved.^[36-37]

Figure 2.9 (a) The AFM height image of metallic WS₂ nanosheet. (b) The STEM image of metallic WS₂ nanosheet. (c) Polarization curves based on different WS₂-based electrocatalysts. (d) The corresponding Tafel slopes obtained from the polarization curves in (c).^[35]

Besides electrocatalysis, Chhowalla and coworkers also demonstrated that the exfoliated MoS₂ nanosheet with high concentration of metallic 1T phase exhibited excellent performance for electrochemical supercapacitor when used as the electrode.^[38] It was found that the conductivity of metallic MoS₂ nanosheet is comparable with rGO electrode, which is $\sim 10^7$ times higher than that of 2H phase MoS₂ one. It was found the metallic MoS₂ nanosheet-based electrode gave much larger capacitance than that of the electrode based on 2H phase MoS₂ with excellent cycling stability. The highest capacitance could reach up to 650 F/cm² in H₂SO₄ aqueous electrolyte. It is believed that the high electrical conductivity and hydrophilicity are responsible for the excellent supercapacitor performance. In addition, the same group also demonstrated the fabrication of low-resistance contact field-effect transistor (FET) devices with much enhanced performance based on MoS₂ nanosheets with metallic 1T phase.^[39] The 2H phase MoS₂ nanosheet was selectively converted into metallic 1T phase in some parts and the metallic 1T phase parts were then used electrodes for the FET devices. It was found that the contact resistances based on metallic 1T phase electrodes is about 200-300Ωμm, which is much lower than that of 2H phase ones (0.7 kΩμm-10kΩμm), thus leading to much enhanced device performance compared with the 2H phase one. Similarly, later on, it was also demonstrated that FET devices based on MoTe₂ nanosheets with 1T' phase electrodes also exhibited superior performance compared to the 2H phase ones by partially transforming 2H phase into 1T' phase in MoTe₂ nanosheets.^[31]

2.1.3 2D metal chalcogenide epitaxial heteronanostructures

It has been proved that transferring a kind of 2D nanosheet to another distinct 2D nanosheet and stacking them in vertical or lateral directions to form Van der Waals (VdW) heteronanostructures is a facile and powerful way to tune the electronic properties of ultrathin 2D nanosheets.^[40] The artificially stacked 2D heteronanostructures have been explored to exhibit some unconventional optical and electronic properties or even new phenomena. However, one of the major disadvantages for preparation of the 2D VdW heteronanostructures is that polymer contaminations will be introduced in the system during the transfer process, which will affect the optical and electronic properties of the

fabricated heteronanostructures.^[41] Even worse, the stacking area and orientation of two nanosheets are hard to be controlled in VdW heteronanostructures, which will also affect the tuning of the optical and electronic properties of heteronanostructures. It is believed that the epitaxial growth of 2D heteronanostructures which possess well-defined structure, interface and crystal orientation could be a promising way to solve the aforementioned drawbacks that involved in 2D VdW heteronanostructures.

Epitaxial growth is defined to the growth of one kind of crystals to another crystalline surface with the same crystalline orientation.^[42] In general, single-crystalline bulk crystals with a single-exposed crystal facet, such as graphite, mica, Si(111), and Au(111), are ideal substrates for the epitaxial deposition of other kind of nanostructures or thin films.^[43-46] Impressively, as a newly emerging class of nanomaterials, ultrathin 2D metal chalcogenide nanosheets possess single-crystalline structure with atomic flat surface with single-exposed crystal facet, which are very similar to those traditionally used bulk crystalline substrates, even their thickness is thinned to single-layer.^[4] Therefore, they might be able used as unique nanostructured templates for epitaxial growth of other kinds of nanostructures to construct heteronanostructures. As known, lower lattice mismatch between two crystals is favorable for the realization of epitaxial growth of heteronanostructures. It is worth pointing out that some metal chalcogenide crystals have similar crystal structures with small lattice mismatch, making them ideal for construction of epitaxial heteronanostructures between them. For example, the calculated lattice mismatch between MoS₂ and MoSe₂ or WS₂ and WSe₂ is as low as ~4%.

Figure 2.10 Schematic illustration of 2D vertical and lateral heteronanostructures between two different single-layer metal chalcogenides.^[41]

As known, the CVD technique is widely used method for growth of highly quality single- or few-layer metal chalcogenide nanosheets (e.g. MoS_2 , WS_2 , MoSe_2 , WSe_2 , *etc.*) on various substrates (e.g. SiO_2/Si).^[47-48] It is believed that 2D metal chalcogenide epitaxial heteronanostructures might be prepared by the further growth of another type of metal chalcogenide nanosheet on the top or at the edge of an as-grown seed metal chalcogenide nanosheet (Figure 2.10).^[41] However, it was found that the edge or surface of the CVD-grown metal chalcogenide nanosheet will become inactive after exposure to ambient conditions, resulting in separate growth of metal chalcogenide nanosheets rather than the formation of epitaxial heteronanostructures. In order to solve this problem, a number of methods were developed. For example, Duan and coworkers developed a CVD method to prepare 2D metal chalcogenide epitaxial heteronanostructures.^[49] This method allows in situ switching of the vapor-phase reactants and thus can avoid the passivation of the seed metal chalcogenide induced by the exposure to ambient conditions. Therefore, single-layer lateral epitaxial WSe_2 - WS_2 and MoSe_2 - MoS_2 heteronanostructures with size in micrometer were prepared. Concurrently, single-layer lateral epitaxial MoSe_2 - WSe_2 heteronanostructure was also prepared by the physical vapor transport method by using MoSe_2 and WSe_2 powders as precursors.^[50] Firstly, single-layer MoSe_2 nanosheet was obtained on the substrate. After a certain time, the growth of WSe_2 dominated the growth process, which was further grown on the edge of existing MoSe_2 seed to form the lateral epitaxial MoSe_2 - WSe_2 heteronanostructure. However, pure WSe_2 nanosheet was also grown on the substrate. At the same time, Ajayan and coworkers developed a single-step vapor phase growth process for preparation of single-layer WS_2 - MoS_2 epitaxial heteronanostructures.^[51] It is believed that the difference in nucleation and growth rates between MoS_2 and WS_2 is the key factor for the formation of epitaxial heteronanostructures rather than alloyed $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ nanosheets. It is worth pointing out that by simply tuning the reaction temperature, the growth mode of the formed heteronanostructures can be controlled. The WS_2 nanosheet tended to grow on the top of single-layer MoS_2 nanosheet to obtain vertically stacked epitaxial WS_2 - MoS_2 heteronanostructure at reaction temperature of about 850°C (Figure 2.11a-d). However, at the reaction temperature of about 650°C , the lateral epitaxial WS_2 - MoS_2

heteronanostructure was obtained since the WS_2 preferred to nucleate at the edge site of the single-layer MoS_2 seed (Figure 2.11e-h). Note that tellurium was added in the tungsten powder to facilitate the growth process, while the exact role of tellurium in the growth process needs further exploration. Of note, this is the first time for the realization of the growth of vertical epitaxial metal chalcogenide heteronanostructures. After that, some other 2D epitaxial heteronanostructures, such as vertical MoS_2 - WS_2 and lateral MoS_2 - WS_2 and MoSe_2 - WSe_2 , have been also fabricated by similar methods.^[52] Of note, all the aforementioned single-layer lateral metal chalcogenide heteronanostructures have an alloy-like structure at the interface region rather than an atomically sharp interface. In order to solve this problem, a two-step CVD method was developed by Li and coworkers, in which the two different metal chalcogenide nanosheets, i.e. WSe_2 - MoS_2 , were grown in separate finance.^[53] In this case, the influence of residual precursor of the seed nanosheet can be totally avoided to realize the atomically sharp composition transition at the interface region.

Figure 2.11 (a-d) Schematic illustration and characterization of the vertical epitaxial WS_2 - MoS_2 heteronanostructure. (e-h) Schematic illustration and characterization of the lateral epitaxial WS_2 - MoS_2 heteronanostructure.^[51]

In addition to simple vertical and lateral epitaxial metal chalcogenide heteronanostructures, complicated patterned single-layer lateral MoSe_2 - MoS_2 epitaxial heteronanostructure array has also been prepared by Geohegan and coworkers recently.^[54]

They first prepared single-layer MoSe₂ nanosheet by the CVD method on a SiO₂/Si substrate (Figure 2.12a). The as-grown MoSe₂ nanosheet was then masked by a conventional patterning technique (Figure 2.12a). The unmasked area of MoSe₂ nanosheet was converted into MoS₂ via sulfidization using a pulsed laser vaporization technique (Figure 2.12a). Very interestingly, the shape of patterned MoS₂ array, such as triangles, circles and ribbons, can be easily tuned by controlling the shape of the mask. As shown in Figure 2.12b, the patterned single-layer lateral MoSe₂-MoS₂ epitaxial heteronanostructure array can be confirmed by the Raman maps.

Figure 2.12 (a) Schematically showing the preparation process of lateral epitaxial MoSe₂-MoS₂ heteronanostructure array. (b) Two examples of lateral epitaxial MoSe₂-MoS₂ heteronanostructure array.^[54]

It is noteworthy that all the aforementioned 2D epitaxial metal chalcogenide heteronanostructures were prepared by the gas-phase epitaxy techniques. Although the gas-phase epitaxy approaches allow us prepare high quality 2D epitaxial metal

chalcogenide heteronanostructures, high temperature/vacuum and certain substrate are required, leading to high cost and relative low output. It is believed that high yield and large amount production of 2D epitaxial heteronanostructures could be realized if liquid-phase epitaxial growth methods can be developed since the high yield and massive preparation of 2D metal chalcogenide nanosheets in solution phase have been achieved. Therefore, these solution-processed 2D metal chalcogenide nanosheets might be used as dispersible templates for epitaxial growth of distinct 2D metal chalcogenide nanostructures to create 2D epitaxial heteronanostructures. Recently, 2D metal chalcogenide nanosheets, such as MoS₂ and WS₂, have been used as templates for the epitaxial deposition of other nanocrystals on their surface via solution-based method. For example, it has been demonstrated single-layer MoS₂ nanosheet could be used a dispersible template for epitaxial growth of noble metal nanocrystals, including Pd and Pt NPs and Ag nanoplate, by wet-chemical synthesis methods in solution phase.^[29] Moreover, PbSe NPs have been epitaxially grown on MoS₂ and WS₂ nanoflakes by a facile wet-chemical synthesis method.^[55] However, no one has reported the liquid-phase epitaxial growth of 2D metal chalcogenide heteronanostructures, which still remains a challenging topic.

2.1.4 Self-assembly of ultrathin 2D nanomaterials into 1D nanostructures

Ultrathin 2D nanosheets, especially graphene and its derivatives (e.g. GO and rGO), have attracted considerable attention in the last decade owing to their distinctive properties and numerous potential applications.^[56] One of the unique advantages of ultrathin 2D nanosheets enabled by the atomic thickness is the ultrahigh flexibility. The large lateral size and excellent flexibility make these ultrathin 2D nanosheets ideal building blocks for the self-assembly via morphology/topology transformation to construct novel nanostructures with reduced dimensionality, such as 1D nanofibers and nanoscrolls.^[57] One of the major advantages of the assembled nanostructures compared to the directly synthesized one is that some of the interesting properties of the ultrathin 2D nanosheets can be maintained. For example, the theoretical calculation suggested that 1D graphene scrolls are expected to keep the same excellent conductivity as graphene sheets.^[58] More

importantly, the assembled novel nanostructures may exhibit some new exciting properties or functions that are not observed in the original form.^[59-60] Therefore, benefiting from the ability for the high yield and large scale production of ultrathin 2D nanosheets in solution phase, much effort has been devoted in developing facile and feasible strategies for the assembly of ultrathin 2D nanosheets into 1D nanostructures. The most widely used ultrathin 2D nanosheets for the assembly are graphene derivatives, i.e. GO and rGO.

Several effective strategies have been developed for direct assembly of graphene-based nanosheets into 1D nanostructures without assistance of any templates or surfactants. Early in 2003, Kaner and coworkers developed a simple sonication-assisted method for assembling graphite nanosheet into nanoscrolls.^[61] Firstly, potassium-intercalated graphite was prepared by intercalation of graphite bulk crystal with KC_8 (Figure 2.13). Then the potassium-intercalated graphite was sonicated in ethanol to form graphite sheets (Figure 2.13). Interestingly, it was found that during the sonication process, the exfoliated graphite sheets can assemble themselves to form nanoscrolls with a yield over 80% (Figure 2.13). Later in 2011, Liu and coworkers reported that graphene nanoscrolls can be directly prepared from natural graphite.^[62] Firstly, the natural graphited dispersed in liquid nitrogen was treated by microwave irradiation. After evaporation of liquid nitrogen, the resultant product was sonicated in ethanol to form graphene nanoscrolls. It is believed that the sonication of graphene nanosheets in ethanol is the key process for the formation of graphene nanoscrolls, which is similar the mechanism for graphite oxide nanoscrolls reported by Kaner and coworkers discussed above. In another example, GO nanoscrolls can be also obtained by sonication of GO nanosheets with the assistance of MnO_2 .^[63] Very interestingly, Xu and coworkers reported a self-assembly strategy for preparation of GO fibers from GO nanosheets.^[64] It was found that GO nanosheets can be self-assembled into GO fibers at the liquid/air interface after about two-week standing of GO solution. Recently, Yan and coworkers developed a simple cold cooling method for assembly of GO nanosheets into nanoscrolls.^[65] The GO aqueous suspension was first heated to about 80°C, which was then immediately quenched by liquid nitrogen to form

frozen suspension. rGO nanoscrolls can be obtained by removing the solvent via vacuum freeze-drying with subsequent thermal annealing at 800°C under Ar.

Figure 2.13 (a) Schematic illustration of the assembly process for nanoscrolls from graphite and (b-d) the corresponding TEM images.^[61]

In addition, 1D nanostructures can be also obtained by inorganic nanomaterial-templated assembly strategies. As a typical example, Wågberg and coworkers reported a magnetic $\gamma\text{-Fe}_2\text{O}_3$ NP-induced rolling approach for the assembly of nitrogen doped rGO (N-rGO) into nanoscrolls.^[66] By simply refluxing the methanol solution containing iron chloride, tungsten hexacarbonyl, and PVP, hydrazine and N-rGO for 24 h, N-rGO nanoscrolls decorated with magnetic $\gamma\text{-Fe}_2\text{O}_3$ NPs can be obtained with a yield nearly 100%. It was suggested that the rolling of N-rGO sheets was induced by the strong mutual magnetic interaction of magnetic NPs decorated on N-rGO at the nitrogen defect sites. It is worth pointing out that the transformation from nanosheets to nanoscrolls is fully reversible if the magnetic NPs were removed from the nanoscrolls. In another example, Mai and coworkers reported a nanowire-templated approach for the assembly of rGO nanosheets into nanoscrolls to form core-shell hybrid nanostructures (Figure 2.14).^[67] The nanowire templates here can be V_3O_7 and MnO_2 . Similarly, the precursors of metal oxide nanowires were reacted in solution containing rGO nanosheets to form the metal oxide-rGO nanoscroll core-shell nanostructures. It was proposed that metal oxide NPs were first synthesized in the solution. Metal oxide nanowires were then obtained by the oriented attachment of metal oxide NPs. Therefore, the obtained nanowire templates can induce the rolling of rGO and wrap on the nanowires. Finally, rGO nanoscrolls wrapped metal

oxide core-shell nanostructures were obtained, which can be used as electrode materials in LIBs with enhanced performance.

Figure 2.14 Schematic demonstration of construction processes of nanowire-templated graphene nanoscroll.^[67]

Besides aforementioned strategies, GO or rGO also can be assembled in nanoscrolls on substrates. Our group developed a molecular combing for the assembly of GO into nanoscroll on hydrophobic substrates (Figure 2.15).^[68] In a typical process, a water suspension containing GO nanosheets was dropped at one end of a hydrophobic substrate. Then a cover slip placed on the substrate with an angle of $\sim 45^\circ$ was moved from one end to another end to spread the solution. After absorption of excess solution by a filter paper, GO nanoscrolls can be obtained on the substrate. The GO nanoscroll can be easily reduced to rGO, which was then used as the channel material for fabrication of electronic sensor for gas sensing. Later on, it was demonstrated that micropatterned GO nanoscroll can be assembled by using the same method by modifying the substrate with hydrophilic-hydrophobic micropatterned self-assembled monolayers (SAMs).^[69] Note that the shape, orientation and position of assembled GO nanostructures can be easily tuned by controlling the hydrophilic-hydrophobic micropatterned SAMs on the substrate.

Figure 2.15 Schematic illustration of the molecular combing method for the assembly of GO nanosheets into nanoscrolls on a hydrophobic substrate.^[68]

Inspired by graphene, single- or few-layer metal chalcogenide nanosheets have also attracted considerable attention over the last few years. Note that single- or few-layer metal chalcogenide nanosheets possess similar structural characteristics to graphene. Therefore, it is believed that they might be also able to be assembled into various 1D nanostructures via morphology/topology transformation. However, the assembly of ultrathin 2D metal chalcogenide nanosheets into 1D nanostructures still remains a challenging topic.

2.2 Questions to Answer Based on Literature

As discussed in the aforementioned literature review, great progress has been made in the synthesis, characterization, assembly of 2D metal chalcogenide nanosheets as well as the exploration of their potential in various applications. However, there are still questions remain unclear.

First, it has been proved that liquid phase exfoliation methods are very effective for the exfoliation of a variety of layered metal chalcogenide bulk crystals into single- or few-layer nanosheets. One may wonder whether these well-developed liquid phase exfoliation methods can be further used to prepare new ultrathin 2D metal chalcogenide nanosheets. Which specific exfoliation method is the most suitable one for the exfoliation of a given layered metal chalcogenide bulk crystal? Moreover, one may wonder which kind of application of the exfoliated new nanosheets can be applied.

Second, a number of 2D metal chalcogenide nanosheets with metallic 1T phase have been prepared, which have shown much enhanced performance in some specific applications. One may wonder whether alloyed metal chalcogenide nanosheets with metallic 1T phase can be prepared by the currently reported methods for phase engineering. Except the proved applications, whether they show enhanced performance in other applications. Are there any other strategies that are able to induce the phase transformation from 2H to 1T on 2D metal chalcogenides? Are there any advantages of the alloyed metal chalcogenide nanosheets with metallic 1T phase compared with the pure metal chalcogenide nanosheets?

Third, a lot of 2D metal chalcogenide epitaxial heteronanostructures have been prepared by the gas-phase epitaxy methods. One may wonder whether we can achieve the preparation of 2D metal chalcogenide epitaxial heteronanostructures by wet-chemical methods. If yes, which kind of method might be effective for the epitaxial growth? What is the mechanism behind the epitaxial growth of 2D metal chalcogenide heteronanostructures? Are there any advantages of the 2D epitaxial heteronanostructures compared with the non-epitaxial ones?

Last, various kinds of 1D nanostructures have been prepared from graphene and its derivatives via various kinds of assembly strategies. One may wonder whether 2D metal chalcogenide nanosheets into 1D nanostructures via assembly strategies. What kind of 2D nanostructures can be formed? What is mechanism underlying the assembly process of 2D metal chalcogenide nanomaterials into 1D nanostructures? Are there any advantages of the assembled 1D nanostructures compared with the original 2D nanomaterials?

2.3 PhD in Context of Literature

In my thesis, I focus on the synthesis of novel 2D metal chalcogenide nanosheets and epitaxial heteronanostructures, the assembly of 2D metal chalcogenide nanomaterials into 1D chiral nanostructures and then exploration of these as-prepared nanomaterials or

nanostructures in some applications like fluorescent sensors, DSSCs, LIBs and memory devices. The contribution of my thesis in this area is list as follow:

First, I identified that the electrochemical Li-intercalation and exfoliation method is suitable for preparation of novel ultrathin 2D ternary metal chalcogenide nanosheets from the layered bulk crystals. This study further proved the wide applicability of this method for the exfoliation of new layered materials. Moreover, two ternary metal chalcogenide nanosheets were prepared for the first time in high yield, which can be explored for a wide range of applications. In addition, the potential of application of the single-layer Ta_2NiS_5 nanosheet has also been proved.

Second, I proved that the electrochemical Li-intercalation and exfoliation method can be used for the preparation of single-layer alloyed metal chalcogenide nanosheets with metallic 1T phase via phase engineering. This method might be able to be further extended to prepare other 2D metal chalcogenide nanosheets with metallic 1T phase (e.g. WS_2). Single-layer alloyed metal chalcogenide nanosheets were prepared in high yield and large scale for the first time. It has been proved that 2D metal chalcogenide nanosheets with metallic 1T phase exhibited enhanced PCEs compared with 2H phase ones when used as electrocatalysts on the counter electrodes in DSSCs.

Third, I identified that an electrochemical method can be used for the preparation 2D metal chalcogenide epitaxial heteronanostructures in liquid. This is the first report on the liquid phase epitaxial growth of 2D metal chalcogenide heteronanostructures. It has been proved that the prepared 2D metal chalcogenide epitaxial heteronanostructures exhibited enhanced performance when used as anode electrode in LIBs.

Last, I developed a simple and general assembly approach for assembly of a number of ultrathin 2D nanomaterials into 1D nanostructures. For the first time, chiral nanostructures, including nanofibers and nanorings, were assembled from 2D nanomaterials. This method might be able to be further extended to assemble other

ultrathin nanomaterials into chiral nanostructures. I also proved that the assembled chiral nanofibers with polymer displayed enhanced performance when used as the active layer in memory devices.

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Chapter 3

Experimental Methodology

In this chapter, the rational for selection of methods and materials is discussed first. The used chemicals and the experimental procedures for synthesis or assembly of ultrathin 2D metal chalcogenide nanosheets are presented, followed with the description of the techniques and equipment used for characterization. Finally, the details of the device fabrication and performance measurements based on ultrathin 2D metal chalcogenide nanomaterials are summarized.

3.1 Rationale for Selection

In the first part of the thesis, Ta_2NiS_5 and Ta_2NiSe_5 were selected as the materials and the electrochemical Li-intercalation and exfoliation method was used to exfoliate them into nanosheets. From the material point of view, exploring new materials is always one of the most promising ways to obtain some interesting results since they have not been explored yet. More of the studies on 2D metal chalcogenide nanosheets focused on binary compounds, such as MoS_2 , TiS_2 , TaS_2 and WS_2 . Ternary metal chalcogenide nanosheets may exhibit some extraordinary properties, functions or applications due to the multicomponent and complex structure. Moreover, it is worth pointing out that both the bulk crystals of Ta_2NiS_5 and Ta_2NiSe_5 have a layered structure similar to the bulk MoS_2 crystal.^[1] Therefore, it might be able to exfoliate them into single- or few-layer nanosheets by these well-developed liquid phase exfoliation methods. From the method point of view, as discussed in Section 2.1.1, there several well-developed liquid phase exfoliation methods for exfoliation of layered metal chalcogenides. Among them, the electrochemical Li-intercalation and exfoliation method was developed in our group,^[2] which is more effective for exfoliation of layered metal chalcogenides into single-layer nanosheets in high yield. Moreover, this method is more controllable compared with other liquid phase exfoliation methods, such as sonication-assisted exfoliation and chemical ion-intercalation and exfoliation method. In addition, this method has been proved to be effective for preparation of single-layer TaS_2 nanosheet with a single-layer yield up to 93%.^[3] With similar elemental composition and layered structure, it is believed that this method should be also effective for the production of single- or few-layer Ta_2NiS_5 and Ta_2NiSe_5 nanosheets from their layered bulk crystals. From the application point of view, it has been proved that single-layer MoS_2 , TiS_2 and TaS_2 nanosheets are good sensing platform for construction of fluorescent sensors for DNA detection.^[4-5] Therefore, this concept could be further extended on single-layer TiS_2 nanosheet.

In the second part of the thesis, alloyed $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ and $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ were selected as the target subjects and the electrochemical Li-intercalation and exfoliation method was also

used for the preparation of single-layer nanosheets with metallic 1T phase. From the material point of view, alloyed $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ and $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ nanosheets have been mostly prepared by CVD method and they have shown some advantages, such as tunable bandgap and enhanced electrocatalytic activity, compared to pure MoS_2 , WS_2 and MoSe_2 .^[6] But the exfoliation of them into single-layer nanosheets in high yield and large scale in liquid phase has not been achieved yet. From the method point of view, I chose the electrochemical Li-intercalation and exfoliation method because it has been proved to be effective for preparation MoS_2 nanosheets with metallic 1T phase.^[7] Therefore, it is reasonable to extend this method to prepare single-layer alloyed $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ and $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ nanosheets with high concentration of metallic 1T phase. For the application point of view, phase-dependent electrocatalytic tri-iodide reduction was explored since the enhanced electrical conductivity due to the presence of metallic 1T phase may delivery enhanced performance.

In the third part of the thesis, CuS , ZnS and Ni_3S_2 were selected to epitaxially grow on TiS_2 and an electrochemical method was also used for the preparation of 2D heteronanostructures. From the material point of view, because the lattice mismatch between CuS , ZnS or Ni_3S_2 and TiS_2 is low, CuS , ZnS or Ni_3S_2 was chose to grow on TiS_2 to form epitaxial heteronanostructures. In principle, lower lattice mismatch is more favorable for the realization of epitaxial effect between two crystals. From the method point of view, I chose an electrochemical method to prepare 2D heteronanostructures in liquid phase since all the current report methods used for preparation of 2D metal chalcogenide epitaxial heteronanostructures are gas-phase based methods. Moreover, it was occasionally observed that CuS crystal can be formed on the TiS_2 nanosheet by simple modification of the experimental conditions for the exfoliation of bulk TiS_2 crystal. Therefore, the modified electrochemical method was systematically explored for the preparation of 2D metal chalcogenide epitaxial heteronanostructures in liquid phase. From the application of view, LIB was used as example to demonstrate the application of the as-prepared 2D heteronanostructures.

In the last part of the thesis, chiral nanostructures were assembled from various ultrathin 2D nanomaterials and a solution-based assembly strategy was used for the assembly.

From the material point of view, all the materials used in this study are ultrathin 2D nanomaterials, which have shown many special properties and wide applications. More importantly, they could be assembled into other kinds of nanostructures via morphology or topology transformation due to their excellent flexibility. In principle, engineering chirality to inorganic nanomaterials to form chiral nanostructures bring some new interesting properties and functions that are not attainable on normal achiral nanomaterials.^[8] From the method point of view, ultrathin 2D nanomaterials were assembled into chiral nanofibers in a highly stirring solution containing P123. Note that under high speed stirring, vortex can be formed in the solution and which is a widely observed naturally chiral object.^[9] Therefore, vortex might be able to be used for the assembly of chiral nanostructures. From the application of view, composites composing of inorganic nanomaterials and polymers have been widely used as the active layers in non-volatile resistive memory devices. Therefore, it is believed that chiral MoS₂ nanofiber with P123 should be also promising for the fabrication of memory devices.

3.2 Synthesis

3.2.1 Chemicals

Tantalum powder (99.9%), molybdenum powder (~22 mesh, 99.9975%, tungsten powder (~22 mesh, 99.999%, Puratronic®), nickel powder (99.9%), sulfur powder (99.995%) and selenium shots (1-3 mm, 99.999%, Puratronic®), titanium sulfide bulk crystal (TiS₂), Pluronic P123 (Mol. Wt. 5800), Triton X-100 (Mol. Wt. 646.8), Tween 20 (Mol. Wt. 1227.5), polyethylene terephthalate film (PET), ethanol (absolute, 99.8%), tetrahydrofuran (THF, 99.8%), phosphate buffer saline (PBS) tablets, acetone and N-methylpyrrolidone (NMP) were purchased from Sigma-Aldrich (Germany). Lithium-ion battery electrolyte that is 1 M of LiPF₆ dissolved in a mixture of ethyl carbonate and dimethyl carbonate (v:v = 1:1) was purchased from Charslton Technologies Pte Ltd (Singapore). Poly (vinylidene fluoride) (PVDF), lithium foil, copper foil, zinc foil and nickel foil were purchased from the ACME Research Support Pte Ltd (Singapore). Molybdenum disulfide (MoS₂) bulk crystal with size of 10-30 mm was purchased from

Rose Mill (USA). Tantalum sulfide (TaS_2), tantalum selenide (TaSe_2), and tungsten selenide (WSe_2) were purchased from Alfa Aesar (USA). DNA sequences were purchased from Shanghai Sangon Biotechnology Co. (China). PBS solution (0.01 M, pH 7.4) was prepared by dissolving PBS tablets in water. All the chemicals were used as received without further purification. All the water used in my experiments is Milli-Q water which was purified by the Milli-Q System, Millipore.

3.2.2 Preparation of Ta_2NiS_5 and Ta_2NiSe_5 layered bulk crystals

The chemical vapor transport technique was employed to grow single crystals of Ta_2NiS_5 and Ta_2NiSe_5 ,^[1] in which iodide was used as the transporting agency. The stoichiometric amounts of high purity Ta, Ni and S (or Se) powders or shots with the molar ratio of Ta:Ni:S (or Se) = 2:1:5 with the total weight of 1 g were mixed together homogeneously and then sealed in an evacuated quartz tube under vacuum of 10^{-6} Torr, in which 40 mg iodide was also added in the tube as the transporting agency. The sealed tube was then put in a three-zone furnace. At the first stage, the reaction zone was heated at 850 °C for 30 h, while the growth zone was heated to 900 °C. After that, reaction zone was reacted to 1030 °C for 4 days, while the growth zone still kept at 900 °C and single crystals of Ta_2NiS_5 or Ta_2NiSe_5 were grown in the growth zone. Finally, the furnace was naturally cooled down to room temperature for the collection of the single crystals. Micro-sized crystals were obtained by grinding the big single crystals for the further characterizations and experimental usage.

3.2.3 Preparation of ultrathin 2D Ta_2NiS_5 and Ta_2NiSe_5 nanosheets

The as-prepared micro-sized layered bulk crystals of Ta_2NiS_5 and Ta_2NiSe_5 were used as the sources to prepare ultrathin 2D nanosheets by using our developed electrochemical Li-intercalation and exfoliation method.^[2] The experimental process is similar to the process for preparation of single-layer MoS_2 nanosheet reported in our previous paper.^[2] In a typical process, the Ta_2NiS_5 or Ta_2NiSe_5 powder of bulk crystal, PVDF and acetylene black were homogeneously mixed in NMP with the mass ratio of 8:1:1. The

homogeneous slurry was then uniformly coated onto copper foil disc. The copper foil disc coated with Ta_2NiS_5 or Ta_2NiSe_5 crystal was first dried naturally for several days and then dried in a vacuum oven at 90 °C overnight. A battery cell was assembled in a glove box by using the as-fabricated electrode, Li foil and 1 M of LiPF_6 as the cathode, anode and electrolyte, respectively, in which the PDVF membrane was used as the separator to separate the cathode and anode. The discharge process was conducted to intercalate Li ions into the layered bulk crystal to form Li-intercalation compound at the current of 0.025 mA with a cut-off voltage of 0.9 V. After taken out, the electrode was then put in water for the further sonication to get nanosheet suspension. A centrifugation process was used to remove thick flake and residual chemicals to get the final product, i.e. Ta_2NiS_5 or Ta_2NiSe_5 nanosheet, which was collected for further characterization and experimental usage.

3.2.4 Preparation of alloyed $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ and $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ bulk crystals

Similar to the Ta_2NiS_5 , micro-sized alloyed $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ and $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ layered bulk crystals were also grown by the chemical vapor transport method by using their elementary powders or shots as the precursors.^[10] Stoichiometric amounts of Mo, S and Se (or Mo, W and S) in the total weight of 1 g were sealed in quartz ampoule with an internal pressure in the range of 10^{-5} to 10^{-6} torr, in which 40 mg of iodine was added in the tube as the transport agent. The sealed tube was then put into a two-zone horizontal tube furnace. Firstly, the source zone was heated to 800 °C and the growth zone was kept at 950 °C for 48 h. After that, the temperature of source zone was gradually increased to 1030 °C at increasing rate of 10 °C/min, while the growth zone was still kept at 950 °C for another 120 h. After that, both of two zones were naturally cooled down to room temperature. The final product, i.e. $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ (or $\text{Mo}_x\text{W}_{1-x}\text{S}_2$) bulk crystal, was taken out from the tube. It is noteworthy that unlike the Ta_2NiS_5 crystal, the as-grown $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ and $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ crystals have sizes in micrometer ranges, which can be directly used for further characterization and exfoliation.

3.2.5 Preparation of single-layer alloyed $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ and $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ nanosheets

with high-concentration metallic 1T phase

Single-layer alloyed $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ and $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ nanosheets with high concentration of metallic 1T phase were produced by exfoliating their 2H-phase layered bulk crystals by using the electrochemical Li-intercalation and exfoliation method.^[2] The procedure is quite similar to the process for the preparation of single-layer Ta_2NiS_5 described in section 3.2.3. The only difference is to place the Ta_2NiS_5 crystal with micro-sized $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ or $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ layered bulk crystal.

3.2.6 Preparation of 2D metal chalcogenide epitaxial heteronanostructures

The epitaxial growth of metal sulphide nanoplates on TiS_2 nanosheets was achieved by an electrochemical method. The synthetic procedure is similar the process for preparation of single-layer Ta_2NiS_5 described in section 3.2.3.^[2] Generally, the bulk TiS_2 crystal was mixed with acetylene black and PVDF binder in NMP with the mass ratio of 8:1:1 and stirred for 24 h. The obtained slurry was then coated onto metal foils. Based on the growth of different metal sulphides, different metal foils were used. Copper, zinc, nickel foil discs were used for growth of CuS , ZnS and Ni_3S_2 nanoplates, respectively. The coated electrodes were dried in air and then in a vacuum oven at 90°C for 8 h. The battery cells were assembled by using the fabricated electrode as the cathode, Li foil as the anode and 1 M of LiPF_6 as the electrolyte, respectively. The assembling process was conducted in a glove box filled with Ar with oxygen and moisture less than 0.1 p.p.m. The Li-intercalation of TiS_2 crystal was conducted on a Neware battery test system via a discharge process at the current of 0.025 mA and cut-off voltage of 0.9 V. Unlike for the preparation of single-layer nanosheets, the battery cells were kept undisturbed for a given time (e.g. 15 days) after the discharge process rather than treated with sonication immediately. After that, the electrodes were taken out from the battery cells. After washing with acetone, the electrodes were sonicated in water to get aqueous suspension containing 2D metal chalcogenide heteronanostructures. The suspension was then purified by centrifugation, and the final product, i.e. CuS-TiS_2 , ZnS-TiS_2 or $\text{Ni}_3\text{S}_2\text{-TiS}_2$ hetero-nanostructure, was obtained.

3.2.7 Preparation of chiral nanofibers from ultrathin 2D nanomaterials

Single- or few-layer metal chalcogenide nanosheets, including MoS₂, TiS₂, TaS₂, TaSe₂ and WSe₂ were exfoliated from their layered bulk crystals by the electrochemical Li-intercalation and exfoliation method according to our previously reported papers.^[2-3] Pt NPs were deposited on single-layer MoS₂ nanosheets by the photochemical reduction method according to the previously reported method.^[7] These 2D nanomaterials were then used as the starting materials for the preparation of chiral nanofibers via self-assembly. In a typical process, ultrathin 2D metal chalcogenide nanomaterials were dispersed into water with a given concentration (e.g. 0.1 µg mL⁻¹) to form suspension. Meanwhile, 8 mg mL⁻¹ P123 aqueous solution was prepared by dissolving P123 in water. Then, 2 mL of suspension containing 2D nanomaterials was added dropwise into 5 mL of P123 solution under stirring at high speed (~1,500 r.p.m) on a magnetic stirrer at room temperature. After addition of 2D nanomaterials, the mixed solution was further stirred for 20 min. During this process, the ultrathin 2D metal chalcogenide nanomaterials were assembled into chiral nanofibers. The final product was washed twice with water and then once with THF via centrifugation. In the control experimental, the experimental was conducted at the same conditions only by replacing P123 with Triton X-100 and Tween 20.

3.2.8 Preparation of chiral nanorings via the assembly of nanofibers

The chiral nanofibers were further assembled into chiral nanorings via a secondary self-assembly process. 400 µL of the as-prepared chiral nanofiber solution was transferred into a 1.5 mL centrifugal tube. The chiral nanofiber suspension was then washed with water with the assistance of 1 min sonication and 5 min vortexing on a Vortex Mixer at low speed. After that, the nanofiber suspension was centrifuged at 13,000 r.p.m for 2 min to remove the upper solution. This procedure was repeated once. 980 µL of THF and 20 µL of ethanol were then added consecutively into the centrifugal tube to disperse the chiral nanofibers. The obtained suspension was sonicated for 1 min and oscillated on a

Vortex Mixer for about 30 min. The upper solution was removed after centrifugation at 13,000 r.p.m for 2 min. Finally, 990 μL of THF and 10 μL of ethanol were added consecutively into the centrifugal tube, which was sonicated for 1 min and then oscillated on a Vortex Mixer for 5 min. The final product, i.e. chiral nanorings, was obtained by removing the upper solution after centrifugation at 13,000 r.p.m for 2 min.

3.3 Characterization

After the preparation of ultrathin 2D metal chalcogenide nanomaterials, using suitable techniques to well characterize them is of particular importance to give the detail information on the morphology, compositions, crystal phase, surface properties, optical properties and electronic properties. Since each technique can give a specific or some specific information, the combination of different characterization techniques is necessary to fully understand different structural features or properties. Each technique has its own advantages and limitations. It is also important to understand the stand conditions to obtain reliable data for each technique. Therefore, in this section, I will introduce the different techniques that were used to characterize the prepared ultrathin 2D metal chalcogenide nanomaterials in this thesis.

3.3.1 Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) images and energy-dispersive x-ray spectra (EDS) were recorded on a JEOL JSM-7600 field-emission scanning electron microanalyzer coupling of an EDS detector. The SEM is a widely used equipment to characterize the morphology, topology and detail surface structure of solid materials. SEM can scan or raster a fine electron probe of over a material, in which the electrons will interact with the sample to generate a variety of signals. Then these signals are collected using different detectors, and an image can be created by reconstructing the signals generated within the sample.

For the SEM images in this thesis, secondary electrons were always used as the signal for

imaging the morphology of layered bulk crystals of Ta_2NiS_5 , Ta_2NiSe_5 , $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ and $\text{Mo}_x\text{W}_{1-x}\text{S}_2$, exfoliated nanosheets of Ta_2NiS_5 , Ta_2NiSe_5 , $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ and $\text{Mo}_x\text{W}_{1-x}\text{S}_2$, and assembled chiral nanofibers and nanorings. For the characterization of bulk crystals of Ta_2NiS_5 , Ta_2NiSe_5 , $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ and $\text{Mo}_x\text{W}_{1-x}\text{S}_2$, the powders of them were directly casted on the conductive adhesive to record the images at the accelerating voltage of 5 keV with a working distance of 6 cm and a probe current of 6 μA . The energy-dispersive x-ray spectroscopy was used to characterize the elemental compositions and the ratios between different elements in the compounds. The EDS spectra were collected at the accelerating voltage of 15 keV, a working distance of 15 cm and a probe current of 9 μA . Note that for the bulk crystals, surface coating is unnecessary since they all have good conductivity and the surface coating will affect the accuracy of the EDS test. SEM images of exfoliated nanosheets deposited on SiO_2/Si substrates were also recorded at the accelerating voltage of 5 keV with a working distance of 6 cm and a probe current of 6 μA . Although SiO_2/Si substrates are non-conductive, they are positive-charged after the modification with (3-aminopropyl)triethoxysilane (APTES). The detail modification process will be described in the Section 3.3.4. Due to the positive charge, the deposited nanosheets will give a darker contrast compared with the substrate, thus we can clearly identify the nanosheets from the SEM images. For the characterization of assembled chiral nanostructures, all the samples were drop-coated on Si substrates, dried naturally, and imaged with the accelerating voltage of 5 keV with a working distance of 6 cm. Note that the assembled nanostructures have residual polymer on their surface, making them non-conductive. Therefore, a thin layer of Pt with thickness of 3-5 nm was deposited on the surface to make it conductive.

3.3.2 Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) images were collected on either a JEOL JEM-2010 or JEM 2100F instrument. EDS spectra and elemental mappings were recorded on a JEM 2100F instrument coupling with an EDS detector. Generally, for the preparation of TEM samples, a drop of solution containing specific sample was dropped on a holey carbon film supported by copper grids and dried naturally for the further TEM

characterization. The used accelerating voltage is 200 keV. In TEM technique, a beam of electrons is passed through the sample with thin thickness and the electrons interact with sample. Signals of interaction of electrons transmitting sample were collected to generate an image, which can be recorded by a CCD camera. Several kinds of information can be obtained from a TEM on ultrathin 2D metal chalcogenide nanosheets.

First, the low magnification TEM images can be used to study the size of nanosheets and roughly study the thickness. The lateral size of the exfoliated nanosheets can be precisely measured from the low magnification TEM images. The contrast of the nanosheets can be used to evaluate the thickness of the nanosheets. As known, in bright field TEM images, thicker thickness and larger Z number give darker contrast. For the same material, the contrast is only related to the thickness. In this case, the thickness of the nanosheets in TEM images can be roughly estimated from its contrast. Moreover, Moiré patterns in low magnification TEM images can be used to roughly confirm the epitaxial growth effect of 2D epitaxial heteronanostructures.

Second, the HRTEM images and SAED patterns can be used to study the crystal structure, crystal orientation and exposed crystal facets. Nanocrystals normally give clear crystal lattice fringes, while amorphous materials do not show any crystal lattices. Single-crystalline crystals show continuous lattice fringes with the same orientation, while polycrystalline crystals give incontinuous lattice domains with random orientations. By measuring the distance of crystal lattice fringes, the exposed crystal facets can be confirmed. The single-crystalline, polycrystalline and amorphous structure of a material can be studied by the SAED pattern. Single-crystalline materials give clear bright dot patterns in the SAED pattern images. Polycrystalline materials display ring-like pattern and amorphous materials do not show any SAED patterns. For a single-crystalline material, SAED pattern can also give crystal orientation and growth direction. For 2D metal chalcogenide heteronanostructures, the SAED pattern is the more straightforward information to study the epitaxial growth effect. The two different crystals should have the same crystal orientation if they have the epitaxial effect. However, in this case of single-layer alloyed metal chalcogenide nanosheets with metallic 1T phase, the different

phases, i.e. 1T phase and 2H phase, can be distinguished in the HRTEM images. Only the atomic scale STEM images can be used to image the two different phases, which will be described in Section 3.3.3.

Third, the EDS spectra and corresponding elemental mapping can be used to study the elemental compositions and distribution of the ultrathin 2D metal chalcogenide nanosheets. For example, by measuring the EDS spectrum of a single nanosheet, we see the elemental compositions of it and whether it has been oxidized or not. Moreover, elemental mapping can be used to imaging the distribution of each element in the whole nanosheets.

3.3.3 Scanning transmission electron microscopy (STEM)

All of the scanning transmission electron microscopy (STEM) characterization of single-layer alloyed $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ and $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ nanosheets at atomic scale were carried out with a probe-corrected Titan ChemiSTEM (FEI, USA). This microscope was operated at an acceleration voltage of 200 keV to achieve better resolution (smaller probe size). To get sharper contrast of atomic images, the two images on the top were acquired through superposition of a slice of drift corrected images.

The STEM was used to characterize the atomic distribution of S and Se or M and W in single-layer $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ and $\text{M}_x\text{W}_{1-x}\text{S}_2$ nanosheets, respectively. It is worth pointing out that different atoms cannot be distinguished from normal HRTEM images. However, in STEM mode, the contrast of atoms is related to the Z number of the atoms. The larger Z number gives bright contrast in the atomic STEM images.

3.3.4 Atomic force microscopy (AFM)

Atomic force microscopy (AFM) images were recorded on a Dimension 3100 AFM (Veeco, CA, USA), NSCRIPTOR system with a Si tip (resonance frequency: 320 kHz; spring constant: 42 N/m) in the tapping mode. Images were acquired under ambient

conditions with a scanning rate of 1 Hz and scanning line of 512. AFM is the most commonly used equipment to characterize the thickness of nanomaterials, which has ultrathin vertical resolution.

In this thesis, the AFM height images were used to characterize the thickness of exfoliated nanosheets. By analyzing the height profiles, the layer number of the exfoliated nanosheets can be confirmed. It is worth pointing out the thickness of the measured thickness of exfoliated nanosheets deposited on Si/SiO₂ substrates normally are a little bit thicker than the real or calculated thickness of the nanosheets. For example, the calculated thickness of single-layer Ta₂NiS₅ is about 0.63 nm, while the measured thickness from AFM height images is normally about 1 nm. Moreover, the yield of single-layer nanosheets can be also calculated by measuring the height profiles a large number of nanosheets (e.g. more than 50 nanosheets). As known, the exfoliated nanosheets tend to aggregate together after drying due to strong Van der Waals interaction if they were drop-casted on substrates. The aggregation of nanosheets will significantly affect the accuracy of the AFM measurement. Therefore, in order to get well-dispersed nanosheets on Si/SiO₂ substrates, the substrates were first modified with APTES to make the surface positive-charged. In a typical process, Si/SiO₂ substrates were first cut into pieces of about 1×1 cm. Then they were sonicated in acetone for 30 min to remove the fragments. After that, they were boiled in a mixture of sulphuric acid and hydrogen peroxide with volume ratio of 1:1 at 120°C for 2h to remove residual organic contaminations. Finally, the cleaned substrates were rinsed with DI water for five times and then dried under N₂ flow. The freshly cleaned Si/SiO₂ substrates were immersed into an APTES water solution with a volume ratio of 1:100 for 10 min and then rinsed with water. The Si/SiO₂ substrates absorbed with APTES were then dried at 100°C for 2h to ensure the tight functionalization of APTES on Si/SiO₂ substrates to obtain positive-charged APTES-modified Si/SiO₂ substrates. In this case, the negative-charged metal chalcogenide nanosheets can be easily adsorbed on their surface via the electrostatic force. Well-dispersed monolayer nanosheets deposited on APTES-modified Si/SiO₂ substrates can be obtained after rinsing excess nanosheet solution, which were then used for the further AFM and SEM test.

Of note, AFM phase images rather than the height images were used to characterize the spiral structure of the chiral nanostructures, because the residual polymer on the surface of chiral nanostructures significantly affected the accuracy of the height profile analyses. The phase images is mainly based on the different material composition, thus the structure can be well distinguished from the AFM phase images. Moreover, the pitch length of the chiral nanostructures can be also obtained based the profiles of the AFM phase images.

3.3.5 X-Ray diffraction (XRD)

The crystal phase of layered bulk crystals were characterized by a Bruker D8 diffractometer (German) with a Cu K α ($\lambda=1.54178$ Å) X-ray source. The XRD patterns were recorded using CuK α radiation by step-scanning over the range of 10° to 80° in 0.05° intervals, at a dwell time of 1s.

The XRD patterns were used to identify the crystal phase of the layered bulk crystals of Ta₂NiS₅, Ta₂NiSe₅, MoS_{2x}Se_{2(1-x)} and Mo_xW_{1-x}S₂ in this thesis. The powders of the micro-sized layered bulk crystals were directly put on the XRD sample holders for the test. The experimental XRD patterns were compared with simulated XRD patterns based on its crystal structure information to confirm the crystal phase.

3.3.6 X-Ray photoelectron spectroscopy (XPS)

A VG ESCALAB 220i-XL instrument (base pressure $<5\times10^{-10}$ mbar) equipped with a monochromatic Al K α (1486.7 eV) X-ray source was used to measure the x-ray photoelectron spectroscopy (XPS) spectra of our samples. All the samples were measured an area of $300 \times 700 \mu\text{m}^2$. All the spectra were calibrated by using the C1s peak (284.5 eV) as the reference. For preparation of XPS samples, a drop of solution containing exfoliated nanosheets was drop-casted on a clean Si substrate and then naturally dried in air, which then can be used for XPS measurement.

XPS is a widely used technique to measure the binding energies of a material that can be used to analyze the chemical composition, oxidation state, electronic state and even crystal phase of each element. Note that XPS is very sensitive to study the surface of a material but cannot go deep into material no more than few nanometers. XPS can be used to quantitatively determine the chemical composition in materials. In this thesis, the XPS was mainly used to characterize the oxidation state of elements in exfoliated nanosheets (e.g. Ta_2NiS_5 and Ta_2NiSe_5) or heteronanostructures (e.g. CuS-TiS_2). In general, detail fitting analyses are necessary to investigate the obtained XPS spectra to get more precise information about the compositional and structural features of the studied materials. More importantly, by the integration of area of each component, the composition ratio for each component can be calculated based on XPS spectra.

In addition, it has been proved that XPS is a powerful technique to explore crystal phase of ultrathin 2D metal chalcogenide nanosheets. Therefore, both the composition and crystal phase of the exfoliated single-layer alloyed $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ and $\text{M}_x\text{W}_{1-x}\text{S}_2$ nanosheets were studied by XPS. The XPS signals of metallic 1T phase $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ and $\text{M}_x\text{W}_{1-x}\text{S}_2$ nanosheets will show big shift to lower binding energies compared to 2H phase. More importantly, the integral areas of 2H and 1T phase after the deconvolution can be used calculate the concentration of metallic 1T phase in the exfoliated nanosheets. Therefore, it provides a facile and reliable way to identity the presence of different phases in exfoliated metal chalcogenide nanosheets.

3.3.7 Raman spectroscopy

The Raman spectra was measured on A WITec CRM200 confocal Raman microscopy system with the excitation line of 488 nm or 532 nm and air cooling charge coupled device as the detector (WITec Instruments Corp, Germany). All the Raman spectra were calibrated by the Raman band of a silicon wafer at 520 cm^{-1} as the stand peak. The sample preparation for Raman spectroscopy is the same for the preparation of samples for XPS test described in Section 3.3.6. Raman spectroscopy is a spectroscopic technique to

study the vibration, rotation and other low-frequency modes in materials. In this thesis, the Raman spectroscopy was used to investigate the composition and crystal phase information of exfoliated nanosheets.

Generally, both the bulk crystals and exfoliated nanosheets were explored by Raman spectroscopy. For example, the exfoliated Ta_2NiS_5 nanosheets show have similar characteristic Raman peaks due to the same composition and crystal structure. However, after exfoliation, the Raman peaks of the nanosheets will give some small shift compared to that of the bulk crystals due to the reduced dimensionality. For the chiral nanostructures, Raman spectroscopy was used to confirm that the assembled chiral nanostructures have the same composition with the original nanosheets.

Moreover, in the study about single-layer alloyed metal chalcogenide nanosheets with metallic 1T phase, Raman spectroscopy not only can be used to exam the composition, but also to identify the presence of different crystal phases in the exfoliated nanosheets. For example, in the Raman spectrum of exfoliated $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheets, both the MoS_2 -like and MoSe_2 -like Raman peaks can be observed due to different vibrational modes in different structures. More importantly, even having the same composition, the $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheets with metallic 1T phase show different Raman peaks compared to the 2H phase one due to the different coordination mode-induced difference in vibrational modes. Therefore, in this study, the coexistence of the metallic 1T phase and semiconducting 2H phase can be clearly evidenced by the Raman spectroscopy.

3.3.8 UV-vis absorption spectroscopy

A UV-2700 (Shimadzu) with QS-grade quartz cuvettes (111-QS, Hellma Analytics) was used to record the UV-vis absorption spectra at room temperature. The UV-vis spectroscopy is used the characterize the UV-vis absorption spectra of single-layer alloyed metal chalcogenide nanosheets with metallic 1T phase and pure 2H phase. As known, the characteristic absorption peaks of a material are close related to its electronic structure, i.e. band gap. Due to the presence of high concentration of metallic 1T phase,

single-layer alloyed metal chalcogenide do not give any characteristic absorption peaks since the 1T phase is metallic. In contrast, after annealing, the metallic 1T phase is fully transformed into semiconducting 2H phase. Single-layer alloyed metal chalcogenide nanosheets with 2H phase give three main characteristic peaks due to its semiconducting properties. Therefore, in this thesis, the UV-vis absorption spectroscopy was used as one of the useful technique to identify the crystal phase of single-layer alloyed metal chalcogenide nanosheets. The as-exfoliated nanosheets were drop-casted on glass substrate as thin films for the UV-vis absorption measurement. The pure 2H phase samples were prepared by annealing the nanosheet thin films coated glass at 300°C for 1h under Ar atmosphere.

3.3.9 Circular dichroism (CD) spectroscopy

CD measurements were conducted on Jasco J-810 spectropolarimeter (using a quartz cuvette with an optical length of 10 mm). CD spectra only can be observed in chiral molecules and materials. In the thesis, the CD spectroscopy was used to confirm the chirality of the assembled chiral MoS₂ nanofibers. Chiral MoS₂ nanofibers dispersed in THF with a concentration 0.1 µg mL⁻¹ were used for the CD spectroscopy test at room temperature.

3.4 Applications

3.4.1 Fabrication and performance measurement of fluorescent biosensors

In a typical process, 10 µL of probe (P, 1 µM) and 10 µL of target DNA (T, 0-5 µM) were added into 972 µL of PBS solution (0.01 M, pH 7.4) and then hybridized for 30 min. 8 µL of single-layer Ta₂NiS₅ nanosheet suspension with a concentration of 0.5 mg mL⁻¹ was then added into the aforementioned mixed solution, which was incubated for 10 min before the measurement of fluorescence spectra. Note that the final concentration of T is ranging from 0 to 50 nM. The used excitation wavelength was 596 nm. The concentration-dependent fluorescence intensity was explored to find out the optimal

concentration of single-layer Ta₂NiS₅ nanosheet for the fluorescent sensors. It revealed that at the concentration of 4.0 $\mu\text{g mL}^{-1}$, the fluorescent sensors gave the best performance because it exhibited highest signal to noise ratio. Therefore, the concentration of the single-layer Ta₂NiS₅ nanosheet was fixed to 4.0 $\mu\text{g mL}^{-1}$ in the DNA detection. The selectivity of the fluorescent sensors was measured by hybridizing probe (P, 1 μM) with the same concentration of different DNA, including target DNA (T, 1 μM), single-base mismatch DNA (SM, 1 μM) and random DNA (R, 1 μM). All the final concentrations of T, SM and R for the selectivity measurement were fixed to 10 nM.

3.4.2 Fabrication and performance measurement of DSSCs

A screen printing method was used to fabricate the TiO₂ photoanode according to previously reported literature.^[11] There are three layers in the TiO₂ photoanode, including the blocking layer, transparent layer and scattering layer. First, the cleaned FTO substrates were soaked in a 40 mM aqueous TiCl₄ solution at 70 °C for 30 min. Then they were washed with water and ethanol. The blocking layer with thickness of about 50 nm was obtained. The transparent TiO₂ layer (Dyesol, 18NR-T paste) was coated on the top of the blocking layer coated FTO substrates via a screen printing method, which was then dried at 125 °C for 6 min. The thickness of the transparent layer is about 10 μm . After that, the scattering TiO₂ layer was further deposited on the surface of the transparent layer by the screen-printing method. The thickness of the scattering layer is about 4 μm . The FTO substrates coated with TiO₂ was successively annealed under air at 125°C for 10 min, 325°C for 5 min, 375°C for 5 min, 450°C for 15 min, and finally 500°C for 15 min. When the temperature decreased to about 80°C, the ruthenium dye N719 was loaded on the TiO₂ photoanode by immersing them into 0.3 mM of ruthenium dye N719 solution in a mixture of acetonitrile and tert-butyl alcohol (volume ratio, 1:1) at room temperature for 24 h.

The MoS_{2x}Se_{2(1-x)}-based counter electrodes (CEs) were prepared by drop-casting MoS_{2x}Se_{2(1-x)} nanosheet suspension on cleaned FTO substrates. The area of the films is about 1 cm², which was confined by mask. Pt sputtered on FTO (FTO-Pt) was used as the

CE for comparison. The concentration of the used $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheet suspension was $\sim 0.5 \text{ mg mL}^{-1}$. 100 μL of the nanosheet suspension was drop-casted on the confined area and then dried at room temperature overnight. Note that the as-exfoliated $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheet contained a high concentration of metallic 1T phase and the fabricated electrode was referred as FTO-Exfoliated- $\text{MoS}_{2x}\text{Se}_{2(1-x)}$. In order to get 2H phase $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheet for comparison, the FTO-Exfoliated- $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ electrode was treated at 300°C under Ar atmosphere for 1 h. The annealed electrode was referred as FTO-Annealed- $\text{MoS}_{2x}\text{Se}_{2(1-x)}$. A mixture containing 0.1 M of lithium iodide (LiI), 0.6 M of tetrabutylammonium iodide (TBAI), 0.05 M of iodine (I_2), and 0.5 M of 4-tert-butylpyridine dissolved in acetonitrile was used as the electrolyte. The sandwich-type solar cell devices were assembled the photoanode and CE together, in which a piece of parafilm as spacer to separate them to prevent the short circuit. The active area of solar cell devices was confined to be 0.138 cm^2 by a circular mask.

A Keithley Model 2440 source meter was used to characterize the photocurrent density-voltage (J - V) characteristics under AM 1.5 illumination. Cyclic voltammetry (CV) measured was conducted on a CHI760D electrochemical workstation in a three-electrode setup at a scan rate of 50 mV s^{-1} . During the test, the FTO-Pt, FTO-Exfoliated- $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ or FTO-Annealed- $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ was used as the working electrode, and a platinum wire and a Ag/AgCl were used as the counter and reference electrode, respectively. A computer-controlled potentiostat (Solartron1287, UK) was used to perform the electrochemical impedance spectroscopy (EIS) measurements in the dark by applying an AC voltage with 10 mV amplitude. The frequency is ranging from 0.1 Hz to 100 kHz. Two identical CEs were assembled together to prepare the symmetrical cell for the measurement of EIS spectra. The effective area is about 1 cm^2 . The Zview software was used to fit the obtained EIS spectra to get the EIS parameters.

3.4.3 Fabrication and performance measurement of Li ion batteries

The CuS-TiS_2 hetero-nanostructure, P2-single-walled carbon nanotube and PVDF binder in a weight ratio of 8:1:1 were mixed in NMP and stirred for 12 h to form homogeneous

slurry. The obtained slurry was then coated onto Cu foil disc. The coated Cu foil electrode was dried naturally, and then dried in a vacuum oven at 50 °C for 12 h. The fabricated electrode was used as the working electrode in a Li battery cell. Li ion batteries in the CR2032 (3 V) coin-type cells were fabricated by using the Li foil and 1M LiPF₆ as the counter electrode and the electrolyte, respectively. The assembly process of Li ion batteries were carried out in an Ar-filled glove box with moisture and oxygen below 1.0 p.p.m. A NEWARE battery testing system was used to record the charge/discharge curves at a voltage window of 0.005-3.0V.

3.4.4 Fabrication and performance measurement of memory devices

The patterned rGO films on a PET substrate (PET/rGO) were prepared according to our previously reported procedure,^[12] which was used as the bottom electrode in our device. The THF suspension containing MoS₂ chiral nanofibers with P123 (~2 µgmL⁻¹) was deposited on the surface of patterned rGO electrodes via the spin-coating technique at 500 r.p.m for 5 s, followed by 1,000 r.p.m for 30 s and then 3,000 r.p.m for 30 s. The PET/rGO electrodes deposited with the active layer were then dried in a vacuum oven at 60 °C for 12 h. Thereafter, another patterned rGO electrodes were transferred onto the top of the active layer in a perpendicular direction. Finally, devices with the structure of PET/rGO/chiral MoS₂ nanofiber-P123/rGO were obtained, which were dried in a vacuum oven at 60 °C for 12 h prior to the *I-V* measurements. The *I-V* characteristics of the fabricated resistive memory devices were characterized on a Keithley 4200 semiconductor parameter analyzer under ambient conditions at room temperature.

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Chapter 4

Ultrathin 2D Ternary Metal Chalcogenide Nanosheets

In this chapter, the synthesis and characterization of two novel ultrathin 2D ternary metal chalcogenide nanosheets, i.e. Ta_2NiS_5 and Ta_2NiSe_5 , and the potential application of single-layer Ta_2NiS_5 nanosheet as the sensing platform for fluorescent sensors are presented. Micro-sized layered bulk crystals of Ta_2NiS_5 and Ta_2NiSe_5 are exfoliated into ultrathin 2D nanosheets in via the electrochemical Li-intercalation and exfoliation method. The as-prepared nanosheets are characterized by SEM, AFM, TEM, XPS and Raman spectroscopy. Moreover, a novel fluorescent sensor is developed based on the single-layer Ta_2NiS_5 nanosheet for DNA detection, which exhibits good selectivity and a detection limit of 50 pM.

4.1 Introduction

Single- or few-layer nanosheets of layered metal chalcogenides, such as MoS₂, WS₂, TiS₂, TaS₂ and MoSe₂, have attracted considerable attention in the last few years due to their unique structural features and versatile functionalities.^[1-3] These 2D metal chalcogenide nanosheets have been explored in a wide spectrum of applications including electronics,^[4-6] optoelectronics,^[7-8] electrocatalysis,^[9-10] sensing platforms,^[11-13] batteries,^[14-15] supercapacitors^[16-17] and biomedicines.^[18-19] Of note, layered metal chalcogenides are a big family of materials, which contain several tens of compounds based on the combination between different metals and chalcogen atoms.^[1] Their properties are different from each other, making them promising for varying specific application. In the light of this, it is believed that new properties, functions or applications are expected to be identified or discovered on new metal chalcogenide materials.

The ability to prepare ultrathin 2D metal chalcogenide nanosheets is the precondition for the further investigation of various properties and applications. Therefore, over the past few years, a wide range of effective methods have been developed or identified for preparation of ultrathin 2D metal chalcogenide nanosheets.^[1-3] Importantly, the layered nature of metal chalcogenide bulk crystals enables them easy to be exfoliated into single- or few-layer nanosheets by various kinds of exfoliation techniques, including micromechanical cleavage,^[20-21] sonication-assisted exfoliation,^[22-23] surfactant/polymer-assisted exfoliation,^[24-25] Li/Na-intercalation and exfoliation,^[26-28] and electrochemical Li-intercalation and exfoliation.^[29-31] Among those exfoliation methods, the electrochemical Li-intercalation and exfoliation method developed in our group in 2011 has been proved to be a general method for exfoliation of a number of metal chalcogenide layered bulk crystals into nanosheets, such as MoS₂, WS₂, TaS₂, TiS₂, WSe₂, NbSe₂ and Sb₂Se₃.^[29-31] Considering its wide applicability, it is believed that this method is able to further extend to exfoliate new metal chalcogenide layered bulk crystals into ultrathin 2D nanosheets.

In this chapter, we use the electrochemical Li-intercalation and exfoliation method to prepare two new ultrathin 2D ternary chalcogenide nanosheets, i.e. Ta_2NiS_5 and Ta_2NiSe_5 , by exfoliating their micro-sized layered bulk crystals in solution. The single-layer Ta_2NiS_5 nanosheet displays excellent fluorescence quenching ability toward probe DNA, which can be used to develop fluorescent sensor for DNA detection. The constructed sensor exhibits excellent sensitivity with a detection limit of 50 pM and good selectivity.

4.2 Results and Discussion

4.2.1 Synthesis and characterization of Ta_2NiS_5 and Ta_2NiSe_5 layered bulk crystals

The two bulk crystals I chose here, i.e. Ta_2NiS_5 and Ta_2NiSe_5 , both have a layered structure.^[32] Although they have similar crystal structure, the two crystals belong to different space groups. The Ta_2NiS_5 crystallizes in the orthorhombic space group *Cmcm* (63), while the Ta_2NiSe_5 crystallizes in the monoclinic space group *C2/c* (15). The crystal structures of them are shown in Figure 4.1. Both the Ta_2NiS_5 and Ta_2NiSe_5 consist of stacked zigzag waved 2D layers (Figure 4.1a,b). In each layer, it is built from NiS_4 or NiSe_4 tetrahedral single chains and $[\text{TaS}_6]_2$ or $[\text{TaSe}_6]_2$ dimer chains. The NiS_4 or NiSe_4 tetrahedral single chains located between in the two $[\text{TaS}_6]_2$ or $[\text{TaSe}_6]_2$ dimer chains via sharing Q–Q edges (Figure 4.1c,d). As shown in Figure 4.1, the two compounds have similar constituent units and combination mode. However, they have different symmetry operations, making them in different space groups. The structure of Ta_2NiS_5 exhibits a twofold screw axis along the *c* axis, which do not exist in Ta_2NiSe_5 crystal, This major different might be induced by the radius difference of Se^{2-} and S^{2-} anions (Figure 4.1a,b). The calculated thickness of single-layer Ta_2NiS_5 and Ta_2NiSe_5 are about 0.63 and 0.66 nm, respectively (Figure 4.1a,b).

Figure 4.1. The crystal structures of (a) Ta₂NiS₅ and (b) Ta₂NiSe₅. (c) Projection of the layered Ta₂NiS₅ structure along the b axis. (d) The NiS₄ tetrahedra (blue) and TaS₆ octahedra (pink) in the layered Ta₂NiS₅ structure.

A chemical vapor transport technique was used to prepare micro-sized layered bulk crystals of Ta₂NiS₅ and Ta₂NiSe₅ from their elementary powders.^[32] The detail procedure is described in Section 3.2.1. The synthesized bulk crystals were characterized by SEM, EDS and XRD. As shown in Figure 4.2a,b, SEM images show that the obtained Ta₂NiS₅ crystal has a size of 5-30 μm with an irregular shape. A layered structure can be observed from the enlarged SEM image in Figure 4.2b. The elemental compositions were confirmed by EDS and the resultant spectrum gives obvious signals of Ta, Ni and S (Figure 4.2c). The mole ratio of Ta:Ni:S is very close to its chemical formula, that is 2:1:5 (inset in Figure 4.2c). The crystal phase of the Ta₂NiS₅ bulk crystal was characterized by XRD. The peaks of experimental XRD pattern of the Ta₂NiS₅ crystal matches well with simulated pattern (Figure 4.2d). Similarly, SEM, EDS and XRD were also used to characterize the obtained Ta₂NiSe₅ crystal (Figure 4.3). The Ta₂NiSe₅ crystal have a flake like morphology with a size of 20-500 μm (Figure 4.3a,b), which is larger

than the Ta_2NiS_5 crystal. Its EDS spectrum shows strong signals of Ta, Ni and Se (Figure 4.3c) and the calculated mole ratio is very close to its chemical formula. The experimental XRD pattern of Ta_2NiSe_5 crystal can be indexed to its simulated pattern (Figure 4.3d).

Figure 4.2 (a,b) SEM images of micro-sized Ta_2NiS_5 layered bulk crystal. (c) EDS spectrum of Ta_2NiS_5 layered bulk crystal. Inset in (c): The elemental weight and atomic ratio obtained from its EDS spectrum. (d) Simulated and experimental XRD patterns of Ta_2NiS_5 layered bulk crystal.

Figure 4.3 (a,b) SEM images of micro-sized Ta_2NiSe_5 layered bulk crystal. (c) EDS spectrum of Ta_2NiSe_5 layered bulk crystal. Inset in (c): The elemental weight and atomic ratio obtained from its EDS spectrum. (d) Simulated and experimental XRD patterns of Ta_2NiSe_5 layered bulk crystal.

4.2.2 Preparation and characterization of Ta₂NiS₅ and Ta₂NiSe₅ nanosheets

Ultrathin 2D Ta₂NiS₅ and Ta₂NiSe₅ nanosheets were exfoliated from the as-grown Ta₂NiS₅ and Ta₂NiSe₅ micro-sized layered bulk crystals by using the electrochemical Li-intercalation and exfoliation method. The detail experimental procedure of the exfoliation process is described in Section 3.2.2. The size, thickness and elemental composition of the exfoliated Ta₂NiS₅ nanosheets were characterized by SEM, AFM and EDS (Figure 4.4). From the SEM images in Figure 4.4a,b, we can clearly see that 2D nanosheet-like structure with irregular shape is well dispersed on the SiO₂/Si substrate. The size of the Ta₂NiS₅ nanosheet is ranging from tens of nanometer to several micrometers. The thickness of the exfoliated nanosheet was confirmed by AFM. The measured thickness from the AFM height image of Ta₂NiS₅ nanosheet is 1.1 ± 0.1 nm (Figure 4.4c, 4.5), indicating that Ta₂NiS₅ nanosheet is single-layer. The calculated yield of single-layer from AFM height images by measuring more than 50 nanosheets is as high as 86%. The exfoliated nanosheet was further characterized by TEM. The low-magnification TEM image shows a consistent result with the SEM and AFM results (Figure 4.4d). A typical Tyndall phenomenon was observed when a green laser passes through the single-layer Ta₂NiS₅ nanosheet water suspension, as shown in inset in Figure 4.4d. Clear bright spots, which are assignable to (200) and (004) planes of Ta₂NiS₅ crystal, can be observed from the selected area electron diffraction (SAED) pattern of a typical nanosheet (Figure 4.4e,f). The high-resolution TEM (HRTEM) image shows continuous lattice fringes, indicating the single-crystalline nature of the Ta₂NiS₅ nanosheet. The lattice distance measured from the HRTEM image is ~ 0.25 nm, which is assignable to the (006) planes of the Ta₂NiS₅ crystal. The EDS spectrum of a typical Ta₂NiS₅ nanosheet gives obvious elemental signals of Ta, Ni and S (Figure 4.6). The corresponding elemental mapping reveals the homogenous distribution of Ta, Ni and S in the Ta₂NiS₅ nanosheet (Figure 4.4g).

Figure 4.4 (a,b) SEM images of exfoliated Ta_2NiS_5 nanosheet. (c) AFM height image of exfoliated Ta_2NiS_5 nanosheet. (d) TEM image of exfoliated Ta_2NiS_5 nanosheet. Inset: Photograph of Tyndall effect of the suspension containing Ta_2NiS_5 nanosheet. (e) TEM image of a typical Ta_2NiS_5 nanosheet. Inset: The corresponding SAED pattern of the Ta_2NiS_5 nanosheet. (f) HRTEM image of a typical Ta_2NiS_5 nanosheet. (g) EDS elemental mapping of a typical Ta_2NiS_5 nanosheet.

Figure 4.5 (a-c) AFM height images of Ta₂NiS₅ nanosheets. (d) The thickness distribution of 50 Ta₂NiS₅ nanosheets calculated from AFM data, which indicate that 86% of Ta₂NiS₅ nanosheets are single-layer with a thickness of 1.1 ± 0.1 nm.

Figure 4.6 EDS spectrum of a typical Ta₂NiS₅ nanosheet.

The oxidation states of exfoliated Ta₂NiS₅ nanosheet were characterized by XPS. Strong signals of Ta, Ni, and S can be clearly observed from the XPS survey spectrum (Figure 4.7a). The high-resolution XPS Ta 4f spectrum gives three peaks at 24.1 eV, 26.1 eV and

28.0 eV, respectively (Figure 4.7b). The peaks at 24.1 eV and 26.1 eV are corresponding to the Ta $4f_{7/2}$ and Ta $4f_{5/2}$ of Ta⁴⁺ of Ta₂NiS₅ nanosheet, respectively (Figure 4.7b).^[33-34] Similarly, three peaks can be also observed in the high-resolution XPS Ni 2p spectrum, which located at 853.5 eV, 856.2 eV and 861.3 eV, respectively (Figure 4.7c). The peak at 853.5 eV along with a satellite peak at 861.3 eV is assignable to the binding energies of Ni²⁺ of Ta₂NiS₅ nanosheet.^[33-34] The high-resolution S 2p spectrum shows two main peaks at 161.5 eV and 162.7 eV, which are fitted to the binding energies of S²⁻ of Ta₂NiS₅ nanosheet (Figure 4.7d).^[34-35] The additional peaks at 28.0 eV of Ta 4f spectrum, at 856.2 eV of Ni 2p spectrum and at 168.3 eV of S 2p spectrum are to the binding energies of them in Ta₂O₅, NiO and SO₄²⁻, respectively (Figure 4.7b,c,d),^[33-35] which may be due to the oxidation of the sample before characterization. In addition, Raman spectroscopy was also used to characterize the Ta₂NiS₅ bulk crystal and single-layer nanosheet. As shown in Figure 4.8, the Raman spectrum of the Ta₂NiS₅ bulk crystal gives two sharp peaks at 126.6 and 148.7 cm⁻¹ as well as three small peaks at 293.2, 342.5, and 396.1 cm⁻¹. The single-layer nanosheet shows a very similar Raman spectrum to the bulk crystal but with small shift, which might be induced by the decrease of thickness.

Figure 4.7 (a) XPS survey spectrum of single-layer Ta₂NiS₅ nanosheet. (b-d) High-resolution XPS Ta, Ni and S spectra of Ta₂NiS₅ nanosheet.

Figure 4.8 Raman spectra of Ta_2NiSe_5 bulk crystal and single-layer nanosheet.

The electrochemical Li-intercalation and exfoliation method could be also used to exfoliate Ta_2NiSe_5 layered bulk crystal into nanosheet. The exfoliated Ta_2NiSe_5 nanosheet was characterized by SEM, AFM, TEM and XPS. As shown in Figure 4.9a,b,c, both the SEM and TEM images confirmed that the exfoliated nanosheet has a lateral size ranging from tens of nanometers to one micrometer. The thickness of the exfoliated Ta_2NiSe_5 nanosheet measured from its AFM height image is 1.9-3.5 nm (Figure 4.10), which means that the exfoliated Ta_2NiSe_5 nanosheet is few-layer thick. It is worth pointing out that there is small amount of nanoparticle byproduct existing along with the nanosheet (Figure 4.9a), which might be generated due the oxidation-induced decomposition of the nanosheet. The colloidal nature of the Ta_2NiSe_5 nanosheet suspension was also confirmed by the Tyndall effect, as shown in inset in Figure 4.9b. As shown in the HRTEM image in Figure 4.9d, the Ta_2NiSe_5 nanosheet shows continuous lattice fringes with a measured lattice spacing of ~ 0.26 nm, which is corresponding to the (006) planes of Ta_2NiSe_5 crystal. Similarly, intensive signals of Ta, Ni and Se were observed from the EDS spectrum of a typical Ta_2NiSe_5 nanosheet (Figure 4.11), further confirming its elemental composition. The homogeneous distribution of the Ta, Ni and Se elements in the Ta_2NiSe_5 nanosheet is evidenced by its elemental mapping (Figure 4.9e).

Figure 4.9 (a) SEM image of exfoliated Ta_2NiSe_5 nanosheet. (b) TEM image of Ta_2NiSe_5 nanosheet. Inset: Photograph of Tyndall effect of the suspension containing Ta_2NiSe_5 nanosheet. (c) TEM image of a typical Ta_2NiSe_5 nanosheet. (d) HRTEM image of a typical Ta_2NiSe_5 nanosheet. (e) EDS elemental mapping of a typical Ta_2NiSe_5 nanosheet.

Figure 4.10 (a) AFM height image of Ta_2NiSe_5 nanosheet and (b) the corresponding height profiles.

Figure 4.11 EDS spectrum of a typical Ta₂NiSe₅ nanosheet.

The chemical composition of exfoliated Ta₂NiSe₅ nanosheet was also studied by XPS. As shown in Figure 4-12a, obvious Ta, Ni and Se signals can be observed from the XPS survey spectrum of Ta₂NiSe₅ nanosheet. The high-resolution XPS Ta 4f spectrum gives four peaks at 23.7 eV, 25.7 eV, 26.4 eV and 28.1 eV. The two peaks at 23.7 eV, 25.7 eV are assignable to the binding energies of Ta⁴⁺ of Ta₂NiSe₅ nanosheet.^[36] Another two peaks located at 26.4 eV and 28.1 eV belong to the binding energies of Ta₂O₅,^[37] which might be generated due to the oxidation of the Ta₂NiSe₅ nanosheet before XPS measurement. As shown in Figure 4-13b, there are three peaks at 853.3 eV, 856.5 eV and 861.6 eV in the high resolution XPS Ni 2p spectrum. The peaks at 853.3 eV and 861.6 eV are corresponding to the binding energies of Ni²⁺ of Ta₂NiSe₅ nanosheet.^[36] Similarly, due to the oxidation of the sample, the addition peak at 856.5 eV is fitted to the binding energy of NiO.^[38] The high resolution Se 3d spectrum also gives three peaks at 53.8 eV, 54.7 eV and 55.7 eV, in which the former two peaks can be indexed to the binding energies of Se²⁻ of Ta₂NiSe₅ nanosheet.^[36] All the aforementioned XPS analysis reveals that the main composition of Ta₂NiSe₅ still kept unchanged after the exfoliation but with partial oxidation.

Figure 4.12 (a) XPS survey spectrum of Ta_2NiSe_5 nanosheet. (b-d) High-resolution XPS Ta, Ni and Se spectra of Ta_2NiS_5 nanosheet.

4.2.3 Single-layer Ta_2NiS_5 nanosheet-based fluorescent sensor

The development of fluorescent sensors capable of simply, rapidly, and selectively detection of biomolecules is the central topic in clinical diagnostics, gene profiling, and environmental monitoring.^[39] Previously, our group first reported the construction of fluorescent biosensors for DNA detection based on single-layer MoS_2 nanosheet due to its different fluorescence quenching ability toward different DNA chains.^[12] Later on, it has been proved that besides MoS_2 , other single-layer metal chalcogenide nanosheets, including TaS_2 and TiS_2 , could be also used as promising candidates for development of fluorescent sensors for the detection of DNA, in which TaS_2 nanosheet-based sensor gave superior sensitivity compared to MoS_2 and TiS_2 .^[40] Given the similar structural feature and chemical composition, the single-layer Ta_2NiS_5 nanosheet is used as a new sensing platform to construct fluorescent sensor. Figure 4.13a schematically shows the design principle of the sensor based on single-layer Ta_2NiS_5 nanosheet. The Texas red-labeled ssDNA was used as the probe (P). The detail sequence information of all the DNAs used

in this chapter is shown in Table 4.1. First, the fluorescence quenching ability of single-layer Ta_2NiS_5 nanosheet toward the probe was studied. The fluorescent spectrum of P gave rise to intense fluorescence emission itself, as shown in Figure 4.13b. In contrast, the fluorescence of P was quenched after addition of $4.0 \mu\text{g mL}^{-1}$ of single-layer Ta_2NiS_5 nanosheet within 10 min (Figure 4.13b and inset in Figure 4.13b), which indicates that the Ta_2NiS_5 nanosheet has excellent fluorescence quenching ability toward the P. The excellent quenching ability might be due to the strong interaction between single-layer Ta_2NiS_5 nanosheet and ssDNA. Importantly, the fluorescence of P was recovered when an equal amount of T was added. It is believed that the P was hybridized with T after its addition to form the dsDNA (P/T duplex) and the formed P/T duplex can easily fall off from the single-layer Ta_2NiS_5 nanosheet, resulting in the recovery of fluorescence intensity (Figure 4.13b). The results uncover that the interaction between single-layer Ta_2NiS_5 nanosheet and dsDNA is much weaker compared to the interaction between single-layer Ta_2NiS_5 nanosheet with ssDNA. Figure 4.14a shows the fluorescent intensity of P and P/T at different concentration of single-layer Ta_2NiS_5 nanosheet. The highest signal to noise ratio was obtained at the concentration of $4.0 \mu\text{g mL}^{-1}$, which was used as the optimal concentration for the DNA detection. It is noteworthy that the recovered fluorescence intensity of P/T duplex is about 82% of the original fluorescence intensity of P (Figure 4.13b). The slight decrease of fluorescence intensity might be due to the different effect of the primary and secondary structures of DNA on the fluorescence intensity of the labeled dye.^[41]

Figure 4.13 (a) Schematic illustration of single-layer Ta_2NiS_5 nanosheet-based fluorescent sensor. (b) Fluorescence spectra of P (10 nM) and P/T (10 nM) with and without Ta_2NiS_5 nanosheet. Inset: The fluorescence quenching curves of P and P/T with of Ta_2NiS_5 nanosheet. (c) Fluorescence spectra of P with varying concentrations of T (0-50 nM) in present of Ta_2NiS_5 nanosheet. (d) Calibration curve of the DNA detection. Inset: The linear plot of fluorescence peak intensity of P vs. the concentration of T. The excitation wavelength is 596 nm.

The aforementioned results are similar to our previously reported work, which means the single-layer Ta_2NiS_5 nanosheet could be a promising sensing platform for the construction of fluorescent sensor for measurement of DNA. Figure 4.13c shows the fluorescence intensity of P in presence of single-layer Ta_2NiS_5 nanosheet with addition of different concentration of T varying from 0 to 50 nM. It revealed that the recovered fluorescence intensity of P is highly dependent on the concentration of T, making it promising for quantitative detection of DNA. The fluorescence intensity shows a linear relationship with the concentration of T in the range of 0 to 5 nM. Importantly, the calculated detection limit of this sensor is 50 pM, which is much better than that of the sensor based on single-layer MoS_2 nanosheet (0.5 nM).^[12] The result is also comparable the sensor constructed from single-layer TaS_2 nanosheet (50 pM).^[40] Table 4.2 shows the comparison of this work with some other reported 2D nanomaterial-based fluorescent

sensors. Moreover, the selectivity of the sensor was also investigated. As shown Figure 4.14b, only T could give rise to significant recovery of fluorescence intensity of P when addition of same amount of SM, R and T. This result demonstrates that the single-layer Ta_2NiS_5 nanosheet-based fluorescent sensor has good selectivity toward different DNA chains.

Table 4.1 Detail information of DNA sequences used in this chapter.

Name	Sequence (5'-3')
Probe (P)	TTCTTCATCGAGAGTGTAGTCG-Texas Red
Target (T)	CGACTACACTCTCGATGAAGAA
Single-base mismatch DNA (SM)	CGACTACACTCTTGATGAAGAA
Random DNA (R)	TAGCTTATCAGACAGATGTTGA

Figure 4.14 (a) Fluorescence intensity of P+ Ta_2NiS_5 (black) and P/T+ Ta_2NiS_5 (red) at different final concentration of Ta_2NiS_5 nanosheet (1.0, 2.0, 3.0, 4.0, 5.0 and 6.0 $\mu\text{g mL}^{-1}$) (P: 10 nM, T: 10 nM). Inset: The fluorescence intensity ratio ($F_{P/T}/F_P$) at 610 nm with different concentration of Ta_2NiS_5 nanosheet. (b) Fluorescence intensity of the sensor with complementary target DNA (T), single-base mismatched DNA (SM) and random DNA (R). The excitation wavelength is 596 nm.

Table 4.2 Comparison of fluorescent DNA sensors based on ultrathin 2D nanomaterials.

Materials	Fluorescent reporter	Sensitivity (Detection limit)	Detection time	Comments	Ref.
GO	FAM, ROX,	100 pM	1 min	Multiplexed analysis	42
GO	FAM	2 nM	5 min	-	43
GO	Silver	0.5 nM	1-1.5 h	Multiplexed analysis	44
GO	FITC	6.25 pM	20 min	-	45
GO	SYBR Green I	0.25 pM	5 min	DNA intercalating dye	46
GO	Graphene quantum dots	75 pM	30 min	-	47
GO	FAM	0.2 nM	20 s	-	48
GO	FAM, ROX	5 pM	90 min	Exonuclease III amplification	49
g-C ₃ N ₄	FAM, ROX	81 pM	30 min	Exonuclease III amplification	50
MoS ₂	FAM	0.5 nM	5 min	-	12
TiS ₂	FAM, Texas	0.2 nM	5 min	Multiplexed analysis	40
TaS ₂	FAM, Texas	50 pM	5 min	Multiplexed analysis	40
Ta ₂ NiS ₅	Texas red	50 pM	10 min	-	This work

Abbreviations:

FAM: carboxyfluorescein; ROX: 6-carboxyl-x-rhodamine; Cy5: cyanine 5; FITC: fluorescein isothiocyanate.

4.3 Conclusion

The electrochemical Li-intercalation and exfoliation method has been successfully exploited for the high-yield and scalable exfoliation of two new micro-sized ternary chalcogenide layered bulk crystals into ultrathin 2D nanosheets, i.e. Ta₂NiS₅ and Ta₂NiSe₅. The characterization results revealed that the Ta₂NiS₅ nanosheet is single-layer in thickness, while the Ta₂NiSe₅ nanosheet is few-layer thick. Importantly, the single-layer Ta₂NiS₅ nanosheet had high fluorescence quenching ability, which thus could be used as sensing platform to develop a novel fluorescent sensor for detection of DNA. A detection limit of 50 pM was achieved on the resultant sensor, which is better than that of

the previously reported single-layer MoS₂-based biosensor.^[12] These novel ternary metal chalcogenide nanosheets produced in high yield and large scale may be also promising in some other applications like electronics, electrocatalysis, supercapacitors and biomedicines, which are expected to be explored in the near future.

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Chapter 5

Single-Layer Alloyed $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ and $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ Nanosheets with Metallic 1T Phase

This chapter describes the preparation of single-layer alloyed $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ and $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ nanosheets with high-concentration metallic 1T phase from their layered bulk 2H-phase crystals via phase engineering. The exfoliated alloyed $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ and $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ nanosheets are characterized by SEM, TEM, STEM, XPS and UV-vis spectroscopy. The phase-dependent electrocatalytic activity of single-layer $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheet toward the tri-iodide reduction on the counter electrode in a dye-sensitized solar cell is studied. The thin film of exfoliated $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheet with high-concentration of metallic 1T phase exhibits an enhanced power conversion efficiency (6.5%) in contrast to the 2H-phase one (5.4%).

5.1 Introduction

Over the past few year, ultrathin 2D alloyed metal chalcogenide nanosheets, including $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ and $\text{Mo}_x\text{W}_{1-x}\text{S}_2$, have attracted much attention owing to their interesting properties such as composition-dependent bandgaps and enhanced electrocatalytic activities.^[1-10] Till now, ultrathin 2D alloyed metal chalcogenide nanosheets have been mostly prepared by the mechanical exfoliation^[2-3] and chemical vapor deposition.^[4-7] Moreover, sonication-assisted exfoliation and wet-chemical synthesis method have been also used to prepare alloyed metal chalcogenide nanosheets.^[8-10] However, only thick flakes can be obtained. Therefore, the high-yield and massive production of single-layer alloyed metal chalcogenide nanosheets in solution still remains a big challenge.

Layered metal chalcogenide bulk crystals, such as MoS_2 , WS_2 , MoSe_2 and WSe_2 , normally crystallize into a hexagonal 2H crystal phase, which exhibit semiconducting properties.^[11] After being exfoliated, single- or few-layer metal chalcogenide nanosheets have bandgaps ranging from 1 to 2 eV, rendering them compelling for the fabrication of electronic and optoelectronic devices.^[12] However, the large bandgaps enable them with low intrinsic electrical conductivity, which hindered their potentials in those applications that need high electrical conductivity, such as electrocatalysis, electrochemical supercapacitors and low-resistance contact transistors. Promisingly, recent studies have proved that the semiconducting 2H phase of metal chalcogenide nanosheets can be partially converted into metallic 1T phase via phase engineering,^[11] in which can significantly enhance the conductivity of metal chalcogenide nanosheets. More importantly, the obtained metal chalcogenide nanosheets (e.g. MoS_2 and WS_2) with high concentration of metallic 1T phase have shown much enhanced performance in applications like electrocatalytic hydrogen evolution,^[13-15] supercapacitors^[16] and high-performance transistors.^[17-18] Currently, several strategies, including Li-intercalation by using n-butyllithium, laser irradiation, electron beam irradiation, and gate-driven Li-intercalation, have been developed or identified to induce the phase transformation from 2H to 1T phase.^[18-21] The exploration and identification of new methods for phase

engineering is fundamentally and technologically intriguing for fully exploitation of the potential of metallic metal chalcogenide nanosheets.

In this chapter, single-layer alloyed $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ and $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ nanosheets with high concentration (~66%) of metallic 1T phase are exfoliated from their micro-sized 2H-phase layered bulk crystals in solution phase by using the electrochemical Li-intercalation and exfoliation method. The exfoliated $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheet is coated on a FTO substrate as a thin film by simple drop-coating method, which is then used as the electrocatalyst for the tri-iodide reduction on the counter electrode in a DSSC. The phase-dependent catalytic activities of $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheet thin films for the tri-iodide reduction is investigated.

5.2 Results and Discussion

5.2.1 Preparation and characterization of 2H-phase alloyed $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ and $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ layered bulk crystals

Similar to the Ta_2NiS_5 layered bulk crystal, micro-sized alloyed $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ and $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ layered bulk crystals with a 2H-phase were grown by the chemical vapor transport method by using the corresponding elementary powders as the starting materials.^[22] The growth procedure is described in detail in Section 3.2.4. The morphology, chemical composition and crystal phase of the two alloyed crystals were characterized by SEM, EDS and XRD. As shown in Figure 5.1a,b, the $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ bulk crystal has a plate-like structure with a lateral size of 5-30 μm and a thickness of 1-2 μm . The elemental composition of Mo, S and Se of the bulk crystal is evidenced by its EDS spectrum (Figure 5.1c). The calculated chemical formula based on its EDS result is $\text{MoS}_{1.35}\text{Se}_{0.65}$ (inset in Figure 5.1c). Figure 5.1d shows the XRD pattern of the $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ bulk crystal. All the peaks can well match with stand peaks of 2H-phase MoSe_2 crystal but with some shift, indicating its 2H-phase crystal structure. Note that the peak shift in XRD pattern is induced by the change of the inter-layer lattice spacing due to the substitution of Se atoms with S atoms. This phenomenon is quite similar to solid

solutions of $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ prepared by similar methods reported in literature,^[23-24] which can be explained by the Vegard's law. Similarly, the successful preparation of micro-sized $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ bulk crystal with a 2H phase was confirmed by SEM, EDS and XRD characterization, which are shown in Figure 5.2. The calculated chemical formula based on its EDS result is $\text{Mo}_{0.65}\text{W}_{0.35}\text{S}$ (inset in Figure 5.2c).

Figure 5.1 (a,b) SEM images of micro-sized 2H-phase layered bulk crystal of $\text{MoS}_{2x}\text{Se}_{2(1-x)}$. (c) Its corresponding EDS spectrum. Inset in (c): The elemental ratio calculated from the EDS spectrum. (d) Its XRD pattern. The standard patterns of MoS_2 (JCPDS #00-009-0312) and MoSe_2 (JCPDS #00-017-0887) are inserted as references.

Figure 5.2 (a,b) SEM images of micro-sized 2H-phase layered bulk crystal of $\text{Mo}_x\text{W}_{1-x}\text{S}_2$. (c) Its corresponding EDS spectrum. Inset in (c): The elemental ratio calculated from the EDS spectrum. (d) Its XRD pattern. The standard patterns of MoS_2 (JCPDS #00-009-0312) and WS_2 (JCPDS #00-008-0237) are inserted as references.

5.2.2 Preparation and characterization of single-layer alloyed $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ and $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ nanosheets with high-concentration metallic 1T phase

Micro-sized layered bulk crystals of $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ and $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ were exfoliated into single-layer alloyed nanosheets with high concentration of metallic 1T phase by using the electrochemical Li-intercalation and exfoliation method,^[25] which is schematically shown in Figure 5.3. The detail exfoliation procedure is described in Section 3.2.5. The exfoliated single-layer alloyed nanosheets were then characterized by SEM, AFM, TEM, STEM, XPS and UV-vis spectroscopy. As shown in Figure 5.4a,b,c, the SEM, AFM height, and TEM images suggest that the exfoliated $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheet has a lateral size of 0.1-2 μm. The AFM height image and its corresponding height profiles indicate that the exfoliated $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheet has a thickness of 1.1-1.2 nm (Figure 5.4b and Figure 5.5), which means that the exfoliated $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheet is single-layer. The

photograph in inset of Figure 5.4a shows the stable suspension of the exfoliated $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheet, indicating its colloidal nature. The SAED pattern of a typical $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheet shown in Figure 5.4d is shown in Figure 5.4e. It gives clear diffraction spots with hexagonal shape, indicating its single-crystalline nature. The outer and inner six spots are corresponding to the (110) and (100) planes of $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ crystal, respectively. Continuous lattice fringes can be observed from its HRTEM image and the measured lattice distance is about 0.276 nm, which is indexed to the (100) planes of $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ crystal. The elemental composition of the $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheet is confirmed by its EDS spectrum, as shown in Figure 5.6. The corresponding elemental mapping clearly shows the uniform distribution of Mo, S and Se in the nanosheet (Figure 5.4g). The atom arrangement of the exfoliated $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheet was imaged by the high-angle annual dark-field (HAADF) aberration-corrected STEM. As shown in Figure 5.7a, the atomic scale STEM image of a typical $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheet shows the triangular arrangement of atoms,^[11,14] which means that metallic 1T phase is presence in the exfoliated nanosheet. Note that S atoms give negligible contrast in 1T phase structure, while Se atoms give brighter contrast than Mo atoms since it has larger Z number (Figure 5.7a).^[4] As shown Figure 5.7b, the enlarged STEM image clearly shows the locations of Mo and Se atoms, which are labelled by light blue and orange dots, respectively. The STEM analysis reveals the alloyed structure of $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheet and the presence of metallic 1T phase of in the exfoliated nanosheet.

Figure 5.3 Schematic demonstration of the exfoliation of 2H-phase layered bulk crystals into single-layer alloyed metal chalcogenide nanosheets with high-concentration metallic 1T phase by using the electrochemical Li-intercalation and exfoliation method. $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ is used as an example in the scheme.

Figure 5.4 (a) SEM image of exfoliated $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheet. Inset is the photograph of $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheet suspension. (b) AFM height image of exfoliated $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheet. (c) TEM image of exfoliated $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheet. (d) TEM image of a typical $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheet. (e) The corresponding SAED pattern of (d). (f) HRTEM image of a typical $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheet. (g) EDS elemental mapping of a typical $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheet.

Figure 5.5 (a) AFM height image of the exfoliated $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheet and (b-d) its corresponding height profiles.

Figure 5.6 EDS spectrum of a typical $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheet.

Figure 5.7 (a) Atomic STEM image of a typical exfoliated $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheet. (b) Enlarged STEM image in the white square in (a). The Mo and Se atoms are labeled by light blue and orange dots, respectively.

In addition, XPS, Raman spectra and UV-vis absorption analyses also confirmed the coexistence of 2H and 1T phases in the exfoliated nanosheets. The XPS spectra of $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ bulk crystal, exfoliated nanosheet and annealed nanosheet are shown in Figure 5.8a,b,c. According to previous report,^[19] the metallic 1T phase is metastable, which can be fully converted into 2H phase at mild annealing treatment (e.g. 300°C) under inert atmosphere. Therefore, the exfoliated nanosheets with metallic 1T phase deposited on Si substrates were annealed at 300°C under Ar for 1h to prepare 2H-phase nanosheets, which are labeled as annealed nanosheet in this chapter. Figure 5.8a shows the high-resolution XPS Mo 3d spectra of the three samples. As shown in Figure 5.8a, the bulk crystal gives two peaks at 229.0 and 232.1 eV, which are corresponding to the $\text{Mo}^{4+} 3d_{5/2}$ and $\text{Mo}^{4+} 3d_{3/2}$ peaks of 2H-phase $\text{MoS}_{2x}\text{Se}_{2(1-x)}$, respectively. After exfoliation, the two peaks of the exfoliated nanosheet can be fitted into four peaks at 229.0, 228.2, 232.1 and 231.3 eV (Figure 5.8a). The two main peaks at 228.2 and 231.3 eV (red peaks) shifted to lower binding energy by 0.8 eV in contrast to the peaks of 2H-phase $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ (Figure 5.8a), which are assignable to the metallic 1T phase $\text{MoS}_{2x}\text{Se}_{2(1-x)}$. In addition, there are still two peaks at 229.0 and 232.1 eV that belongs to 2H-phase $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ in its XPS spectrum (Figure 5.8a). Similar shifting phenomena were also observed in the high-resolution XPS S 2p and Se 2d spectra (Figure 5.8b,c). All the aforementioned XPS analyses suggested that the metallic 1T phase and semiconducting

2H phase coexist in the exfoliated $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheet, which is similar to that of chemically exfoliated MoS_2 nanosheet.^[19] According to high-resolution XPS Mo 3d spectrum, the concentration of metallic 1T phase in the exfoliated was calculated to be ~66% (Figure 5.8a).^[19,26] After annealing, the XPS peaks belong to metallic 1T phase disappeared in all the XPS spectra (Figure 5.8a,b,c), indicating that the metallic 1T phase was restored to 2H phase after annealing treatment. Moreover, the exfoliated and annealed $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheets were also characterized by UV-vis spectroscopy. As shown in Figure 5.8d, except a small peak at round 380 nm, the characteristic 2H-phase peaks of $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheet cannot be observed from the UV-vis spectrum of the exfoliated nanosheet film.^[19] In contrast, the UV-vis spectrum of annealed nanosheet film gives obvious characteristic A and B excitonic peaks at 650 and 715 nm and convoluted C and D excitonic peaks at around 443 nm of 2H-phase $\text{MoS}_{2x}\text{Se}_{2(1-x)}$, respectively.^[19] The UV-vis spectra analyses revealed that the exfoliated $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheet possesses high concentration of metallic 1T phase and the restoration of 2H phase occurred during the annealing process.

Figure 5.8 High-resolution XPS (a) Mo 3d, (b) S 2p and (c) Se 2d spectra of bulk crystal of $\text{MoS}_{2x}\text{Se}_{2(1-x)}$, and the exfoliated and annealed $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheet. (d) UV-vis spectra of as-deposited and annealed thin films of $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheet on glass.

By using the same method, micro-sized layered bulk crystal of $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ with a 2H phase was also exfoliated into single-layer nanosheets with high-concentration metallic 1T phase. The SEM, AFM and TEM characterizations of the exfoliated $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ nanosheet are shown in Figure 5.9. As shown in the photograph (inset in Figure 5.9a), the $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ nanosheet can form stable colloidal suspension when dispersed in water. As shown in Figure 5.9a,b,c, the SEM, AFM height and TEM images clearly show that the exfoliated $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ nanosheet has a similar lateral size to that of the $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheet. The measured thickness of the $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ nanosheet from AFM height image is 0.9-1.2 nm (Figure 5.9b and Figure 5.10), indicating that the $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ nanosheet is single-layer thick. The SAED pattern of a typical $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ nanosheet (Figure 5.9d) gives hexagonal diffraction spots (Figure 5.9e), in which the outside and inner six spots are corresponding to the (110) and (100) planes of $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ crystal, respectively. Continuous lattice fringes can be observed from its HRTEM image and the measured lattice spacing is about 0.272 nm, which can be indexed to the (100) planes of the $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ crystal. Strong signals of Mo, W and S were detected in the EDS spectrum of a typical $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ nanosheet (Figure 5.11a) and the corresponding elemental mapping demonstrates the homogeneous distribution of the three elements in the alloyed nanosheet (Figure 5.11b). Similarly, the locations of Mo and W atoms were visualized by atomic scale STEM image in the single-layer $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ nanosheet. Note that W atoms show brighter contrast than the Mo atoms due to its greater Z number.^[2] As shown in Figure 5.12, the W (bright dots) and Mo (dark dots) atoms are randomly distributed along the nanosheet and form a triangular lattice arrangement. It is worth pointing out that S atoms give negligible contrast in the STEM image due to its lower Z number and the 1T phase crystal structure.

Similarly, the presence of metallic 1T phase in the exfoliated $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ nanosheet was also evidenced by the XPS and UV-vis absorption analyses, which are shown in Figure 5.13. As shown in Figure 5.13a,b,c, the binding energies belong to metallic 1T phase can only be observed in the exfoliated $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ nanosheet and both the bulk crystal and annealed nanosheet only give the 2H phase peaks in all the high-resolution XPS Mo 3d, S

2p and W 4f spectra.^[14,19] The concentration of metallic 1T in the $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ nanosheet is calculated to be ~66% based on the Mo 3d spectrum (Figure 5.13a). The UV-vis absorption spectra of the thin films of exfoliated and annealed $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ nanosheets display similar results to that of the $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheet thin films.^[19] The annealed nanosheet gives clear characteristic 2H phase absorption peaks in contrast to the exfoliated $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheet with high concentration of metallic 1T phase (Figure 5.13d). This result clearly proved that the metallic 1T phase was converted to 2H phase after annealing treatment.

Figure 5.9 (a) SEM image of exfoliated $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ nanosheet. Inset is the photograph of $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ nanosheet suspension. (b) AFM height image of exfoliated $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ nanosheet. (c) TEM image of exfoliated $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ nanosheet. (d) TEM image of a typical $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ nanosheet. (e) The corresponding SAED pattern of (d). (f) HRTEM image of a typical $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ nanosheet.

Figure 5.10 (a) AFM height image of the exfoliated $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ nanosheet and (b) its corresponding height profiles.

Figure 5.11 EDS spectrum and corresponding elemental mapping of a typical $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ nanosheet.

Figure 5.12 STEM image of a typical $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ nanosheet at atomic scale.

Figure 5.13 High-resolution XPS (a) Mo 3d, (b) S 2p and (c) W 4f spectra of $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ bulk crystal, and the exfoliated and annealed nanosheets. (d) UV-vis spectra of as-deposited and annealed thin films of $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ nanosheets on glass.

The electrochemical Li-intercalation and exfoliation method was developed by our group in 2011 for exfoliation of single-layer metal chalcogenide nanosheets, such as MoS_2 , WS_2 , TiS_2 and TaS_2 .^[25] It has been found that the 2H and 1T phase coexist in the exfoliated single-layer nanosheets.^[27] Therefore, this method is used here to prepare single-layer alloyed metal chalcogenide nanosheets that contain high concentration of metallic 1T phase. It has been proved that the bulk crystals of $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ and $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ have a 2H phase, while single-layer alloyed nanosheets with concentration of metallic 1T phase were obtained after the exfoliation. It is suggested that the metal chalcogenides underwent a partial phase transformation from semiconducting 2H phase to metallic 1T phase during the electrochemical Li-intercalation process. This phenomenon is similar the Li intercalation of bulk metal chalcogenides with n-butyllithium.^[26,28] It is believed that the electron was transferred from the butyl to metal chalcogenides during the

intercalation process with n-butyllithium.^[11] Therefore, the pristine 2H phase was destabilized, thus inducing the phase transformation from 2H to metallic 1T phase. In our case, it is believed that the electrons should be donated from Li foil to bulk metal chalcogenide crystals (i.e., $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ and $\text{Mo}_x\text{W}_{1-x}\text{S}_2$) during the discharge process, thus leading to the phase transformation. This method might be a general method that can be extended to engineer the crystal phase of other metal chalcogenides, such as TaS_2 , TiS_2 , WS_2 and their alloyed crystals, since it has been proved to be effective for the exfoliation of these bulk crystals into single-layer nanosheets.^[25]

5.2.3 Phase-dependent electrocatalytic activity of thin films based on $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheets

Previous studies have demonstrated the advantages of the presence of metallic 1T phase in metal chalcogenide nanosheets a number of applications, including electrocatalytic hydrogen evolution, electrochemical supercapacitors and low-resistance contact transistors.^[13-18] Herein, the advantage of metallic 1T phase in $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheet for the electrocatalytic tri-iodide reduction on the counter electrode in a DSSC is presented. The single-layer $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheet with 66% of metallic 1T phase was deposited on a FTO substrate to form a thin film by the simple drop-casting method (FTO-Exfoliated- $\text{MoS}_{2x}\text{Se}_{2(1-x)}$), which was then used as the electrocatalyst for tri-iodide reduction in I^-/I_3^- redox electrolyte in DSSCs. For comparison, the 2H-phase $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheet thin film deposited on FTO (FTO-Annealed- $\text{MoS}_{2x}\text{Se}_{2(1-x)}$) was prepared by annealing the as-deposited $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheet thin film under Ar atmosphere at 300°C for 1 h. The thickness of the deposited is about 50 nm, which is confirmed by the SEM cross-sectional view (Figure 5.14). The DSSC device structure is schematically shown in Figure 5.15a, in which the $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheet thin film coated FTO and N719 dye-sensitized mesoporous TiO_2 electrode were used as the counter electrode and photoanode, respectively.^[29] The electrocatalytic activities of $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheet-based electrodes toward the tri-iodide reduction was studied by CV measurement in I^-/I_3^- redox electrolyte. As shown in Figure 5.15b, the CV curve of the FTO-Exfoliated- $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ electrode give two typical pairs of redox peaks, which are very similar to the FTO-Pt electrode,

indicating its Pt-like electrocatalytic activity for the tri-iodide reduction. The two pair peaks are assignable to the two-step reversible redox reaction in I^-/I_3^- electrolyte solution. The left pair (Ox-1 and Red-1) is due to the reaction of $I_3^- + 2e^- \leftrightarrow 3I^-$, and the right pair (Ox-2 and Red-2) is corresponding to the reaction of $3I_2 + 2e^- \leftrightarrow 2I_3^-$ (Figure 5.15b). The FTO-Annealed-MoS_{2x}Se_{2(1-x)} electrode also gives similar CV curve, but the anodic peak (Ox-2) disappeared. Note that in FTO-Exfoliated-MoS_{2x}Se_{2(1-x)} gives higher cathodic peak density of Red-1 than that of the FTO-Annealed-MoS_{2x}Se_{2(1-x)}, indicating its faster redox reaction. All the CV analyses revealed that the FTO-Exfoliated-MoS_{2x}Se_{2(1-x)} exhibits better electrocatalytic activity toward the tri-iodide reduction compared to FTO-Annealed-MoS_{2x}Se_{2(1-x)}, which is comparable with FTO-Pt electrode. Considering its good electrocatalytic activity, the FTO-Exfoliated-MoS_{2x}Se_{2(1-x)} electrode was then assembled into a DSSC device as the CE. For comparison, FTO-Annealed-MoS_{2x}Se_{2(1-x)} and FTO-Pt were also used as CEs in DSSC devices. The photocurrent density-voltage (*J-V*) characteristic curves of DSSCs based on different CEs are shown in Figure 5.15c. Table 5.1 shows and compares the detailed photovoltaic parameters. Note that the DSSC by using FTO-Exfoliated-MoS_{2x}Se_{2(1-x)} as CE has an open-circuit voltage (V_{oc}) of 0.75 V, a short-circuit current density (J_{sc}) of 13.40 mA cm⁻², a fill factor (*FF*) of 0.65 and a PCE of 6.5%, which all are close to that of the DSSC using FTO-Pt that are 0.80 V, 12.82 mA cm⁻², 0.69, and 7.0%, respectively (Table 1 and Figure 5.15c). In contrast, the DSSC has a PCE only about 5.4% with V_{oc} =0.76 V, J_{sc} =13.52 mA cm⁻², and *FF*=0.52 when using the FTO-Annealed-MoS_{2x}Se_{2(1-x)} as CE (Table 1 and Figure 5.15c). The aforementioned results demonstrated that the exfoliated MoS_{2x}Se_{2(1-x)} nanosheet thin film with high concentration of metallic 1T phase gave much enhanced photovoltaic performance compared with the 2H phase one, which is also comparable with Pt-based CE.

The electrochemical impedance spectroscopy (EIS) was used to study the electron transport process at the CE/electrolyte interface. The measurement was conducted in a symmetric dummy cell consisting of two identical CEs. The Nyquist plots for the three samples measured in dark without bias potential are shown in Figure 5.15d. The data were fitted with the equivalent circuit inset in Figure 5.15d.^[30] The semicircle in the high

frequency region presents the charge transfer resistance (R_{ct}) and the corresponding constant phase angle element (CPE) at the CE/electrolyte interface. The electrocatalytic activity toward the tri-iodide reduction can be evaluated by the parameters of R_{ct} and the ohmic series resistance (R_s). The obtained R_{ct} and R_s of all the three CEs are summarized in Table 5.1. Note that all the three CEs have a similar value of R_s . However, the FTO-Exfoliated-MoS_{2x}Se_{2(1-x)} has a much lower R_{ct} (4.60 $\Omega \text{ cm}^2$) compared with the FTO-Annealed-MoS_{2x}Se_{2(1-x)} (23.25 $\Omega \text{ cm}^2$), which is very close to the FTO-Pt CE (2.28 $\Omega \text{ cm}^2$), suggesting its higher electrocatalytic activity. It is believed that the higher R_{ct} may be ascribed to the lower conductivity of the semiconducting 2H-phase MoS_{2x}Se_{2(1-x)} after annealing of the exfoliated-MoS_{2x}Se_{2(1-x)}, which induces the sluggish electron transfer process. In contrast, the high concentration of metallic 1T phase in the FTO-Exfoliated-MoS_{2x}Se_{2(1-x)} (~66%) renders its higher conductivity, which can facilitate the electron transport from the CE surface to the redox electrolyte for the tri-iodide reduction.

Based on all the aforementioned discussion, we uncover that the exfoliated MoS_{2x}Se_{2(1-x)} nanosheet with high concentration of metallic 1T phase gives higher electrocatalytic activity towards the tri-iodide reduction compared to the 2H phase one. Therefore, the FTO-Exfoliated-MoS_{2x}Se_{2(1-x)} exhibits a higher photovoltaic performance (PCE=6.5%) compared with the FTO-Annealed-MoS_{2x}Se_{2(1-x)}. Although the PCE of the DSSC device reported here is still lower than that of the DSSCs based MoS₂, WS₂, and MoSe₂ CEs,^[31-32] this study provided a promising way via phase engineering to enhance the PCEs of DSSCs by using metal chalcogenide-based nanosheets as CEs. Intriguingly, considering the MoS_{2x}Se_{2(1-x)} nanosheet thin film was deposited by simple drop-casting method at room temperature, the as-prepared nanosheet might be promising candidate for the construction of flexible photovoltaic devices in the near future.

Figure 5.14 SEM image of cross-sectional view of the thin film of exfoliated $\text{MoS}_2\text{S}_{2(1-x)}$ nanosheet deposited on a FTO.

Figure 5.15 (a) Schematic illustration of a typical fabricated DSSC. (b) CV curves of different electrodes. (c) $J-V$ curves of DSSCs based on different CEs. (d) Nyquist plots of different CEs (inset: a fitting equivalent circuit).

Table 5.1 Photovoltaic parameters of DSSCs with the three different CEs.

Counter electrode	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE (%)	R_s (Ω cm ²)	R_{ct} (Ω cm ²)
FTO-Pt	0.80	12.82	0.69	7.0	27.07	2.28
FTO-Exfoliated-MoS _{2x} Se _{2(1-x)}	0.75	13.40	0.65	6.5	28.40	4.60
FTO-Annealed-MoS _{2x} Se _{2(1-x)}	0.76	13.52	0.52	5.4	27.92	23.25

5.3 Conclusion

The electrochemical Li-intercalation and exfoliation method has been provide to be effective for the exfoliation of micro-sized layered bulk crystals of alloyed MoS_{2x}Se_{2(1-x)} and Mo_xW_{1-x}S₂ into single-layer nanosheets. More importantly, the Li-intercalation into bulk crystals MoS_{2x}Se_{2(1-x)} and Mo_xW_{1-x}S₂ can induce the partial phase transformation from 2H phase to 1T phase, resulting in the formation of single-layer alloyed nanosheets with high-concentration metallic 1T phase. The metallic 1T can be restored into 2H phase via simple annealing treatment. When coated on a FTO as a thin film by the simple drop-coating method and then used as the counter electrode in a DSSC, the exfoliated MoS_{2x}Se_{2(1-x)} nanosheet gave a higher PCE (6.5%) than that of the annealed one (5.4%) due to its enhanced electrocatalytic activity toward the tri-iodide reduction. The enhanced electrocatalytic activity is attributed to the much enhanced electrical conductivity of the exfoliated MoS_{2x}Se_{2(1-x)} nanosheet enabled by the metallic 1T phase. It is believed that the exfoliated single-layer alloyed metal chalcogenide nanosheets with high concentration of metallic 1T phase might also be promising for other applications like electrocatalytic hydrogen evolution, supercapacitors and electrochemical sensors.

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Chapter 6

Liquid-Phase Epitaxial Growth of 2D Metal Chalcogenide Heteronanostructures

This chapter introduces the epitaxial growth of 2D metal chalcogenide heteronanostructures via a solution-based method. The in-situ deposition of 2D metal sulphide nanoplates, including CuS, ZnS and Ni_3S_2 , on TiS_2 nanosheet to form 2D epitaxial heteronanostructures is achieved via an electrochemical approach using the bulk TiS_2 crystal and metal foils. These epitaxial 2D metal chalcogenide heteronanostructures are characterized by TEM, EDS and XPS. When used as the electrode in a LIB, the CuS- TiS_2 heteronanostructure exhibits good performance.

6.1 Introduction

Epitaxial growth of one kind of nanomaterial on another crystalline nanostructure is a promising way to construct epitaxial heteronanostructures.^[1] Due to well-defined structure, interface and crystal orientation, these epitaxial heteronanostructures have been demonstrated to be promising in a number of applications like phasmonics, catalysis, electronics and sensors.^[1] From a method point of view, gas-phase epitaxy methods are the most commonly used methods for epitaxial growth of crystals on bulk substrates.^[2-5] However, the gas-phase epitaxy approaches need high temperature and high vacuum, yielding a low production yield with relatively high cost. In contrast, the liquid-phase epitaxy methods are able to produce epitaxial heteronanostructures in high yield and large scale with relative low cost in solution phase. Till now, solution-phase epitaxy methods have been used to prepare various kinds of epitaxial heteronanostructures, such as chalcogenide-chalcogenide, metal-metal, metal-metal oxide and metal-chalcogenide heteronanostructures.^[6-13] However, all the aforementioned epitaxial heteronanostructures were grown based on nanoparticles, nanorods or nanocubes and the epitaxial growth of heteronanostructures based on 2D nanomaterials still remains a challenging topic.

Over the past few years, single- or few-layer nanosheets of layered metal chalcogenides, such as MoS₂, WS₂, TiS₂, TaS₂, etc. have become a key class of nanomaterials in physics, materials science and chemistry.^[14-16] Thanks to their extraordinary properties, these newly emerging 2D nanomaterials have shown much potential for many promising applications, due to their outstanding physical, chemical and electronic properties.^[14-16] It is worth pointing out that although being atomically thin, these 2D metal chalcogenide nanosheets still keep the single-crystalline nature with atomically flat surface due to its 2D structural features, rendering them ideal templates for the epitaxial growth of other nanostructures on their surface.^[17-19] Recently, a number of 2D lateral or vertical epitaxial metal chalcogenide heteronanostructures, such as MoS₂-MoSe₂, WS₂-WSe₂, MoSe₂-WSe₂ and WS₂-MoS₂, have been successfully prepared by the CVD method.^[20-28] The resultant 2D heteronanostructures have shown great potential in applications like p - n diodes, photovoltaic devices, and light-emitting diodes.^[20-28] However, the preparation of 2D

metal chalcogenide epitaxial heteronanostructures by liquid-phase epitaxial approaches still remains a big challenge.

In this chapter, a facile electrochemical method is exploited to prepare 2D metal chalcogenide epitaxial heteronanostructures in liquid phase by epitaxially growing metal sulphide nanoplates, including CuS, ZnS and Ni₃S₂, on the TiS₂ nanosheet. Metal sulphide nanoplates are deposited on TiS₂ nanosheet with perfect epitaxial effect. The growth process is explored by studying the time-dependent morphology evolution of the CuS-TiS₂ heteronanostructure. The potential application of the CuS-TiS₂ heteronanostructure as the anode in a Li-ion battery is investigated.

6.2 Results and Discussion

6.2.1 Preparation and characterization of 2D metal chalcogenide epitaxial heteronanostructures

2D metal chalcogenide epitaxial heteronanostructures were prepared via an electrochemical method by using metal foils and bulk TiS₂ crystal as starting materials. The detail experimental procedure is described in Section 3.2.6. After the preparation, the obtained 2D heteronanostructures were characterized by TEM, EDS and XPS. The TEM characterization of CuS-TiS₂ heteronanostructure is shown in Figure 6.1. Figure 6.1a,b show the TEM images of the CuS-TiS₂ heteronanostructure at different magnifications. From Figure 6.1a, we can clearly see that CuS nanoplates are deposited on a large TiS₂ nanosheet. The CuS nanoplates have a regular triangular or hexagonal shape. The measured lateral size of CuS nanoplates on TiS₂ nanosheet is about 50-120 nm. The photograph of the CuS-TiS₂ heteronanostructure solution indicates the formation of stable colloidal suspension when dispersing in water (inset in Figure 6.1a). Two sets of hexagonal diffraction spots can be clearly observed from the SAED pattern of Cu-TiS₂ heteronanostructure (Figure 6.1c). The inner and outside diffraction spots are assignable to the CuS and TiS₂ crystals, respectively. It is clear that the two sets of diffraction spots are well aligned in the same orientation without any misorientation, suggesting the

perfect epitaxial alignment of CuS nanoplates on TiS_2 nanosheet, as shown in Figure 6.1c. Continuous lattice fringes can be observed from the HRTEM of a CuS nanoplate on TiS_2 nanosheet (Figure 6.1d), which means that the CuS nanoplates have a single-crystalline structure. The measured lattice distance from the HRTEM is ~ 0.19 nm, which corresponds to the (110) planes of hexagonal CuS (JCPDS 06-0464 with $a = 3.792$ Å and $c = 16.34$ Å) (Figure 6.1d). Continuous lattice fringes of both CuS and TiS_2 can be also observed from the HRTEM image at the interface area of them, indicating the single-crystalline nature of them (Figure 6.1e). The measured lattice fringes of CuS and TiS_2 are 0.33 and 0.29 nm, corresponding to (100) planes of them, respectively. As shown Figure 6.1f, the fast Fourier transfer (FFT)-generated SAED pattern from the HRTEM in Figure 6.1e gives two sets of well aligned spots similar to its SAED pattern showing in Figure 6.1c. This result further supports the epitaxial growth effect between CuS and TiS_2 . The epitaxial growth effect between CuS and TiS_2 is also evidenced by the Moiré pattern fringes observed in TEM image.^[29] The TEM image in Figure 6.2 clearly shows the presence of Moiré pattern fringes induced by the superposition of misfitted CuS nanoplates on grown on TiS_2 nanosheet. The measured fringe distance from the Moiré pattern is about 1.52, close to value (1.615 nm) calculated between the (110) planes of CuS and TiS_2 crystal according to the reported method.^[30] The schematic illustration of the CuS- TiS_2 heteronanostructure is shown in Figure 6.3a. The crystal structure mode for the epitaxial growth of CuS on TiS_2 is shown in Figure 6.3b. As shown in Figure 6.3b, both the sulfur layers of CuS and TiS_2 have the same six-fold symmetry with the same orientation. The calculated lattice mismatch of (110) planes between CuS and TiS_2 is about 10%.

Figure 6.1 (a,b) TEM images of CuS-TiS₂ heteronanostructure. Inset in (a): photograph of CuS-TiS₂ suspension. (c) The SAED pattern of (b). (d) HRTEM image of CuS-TiS₂ heteronanostructure focused on a CuS nanoplate. (e) HRTEM image and (f) FFT-generated SAED pattern of the CuS-TiS₂ heteronanostructure at the interface between CuS and TiS₂.

Figure 6.2 Moiré patterns observed in TEM image of CuS-TiS₂ heteronanostructure.

Figure 6.3 (a) Scheme showing CuS-TiS₂ heteronanostructure composing of CuS nanoplates epitaxially grown on TiS₂ nanosheet. (b) Azimuthal orientation of the CuS-TiS₂ heteronanostructure.

The chemical compositions and binding energies of the prepared CuS-TiS₂ heteronanostructure were studied by EDS and XPS, respectively. Figure 6.4 shows the EDS elemental mapping and corresponding EDS spectrum of the CuS-TiS₂ heteronanostructure. The elemental mapping clearly shows the homogeneous distribution of S, Ti and Cu elements in the heteronanostructure (Figure 6.4a). The presence of intense signals of S, Ti and Cu further confirms its chemical composition. Off note, there is a weak O signal (Figure 6.4b), which may due to oxidation of the sample before the test. Figure 6.5 shows the XPS spectra of CuS-TiS₂ heteronanostructure. Similarly, intense Cu, Ti and S signals can be clearly observed from the XPS survey spectrum of the CuS-TiS₂ heteronanostructure, as shown in Figure 6.5. The high-resolution XPS Cu 2p spectrum shows two peaks at 931.5 eV and 951.5 eV (Figure 6.5b), which can be fitted to the binding energy of Cu²⁺ of CuS.^[31] Three peaks at 455.6 eV, 458.3 eV and 464.2 eV were detected in the high-resolution XPS Ti 2p spectrum (Figure 6.5c).^[32-33] The peak at 455.6 eV and 464.2 eV are assignable to the binding energies of Ti⁴⁺ of TiS₂ and TiO₂, respectively.^[32-33] The peak at 458.3 eV can be fitted to the mixed state of Ti⁴⁺ of TiS₂ and TiO₂.^[32-33] The presence of TiO₂ might be due to oxidation of the sample before XPS test. The high-resolution XPS S 2p spectrum gives two main peaks at 160.6 eV and 161.7 eV, which can be indexed to the binding energies of S²⁺ of TiS₂ and CuS.^[31-33] Both the

EDS and XPS analyses suggested that the obtained heteronanostructure is mainly composed of CuS and TiS₂.

Figure 6.4 (a) EDS elemental mapping of the CuS-TiS₂ heteronanostructure. (b) EDS spectrum of the CuS-TiS₂ heteronanostructure.

Figure 6.5 (a) Survey XPS spectrum of CuS-TiS₂. (b-d) High-resolution XPS Cu, Ti and S spectra of CuS-TiS₂ heteronanostructure.

Time-dependent structural evolution was used to study the growth process of the CuS-TiS₂ heteronanostructure. In our previous report, it has been demonstrated that pure TiS₂

nanosheet was obtained if the Li-intercalated TiS_2 crystal was sonicated in water immediately after the discharge process.^[34] In our current experiment, the key step for achieving epitaxial growth of CuS on TiS_2 is that the battery cell kept undisturbed from a given time (e.g. 15 days) after the intercalation of Li ions to form Li-intercalated compound during the discharge process. Therefore, samples were taken out from battery cells at different reaction time for the TEM characterization. Note that the reaction time here represents the undisturbed time that the battery cell kept after the discharge process, in which CuS crystal continuously grows on the TiS_2 nanosheet. TEM analyses of the samples produced at different reaction time are shown in Figure 6.6.

As shown in Figure 6.6a,b, there is no CuS crystal grown on the TiS_2 nanosheet for 1 day and the SAED pattern only gives one set of diffraction spot, which is corresponding to TiS_2 nanosheet. This result is consistent with our previous report on the exfoliation of TiS_2 . Interestingly, after 5 days, we can clearly see that there are some small CuS nanocrystals grown on the TiS_2 nanosheet (Figure 6.6c). Its corresponding SAED pattern shows two sets of diffraction spots that are similar to that of the CuS- TiS_2 heteronanostructure, suggesting that these small CuS nanocrystals are epitaxially grown on the TiS_2 nanosheet. It was found that after 10 days, the small CuS crystals can further grow into triangular nanoplates with remained epitaxial growth effect (Figure 6.6e,f). After 15 days, the final product was obtained and the structure has been discussed above (Figure 6.6g,h). Note that the growth of CuS nanoplates is slow process, which needs about 15 days.

Figure 6.6 TEM characterization of time-dependent structure evolution of CuS-TiS₂ heteronanostructure.

In addition to CuS, other metal sulphide nanoplates, including ZnS and Ni₃S₂, can be also epitaxially grown on TiS₂ nanosheet to form Zn-TiS₂ and Ni₃S₂-TiS₂ heteronanostructures via the same method by using Zn or Ni foil to replace the Cu foil. The characterization of Zn-TiS₂ and Ni₃S₂-TiS₂ heteronanostructures are shown in Figure 6.7. The TEM image shows ZnS nanoplates deposited on TiS₂ nanosheet (Figure 6.7a). The size of the ZnS nanoplates is about 70-150 nm. Its corresponding SAED pattern gives two sets of well-oriented diffraction spots (Figure 6.7b), which is similar to that of the CuS-TiS₂ heteronanostructure. The inner and outer sets of diffraction spots can be indexed to ZnS and TiS₂ crystals, respectively. Both the inner and outer six spots of ZnS and TiS₂ crystals are assignable to the (100) and (110) planes of them, respectively. The well alignment of the two sets of diffraction spots clearly indicates the epitaxial growth of ZnS nanoplates on TiS₂ nanosheet. Figure 6.7c shows the HRTEM image of ZnS-TiS₂ heteronanostructure at the interface area, indicating the crystalline structure of both of them. The measured lattice fringes of ZnS and TiS₂ are 0.27 and 0.29 nm, which are corresponding to their (100) planes (inset in Figure 6.7c). The chemical composition of the ZnS-TiS₂ heteronanostructure is confirmed by EDS spectrum. As shown in Figure 6.8, its EDS spectrum gives intense signals of Zn, Ti and S. Similarly, the Ni₃S₂-TiS₂

heteronanostructure was also prepared by epitaxially growing Ni_3S_2 on TiS_2 nanosheet. The detail TEM, HRTEM, SAED and EDS analyses of the Ni_3S_2 - TiS_2 heteronanostructure are shown in Figure 6.7d-f and Figure 6.9.

Figure 6.7 (a) TEM image and of ZnS-TiS₂ heteronanostructure. (b) The corresponding SAED pattern of ZnS-TiS₂ heteronanostructure. (c) HRTEM image of ZnS-TiS₂ heteronanostructure at interface area of ZnS and TiS₂. Inset: the enlarged HRTEM in the white square. (d) TEM image and of Ni₃S₂-TiS₂ heteronanostructure. (e) The corresponding SAED pattern of Ni₃S₂-TiS₂ heteronanostructure. (f) HRTEM image of Ni₃S₂-TiS₂ heteronanostructure at interface area of Ni₃S₂ and TiS₂. Inset: the enlarged HRTEM in the white square.

Figure 6.8 EDS spectrum of ZnS-TiS₂ heteronanostructure.

Figure 6.9 EDS spectrum of Ni_3S_2 - TiS_2 heteronanostructure.

The mechanism for the epitaxial growth of metal sulphide nanocrystals on TiS_2 nanosheet is not very clear. Here I propose a possible mechanism for the preparation of 2D metal chalcogenide epitaxial heteronanostructures from metal foils and the bulk TiS_2 crystal. Previous study has proved that S powder can react with Cu foil to form CuS nanocrystal after the discharge process by using the S powder-coated Cu foil as the electrode in a LIB.^[35] It is believed that Li_2S was formed by reacting the S powder with Li ions. CuS crystal was then prepared due to the reaction between the formed Li_2S and Cu foil. In our experiment, the 2D metal chalcogenide heteronanostructures were prepared from the bulk TiS_2 crystal and metal foils. The Li ions were intercalated into the layered TiS_2 crystal to form Li-intercalated compound, i.e. Li_xTiS_2 . The Li_xTiS_2 has an expanded interspacing during to the Li intercalation. Meanwhile, it is believed that Li ions can react with TiS_2 to form Li_2S after the discharge process. According to previous report,^[36-37] Li ions can reaction with TiS_2 to form Li_2S via the following three reactions: 1) $\text{Li} + \text{TiS}_2 \rightarrow \frac{1}{2}\text{Ti}_2\text{S}_3 + \frac{1}{2}\text{Li}_2\text{S}$; 2) $\text{Li} + \frac{1}{2}\text{TiS}_2 \rightarrow \frac{1}{2}\text{TiS} + \frac{1}{2}\text{Li}_2\text{S}$; 3) $\text{Li} + \frac{1}{4}\text{TiS}_2 \rightarrow \frac{1}{4}\text{Ti} + \frac{1}{2}\text{Li}_2\text{S}$. In this case, the Cu foil then can react with the formed Li_2S to produce CuS nanoplate. Note that CuS crystal has similar crystal symmetry with TiS_2 crystal and the lattice mismatch between them is $\sim 10\%$. Therefore, the CuS crystal was epitaxially grown on TiS_2 nanosheet, in which the free energy at their interface was minimized. The possible reason for the CuS crystal grown into nanoplate nanostructure might be due to the template effect of the TiS_2 nanosheet.

6.2.2 Li ion batteries based on the CuS-TiS₂ heteronanostructure

The potential application of the CuS-TiS₂ heteronanostructure as the anode material in a LIB was explored. The fabrication of the anode electrode and battery cell was described in Section 3.4.3. The CuS-TiS₂ electrode gave a first discharge capacity of 1158 mAhg⁻¹, while the first charge capacity decreased to 584 mAhg⁻¹ (Figure 6.10a). The capacity of the electrode becomes stable after the second cycle. Note that the capacity of the CuS-TiS₂ electrode obtained here is better compared to CuS nanosheet and TiS₂ bulk crystal-based electrodes.^[38-39] Moreover, excellent cycling performance was observed on the CuS-TiS₂ electrode. As shown in Figure 6.10b, the CuS-TiS₂ electrode gave a stable capacity of around 600 mAhg⁻¹ without obvious degradation even after 100 cycles at the current of 0.1 Ag⁻¹. The rate capability of the CuS-TiS₂ electrode also proved its high reversible capacity. Figure 6.11 shows the cycling behavior of the CuS-TiS₂ electrode at different current densities. As we can see from Figure 6.11, the CuS-TiS₂ electrode still delivered capacities up to ~350 and ~260 mAhg⁻¹ at 3 and 6 Ag⁻¹, respectively. More importantly, the capacity of the CuS-TiS₂ electrode was recovered to its initially stable value even after charge-discharge process at different high current densities. It is worth pointing out that the obtained performance here is much better than the CuS nanosheet.^[38]

Figure 6.10 (a) The first two cycle charge-discharge voltage profiles of the electrode based on CuS-TiS₂ heteronanostructure (0.3 Ag⁻¹). (b) Cycling test of the electrode based on CuS-TiS₂ heteronanostructure.

Figure 6.11 Rating test of CuS-TiS₂ electrode.

6.3 Conclusion

A facile and general electrochemical method has been developed for the preparation of 2D metal chalcogenide epitaxial heteronanostructures, including CuS-TiS₂, ZnS-TiS₂ and Ni₃S₂-TiS₂. Metal sulphide nanoplates were aligned on TiS₂ nanosheet with perfect epitaxial growth effect. This approach is a solution-based method, allowing for the high-yield and massive production in liquid phase at relatively low cost. The CuS-TiS₂ heteronanostructure could be used as a promising anode material in a LIB. This method might be further exploited to prepare some other 2D metal chalcogenide epitaxial heteronanostructures, which might exhibit enhanced performance in some applications due to their well-defined structural features.

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Chapter 7

Chiral Nanofibers Assembled from Ultrathin 2D Nanomaterials

This chapter introduces a facile and versatile approach for high-yield and scalable assembly of ultrathin 2D metal chalcogenide nanomaterials into chiral nanofibers in highly stirred polymeric solutions. The assembled chiral nanofibers are characterized by SEM and AFM. Interestingly, the obtained chiral nanofibers are further transformed into same-handed chiral nanorings through a second assembly process. The chiral MoS₂ nanofiber with P123 is used as promising active material in a flexible non-volatile data storage device, exhibiting a non-volatile flash memory behavior with excellent reproducibility and stability.

7.1 Introduction

Self-assembly of nanomaterials is one of the most attractive strategies to create highly ordered complex architectures or super-lattices in high-yield and large-scale, in which the size, morphology and composition of the assembling materials can be selectively designed.^[1-2] The emerging of ultrathin 2D nanosheets over the last decade, especially graphene, offers great opportunities for construction of various kinds of novel nanostructures based on them via self-assembly processes.^[3-5] Due to their giant, 2D feature and fluid-like flexibility derived from its atomic thickness, chemically converted graphene-related sheets, such as graphene oxide (GO) and reduced GO (rGO), have been demonstrated to be fascinating building blocks for self-assembling nanostructures with different dimensionalities, including three-dimensional (3D) frameworks,^[6-8] 1D fibers or scrolls,^[9-16] and zero-dimensional (0D) particles.^[17] In contrast to the direct synthesis, these assembled architectures could retain some of the unique properties from the 2D nanosheets. For example, 1D graphene scrolls are expected to keep the same excellent conductivity as graphene sheets.^[18] More intriguingly, some new fascinating properties or functions also could be generated on these novel nanostructures. Representatively, 3D graphene aerogels presented superior performances in supercapacitors and recyclable sorbent for oils and organic solvents.^[7-8] It should be noted that no one has been reported the assembly of GO or rGO into ring-like structures yet, despite many assembled nanostructures have been prepared.

Besides graphene, single- and few-layer nanosheets of layered metal chalcogenides, such as MoS₂, TiS₂, TaS₂, *etc.*, are receiving explosive attention in past few years due to their unique chemical and electronic properties originated from the quantum confinement in two-dimensions,^[19-20] endowing them with great potential in a variety of applications such as catalysis, electronic/optoelectronic devices and energy storage devices.^[19-20] Having similar configuration with GO and rGO, it is expected that metal chalcogenide nanosheets also could serve as a new class of promising building blocks to be assembled into various nanostructures.^[19] However, till now, no one has been reported the assembly of other kinds of nanostructures from ultrathin 2D metal chalcogenide nanomaterials.

In this chapter, a facile and general assembly approach is developed for preparation of chiral nanofibers from ultrathin 2D nanomaterials, including single-layer GO, MoS₂, TaS₂ and TiS₂, few-layer TaSe₂ and WSe₂ as well as Pt-GO and Pt-MoS₂ composites. A second assembly strategy is also developed for the further assembly of some of the assembled chiral nanofibers into chiral nanorings. The mechanism behind the assembly process is explored by conducting a series of control experiments. Moreover, the potential application of the chiral MoS₂ nanofiber with P123 in flexible non-volatile resistive memory devices is explored.

7.2 Results and Discussion

7.2.1 Preparation and characterization of chiral nanofibers

Ultrathin 2D nanomaterials, including single-layer graphene oxide (GO), MoS₂, TaS₂ and TiS₂, few-layer TaSe₂ and WSe₂ as well as Pt-GO and Pt-MoS₂ composites were used as the starting materials for the assembly of chiral nanofibers. In a typical process, suspension by dispersing ultrathin 2D nanomaterials in water with a given concentration was added dropwise into a polymer solution under high speed stirring. The detail procedure for the preparation of chiral nanofibers via self-assembly is described in Section 3.2.7. Pluronic P123, an achiral triblock copolymer (PEO₂₀PPO₇₀PEO₂₀), was used as the polymer to assist the assembly process and the molecular structure of P123 is shown in Figure 7.1. The assembled chiral nanofibers were characterized by SEM and AFM. Figure 7.2 shows the SEM and AFM phase images of assembled GO, MoS₂ and TaS₂ chiral nanofibers. As shown in Figure 7.2a,b, GO nanofiber has a helical structures with a length of 10-50 μm and diameter of 40 ± 12 nm. Importantly, by randomly measuring more than 200 nanofibers by SEM, all the nanofibers have a left-handed spiral structure, yielding a 100% enantiomeric purity. The helical structure of the GO nanofiber is further demonstrated by its AFM phase image (Figure 7.2c). The measured average pitch length of GO nanofiber is about 42 nm (Figure 7.2c and Figure 7.3). Chiral GO nanofiber shows a similar Raman spectrum to the GO nanosheet (Figure 7.4), indicating

that the GO nanofiber is constructed from GO nanosheet. Intriguingly, by tuning the initial concentration of GO nanosheet, the diameter of GO nanofiber can be roughly tuned. Figure 7.5 shows the GO nanofibers prepared from different concentrations of GO nanosheet solutions. The diameter of GO nanofiber is about 80, 55 and 38 nm, when GO nanosheet with a concentration of about 0.25, 0.1 and 0.05 $\mu\text{g mL}^{-1}$ was used, respectively. Similarly, chiral MoS_2 nanofiber was also prepared by the same assembly process. As shown Figure 7.2d,e, the assembled chiral MoS_2 nanofiber has a similar structural features with that of the GO nanofiber. The measured length and diameter of the MoS_2 nanofiber is 10-20 μm and $\sim 30 \pm 11$ nm, respectively. The helical structure is further evidenced by the AFM phase image and the measured pitch length is about 34 nm (Figure 7.2f and Figure 7.6). The circular dichroism (CD) spectroscopy was used to further study the chirality of the MoS_2 nanofiber. Figure 7.7a shows the CD spectrum of the MoS_2 nanofiber. Two obvious broad bands at round 253 and 298 nm were detected in its CD spectrum, clearly indicating its chiral nature.^[21] Both the MoS_2 nanosheet and nanofiber give similar Raman spectra (Figure 7.7b), indicating that they have the same composition. More importantly, chiral TaS_2 , TiS_2 , TaSe_2 and WSe_2 nanofibers were also assembled from their single- or few-layer nanosheets in high-yield by the same assembly process. The SEM and AFM characterizations of these nanofibers are shown in Figure 7.2g,h,i, Figure 7.8 and Figure 7.9. More intriguingly, this assembly strategy can be further extended to assemble ultrathin hybrid nanosheets, including Pt- MoS_2 and Pt-rGO, into chiral nanofibers. The obtained hybrid chiral nanofibers have similar morphology and spiral structure to that of the MoS_2 nanofiber. The SEM images of the two hybrid nanofibers are shown in Figure 7.10. It is worth pointing out that the yield of the production of chiral nanofibers from aforementioned ultrathin 2D nanomaterials is 100%.

Figure 7.1 The molecular structure of Pluronic P123.

Figure 7.2 (a,b) SEM images of chiral GO nanofiber. (c) AFM phase image of chiral GO nanofiber. (d,e) SEM images of chiral MoS₂ nanofiber. (f) AFM phase image of chiral MoS₂ nanofiber. (g,h) SEM images of chiral TaS₂ nanofiber. (i) AFM phase image of chiral TaS₂ nanofiber.

Figure 7.3 (a) AFM phase image and (b) the corresponding cross-section profile of chiral GO nanofiber

Figure 7.4 Raman spectra of GO nanosheet and chiral nanofiber.

Figure 7.5 SEM images of chiral GO nanofiber assembled with different concentration of GO nanosheet: (a) $0.25 \mu\text{g mL}^{-1}$, (b) $0.1 \mu\text{g mL}^{-1}$ and (c) $0.05 \mu\text{g mL}^{-1}$.

Figure 7.6 (a) AFM phase image and (b) the corresponding cross-section profile of chiral MoS₂ nanofiber.

Figure 7.7 (a) CD spectrum of chiral MoS₂ nanofiber. (b) Raman spectra of MoS₂ nanosheet and chiral nanofiber.

Figure 7.8 (a) AFM phase image and (b) the corresponding cross-section profile of chiral TaS₂ nanofiber.

Figure 7.9 SEM images of chiral (a,b) TiS₂, (c,d) TaSe₂ and (e,f) WSe₂ nanofibers.

Figure 7.10 SEM images of chiral (a,b) Pt-rGO and (c,d) Pt-MoS₂ nanofibers.

7.2.2 Mechanism study for the assembly process

Taking MoS₂ a typical example, a series of control experiments were conducted to investigate the mechanism underlying the self-assembly process. For the preparation of chiral nanofiber, MoS₂ nanosheet was added dropwise in the solution containing polymer like P123, which was under vigorous stirring (~1500 r.p.m). It was found that MoS₂ nanosheet did not undergo a topological transformation from nanosheet to nanofiber without stirring or without addition of P123. As shown in Figure 7.11a,b,c,d, the MoS₂ nanosheet still has a sheet-like structure after the assembly process similar to that of for chiral nanofiber except without stirring (Figure 7.11a,b) or without addition of P123 in the solution (Figure 7.11c,d). As shown in Figure 7.11e,f, the Pure P123 itself shows a micro-particle morphology after precipitation from its stirred aqueous solution, indicating that the P123 plays as the template for directing the assembly of ultrathin 2D nanomaterials rather than forms chiral nanofiber itself. The results suggested that both the stirring and the presence of polymer template are essential for the creation of chiral nanofibers. It has been reported that vortex will be generated when a solution stirred at high speed and it has been regarded as a typical naturally macroscopic chirality.^[22] It has been also proved that dynamic chiral architectures can be formed in vortex if aqueous solution containing achiral organic molecules was stirred, resulting in detectable dynamic

chiral signals.^[23] However, the chiral signals will disappear once the stirring stop.^[23] Based on all the aforementioned analyses, it is believed that in our case, ultrathin 2D nanomaterials are twisted under torsional flow of vortex to form assembled chiral nanofibers, in which the highly adhesive P123 plays as the soft template to keep the morphology of the chiral nanofibers. In contrast, although chiral nanofibers also can form in the vortex, they will release back to nanosheets in the absence of P123. In order further prove the function of P123 in the assembly process, two other commonly used achiral polymers that also are highly adhesive, including Tween 20 and Triton 100-X, were used to replace the P123 in the assembly process. The molecular structures of Tween 20 and Triton 100-X are shown in Figure 7.12. As expected, chiral nanofibers can be also obtained similarly. For example, chiral MoS₂ nanofiber with similar structural features was also prepared from single-layer MoS₂ nanosheet by replacing P123 with Tween 20 (Figure 7.13a,b) and Triton X-100 (Figure 7.13c,d), respectively.

Figure 7.11 (a,b) SEM images of MoS₂ nanosheet after vigorously stirring in pure water. (c,d) SEM images of MoS₂ nanosheet mixed with P123 without stirring. (e,f) SEM images of pure P123.

Figure 7.12 Molecular structures of Tween 20 and Triton X-100.

Figure 7.13 SEM images of chiral MoS₂ nanofibers prepared by replacing P123 with (a,b) Triton X-100 or (c,d) Tween-20.

7.2.3 Preparation and characterization of chiral nanorings

Very interestingly, it was found that some of the prepared chiral nanofibers were further assembled into chiral nanorings via a second assembly process. The detail assembly procedure is described in Section 3.2.8. Figure 7.14 shows the SEM images of the as-prepared chiral GO and WSe₂ nanorings. As shown in Figure 7.14a,b, chiral GO nanoring has a ring-like structure and the nanofiber in the nanoring still kept the spiral structure with the same left-handedness after the second assembly process. The measured ring diameter from the SEM image is about 400-600 nm (Figure 7.14a). The measured diameter of the nanofiber in the nanoring is about 40±12 nm (Figure 7.14b), which is consistent with that of the chiral GO nanofiber. Note that the yield of the assembly of nanorings from nanofibers is almost 100%. Importantly, this assembly strategy was further extended to assembly other nanofibers, including WSe₂, TaSe₂ and MoS₂, into nanorings. The SEM images of chiral WSe₂, TaSe₂ and MoS₂ nanorings are shown in Figure 7.14c,d, Figure 7.15a,b and Figure 7.15c,d, respectively, demonstrating the similar structural characteristics with the chiral GO nanoring.

Figure 7.14 SEM images of chiral (a,b) and GO, (c,d) WSe₂ nanorings.

Figure 7.15 SEM images of chiral (a,b) TaSe₂ and (c, d) MoS₂ nanorings.

7.2.4 Chiral MoS₂ nanofiber with P132-based memory devices

It has been demonstrated that organic-inorganic hybrid materials by hybridizing inorganic conducting or semiconducting nanomaterials with polymers could be appealing active materials for integration of high-performance non-volatile resistive diodes.^[24-25] Herein, the chiral MoS₂ nanofiber with P123 was used the active layer for fabrication of resistive diodes. By using flexible rGO films as electrodes, flexible memory devices with a configuration of rGO/chiral MoS₂ nanofiber-P123/rGO on a flexible polyethylene terephthalate (PET) substrate were constructed by using the chiral MoS₂ nanofiber with P123 as the active layer. Figure 7.16a shows the photograph of the fabricated memory devices with a 6×6 array and the device with a sandwich-like structure is schematically shown in inset in Figure 7.16a. The characterization of the performance of the fabricated diode is shown in Figure 7.16b,c,d. Figure 7.16a shows the typical I-V characteristic of the memory device based on chiral MoS₂ nanofiber with P123, indicating a typical flash memory effect. As shown Figure 7.16b, by applying a positively potential sweep from 0 to 4 V, the current of the device increased gradually from $\sim 5 \times 10^{-11}$ to $\sim 10^{-4}$ (stage 1), which is corresponding to the low-resistance state (LRS), also referred as the ON state. This process represents the “Write” process in memory devices. The device kept in the

LRS when a backward sweep from 4 to 0 V was applied (stage 2), which still kept in the LRS state in a following sweep from 0 to -4 (stage). Interestingly, the current went back the high resistance state (HRS), i.e. the OFF state, during the backward sweep from -4 to 0 V, which is defined as the “Erase” process. The whole process is corresponding to the characteristic of the flash memory effect. The calculated ON/OFF current ratio of the device is about 5.5×10^2 . Moreover, the producibility of the device was explored by consecutive cyclic sweep. As shown in Figure 7.16c, the *I-V* curves of the device did not undergo any our degradation even after more 50 consecutive cycles. The result revealed that the chiral MoS₂ nanofiber-based memory device has excellent reproducibility. The stability of the device was studied by recording its retention time. The retention time at a read voltage of -0.5 V of the device is shown in Figure 7.16d. It clearly shows that both the ON and OFF states of the device did not undergo an obvious change even after a test period of more than 4×10^3 s, providing the good stability of the device. Note that, the pure MoS₂ nanosheet itself is a semiconducting material, is not active when it was used as the active layer,^[26] which means that the dielectric P123 played a crucial role in the device.

Figure 7.16 (a) Photograph of the fabricated device array. Inset: The representative scheme of a typical device. (b) The first *I-V* characteristics of the memory cell. (c) Consecutive 50 cycle *I-V* measurements of the memory cell. (d) Retention test of chiral MoS₂ nanofiber-based memory device.

In order to investigate the carrier transport mechanism, the I - V characteristic in the OFF and ON states was fitted (Figure 7.17). As shown in inset in Figure 7.17a, a straight line can be fitted from 0 to 0.8 V on the plot of $\ln(I)$ versus $V^{1/2}$ in the OFF state. In this range, the thermionic emission might be the dominated conduction mechanism of the device, in which the charge injected from the rGO electrode to the active layer.^[27] As shown in Figure 7.17a, from 0.9 to 2.5, the plot of $\ln(I)$ versus $\ln(V)$ can be fitted into a linear relation with a slope of 3.89, which means that the space-charge limited current (SCLC) model dominated the carrier transport mechanism in this stage.^[28] The Ohmic conduction behavior in the ON state was observed on the device (Figure 7.17b).^[27] Note that the trapped charges in MoS₂ retained even after the power was turned off, so the device can maintain the high conductivity and non-volatility. In contrast, when applying a reverse bias sweep, the trapped charges can be detrapped, resulting in a flash memory effect. Therefore, it is believed that the charge trapping and detrapping behavior of MoS₂ in P123 generated the electrical switching effect, which is similar to the previously reported PVP-MoS₂-based flash memory device.^[29]

Figure 7.17 Experimental and fitted data of I - V curve shown in Figure 7.16b in the (a) OFF state and (b) ON state.

7.3 Conclusion

In summary, various ultrathin 2D nanomaterials have been assembled into chiral nanofibers in high yield through a facile and universal assembly approach with the

assistance of P123. The obtained chiral nanofibers have a left-handed chirality with 100% enantiomeric purity. Some of the chiral nanofibers were further transformed into chiral nanorings via a second assembly process. The control experiments suggested that the stirring and polymer template (e.g. P123) played key roles in the formation of chiral nanostructures. The chiral MoS₂ nanofiber with P123 has been proved to a promising active material for the construction of flexible resistive memory devices. The constructed memory device exhibited a flash memory effect with good stability and excellent reproducibility. It is believed that this simple and versatile assembly way is able to further extend to assemble other kinds of ultrathin 2D nanomaterials, such as organic materials, metal oxides, metals and their composites into chiral nanofibers, which may have great potential in a variety of applications like catalysis, chiral separation, chiral sensing and electronic devices.

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Chapter 8

Discussion and Future Work

The chapter gives a general discussion to conclude the whole thesis and discusses the originality of the research works in this thesis. Based on the current research status, the future work that can be focused on in the near future is also discussed.

8.1 General Discussion

In this thesis, I am focusing on the synthesis of new ultrathin 2D metal chalcogenide nanosheets, preparation of alloyed metal chalcogenides nanosheets with metallic 1T phase, epitaxial growth of 2D metal chalcogenide heteronanostructures, and assembly of ultrathin 2D nanomaterials into 1D chiral nanostructures. Meanwhile, I also explore the prepared 2D metal chalcogenide nanomaterials for some potential applications, such as fluorescent DNA sensors, solar energy conversion devices, LIBs and data storage devices.

First, two new ternary metal chalcogenide bulk crystals were grown from the corresponding elementary powders. Both the Ta_2NiS_5 and Ta_2NiSe_5 bulk crystals were exfoliated by using the electrochemical Li-intercalation and exfoliation method for production of single- or few-layer nanosheets. For the first time, single-layer Ta_2NiS_5 and few-layer Ta_2NiSe_5 nanosheets have been prepared in high yield and large amount. It has proved that the electrochemical Li-intercalation and exfoliation method could be used for exfoliating new metal chalcogenide bulk crystals. However, due to the different properties, Ta_2NiS_5 and Ta_2NiSe_5 nanosheets with different thickness were obtained. It was also found that the exfoliated Ta_2NiS_5 nanosheet is much more stable compared to the Ta_2NiSe_5 nanosheet. The single-layer Ta_2NiS_5 nanosheet displayed strong fluorescence quenching ability towards probe DNA. Therefore, it was used as quenching platform to establish a fluorescent sensor for DNA detection. The sensitivity of the constructed fluorescent sensor is comparable with the best one based on 2D metal chalcogenides. Besides fluorescent sensors, single-layer Ta_2NiS_5 nanosheet could be also used for other applications. For example, single-layer Ta_2NiS_5 nanosheet has a small band gap about 0.3 eV, which is semimetal and possess good electrical conductivity. Therefore, it can be used for fabrication of flexible devices, such as electronic gas sensors and supercapacitors.

Second, single-layer alloyed $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ and $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ nanosheets have been prepared in high yield and large scale in solution phase first the first time via liquid exfoliation of the bulk crystals. More importantly, both the exfoliated $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ and $\text{Mo}_x\text{W}_{1-x}\text{S}_2$

nanosheets contains high concentration (66%) of metallic 1T phase, making them much more conductivity compared with 2H phase ones. The electrochemical Li-intercalation was regarded to induce the partial phase transformation from 2H to 1T phase. This is the first time for the realization of the preparation of single-layer alloyed metal chalcogenide nanosheets with high-concentration metallic 1T phase. This method could be further extended to prepare other 2D metal chalcogenide nanosheets with metallic 1T phase (e.g. WS_2 and MoSe_2). It was demonstrated that the exfoliated $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheet containing metallic 1T phase exhibits much enhanced electrical conductivity compared with the 2H phase counterpart. Thus, it was used as an efficient electrocatalyst toward tri-iodide reduction when deposited on a FTO substrate as a thin film. Due to its enhanced electrocatalytic activity, the DSSC device presented a higher PCE than the 2H phase one when the $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ thin film coated on FTO was incorporated into a DSSC device as the counter electrode. This is the first time the demonstration of advantage of metallic 1T phase in 2D metal chalcogenides in electrocatalytic tri-iodide reduction reaction. These exfoliated single-layer alloyed metal chalcogenide nanosheets with good conductivity might be also promising other applications like electrocatalytic hydrogen evolution, electrochemical sensors and electronic gas sensors.

Third, an electrochemical method was developed for the preparation of 2D metal chalcogenide heteronanostructures with epitaxial growth effect. Compared to the widely used gas-phase epitaxy methods, this method allows for the high yield and large scale production at room temperature with relatively low cost in solution phase. This is the first report on the synthesis of 2D metal chalcogenide epitaxial heteronanostructures in solution phase. Moreover, three new 2D epitaxial heteronanostructures, i.e. CuS-TiS_2 , ZnS-TiS_2 and $\text{Ni}_3\text{S}_2\text{-TiS}_2$, were prepared for the first time. Some other metal sulphide nanostructures might be also epitaxially grown on TiS_2 nanosheet to form new 2D metal chalcogenide heteronanostructures by a similar method. It has been demonstrated that when incorporated into a LIB as the anode electrode, the CuS-TiS_2 heteronanostructure gave large capacity and excellent cycling performance. These 2D heteronanostructures may also exhibit enhanced performance in some other applications like electrocatalysis, solar cell and sensors.

Last, a simple and general assembly strategy was developed for the assembly of ultrathin 2D nanomaterials to form chiral 1D nanostructures including nanofibers and nanorings with the assistance of highly adhesive polymers (e.g. P123). This method is widely applicable for a number of ultrathin 2D nanomaterials, including single-layer GO, MoS₂, TaS₂, TiS₂ and few-layer TaSe₂, WSe₂ as well as hybrid nanosheets, i.e. Pt-rGO and Pt-MoS₂. This method could be further extended to assemble other ultrathin 2D nanomaterials into chiral nanostructures. Moreover, this is the first time the realization of symmetry breaking in all the aforementioned inorganic nanomaterials to form chiral nanostructures. It has been proved that flexible memory diodes could be fabricated by using the chiral MoS₂ nanofiber with P123 at the active layer and conductive rGO films as the electrodes. These assembled chiral nanostructures may have potential in other applications like chiral separation, chiral sensors and electronic gas sensors.

8.2 Reconnaissance Work not Included in Main Chapters

Although some interesting works have been done in this thesis, there are still many opportunities remaining in this promising field. Based on the current status discussed in this thesis, I will also give a general discussion on the future works which can be conducted in the near future.

Previous studies have demonstrated that single-layer metal chalcogenide nanosheets with solution-processibility (e.g. MoS₂, TiS₂ and TaS₂) can be attractive dispersible 2D nanotemplates for the further deposition of noble metal nanostructures (e.g. Au, Ag, Pt and Pd). The hybrid nanostructures of noble metal nanostructure-decorated single-layer nanosheets could be used as efficient electrocatalysts for electrochemical hydrogen generation. Therefore, the high yield produced single-layer Ta₂NiS₅ nanosheet could be also exploited as a promising template for directing the deposition of noble metal nanostructures. Similar to single-layer MoS₂, noble metal nanocrystals might be also able to epitaxially grow on the surface of single-layer Ta₂NiS₅ nanosheet. More intriguingly, single-layer Ta₂NiS₅ has a unique crystal structure compared with these binary metal

chalcogenide nanosheets. As shown, the Mo atoms are homogeneously distributed in the single-layer MoS_2 nanosheet with six-fold symmetry. However, unlike MoS_2 , Ta_2NiS_5 contains two different types of metal atoms, i.e. Ta and Ni. More importantly, as shown in Figure 4.1c, Both the Ta and Ni atoms form long line chains in the single-layer nanosheet, in which one long line chain of Ni is located in the between of two long line chains of Ta atoms. This unique structure can be regards as a kind of superlattice. Therefore, when used as the template for growth of noble metal nanostructures, it is possible that the noble metal crystals will align on the single-layer Ta_2NiS_5 along with long line chains of metal atoms to form long line chain superlattices. The single-layer Ta_2NiS_5 nanosheet decorated with noble metal nanocrystals may exhibit good catalytic activity toward electrochemical hydrogen evolution reaction. Moreover, the deposited noble metal superlattices might be able to tune the optical properties of the single-layer Ta_2NiS_5 nanosheet, making it promising for the fabrication of high performance optoelectronic devices, such as photodetectors.

Recently, some metal chalcogenide materials (e.g. MoS_2 and WS_2) have been identified to be active for electrocatalytic hydrogen evolution. With the development of nanotechnology, nanostructured metal chalcogenides have been proved to be much more active in electrocatalytic hydrogen evolution owing to the increased active sites. Especially, single- or few-layer metal chalcogenide nanosheets have shown much enhanced catalytic activity due to their large-exposed surface area. However, due to the semiconducting property, 2D metal chalcogenide nanosheets normally have low electrical conductivity, which is not favorable in electrocatalysis. One of the promising ways to solve this problem is to prepare metal chalcogenide nanosheets with metallic 1T phase via phase engineering. The single-layer alloyed $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ nanosheet with high concentration of metallic 1T phase has been prepared in this thesis, which might be a good electrocatalyst for hydrogen evolution reaction. The catalytic ability of alloyed $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ nanosheets for hydrogen evolution will be explored and the atom ratio between Mo and W on catalytic activity will be investigated in details. Besides, ternary alloyed nanosheets, quaternary metal chalcogenide nanosheets (e.g. $\text{Mo}_x\text{W}_{1-x}\text{S}_{2y}\text{Se}_{2(1-y)}$) with metallic 1T phase might be also prepared from their bulk crystals by the electrochemical Li-

intercalation and exfoliation method. The catalytic ability of the exfoliated quaternary nanosheets will be also explored, which may show enhanced catalytic activity compared with binary and ternary nanosheets.

For the preparation of chiral nanostructures from ultrathin 2D nanomaterials, the key point of the 2D nanomaterials is the excellent flexibility. The excellent flexibility can ensure the assembly via morphology or topology transformation. Beside ultrathin 2D nanomaterials, ultrathin 1D nanostructures, such as carbon nanotubes and noble metal nanowires, have also attracted numerous attention in last decades. Similarly, these ultrathin 1D nanostructures also possess excellent flexibility due to their ultrathin characters. Therefore, it is anticipated that they could be also assembled into chiral nanostructures via the assembly strategy discussed in chapter 7. Carbon nanotubes and ultrathin Au nanowires will be used as the building blocks to prepare chiral nanofibers via the assembly strategy. In the thesis, the assembled chiral MoS₂ nanofiber with polymer was utilized as the active material to fabricate flexible data storage devices. However, the device performance has no relationship with the chirality of the chiral nanofiber. Therefore, the assembled carbon nanotube and Au nanofibers could be used for some chirality-related applications, such as chiral catalysis, chiral sensors and chiral separation.

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