Synthesis and applications of multinary layered metal chalcogenide nanomaterials

Lai, Zhuangchai

2018

Lai, Z. (2018). Synthesis and applications of multinary layered metal chalcogenide nanomaterials. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/89688>

<https://doi.org/10.32657/10220/46339>

**NANYANG
TECHNOLOGICAL
UNIVERSITY**

SINGAPORE

**SYNTHESIS AND APPLICATIONS OF MULTINARY LAYERED
METAL CHALCOGENIDE NANOMATERIALS**

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2018

SYNTHESIS AND APPLICATIONS OF MULTINARY LAYERED METAL CHALCOGENIDE NANOMATERIALS

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

A thesis submitted to the Nanyang Technological University
in partial fulfilment of the requirement for the degree of
Doctor of Philosophy

2018

Statement of Originality

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

21-Aug-2018

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Supervisor Declaration Statement

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

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Prof. Zhang Hua

Authorship Attribution Statement

This thesis contains material from papers published in the following peer-reviewed journals where I was the first and/or corresponding author.

Chapter 2 is published as C. Tan, Z. Lai, H. Zhang, Ultrathin Two-Dimensional Multinary Layered Metal Chalcogenide Nanomaterials. *Adv. Mater.* **29**, 1701392 (2017). DOI: 10.1002/adma.201701392.

The contributions of the co-authors are as follows:

- Prof. Zhang Hua proposed the initial idea and edited the manuscript drafts.
- I wrote the section 4 of the manuscript drafts and co-wrote section 1, 2, 3 and 5 with Dr. Tan Chaoliang.
- All the authors gave suggestions to revise the manuscript together.

Chapter 4 is published as Z. Lai, A. Chaturvedi, Y. Wang, T. H. Tran, X. Liu, C. Tan, Z. Luo, B. Chen, Y. Huang, G.-H. Nam, Z. Zhang, Y. Chen, Z. Hu, B. Li, S. Xi, Q. Zhang, Y. Zong, L. Gu, C. Kloc, Y. Du, H. Zhang, Preparation of 1T'-Phase $\text{ReS}_{2x}\text{Se}_{2(1-x)}$ ($x = 0-1$) Nanodots for Highly Efficient Electrocatalytic Hydrogen Evolution Reaction. *J. Am. Chem. Soc.* **140**, 8563-8568 (2018). DOI: 10.1021/jacs.8b04513.

The contributions of the co-authors are as follows:

- Prof. Zhang Hua proposed the idea, supervised the whole project and edited the manuscript drafts.
- I performed the materials preparation, characterizations and analysis of all the experimental data. I wrote the drafts of the manuscript. The manuscript was revised together with Prof. Zhang Hua.
- Dr. Du yonghua helped to measure the XANES and EXAF of all the samples, and help to analyze the data.
- Dr. Chaturvedi Apoorva helped to prepare all the bulk crystals of $\text{ReS}_{2x}\text{Se}_{2(1-x)}$ ($x = 0-1$).

- Ms Tran Thu Ha helped to do the experiments related to materials preparations.
- Dr. Wang Yun conducted the theoretical simulations for the manuscript.
- All the authors gave suggestions to revise the manuscript together.

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Abstract

Preparation of novel layered transition metal chalcogenide nanomaterials is of great importance for the exploration of new properties of nanomaterials for a wide range of applications. Inspired by this, the aim of this thesis is to synthesize novel layered metal chalcogenide nanomaterials with new functionalities and then explore their potential applications in catalysis and energy storage devices.

First, I prepared the large-scale and solution-processable alloyed 1T'-phase $\text{ReS}_{2x}\text{Se}_{2(1-x)}$ ($x=0-1$) nanodots via combining the chemical vapor transport (CVT) and chemical Li-intercalation and exfoliation method. The produced ReSSe nanodots possess the ultrasmall size of around 1.7 nm and the ultrathin thickness of around 1.2 nm. As characterized by the XPS and XANES techniques, some chalcogen atoms are lost due to the vigorous exfoliation process, resulting in the asymmetric S vacancy. More importantly, as predicted by the DFT calculation, the low site S vacancy in the ReSSe nanodots is the most active sites for electrocatalytic HER. Significantly, the 1T'-phase ReSSe nanodots show the best water-splitting performance with a small Tafel slope of 50.1 mV dec⁻¹. Moreover, a low overpotential of 84 mV can be achieved at current density of 10 mA cm⁻². The optimal hydrogen absorption energy of the active site is concluded to be the reason for the great hydrogen evolution performance, which is resulted from by the asymmetric S vacancy in the highly asymmetric 1T' structure.

Second, I obtained the large-scale production of single-layer $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ and $\text{Ni}_3\text{Cr}_2\text{P}_2\text{Se}_9$ nanosheets by exfoliation of the corresponding bulk crystals prepared by CVT method. The prepared $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ nanosheets possess the narrow distribution on thickness of around 1.4 nm, which corresponds to the single-layer thickness. The obtained $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ nanosheets were restacked by the vacuum filtration method to form a freestanding film. The prepared freestanding film was then supported on the conductive carbon paper for electrochemical measurements in 1.0 M H_2SO_4 electrolyte, delivering a high specific capacitance of 160.7 and 51.3 mF cm⁻², at the scan rate of 20 mV s⁻¹ and current density of 0.9 mA cm⁻²,

respectively. The galvanostatic charge/discharge measurements also reveal the good rate capacity of the fabricated device based on restacked $\text{Ni}_3\text{Cr}_2\text{P}_2\text{Se}_9$ film.

Lay Summary

The current economic prosperity all over the world is established on the fast depletion of a huge amount of unsustainable fossil fuels, such as petroleum. However, this development is being exchanged with the severe energy crises and the damage of Mother Nature, such as air pollution and water contamination. Therefore, how to find the alternative sustainable and clean energy resources to support the development of the economy and society is the current and urgent demand on the scientific community. As known, the burning of hydrogen only gives birth to water as the final product, which can be decomposed into hydrogen and oxygen under certain conditions. This makes it a sustainable cycle for utilization of energy. Hence, hydrogen is considered as one of cleanest renewable energy sources, due to a huge amount of water in our planet. To successfully utilize hydrogen, the highly efficient and durable catalyst is most desired. In this thesis, the work of preparation of $\text{ReS}_{2x}\text{Se}_{2(1-x)}$ nanodots aims to solve this problem. The test results also confirmed our assumption, in which the prepared catalyst can give a high efficiency for producing hydrogen with lower energy consumption. The prepared catalyst can also survive even after 20,000 cycles of producing hydrogen, which can greatly reduce the production cost. Hence, this research may inspire the development in the production of sustainable and renewable hydrogen source.

Beside the invention and discovery of new clean and renewable energy source, the energy storage devices are also important for the improvement of the economic development and the quality of life. It is well known that the energy storage is an important supplementary stage for electric power generation, since the power needs to be planed and directed to the areas on demand. Especially in modern society, the population of portable and wearable devices poses more pressure on the development of high-performance energy devices, such as the rechargeable batteries and mobile power banks for mobile phones and ultrathin skin detectors. In this thesis, the work of preparation of $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ nanosheets can be used for energy storage, because the device based on $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ nanosheets can be charged and discharged to generate the power cycle, which can be utilized to power the electronic devices. Generally, the ability of storing more electrical power and the releasing more

power in short time is the characteristics of a good energy storage device. Our energy device based on prepared $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ nanosheets can deliver high specific capacitance of 160.7 and 51.3 mF cm^{-2} , at the scan rate of 20 mV s^{-1} and current density of 0.9 mA cm^{-2} , respectively, which show great potential for application in energy storage.

Acknowledgements

2014 is a critical turning point in my whole life. Standing at the crossroads, I received the research scholarship from Nanyang Technological University, and did not hesitate for a while to decide to pursue my dream at Singapore. During the four years PhD study, I am so fortunate to have many people's help. Herein, I would like to express my most sincere thanks to them.

First and most importantly, the sincerest gratitude should be given to my supervisor Prof. Zhang Hua, for his continual support, incisive suggestions, extraordinary guidance and extensive encouragement on my research and life, which undoubtedly lead my research envision into a new stage.

I also want to thank Prof. Christian Kloc, Asst. Prof. Zheng Liu, Dr. Yonghua Du, Dr. Tay Yee Yan for their professional help and instructive discussions on my research work. I also thank all the technicians in the FACTS and the B2 organic lab of MSE for their help on my research.

I appreciate the great help from Dr. Chaoliang Tan, Dr. Xiao Zhang, Dr. Zhimin Luo, Dr. Xuejun Wu, Dr. Wei Zhao, Dr. Yifu Yu, Dr. Ying Huang, Dr. Shikui Han, Dr. Zhicheng Zhang, Dr. Meiting Zhao, Dr. Qipeng Lu, Dr. Peng Yu, Dr. Bing Li, Dr. Zhanxi Fan, Dr. Apoorva Chaturvedi, Dr. Nailiang Yang, Dr. Bo Chen, Dr. Junze Chen, Dr. Jian Yang, Dr. Qinglang Ma, Dr. Xiehong Cao, Dr. Qiyuan He, Dr. Anliang Wang, Dr. Guigao Liu, Dr. Zhiqi Huang, Dr. Zhengqing Liu, Mr. Gwang-Hyeon Nam, Ms. Ye Chen, Ms. Jie Wang, Mr. Qinbai Yun, Ms. Xiaoya Cui, Mr. Zhaoning Hu, Ms. Thu Ha Tran and all other colleagues.

Last but not least, I would like to give deep thanks to my family. Thank my parents for the unlimited support. Thank my brother for taking care of the whole family, so that I can pursue my PhD degree without worry. I also would like to thank Yingsi Wu my beloved

wife for her accompanying with me and the strongest support no matter how many obstacles we met. You are my destined soulmate. This dissertation is dedicated to you.

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Figure 5.9 Comparison of XPS survey spectrum of prepared Ni₃Cr₂P₂S₉ bulk crystals exfoliated Ni₃Cr₂P₂S₉ nanosheets.

Figure 5.10 Comparison of high-resolution XPS spectrum of prepared Ni₃Cr₂P₂S₉ bulk crystals exfoliated Ni₃Cr₂P₂S₉ nanosheets. (a) Cr 2p. (b) P 2p. (c) Ni 2p. (S) S 2p.

Figure 5.11 Morphology and chemical composition characterization of the Ni₃Cr₂P₂Se₉ bulk crystals prepared by CVT method. (a), (b) the SEM images of the prepared Ni₃Cr₂P₂Se₉ bulk crystals. (c) EDS spectrum of the Ni₃Cr₂P₂Se₉ bulk crystals. (d) The exact ratio of different elements of the prepared Ni₃Cr₂P₂Se₉ bulk crystals.

Figure 5.12 XRD pattern of the Ni₃Cr₂P₂Se₉ bulk crystals prepared by CVT method.

Figure 5.13 Structure analysis of the exfoliated Ni₃Cr₂P₂Se₉ nanosheets. (a) Low magnification TEM image of the exfoliated Ni₃Cr₂P₂Se₉ nanosheets. (b) TEM image of an individual Ni₃Cr₂P₂Se₉ nanosheet. (c) HRTEM image of a Ni₃Cr₂P₂Se₉ nanosheet. Inset in (c): the corresponding FFT pattern. (d) The SAED pattern of a Ni₃Cr₂P₂Se₉ nanosheet.

Figure 5.14 Supercapacitor performance test of restacked film based on Ni₃Cr₂P₂S₉ nanosheets. (a) Cyclic voltammograms (CV) at different voltage range. (b) CVs collected at scan rate ranging from 20 to 500 mV s⁻¹. (c) Plot of specific capacitance (Cs) vs. scan rate. (d) Galvanostatic discharge curves collected at current density of 0.9, 2.25 and 4.5 mA cm⁻².

Abbreviations

2D	Two-Dimensional
AAO	Anodic Aluminum Oxide
AFM	Atomic Force Microscopy
APTES	(3-Aminopropyl)triethoxysilane
CV	Cyclic Voltammetry
CVD	Chemical Vapor Deposition
CVT	Chemical Vapor Transport
DFT	Density function theory
EDS	Energy Dispersive X-ray Spectroscopy
EXAFS	X-ray Absorption Fine Structure
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
LIBs	Li Ion Batteries
NDs	Nanodots
NMP	N-methyl-pyrrolidone
NPs	Nanoparticles
PET	Polyethylene Terephthalate Film
PL	Photoluminescence
PVDF	Poly(vinylidene fluoride)
PVP	Polyvinylpyrrolidone
rGO	reduced graphene oxide
SAED	Selected Area Electron Diffraction
SEM	Scanning Electron Microscopy
SEI	Secondary Electron Images
STEM	Scanning Transmission Electron Microscopy

TEM	Transmission Electron Microscopy
VdW	Van der Waals
XANES	X-ray Absorption Near Edge Structure
XAS	X-ray Absorption Spectroscopy
XRD	X-ray Diffraction
Z	Atomic Number

Chapter 1

Introduction

This chapter gives the brief introduction to this thesis. First, the hypotheses and research background of this thesis are introduced. Second, based on the hypotheses, the objectives and scope of this thesis are described in details. Then, the dissertation overview for each chapter in the whole thesis is also briefly presented. Finally, based on the achieved research results, the findings and outcomes of this thesis are summarized comprehensively.

1.1 Hypothesis/Problem Statement

Recently, the layered metal dichalcogenides (LMDs) have attracted a huge research interest due to their unique physicochemical properties and various promising applications.^[1-15] Among them, the binary transition metal dichalcogenides (TMDs), including MoS₂, MoSe₂, WS₂, WSe₂, TiS₂, TaS₂, NbS₂, etc., have exhibited various properties, from semiconducting (e.g., MoS₂, WS₂) to semimetallic (e.g., WTe₂, TiSe₂), metallic (e.g., NbS₂, VSe₂) and even superconducting (e.g., NbSe₂, TaS₂).^[16-20] Besides that, the ternary alloyed TMD nanomaterials and other multinary LMDs, such as Mo_xW_{1-x}S₂, MoS_{2-x}Se_{2(1-x)}, Ta₂NiS₅, and Cu₂WS₄,^[21-24] also demonstrated fascinating properties and great potentials in many applications. More importantly, the weak van der Waals (vdW) force between neighboring layers endows the possibility to exfoliate the layered metal dichalcogenides to ultrathin nanosheet with monolayer or few-layer thickness, which show unique physical and electronic properties when compared with the bulk counterparts.^[1, 2, 6, 9] Inspired by the importance of these ultrathin LMD nanosheets, various methods have been studied and developed to synthesize ultrathin 2D TMDs and other LMDs, such as mechanical cleavage exfoliation,^[25, 26] sonication-assisted liquid exfoliation,^[8, 27] electrochemical Li-intercalation and exfoliation,^[28, 29] chemical Li-intercalation and exfoliation,^[30, 31] chemical vapor deposition (CVD),^[32-34] chemical vapor transportation (CVT) method^[35, 36] and wet-chemical synthetic method.^[37, 38] The hypothesis based on above discussion is that the well-established chemical Li-intercalation and exfoliation method could be used to exfoliate new LMD bulk crystals for the preparation of ultrathin 2D nanosheets or ultrasmall nanodots, which could have potential on catalysis as well as energy conversion and storage, such as electrocatalysis and supercapacitors.

Rational design and preparation of highly efficient catalysts for electrocatalytic hydrogen evolution reaction (HER) are important for the fulfillment of a sustainable and clean hydrogen economy. The discovery of TMDs nanosheet, such as WS₂ and MoS₂, has raised the increasing research interest on TMDs catalysts due to their earth abundance compared with commercial Pt-based catalysts and high catalytic activities. It has been reported that the edge sites of 2H-phase TMDs and basal planes of 1T-phase TMDs are the active sites

for electrocatalytic HER.^[39, 40] Therefore, preparing small-sized and 1T-phase TMDs is an important way to realize high-performance HER activity. In addition, another important strategy is based on the defect engineering to enhance the activity of TMD catalysts for electrocatalytic HER. For example, inducing S vacancies on the strained 2H-MoS₂ nanosheet can greatly enhance the electrocatalytic activity when compared with the strained 2H-MoS₂ nanosheets without S vacancies.^[41] This is also confirmed by the research on 1T-MoSSe nanodot and porous 1T-MoS₂ nanosheet, suggesting the importance of defect-engineering of TMDs for HER.^[40, 42] But, there is only one kind of anionic vacancies because of the symmetric trigonal prismatic 2H phase and octahedral 1T phase structures. On the other hand, the 1T'-phase TMDs have highly asymmetric structures which could produce different kinds of anionic vacancies since there are different kinds of chalcogen atoms in the crystal structure, which is totally different from the 2H and 1T structures. Hence, the 1T'-phase ReS_{2x}Se_{2(1-x)} may be ideal model catalysts to study the fundamental effect of asymmetric vacancies for electrocatalytic HER. The hypothesis here is that, by using the well-developed chemical Li-intercalation and exfoliation method, the 1T'-ReS_{2x}Se_{2(1-x)} bulk crystals may be exfoliated into ultrathin and ultrasmall nanodots with more edges and asymmetric vacancies, which are beneficial for the enhancement of electrocatalytic activity for HER.

The chemically exfoliated TMD nanosheets usually have good hydrophilicity as well as the ability to accommodate and release various ions in the restacked nanosheets, which is usually beneficial for the fabrication of supercapacitors. However, layered TMDs normally crystallize into a 2H crystal phase, such as MoS₂, WS₂, WSe₂ and MoSe₂, and thus show semiconducting properties with bandgap of 1-2 eV, rendering the exfoliated nanosheets with low electrical conductivity which could restrict the potential in energy storage.^[1] Fortunately, Li-intercalation and exfoliation process can partially transform the semiconducting 2H phase into metallic 1T phase, which can greatly improve the conductivity of these TMD nanosheets.^[43] For example, the Li-assisted exfoliated MoS₂ nanosheets have been proved to be one of the best electrode materials for fabrication of supercapacitors.^[44] Despite that, the obvious bottleneck is that the 2H TMDs usually cannot completely transform into 1T phase, which restricted the application of LMD nanosheets

in energy storage applications. On the other hand, the exfoliation of new LMD materials with intrinsic metallic phase may be the alternative solution to solve this problem. Therefore, layered quaternary $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9/\text{Ni}_3\text{Cr}_2\text{P}_2\text{Se}_9$ nanosheets may be the suitable LMD materials for the fabrication of supercapacitors, because of their intrinsic high conductivity. The hypothesis here is that the chemical Li-intercalation method could be used to exfoliate the bulk LMD crystals to produce intrinsic metallic phase metal chalcogenide nanosheets with high conductivity, which are expected to exhibit high performance in supercapacitors.

1.2 Objectives and Scope

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

First, a series of micro-sized 1T'-phase $\text{ReS}_{2x}\text{Se}_{2(1-x)}$ bulk crystals, including ReS_2 , $\text{ReS}_{1.8}\text{Se}_{0.2}$, $\text{ReS}_{1.4}\text{Se}_{0.6}$, ReSSe , $\text{ReS}_{0.6}\text{Se}_{1.4}$, $\text{ReS}_{0.2}\text{Se}_{1.8}$, and ReSe_2 , will be prepared by a well-developed chemical vapor transport method from the corresponding stoichiometry elementary powder of Re, S and Se. After that, these prepared bulk crystals will be subjected to ball-milling process to reduce the crystal size before intercalated with lithium. The small-size $\text{ReS}_{2x}\text{Se}_{2(1-x)}$ bulk materials will then be exfoliated into ultrathin and ultrasmall nanodots via the *n*-butyl lithium solution assisted chemical Li-intercalation and exfoliation method. These prepared nanodots will then be investigated by SEM, EDS, TEM, AFM, XPS, HAADF-STEM, UV-vis spectroscopy and XAS techniques. As a proof-of-concept application, these prepared nanodots will be used for electrocatalytic HER and the mechanism will also be investigated.

Second, the micro-sized layered bulk crystals of $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ and $\text{Ni}_3\text{Cr}_2\text{P}_2\text{Se}_9$ will be obtained by the well-developed chemical vapor transport (CVT) method using the corresponding elementary powders as precursors. The as-prepared $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ and $\text{Ni}_3\text{Cr}_2\text{P}_2\text{Se}_9$ bulk crystals will then be applied as the raw materials to prepare large-scale monolayer and few-layer nanosheet via the chemical Li-intercalation and exfoliation method by using *n*-butyllithium solution. These prepared nanosheets will then be

characterized and analyzed by SEM, XRD, EDS, TEM, AFM, XPS and Raman spectroscopy. The supercapacitor performance of the prepared nanosheets will then be thoroughly investigated.

1.3 Dissertation Overview

This thesis demonstrates the preparation of novel layered metal chalcogenide nanomaterials by engineering the size, thickness and defects at atomic scale, to enhance their performance for energy conversion and storage. The thesis also addresses how to use suitable and useful analytical techniques to investigate the prepared layered metal chalcogenide nanomaterials. The potentials of the prepared layered metal chalcogenide nanomaterials used in applications of electrocatalysis and supercapacitors will finally be investigated and demonstrated.

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

Chapter 2 reviews the literatures regarding the current research progress on the preparation of novel structured layered metal chalcogenide nanomaterials as well as their applications in energy conversion and storage, especially for TMDs and other multinary metal chalcogenide nanomaterials.

Chapter 3 discusses rational design and selection of experimental methods and target materials, the detailed preparation procedures, characterization techniques, calculation models and principles, as well as the potential applications.

Chapter 4 elaborates the preparation and characterizations of the series of 1T'-phase $\text{ReS}_{2-x}\text{Se}_{2(1-x)}$ nanodots with asymmetric vacancies, and the utilization of the ReSSe nanodots with asymmetric S vacancies as an efficient electrocatalyst for hydrogen evolution reactions (HER).

Chapter 5 elaborates the preparation and characterizations of monolayer multinary metal

chalcogenide nanosheets, including $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ and $\text{Ni}_3\text{Cr}_2\text{P}_2\text{Se}_9$ with large scale, and demonstrates the high performance of $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ nanosheets as electrode materials for the fabrication of supercapacitors.

Chapter 6 summarizes the whole thesis and discuss the reconnaissance research that can be carried out in the near future.

1.4 Findings and Outcomes/Originality

This research led to several novel outcomes by:

1. By combining the CVT and chemical Li-intercalation method, the ultras-small $1\text{T}'$ - $\text{ReS}_{2-x}\text{Se}_{2(1-x)}$ nanodots can be prepared using the corresponding powder of bulk crystals, which include ReS_2 , $\text{ReS}_{1.8}\text{Se}_{0.2}$, $\text{ReS}_{1.4}\text{Se}_{0.6}$, ReSSe , $\text{ReS}_{0.6}\text{Se}_{1.4}$, $\text{ReS}_{0.2}\text{Se}_{1.8}$, and ReSe_2 . Among them, the ReSSe nanodots with active low site S vacancies as well as the rich active edge sites showed better electrocatalytic performance for HER than that of both ReS_2 and ReSe_2 nanodots. Significantly, the $1\text{T}'$ -phase ReSSe nanodots show the best water-splitting performance with a small Tafel slope of 50.1 mV dec^{-1} as well as the great long-term stability. Moreover, a low overpotential of 84 mV can be achieved at current density of 10 mA cm^{-2} . The optimal hydrogen absorption energy of the active site is concluded to be the reason for the great hydrogen evolution performance, which is resulted from by the asymmetric S vacancy in the highly asymmetric $1\text{T}'$ structure. This research could open a new direction to guide the design and preparation of $1\text{T}'$ -phase TMD electrocatalysts with high efficiency via the defect engineering down to the atomic level, and even extend to other catalysts with asymmetric structure.

2. A facile chemical Li-intercalation and exfoliation method for preparation of water-dispersed single-layer $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ and $\text{Ni}_3\text{Cr}_2\text{P}_2\text{Se}_9$ nanosheets from their bulk crystals is developed. Due to the unique electronic structure of the $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ and $\text{Ni}_3\text{Cr}_2\text{P}_2\text{Se}_9$, the exfoliated nanosheets inherited the intrinsic metallic properties from their bulk counterparts. When restacked by the vacuum filtration method, the restacked $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$

film exhibited high rate capacitance in 0.5 M H₂SO₄ electrolyte, indicating its great potential as electrode materials for energy storage.

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Chapter 2

Literature Review

This chapter gives a comprehensive literature review on the recent progress on preparation and structure engineering of layered metal chalcogenide nanomaterials, especially for the TMD nanomaterials. A detailed summary will be presented on the basis of the state-of-the-art research progress of layered 2D multinary layered metal chalcogenide nanomaterials with ultrathin thickness, including the classification and advantages of the layered 2D multinary metal chalcogenide nanomaterials as well as the preparation and characterization techniques. Then, the utilization of these materials in various applications will also be summarized with the emphasis on catalysis, energy storage and conversion fields. Finally, the questions related to the thesis based on literature are also discussed.

*This section published substantially as (C. L. Tan, Z. C. Lai, H. Zhang, *Adv. Mater.* **2017**, 29, 1701392).

2.1 Overview

Two-dimensional (2D) nanosheet of layered transition metal dichalcogenides (TMDs) with ultrathin thickness, including MoS_2 , TiS_2 , TaS_2 , WS_2 , ReS_2 , MoSe_2 and WSe_2 , have been studied intensively during the past five years in the topics of nanotechnology, materials science and chemistry.^[1-6] Because of their unique physicochemical, electronic and optical properties resulting from the various composition, diverse crystal structures and special 2D features of the 2D TMD nanosheets with ultrathin thickness, these 2D metal chalcogenide nanosheets have been utilized in a number of applications, such as optoelectronics/electronics,^[2,7-11] catalysis,^[12-16] energy conversion and storage,^[17-21] sensors,^[22-26] biomedicine,^[27-31] and water remediation.^[32-34] Recent studies have proved that the introduction of heteroatom into/onto the ultrathin 2D metal chalcogenide nanosheet can produce well-defined layered 2D multinary metal chalcogenide nanosheet/heterostructure to optimize their performance for specific applications, since these strategies can further tune their properties.

Recently, a number of multinary ultrathin 2D metal chalcogenide nanosheets have been successfully synthesized, including ternary metal chalcogenides (e.g., Cu_2WS_4 and Ta_2NiS_5),^[35,36] alloyed TMD nanosheets (e.g., $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ and $\text{MoS}_{2x}\text{Se}_{2(1-x)}$),^[37] heteroatom-doped TMD nanosheets (e.g., Co-, Re-, Cr-, V- or Pt-doped MoS_2),^[38-41] and metal chalcogenide heterostructures (e.g., $\text{MoS}_2\text{-WS}_2$ and $\text{MoS}_2\text{-MoSe}_2$).^[42-44] Generally, these 2D multinary layered metal chalcogenide nanosheets can be easily obtained by the well-developed methods which have been used for the synthesis of ultrathin TMDs nanosheets, such like wet-chemical syntheses and chemical vapor deposition (CVD) method. It is noteworthy that these ultrathin 2D multinary layered metal chalcogenide nanomaterials exhibited unique advantages when compared with the 2D binary TMD counterparts to some extent. For instance, the ternary Ta_2NiS_5 nanosheet exhibits a great potential in photothermal and photoacoustic theranostics due to its strong absorption on near-infrared (NIR) range as compared to the binary TMD nanosheets.^[45] Moreover, it has been proved that the bandgaps of the alloyed TMD monolayers can be easily adjusted by finely tuning its precise composition ratio, such as $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ ($x = 0-1$).^[46] As another

example, the introduction of heteroatoms into metal chalcogenide nanosheets is an effective way to increase the number of active sites for catalysis, such as electrocatalytic hydrogen evolution reaction (HER).^[47] On the other hand, the lateral and vertical heterostructures are usually considered as the intrinsic p-n junctions, which show potentials in modern electronics and optoelectronics, such like light-emitting diodes (LEDs), photovoltaics and transistors.^[48] Due to the aforementioned properties and advantages, these 2D multinary layered metal chalcogenide nanomaterials with ultrathin thickness have played an important role on wide applications, such like catalysis, biomedicine, sensors, electronics/optoelectronics, and energy storage and conversion.

2.2 Classification and Advantages

2.2.1 Classification of Multinary Layered Metal Chalcogenides

According to the atom arrangements, all of the 2D multinary layered metal chalcogenide nanomaterials are simply categorized into four kinds: 1) ternary metal chalcogenide nanosheets with well-defined crystal structures, 2) alloyed TMD nanosheets, 3) heteroatom-doped TMD nanosheets and 4) 2D metal chalcogenide heterostructures. First, the ternary metal chalcogenide nanosheets with well-defined crystal structures are defined as that the nanosheet is composed of three or more elements with single-crystalline nature and each kind of element is well aligned within the nanosheets, such as the single-layer Ta_2NiS_5 nanosheet.^[35] As illustrated in **Figure 2.1a**, the $[\text{TaS}_6]_2$ dimer chains are connected by NiS_4 chains on the both sides through the S-S bonds, forming a well-structured individual layer of Ta_2NiS_5 nanosheet. Second, the alloyed TMD nanosheets are also known as solid solutions of TMD nanosheets.^[37] In a typical alloyed TMD nanosheet, one of the elements in binary TMDs is replaced by another element which is close to itself in periodic table. It is worth pointing out that, the crystal structures of the alloyed TMD nanosheets can keep in single homogeneous phase with arbitrary percentages of substitution in alloyed TMDs. Different to well-defined ternary metal chalcogenide nanosheets, the alloyed TMDs usually have two elements randomly distributed in the alloyed nanosheet, such as single-layer $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheet.^[46] As shown in **Figure**

2.1b, both of the S and Se atoms just randomly distributed in the alloyed $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheet with the percentage from 0% to 100%, in which the x value is changing among the range of 0 to 1. Third, heteroatom-doped TMD nanosheets can be prepared by deliberately introducing heteroatoms into the crystal structure of TMD nanosheet. Compared to the alloyed TMDs, the doping heteroatom can be selected on purpose without too strict limitation. However, the percentage of dopants still needs to be lower than a certain concentration. Otherwise, the dopants will transform the crystal structure of the doped host material, which is different from the alloyed TMDs. Mn-doped MoS_2 is one typical example of the heteroatom-doped TMDs and the crystal structure is schematically illustrated in **Figure 2.1c**.^[49] Fourth, 2D metal chalcogenide heterostructures are commonly prepared by one kind of metal chalcogenide nanosheets epitaxially grown on the other metal chalcogenide nanosheet laterally or vertically, forming the vertical or lateral heterostructures. For instance, the vertical and lateral heterostructures of MoS_2 and WS_2 were demonstrated in **Figure 2.1d**.^[50] However, in this thesis, the study will mainly focus on the first three types of multinary layered 2D metal chalcogenide nanomaterials.

Figure 2.1 Schematic illustration of four typical types of multinary ultrathin 2D metal chalcogenide nanomaterials: (a) ternary metal chalcogenide nanosheet with well-defined crystal structures, e.g. Ta_2NiS_5 , (b) alloyed TMD nanosheet, e.g. $\text{MoS}_{2x}\text{Se}_{2(1-x)}$, (c) heteroatom-doped TMD nanosheet, e.g. Mn-doped MoS_2 , and (d) vertical or lateral heterostructures, e.g. MoS_2 - WS_2 .

2.2.1 Advantages of Multinary Layered Metal Chalcogenides

Due to their versatile chemical compositions and unique crystal structures, various advantages have been discovered on the 2D multinary layered metal chalcogenide nanomaterials with ultrathin thickness as compared to the binary TMD nanosheets. First, the chemical, optical and electronic properties of well-structured ternary metal chalcogenide nanosheet can be much different from the binary TMD nanosheet because of their well-defined structures and varying chemical compositions. For instance, the absorption of the ternary Ta_2NiS_5 nanosheets in NIR region was found to be far stronger than that of binary TMD nanosheets.^[45] As another example, the photodetector fabricated using mechanically exfoliated Ta_2NiSe_5 nanosheet exhibited a high external quantum efficiency of 2,645% and great responsivity of 17.21 A W^{-1} .^[51] Second, the tunable bandgap is one of the most attractive advantages of the alloyed TMDs when compared with the binary counterparts. For example, it has been reported that the bandgap of monolayer $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ can change from 1.856 eV (MoS_2) to 1.557 eV (MoSe_2) by simple tuning of the x value from 1 to 0.^[46] Moreover, the lattice strain resulted from the difference of atomic radius between two alloyed atoms, i.e. S and Se, and the synergistic effect between two elements could usually lead to improved electrocatalytic performance toward HER when compared with binary counterparts.^[47] Third, introduction of heteroatom into TMD nanosheet can greatly transform their chemical, physical, and electronic properties. For instance, the band structure of MoS_2 can be altered by the Mn doping into MoS_2 nanosheet.^[49] As another example, both up- and down-conversion photoluminescence (PL) at NIR region could be measured in the Er-doped MoS_2 nanosheet.^[52] Moreover, the activation of basal plane of MoS_2 can be achieved for the electrocatalytic HER through heteroatom doping, such as Pt doping.^[41]

2.3 Preparation and Characterization

There are a number of well-developed preparation methods of 2D multinary layered metal chalcogenide nanomaterials with ultrathin thickness, such as the mechanical exfoliation method,^[53-55] CVD method,^[56-58] sonication-assisted liquid exfoliation method,^[59-61]

chemical Li intercalation and exfoliation method,^[62-64] electrochemical Li intercalation and exfoliation method^[65-67] as well as the wet-chemical syntheses.^[68-71] Note that some of the ultrathin 2D multinary layered metal chalcogenide nanomaterials can be obtained by combining two different methods, such as the combination of electrochemical Li intercalation-assisted exfoliation and CVT method.^[35] Furthermore, the structure, morphology, crystal phase and atomic arrangements of these ultrathin 2D multinary layered metal chalcogenide nanosheets can be studied thoroughly by various characterization techniques. In this part, we will systematically introduce the preparations and characterizations of the 2D multinary layered metal chalcogenide nanomaterials with ultrathin thickness on the basis of the classified structure types.

2.3.1 Ternary Metal Chalcogenide Nanosheets with Well-defined Crystal Structures

First, the preparation of a number of ternary metal chalcogenide nanosheets will be introduced, such as Ta_2NiS_5 , Ta_2NiSe_5 , Cu_2WS_4 , CuSbS_2 , $\text{Pb}_m\text{Bi}_{2n}\text{Te}_{3n+m}$ and ZnIn_2S_4 .^[35,36,51,72-75] As a typical example, the large-scale preparation of ternary metal chalcogenide nanosheets of Ta_2NiS_5 and Ta_2NiSe_5 was first reported via combining the CVT and electrochemical Li-intercalation method.^[35] The layered bulk crystals of Ta_2NiS_5 and Ta_2NiSe_5 were first synthesized by the CVT method from the elementary powders, showing crystal size of tens of micrometers, which were then exfoliated by the Li-assisted intercalation and exfoliation method to produce the ultrathin 2D nanosheets. Moreover, as demonstrated in **Figure 2.2a,b**, the obtained Ta_2NiS_5 nanosheets were characterized by the atomic-force microscopy (AFM), transmission electron microscopy (TEM), high-resolution TEM (HRTEM), showing the single-crystalline structure with the thickness of 1.0-1.2 nm and the size within a few micrometers. The obtained Ta_2NiSe_5 nanosheet exhibited a similar 2D morphology with the Ta_2NiS_5 nanosheet, but thicker on the thickness. After that, Kim and the coworkers used the mechanical exfoliation technique to obtain few-layer Ta_2NiS_5 nanosheets from the CVT-grown bulk crystals.^[72] The thickness of the exfoliated Ta_2NiSe_5 nanosheet was studied by the AFM image, showing the thickness of 4 to 16 layers and the lateral size of around 10 μm (**Figure 2.2c**). The mechanical exfoliation of Ta_2NiSe_5 nanosheet from the CVT-grown bulk crystal were also

reported by Zhai and the coworkers.^[51] As another example, the preparation of Cu_2WS_4 nanosheets was also achieved by combining two different methods in Xie's group.^[36] Specifically, the Cu_2WS_4 bulk crystal was first prepared by a well-developed solvothermal method using copper(I) chloride, thioacetamide and sodium tungstate as precursors. Then, the Cu_2WS_4 nanosheets were prepared from the as-obtained Cu_2WS_4 bulk crystals by the chemical Li-assisted intercalation and exfoliation method, in which butyllithium was used as the intercalating agent. The AFM, TEM and HRTEM characterizations were performed to characterize the exfoliated Cu_2WS_4 nanosheets, revealing the single-crystalline nature of the nanosheet with the monolayer thickness and lateral size of a few hundred nanometers.

Figure 2.2 (a) SEM and (b) AFM height images of single-layer Ta_2NiS_5 nanosheets. Inset in (a): The corresponding HRTEM image.^[35] (c) AFM height image of mechanically-exfoliated Ta_2NiS_5 nanosheets with different thicknesses. Inset: The corresponding optical microscopy image.^[72] (d) TEM and (e) HRTEM images of O-doped ZnIn_2S_4 nanosheets. (f) Zn Kedge extended EXAFS spectra of the O-doped ZnIn_2S_4 nanosheets, the calculated ZnIn_2S_4 , and ZnO .^[75]

It is noteworthy that the top-down methods, such as the mechanical exfoliation and Li intercalation-assisted exfoliation, were most commonly used to prepare the aforementioned ternary metal chalcogenide nanosheets by simply cleaving their layered bulk crystals, which are prepared by other methods, such as CVT method. Alternatively, several other ternary metal chalcogenide nanosheets, including CuSbS_2 , $\text{Pb}_m\text{Bi}_{2n}\text{Te}_{3n+m}$ and ZnIn_2S_4 , can

also be prepared by solution-processed bottom-up methods.^[73-75] For instance, the synthesis of ternary CuSbS₂ nanosheet by a colloidal bottom-up approach was reported by Gupta, Ramasamy and coworkers.^[73] Specifically, the ternary CuSbS₂ nanosheets can be prepared by the reaction of antimony (III) chloride and copper(II) acetylacetonate with the injected sulfur powder in oleylamine at elevated temperature, such as 170 °C. Moreover, the thickness and lateral size of obtained CuSbS₂ nanosheets can be finely tuned by controlling the reaction temperature and/or time. For instance, the thickness of 4 ± 0.8 nm, 7.0 ± 0.7 nm to 10.0 ± 0.5 nm can be easily achieved when the reaction time was changed from 10, 15 to 30 min, respectively, under the same temperature of 170 °C. In addition, the CuSbS₂ microbelts with length of around 10 μ m can also be prepared the similar colloidal synthetic method at a higher elevated temperature of 250 °C, which can then be used to prepare monolayer or few-layer nanosheets by the chemical Li intercalation-assisted exfoliation method. Besides, the preparation of a series of homologous Pb_mBi_{2n}Te_{3n+m} nanosheets, including PbBi₂Te₄, Pb₂Bi₂Te₅, and PbBi₆Te₁₀, by a facile colloidal synthetic method was reported by Biswas and Chatterjee.^[74] Generally, the ternary PbBi₂Te₄, Pb₂Bi₂Te₅, and PbBi₆Te₁₀ nanosheets were synthesized by tuning the molar ratio of Te, Bi and Pb precursors during the synthetic process. Recently, Xie and coworkers reported the preparation of O-doped ZnIn₂S₄ nanosheets from indium (III) chloride, zinc chloride and thioacetamide using the solvothermal method.^[75] The prepared O-doped ZnIn₂S₄ nanosheets were investigated by TEM and HRTEM, showing good crystallinity and the size of around a few hundred nanometers (**Figure 2.2d,e**). The thickness of the obtained O-doped ZnIn₂S₄ nanosheets was confirmed by AFM, showing the ultrathin thickness of about 6 nm. Importantly, the local atomic structure of the O-doped ZnIn₂S₄ nanosheets was revealed by the X-Ray absorption fine structure (XAFS) spectroscopy. Comparison of Zn K-edge extended EXAFS spectra between the O-doped ZnIn₂S₄ nanosheets, calculated ZnIn₂S₄ and ZnO clearly proved the oxygen doping effect in the ZnIn₂S₄ nanosheets (**Figure 2.2f**).

2.3.2 Ultrathin 2D Alloyed Metal Chalcogenide Nanosheets

Although the comprehensive studies of alloyed TMD bulk crystals have been started a few

decades ago,^[76-79] the synthesis and applications of ultrathin 2D alloyed TMD nanosheets just began from past few years. To date, there has been several kinds of alloyed TMD nanosheets prepared and studied, including $\text{MoS}_{2x}\text{Se}_{2(1-x)}$, $\text{Mo}_x\text{W}_{1-x}\text{S}_2$, $\text{WS}_{2x}\text{Se}_{2(1-x)}$, $\text{MoS}_{2x}\text{Te}_{2(1-x)}$ and $\text{ReS}_{2x}\text{Se}_{2(1-x)}$.^[37] As a typical example, the mechanical exfoliation of single-layer $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ nanosheets from their CVT-grown bulk crystals was reported by Suenaga and coworkers.^[80] The high angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) imaging skill in a C_s -corrected TEM was used to characterize the distribution and quantity of Mo and W atoms in monolayer $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ nanosheets. Since the atoms with different Z number can be easily distinguished by the HAADF-STEM due to their different contrast under STEM environment, this technique is one of the most powerful ways to investigate nanomaterials at atomic scale, especially for 2D ultrathin alloyed TMD nanosheets. Therefore, the W and Mo atoms in the single-layer $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ nanosheets could be clearly observed in HAADF-STEM images due to their different brightness and contrast. In addition, using the mechanical exfoliation method, Xie and coworkers also exfoliated the CVT-grown $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ bulk crystals into monolayer nanosheet, which were then well studied by STEM, AFM, optical microscopy, PL spectroscopy and Raman spectroscopy.^[81] As illustrated in **Figure 2.3a**, the optical microscopy image clearly reveals the exfoliated monolayer $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ nanosheet on the SiO_2/Si substrate. The bandgap of the monolayer alloyed $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ nanosheet can be finely tuned from 1.99 eV ($x = 1$) to 1.82 eV ($x = 0.20$) by the change of x value, which was also confirmed by the PL spectroscopy results. Later, the Raman spectroscopy study on mechanically exfoliated monolayer $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ ($x = 0-1$) nanosheets was also conducted by the same group.^[82] As shown in **Figure 2.3b**, the composition-dependent Raman of monolayer $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ nanosheets can be clearly observed. Generally, first-order and second-order Raman modes between 100 and 480 cm^{-1} could be obviously measured, while the disorder-related Raman peaks can be exclusively observed in the alloyed $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ nanosheets but not in the pure MoS_2 and WS_2 nanosheet. The temperature-dependent Raman spectra and PL emission were also studied, revealing the linear relationship with temperature.^[83] In addition to the mechanical exfoliation of corresponding bulk materials, CVD is another effective method used for the preparation of alloyed $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ nanosheets. For example, the preparation of $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ nanosheet by the CVD method was first

reported by Liu and coworkers.^[84] Specifically, the few-layer $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ nanosheets were grown by reacting the as-deposited $\text{Mo}_x\text{W}_{1-x}$ thin films with different compositions ($x = 0, 0.19, 0.55, 0.85, \text{ and } 1$) with the S vapor at the temperature of 950°C in a CVD furnace. Alternatively, Terrones and coworkers prepared alloyed $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ nanosheet by reacting sulfur vapor with MoS_2/WO_3 .^[85] Different from the alloyed $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ with a homogeneous composition in the previous case, the resulting $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ nanosheets have non-uniform elemental distribution, in which W and Mo atoms is dominant at the outside parts and center of the $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ triangular nanosheet, respectively. Moreover, a low-temperature CVD process for the growth of $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ with a wide range of W/Mo ratios at the temperature of 700°C was reported by Chen and coworkers, in which the temperature is slightly lower as compared to previous studies.^[86] It is well known that high temperature and high vacuum is usually desired for the preparation of alloyed TMD nanosheet using CVD method. Impressively, the growth of single-layer alloyed $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ nanosheets by a CVD method at normal pressure was demonstrated by He and coworkers recently, showing the triangle shape and the size of around $20\text{ }\mu\text{m}$.^[87] Furthermore, Tan and coworkers reported the measurement of the precise layer number of $\text{Mo}_{0.5}\text{W}_{0.5}\text{S}_2$ nanosheets by the exploration of the shear and layer-breathing modes under Raman spectroscopy because $\text{Mo}_{0.5}\text{W}_{0.5}\text{S}_2$ nanosheet exhibited layer-dependent signals in two different modes.^[88] Note that the stoichiometry, complex refractive index and substrate of 2D nanosheet cannot affect the layer-dependent Raman signals in the shear and layer-breathing modes, which makes it one of the most useful skill to identify layer-number of 2D nanosheet. As another example, the Raman spectroscopy study under high pressure on the alloyed $\text{Mo}_{0.5}\text{W}_{0.5}\text{S}_2$ nanosheet was performed by Akinwande and coworkers.^[89] It was concluded that there are some new appearing peaks with the increasing of pressure to a certain GPa. For instance, a new peak at 470 cm^{-1} was only observed in the alloyed $\text{Mo}_{0.5}\text{W}_{0.5}\text{S}_2$ nanosheet but not in the pristine MoS_2 and WS_2 nanosheet, which can be assigned to the disorder-activated out-of-plane Raman mode resulted from the pressure.

Figure 2.3 (a) Optical microscopy image of mechanically-exfoliated $\text{Mo}_{0.47}\text{W}_{0.53}\text{S}_2$ nanosheets on Si/SiO₂ substrate.^[81] (b) Raman spectra of $\text{Mo}_{1-x}\text{W}_x\text{S}_2$ monolayers with different W composition, i.e. the x value.^[82] (c) Atomic scale HADDF-STEM image of single-layer $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ with Se concentration of 12%.^[90] (d) SEM image of CVD grown single-layer $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheets. (e) Raman spectra of $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheets with different x values. (f) PL spectra of the $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheets with complete compositions. Inset: A typical PL mapping of a single nanosheet.^[46]

Alloyed $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ ($x = 0-1$) nanosheet with the changing of x values have also been prepared by various methods, especially the CVD method. For instance, the synthesis of alloyed $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheet with different composition, i.e., $x = 0.1, 0.3, 0.50$, and 0.75) has been reported by Ajayan and coworkers through the sulfurization/selenization of MoO_3 at 800°C in a CVD furnace.^[90] Raman spectroscopy, optical microscopy, AFM, PL spectroscopy, HADDF-STEM imaging technique and X-ray photoelectron spectroscopy (XPS) were conducted to investigate the obtained $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheet. As demonstrated in **Figure 2.3c**, the atomic structure of a $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheet and the distribution of Se atoms can be observed by the atomic scale HADDF-STEM. It is noteworthy that the Se atoms in the alloyed nanosheets have a comparable brightness as that of the Mo atoms because of their far larger Z number compared with that of S atoms. Meanwhile, the preparation of $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheet with tunable composition via the CVD method was also achieved by Bartels and coworkers, in which MoO_3 was used as the Mo source and thiophenol/diphenyl-diselenide dissolved in tetrahydrofuran was used as

the S/Se source.^[91] Simultaneously, the large-area growth of alloyed $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheet with tunable composition by the CVD method was reported by Xie, Zhang and coworkers, using MoS_2 and MoSe_2 as precursors.^[92] In addition, the shape-tuning of the prepared alloyed $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheets by simply changing the CVD growth temperature was also demonstrated by the same group.^[93] Generally, alloyed $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheet with different shapes, including hexagons with straight edges, triangles with straight edges and triangles with inward curving edges can be successfully prepared at different growth temperatures, i.e. 670 °C, 630 °C, and 750 °C, respectively. Furthermore, the alloyed $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheet with tunable composition was demonstrated by Li, He and coworkers via the selenization of CVD-grown MoS_2 nanosheet by the vapor Se.^[94] Likely, the $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheet with tunable chemical composition was synthesized by Duan, Pan and coworkers, by the reaction of MoO_3 with S/Se vapor at the temperature of 830 °C.^[46] As shown in **Figure 2.3d**, the prepared $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheet exhibited a triangular shape with the lateral size of a few tens of micrometers. Moreover, these alloyed $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheet demonstrates the gradual change of Raman spectra signals which is dependent on the composition. These alloyed nanosheets exhibited four Raman modes, which can be assignable to MoS_2 -like and MoSe_2 -like A_{1g} and E_{2g} peaks of alloyed $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheets (**Figure 2.3e**). The continuous shifting of PL emission from 668 to 795 nm can be clearly observed on the alloyed $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheet, with the decreasing of x values from 1 to 0, which is presented in **Figure 2.3f**. Notably, the growth of composition-graded bilayer alloyed $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheets was also reported by their group via an modified CVD method,^[95] in which the composition of a individual sheet could be gradually changed from the pure MoS_2 ($x = 1$) to $\text{MoS}_{0.64}\text{Se}_{1.36}$ ($x = 0.32$) from the center to edge of the nanosheet, giving rise to the tunable bandgap at the range of 1.82-1.64 eV.

In addition to the CVD method, the alloyed $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheet can also be synthesized by other methods. For instance, the synthesis of few-layer $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ (with $x = 0, 0.33, 0.5, 0.66$ and 1) nanosheets using the colloidal synthesis method was reported by Li, Liu and coworkers, by the reaction of MoCl_5 with S/Se powders dissolved in a mixed solvent of oleylamine and 1-octadecene at the temperature of 300 °C.^[47] As another example, the

monolayer $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ and $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheets were also prepared by our group via combining the CVT and electrochemical Li intercalation-assisted exfoliation method.^[96] First, the micro-sized 2H-phase $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ and $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ bulk crystals were first prepared by the well-developed CVT method. The electrochemical Li intercalation and exfoliation method was then used to exfoliate the obtained bulk crystals of $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ and $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ into single-layer nanosheets. The whole exfoliation process is schematically presented in **Figure 2.4a**.^[96] The prepared monolayer nanosheets were then investigated by TEM and AFM, showing the lateral size of a few micrometers and the thickness of around 1.1-1.2 nm (**Figure 2.4b,c**).^[96] Energy-dispersive X-ray spectroscopy (EDX) elemental mapping was conducted to reveal the elemental composition of Mo, S and Se (**Figure 2.4d**).^[96] It is noteworthy that the phase of the obtained monolayer $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ and $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheets can transform from original semiconducting 2H phase into metallic 1T phase after exfoliation, which is induced by the Li intercalation (**Figure 2.4a**).^[96] The XPS, UV-vis spectroscopy and HADDF-STEM were used to investigate the monolayer $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ and $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheets, indicating the existence of metallic 1T phase with high concentration. As demonstrated in **Figure 2.4e**, Mo atoms arranging in a triangular shape and Se atoms located at the center of Mo triangles can be observed from the HADDF-STEM image of monolayer $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheet, revealing its 1T phase crystal structure.^[96] It is well known that because of the stacking of two S atoms in the same position in 2H phase $\text{MoS}_{2x}\text{Se}_{2(1-x)}$, S atoms can exhibit comparable brightness in HADDF-STEM image. On the other hand, because of the dislocation of two S atoms and its relatively small Z number than that of Mo and Se atoms, S atoms were invisible in the metallic 1T phase $\text{MoS}_{2x}\text{Se}_{2(1-x)}$. The presence of metallic 1T phase with high concentration (~66%) in obtained $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheet was also confirmed by the XPS spectra (**Figure 2.4f**).^[96] Similarly, the UV-vis spectra of the prepared nanosheet with high-concentration metallic 1T phase exhibited a smooth line without any obvious absorption peaks, while the characteristic A and B excitonic peaks of 2H-phase $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ can be seen in the annealed 2H phase nanosheets (**Figure 2.4g**), which further firmly confirm the existence of metallic 1T phase in the exfoliated nanosheets.^[96]

Figure 2.4 (a) Schematic illustration of preparation of single-layer alloyed $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheets with metallic 1T phase. (b) TEM and (c) AFM images of single-layer $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheets. (d) Atomic scale HADDF-STEM image of $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheets. (e) STEM image and corresponding EDX elemental mapping of $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheets. (f) High-resolution Mo 3d XPS spectra of $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ of bulk crystal, and the exfoliated and annealed nanosheets. (g) UV-vis absorption spectra of the exfoliated and annealed $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheet films on glass.^[96]

Besides $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ and $\text{MoS}_{2x}\text{Se}_{2(1-x)}$, other alloyed TMD nanosheets, such as $\text{MoSe}_{2x}\text{Te}_{2(1-x)}$, $\text{WS}_{2x}\text{Se}_{2(1-x)}$ and $\text{ReS}_{2x}\text{Se}_{2(1-x)}$, have also been synthesized recently. For instance, the preparation of single-layer alloyed triangular $\text{WS}_{2x}\text{Se}_{2(1-x)}$ nanosheet with tunable composition was first reported by Xiang and coworkers via the reaction of WO_3 with S/Se vapor in a CVD system.^[97] Moreover, the synthesis of alloyed $\text{WS}_{2x}\text{Se}_{2(1-x)}$ nanosheet with tunable composition was also demonstrated by Duan and coworkers through the home-made CVD system by using WS_2 and WSe_2 as precursors.^[98] Specifically, the alloyed $\text{WS}_{2x}\text{Se}_{2(1-x)}$ nanosheets were formed on downstream SiO_2/Si substrates by the re-

crystalizing process of the mixed vapors transported from the upstream areas of the CVD furnace, which is produced by the WS_2 and WSe_2 precursors placed separately in upstream areas. The heating temperature of the WS_2 and WSe_2 sources is the key point to control the S/Se ratios in resultant alloyed $\text{WS}_{2x}\text{Se}_{2(1-x)}$ nanosheets. Optical microscopy, Raman spectroscopy, PL spectroscopy and TEM were then used to characterize the alloyed $\text{WS}_{2x}\text{Se}_{2(1-x)}$ nanosheets. Recently, it was found that by combining the CVD method with the chemical Li-intercalation and exfoliation method, few-layer $\text{WS}_{2x}\text{Se}_{2(1-x)}$ nanoribbons with metallic 1T phase can also be successfully synthesized.^[99] In addition, it was reported by Liu and coworkers that the single-layer $\text{MoSe}_{2x}\text{Te}_{2(1-x)}$ nanosheets can be mechanically exfoliated from the CVT-grown bulk crystals.^[100] Typically, the single crystals of $\text{MoSe}_{2x}\text{Te}_{2(1-x)}$ with fully tunable compositions ($x = 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9$ and 1) were first prepared by the CVT method from their corresponding elementary powders. These bulk crystals were then cleaved by the scotch tape to form the single-layer $\text{MoSe}_{2x}\text{Te}_{2(1-x)}$ via the mechanical exfoliation technique. Notably, a phenomenon of composition-dependent crystal phases can be observed from the alloyed $\text{MoSe}_{2x}\text{Te}_{2(1-x)}$ nanosheet. For example, the alloyed $\text{MoSe}_{2x}\text{Te}_{2(1-x)}$ nanosheet crystallized in a metallic 1T' phase when $x = 0.4-0$ and semiconducting 2H phase when $x = 1-0.6$, respectively. More importantly, the mixture of 2H and 1T' phases were obtained in the alloyed $\text{MoSe}_{2x}\text{Te}_{2(1-x)}$ nanosheet when $x = 0.6$ and 0.5 . The composition-dependent crystal phases and electronic properties were fully investigated by HADDF-STEM imaging, Raman spectroscopy, PL spectroscopy and device characteristics. In addition, the synthesis of alloyed $\text{ReS}_{2x}\text{Se}_{2(1-x)}$ nanosheet with tunable bandgap and fully tunable composition ($x = 1.0, 0.82, 0.62, 0.42, 0.19$ and 0) can be achieved by the combination of CVT and mechanical exfoliation methods, which was demonstrated by Xie and coworkers.^[101] The as-prepared alloyed 1T'-phase $\text{ReS}_{2x}\text{Se}_{2(1-x)}$ nanosheet were characterized by HADDF-STEM, TEM, Raman spectroscopy, optical microscopy and PL spectroscopy, exhibiting anisotropic electrical and spectroscopy properties due to its highly asymmetric 1T' crystal structure.

2.3.3 Heteroatom-doped Ultrathin 2D Metal Chalcogenide Nanosheets

Heteroatom doping is an effective way for tuning of the electronic properties of

nanomaterials for the purpose of obtaining better performance in specific applications, such like catalysis and electronic devices.^[102-104] Recently, the doping of heteroatoms into 2D TMD nanosheets has attracted a lot of attentions due to the successfully doping of heteroatoms in other nanomaterials. Consequently, a variety of elements, including Mn, Cr, Er, V, Re, Co, Au and Pt, have been adopted as dopants to modify 2D TMDs by various methods. Among them, exfoliating the heteroatom-doped TMD bulk crystals for the preparation of heteroatom-doped TMD nanosheets is a promising way. For instance, Suenaga and coworkers demonstrated that monolayer Re-doped MoS₂ and Au-doped MoS₂ nanosheets can be prepared by combining the mechanical exfoliation and CVT methods.^[38] Generally, the Au-doped MoS₂ and Re-doped MoS₂ bulk crystals with doping concentration of 0.5~1 at% were first synthesized by the CVT method, followed by the mechanical exfoliation of the grown bulk crystals to form the monolayer nanosheet of Au-doped MoS₂ and Re-doped MoS₂. As demonstrated in **Figure 2.5a,b**, the Au and Re atoms doped in the MoS₂ lattice can be clearly seen in the HADDF-STEM images, due to the brighter contrast of Re and Au atoms than that of Mo atoms.^[38] Moreover, the in-situ TEM technique was used to study the correlation between the energetics and migration behaviors of doped atoms. Similarly, the synthesis of few-layer Mo-doped ReSe₂ was reported by Yang and coworkers via the mechanical exfoliation of the CVT-grown Mo-doped ReSe₂ bulk crystal.^[105] The CVD method is another effective approach to directly prepare heteroatom-doped TMD nanosheet. For instance, the Mn-doped MoS₂ nanosheets were first prepared by Robinson and coworkers by this method.^[49] In their experiments, the used substrate was found to play an crucial role in the fulfillment of Mn doping. As a result, the doping of Mn atoms into MoS₂ could be achieved by using inert substrates, such as graphene (**Figure 2.5c**), while the substrates with reactive surface terminations will give rise to the formation of defective MoS₂ nanosheets without doping, such as SiO₂ and sapphire. Later on, the growth of double-layer Co-doped MoS₂ nanosheets prepared by the CVD method was reported by Li, Wei and coworkers.^[39] It was discovered that the Co atoms mainly doped at the edges sites of nanosheets when the reaction temperature was set at 680 °C. When the growth temperature was set at 750 °C, the CoS₂ film with a cubic pyrite-type structure could be obtained on the surface of Co-doped MoS₂ nanosheet. Similarly, the CVD method was also used to synthesize Er-doped MoS₂ nanosheet from

Er-doped Mo thin film (**Figure 2.5d**).^[52] As illustrated in **Figure 2.5e**, the doped Er atoms in MoS₂ can be clearly observed in the HADDF-STEM image. Interestingly, the Er-doping can lead to the up- and down-conversion NIR PL emission of MoS₂ nanosheet. As another example, Warner, Robertson and coworkers proved the existing of Cr and V doping in the CVD-grown MoS₂ nanosheet, which were prepared from the MoO₃ precursor.^[40] It was found that during CVD growth process, very small amount of Cr and V elements impurities presented in the MoO₃ precursor could be finally doped into the formed MoS₂ nanosheets. The HADDF-STEM and electron energy loss spectroscopy (EELS) spatial mapping were used to identify the truth that some of Mo sites of MoS₂ nanosheets were substituted by Cr and V atoms.

Figure 2.5. Atomic scale HADDF-STEM images of (a) Re- and (b) Au-doped single-layer MoS₂.^[38] (c) Atomic scale HADDF-STEM images of Mn-doped single-layer MoS₂.^[49] (d) Schematic illustration of growth of Er-doped MoS₂. (e) Atomic scale HADDF-STEM image of Er-doped single-layer MoS₂.^[52] (f) TEM image and (g) atomic scale HADDF-STEM image of Pt-doped MoS₂ nanosheets. (h) The comparison k²-weighted EXAFS spectra of Pt-doped MoS₂, Pt foil and commercial 40% Pt/C.^[41]

In addition, besides CVT or CVD combined with exfoliation techniques, various solution-based methods could also be used for the preparation of heteroatom-doped TMD nanosheet. For example, the preparation of O-doped MoS₂ nanosheet via the hydrothermal method using thiourea and ammonium molybdate tetrahydrate as precursors was first reported by Xie and coworkers.^[106] The concentration of O-doping in prepared MoS₂ nanosheet can be finely tuned from 4.18 at%, 3.36 at% and 2.28 at% to 1.92 at% by simple change of the reaction temperature from 140 °C, 160 °C and 180 °C to 200 °C, respectively. Later on, the preparation of S-doped MoS₂ nanosheets by a colloidal synthetic method was demonstrated by Yan and coworkers.^[107] As another example, Chen, Lei and coworkers demonstrated that the N-doped MoS₂ nanosheets can be synthesized via a sol-gel method followed by thermal annealing treatment, with the N doping concentration of 5.8-7.6 at%.^[108] Moreover, Bao, Deng and coworkers showed that the few-layer Pt-doped MoS₂ nanosheets can be prepared by the simple hydrothermal method.^[41] As demonstrated in **Figure 2.5f**, the prepared Pt-doped MoS₂ exhibited a flower-like structure assembled with few-layer nanosheet, in which the doped Pt atoms can be obviously observed by the HADDF-STEM imaging technique (**Figure 2.5g**). Furthermore, only Pt-S bond and no Pt-Pt bond were observed from the extended EXAFS spectra (**Figure 2.5h**), which proved the presence of single-atom doping as well as the disappearing of Pt particles or clusters in Pt-doped MoS₂ nanosheet. As another example, the preparation of a number of few-layer metal-doped WS₂ nanosheet by a colloidal synthetic method was reported by Liu and coworkers, including Ni-, Mn-, Fe-, Co- and Gd-doped WS₂.^[109]

2.4 Applications of Multinary Layered Metal Chalcogenides

It is well known that 2D binary layered TMD nanosheets with ultrathin thickness, such as MoS₂, MoSe₂, WS₂ and WSe₂, have been found to be promising candidates in various applications due to their special physical, chemical and electronic properties. As discussed, the layered multinary metal chalcogenide nanomaterials demonstrated a number of advantages when compared with the 2D binary counterparts. Therefore, they are also expected to be superior in some applications. To date, they have been investigated in a number of applications and did show great performances in most of the examples because

of their multinary chemical compositions, tunable bandgap and doping effect. In this part, the discussion on utilizing the 2D multinary layered metal chalcogenide nanomaterials with ultrathin thickness for various potential applications will be presented.

2.4.1 Catalysis

Ultrathin 2D TMD nanosheets, such as MoS₂, MoSe₂, WS₂ and WSe₂, have showed great potential to be used as catalysts for electrocatalytic HER because of their high catalytic activity and earth abundance.^[110-113] However, there is still a lot of room for the improvement on the catalytic activity of 2D TMD nanomaterials for HER. Therefore, tremendous efforts have been devoted to the research and invention of novel ultrathin multinary layered metal chalcogenide nanomaterials toward HER, for the purpose of achieving higher activity.

Recent research has proved that the heteroatom-doped TMD nanomaterials are promising candidates for the replacement of raw TMD nanosheets for enhanced HER performance. For example, it was found that the O-doping in MoS₂ nanosheets, forming O-doped MoS₂, played an important role on the enhancement of electrocatalytic activity of MoS₂ nanosheets.^[106] A low onset potential of 120 mV and a small Tafel slope of 55 mVdec⁻¹ can be achieved by the optimal O-doped MoS₂ nanosheet, which is labelled as S180 (**Figure 2.6a,b**).^[106] More importantly, the O-doped MoS₂ nanosheet exhibited great long-term stability, in which the HER activity remained almost the same as that of the initial cycles after a continuous test of 3,000 cycles (**Figure 2.6c**).^[106] The proper disorder engineering on MoS₂ nanosheets was found to be the key points to increase the active sites by the increase of the number of unsaturated sulfur atoms. Meanwhile, the intrinsic conductivity of MoS₂ can be greatly enhanced via the oxygen incorporation. The enhancement of HER performance of the O-doped MoS₂ compared with the pure MoS₂ is mainly induced by both of the two synergistically factors. As another example, the enhanced HER catalytic performance was also observed on the ultrathin S-doped MoSe₂ nanosheets when compared with the pure MoSe₂ nanosheets, exhibiting a low onset potential of 90 mV and a small Tafel slope of 58 mV dec⁻¹.^[107] The HER activity only

showed a slight loss after 10,000-cycle test, suggesting its excellent long-term stability. It is concluded that the enhancement on HER performance of the S-doped MoSe₂ resulted from the increase number of unsaturated active sites induced by the sulfur substitution. In addition to the non-metal element doping, the single-metal-atom-doped 2D MoS₂ nanosheet was prepared by Bao and coworkers for the improved electrocatalytic HER performance, including Ni-doped, Co-doped and Pt-doped MoS₂.^[41] Compared with that of pure few-layer MoS₂ nanosheets, the Pt-doped MoS₂ exhibited superior performance with the reduction of 60 mV on the onset potential at the current density of 10 mA cm⁻² as well as the great long-term durability with slight degradation after 5,000 cycling test. It was revealed by the density functional theory (DFT) calculation that the tuned behavior of intermediate H atoms absorbed on the in-plane S sites beside the doped Pt atoms is the reason for the enhancement of activity. Similarly, the Ni-doped MoS₂ and Co-doped MoS₂ also showed improved HER activity compared to the pure MoS₂ nanosheets.^[41]

Figure 2.6 (a) Polarization curves and (b) the corresponding Tafel plots of various O-doped MoS₂ nanosheets. Inset in (a): The enlarged region near the onset. (c) Polarization curves of optimal O-doped MoS₂ nanosheets (S180) before and after 3000 cycles.^[106] (d) Schematic illustration of the electrocatalytic activity of monolayer WS_{2x}Se_{2(1-x)} triangular domains in the HER. (e) The polarization curves after iR correction of monolayer WS_{2x}Se_{2(1-x)} ($x = 0.57$), monolayer WS₂, monolayer WSe₂, Pt and glass carbon (GC) electrode. (f) Tafel plots of the WS_{2x}Se_{2(1-x)} ($x = 0.57$), WS₂ and WSe₂ monolayer, and Pt.^[97]

Besides the heteroatom-doped TMD nanosheets, the alloyed TMD nanosheet also showed

improved catalytic activity for electrochemical HER reaction when compared with the binary TMD nanosheets. For instance, Li and coworkers reported that the improved electrocatalytic HER activity can be obtained by tuning the chemical composition of ultrathin alloyed $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanoflakes.^[47] Notably, the $\text{MoS}_{1.0}\text{Se}_{1.0}$ nanoflake was found to be the best catalyst for HER in the alloyed $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ series in terms of onset potential, showing 50-60 mV smaller than that of MoS_2 and 10-20 mV smaller than that of MoSe_2 . As regards the turnover frequency (TOF) of the reaction at the overpotential of 150 mV, the $\text{MoS}_{1.0}\text{Se}_{1.0}$ nanoflake also exhibited the highest values among all the $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanoflakes, which is about 2 times that of MoS_2 . Moreover, the prepared $\text{MoS}_{1.0}\text{Se}_{1.0}$ nanoflake also showed great durability with the activity after 8,000 cycles almost remaining the same as the first cycle. The optimal hydrogen adsorption behavior caused by the alloying effect is found to be the critical factor for the enhancement of HER activity. In addition, the single-layer CVD-grown $\text{WS}_{2x}\text{Se}_{2(1-x)}$ triangular nanosheets also showed great potential in electrocatalytic HER with improved activity (**Figure 2.6d**).^[97] Specifically, compared to those of WS_2 (100 mV) and WSe_2 (150 mV), the smallest onset potential at around 80 mV can be achieved on $\text{WS}_{2x}\text{Se}_{2(1-x)}$ ($x = 0.57$) nanosheets (**Figure 2.6e**). Regarding of the Tafel slope, the $\text{WS}_{2x}\text{Se}_{2(1-x)}$ ($x = 0.57$) nanosheets also showed enhanced activity with the measured data of 85 mV dec^{-1} , which is smaller than that of monolayer WSe_2 (100 mV dec^{-1}) and WS_2 (95 mV dec^{-1}) (**Figure 2.6f**). It is concluded that, compared to the monolayer WS_2 and WSe_2 , the enhancement on HER activity of $\text{WS}_{2x}\text{Se}_{2(1-x)}$ nanosheet may result from the activation of the inert basal plane, which is originated from the polarized electric field localized in the basal plane. This is mainly caused by the Se-doping induced crystal distortion. Moreover, He and coworkers demonstrated that the metallic 1T phase $\text{WS}_{2x}\text{Se}_{2(1-x)}$ nanoribbon can also be used as catalysts for superior electrocatalytic HER.^[99] Generally, compared to the 2H phase $\text{WS}_{2x}\text{Se}_{2(1-x)}$ ($x = 0.78$) nanoribbons, the exfoliated $\text{WS}_{2x}\text{Se}_{2(1-x)}$ ($x \approx 0.78$) nanoribbons metallic 1T phase showed a lower onset overpotential of $\sim 170 \text{ mV}$ at the current density of 10 mA cm^{-2} , the smallest Tafel slope of around 68 mV dec^{-1} as well as the great long-term stability after 1,000 cycling tests. It was concluded that the enhancement of HER performance is resulted from more active sites induced by the 1T phase as well as the favorable ΔG_{H}^0 caused from the surface tensile regions. This is also proved by the reduced

charge transfer resistance of 50 Ω and the small series resistance of around 1.8 Ω .

Moreover, ultrathin ternary metal chalcogenide nanosheets also showed great potentials for the electrocatalytic HER. For example, it was found that the ternary Cu_2WS_4 nanosheets with body-centered crystal structure obtained via the chemical Li-intercalation and exfoliation method could also be an efficient catalyst for HER. Compared with the bulk counterpart (around 500 mV), the exfoliated ternary Cu_2WS_4 nanosheets showed better catalytic performance with a lower onset potential of ~170 mV.^[114] Furthermore, it was found that the rate-determining step is resulted from the adsorption of protons on the catalyst surface, which is confirmed by the smaller Tafel slope of 95 mV dec⁻¹ of exfoliated ternary Cu_2WS_4 nanosheets when compared with the bulk Cu_2WS_4 (120 mV dec⁻¹). Due to more active sites formed on the prepared nanosheet, Cu_2WS_4 nanosheet exhibited an exchange current density of 177 mA cm⁻², which is 5.8 times higher than that of the bulk counterpart (26 mA cm⁻²). Moreover, a 2,000-cycling test was conducted to evaluate stability of the exfoliated Cu_2WS_4 nanosheets, showing negligible degradation on catalytic activity.

2.4.2 Energy Storage and Conversion

Because of the tunable properties resulted from their versatile composition as well as the rich earth abundance, 2D multinary layered metal chalcogenide nanomaterials with ultrathin thickness are also considered as one of the promising candidates for the energy conversion and storage. For instance, it is reported by Xie and coworkers that the exfoliated hydrogenated- Cu_2WS_4 nanosheet could be used fabricating all-solid-state flexible supercapacitor with high performance.^[36] Impressively, an excellent conductivity up to $2.9 \times 10^4 \text{ S m}^{-1}$, can be measured on the exfoliated hydrogenated- Cu_2WS_4 nanosheet, which is 10^{10} times higher than that of the semiconducting bulk counterparts. Typically, the hydrogenated- Cu_2WS_4 nanosheet film was deposited on the gold-coated PET substrate, in which the fabricated device and the polyvinyl alcohol (PVA)–LiCl gel was utilized as the working electrode and solid-state polymer electrolyte, respectively. Moreover, a specific capacitance as high as of 583.3 F cm⁻³ can be obtained on the hydrogenated- Cu_2WS_4 based

all-solid-state supercapacitor when the tested current density is 0.31 A cm^{-3} , which is showed in **Figure 2.7a-c**.^[36] An energy density of 0.029 Wh cm^{-3} can be achieved at the same current density, resulting in a power density of 0.187 W cm^{-3} . In addition, the supercapacitor fabricated on the hydrogenated- Cu_2WS_4 nanosheets showed great flexibility without evident degradation on capacitance after 500 bending cycles, making it promising for fabrication of wearable devices for energy storage. As another promising example, it was found that monolayer $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheets with metallic 1T phase can be utilized as the cost-effective counter electrode (CE) in fabrication of dye-sensitized solar cell (DSSC) with high efficiency (**Figure 2.7d**).^[96] Typically, the simple drop-casting method was utilized to coat the $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheet onto a fluorine-doped tin oxide (FTO) (FTO-exfoliated- $\text{MoS}_{2x}\text{Se}_{2(1-x)}$) to form the device. A high-power conversion efficiency (PCE) of 6.5% was measured on the DSSC device using the as-fabricated FTO-exfoliated- $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ as the CE, which is much higher than that of the annealed 2H phase $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheet-based CE (FTO-annealed- $\text{MoS}_{2x}\text{Se}_{2(1-x)}$) (5.4%). As demonstrated in **Figure 2.7e**, this result is also close to the data measured on a DSSC device using Pt-decorated FTO (FTO-Pt) as the CE (7.0%).^[96] The higher electrocatalytic activity of the exfoliated nanosheets for tri-iodide reduction was revealed by the cyclic voltammetry (CV) test, which is concluded to be the main factor for the higher photovoltaic performance of the FTO-exfoliated- $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ (**Figure 2.7f**).^[96] Note that the high conductivity caused by the metallic 1T phase of $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheet also played an important role on enhancing the tri-iodide reduction caused by the faster electron transport from the CE surface to the redox electrolyte.

Figure 2.7 (a) CV curves and (b) Galvanostatic charge-discharge curves of the as-fabricated supercapacitor at different scan rates and different current densities, respectively. (c) The Plot of specific capacitance versus current density. Inset: Structural illustration of the as-fabricated supercapacitor. ^[36] (d) Schematic illustration of a typical DSSC device. (e) J - V curves of DSSCs with different CEs. (f) CV curves of different CEs. ^[96]

2.5 Questions to Answer Based on Literature

As discussed in the aforementioned literature review, great research progress has been made on the preparation, characterization and applications of an arising family of layered 2D nanomaterials with ultrathin thickness, i.e. ultrathin multinary layered metal chalcogenide nanomaterials. However, there are still questions remaining unclear and requiring deep research.

First, it has been reported that ultrathin 2D multinary layered metal chalcogenide nanomaterials can be used in many proof-of-concept potential applications, but the performance is still affected by the crystal phase, size, thickness, shape, interface and doping effect. However, the deeper correlated effect between the detailed structural characteristics and a specific application of layered multinary metal chalcogenide nanomaterials is still a mystery. For example, the defect engineering of TMD nanomaterials has attracted much attention due to the great enhancement on electrocatalytic HER. These studies currently only focus on 2H/1T phase TMD nanomaterials, but rarely

on 1T' phase TMDs. Different with 2H and 1T phase structure, there are two types of chalcogenide atoms in 1T' phase TMDs, which can result in different kinds of vacancies. How to understand the fundamental principles is fundamentally crucial for further guidance of the rational design and preparation of ideal ultrathin metal chalcogenide nanomaterials for electrocatalysis to achieve improved or optimal performance.

Second, currently, only a few 2D multinary layered metal chalcogenide nanomaterials with ultrathin thickness, such as 1T-MoS₂ and Cu₂WS₄ nanosheets have been proved to be great candidate of electrode materials for fabrication of supercapacitors, because of their high intrinsic electrical conductivity and the ability of the restacked nanosheets for the intercalation of various ions. One may wonder whether there are some new ultrathin 2D multinary metal chalcogenide nanomaterials with intrinsic metallic phases, which can also be synthesized by the common or newly developed methods. If this is possible, they may be suitable for fabrication of high-performance supercapacitors due to the intrinsic high electrical conductivity. Different from the exfoliated MoS₂ nanosheets by Li-assisted intercalation method, which only have around 60-70% 1T phase, the metallic multinary layered metal chalcogenide nanomaterials may exhibit higher performance if there is not any phase transition causing the reduction of electrical conductivity.

2.6 PhD in Context of Literature

In my thesis, I focus on preparing multinary layered ultrathin metal chalcogenide nanodots and nanosheets, and then exploring the possibility of these nanomaterials in the field of energy storage and conversion, such as electrocatalysis and supercapacitor. The contribution of my thesis in this area is list as follow:

First, it is identified that the 1T'-phase ReS_{2x}Se_{2(1-x)} series, including ReS₂, ReS_{1.8}Se_{0.2}, ReS_{1.4}Se_{0.6}, ReSSe, ReS_{0.6}Se_{1.4}, ReS_{0.2}Se_{1.8}, and ReSe₂, are the ideal catalyst for the investigation of the effects of structural asymmetry on electrocatalytic HER because of their intrinsic 1T' crystal structure. It is also found that the well-developed chemical Li-intercalation and exfoliation method is applicable for the preparation of ReS_{2x}Se_{2(1-x)}

nanodots. This study further proved that defect engineering is an important strategy for TMD-based electrocatalysts. More importantly, this project firmly confirms that the asymmetric vacancy is critical for enhanced electrocatalytic activity, which may guide the rational design and synthesis of more multinary 1T' phase TMD-based electrocatalysts for highly efficient water splitting.

Second, it is proved that the chemical Li-intercalation and exfoliation method can be used for the preparation of single-layer new multinary metal chalcogenide nanosheets with metallic phase, including $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ and $\text{Ni}_3\text{Cr}_2\text{P}_2\text{Se}_9$. It has been proved that these exfoliated 2D metal chalcogenide nanosheets inherit the high electrical conductivity from their bulk counterparts. Moreover, these as-prepared ultrathin multinary nanosheets can easily form a restacked film via vacuum filtration method, which can be used for fabrication of supercapacitors, exhibiting remarkable performance in 0.5 M H_2SO_4 electrolytes. This work may give the guidance for design and preparation of suitable multinary metal chalcogenide nanomaterials for energy storage application such as supercapacitor.

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Chapter 3

Experimental Methodology

In this chapter, the rational selection of synthetic methods and target materials is first discussed. Then, the used chemicals and the experimental procedures for synthesis of ultrasmall metal chalcogenide nanodots as well as the ultrathin metal chalcogenide nanosheets are presented. Subsequently, the description of the techniques and equipment used for characterization will be demonstrated. Finally, the details of the device fabrication and performance measurements based on ultrasmall metal chalcogenide nanodots and ultrathin 2D metal chalcogenide nanosheets are summarized.

3.1 Rationale for Selection of Materials and Methods

In the first part of the thesis, the series of $\text{ReS}_{2x}\text{Se}_{2(1-x)}$ ($x=0-1$) were selected as the target materials and the chemical Li-intercalation and exfoliation method was used to exfoliate these materials into nanodots with desired defects. From the material point of view, it has been pointing out that $\text{ReS}_{2x}\text{Se}_{2(1-x)}$ possess the thermodynamically stable 1T' phase, which is critical for the systematical study of asymmetric vacancy effect on the 1T' TMD nanomaterials. Furthermore, the tunable chemical composition and bandgap may endow them with enhanced electrocatalytic activity and durability compared the binary TMD based catalysts, which makes $\text{ReS}_{2x}\text{Se}_{2(1-x)}$ the ideal catalysts for the fundamental study of the defect-engineering on 1T'-phase TMDs for HER. From the method point of view, previous study has demonstrated that the ReS_2 (nanosheets can be prepared from their bulk crystals using the chemical Li-intercalation and exfoliation method using LiBH_4 as the Li source and the exfoliated ReS_2 nanosheets showed HER activity in acid medium. Moreover, our group has developed a method of combining the ball milling process and Li-intercalation process for the preparation of 1T-MoSSe nanodots for electrocatalytic HER. Therefore, it is reasonable that the chemical Li-intercalation and exfoliation method can be applied in the synthesis of 1T'-phase $\text{ReS}_{2x}\text{Se}_{2(1-x)}$ nanodots. For the application point of view, the asymmetrical vacancy effect on electrocatalytic HER was investigated, since the defect-induced structural change may alter the Gibbs free energies (ΔG_{H^*}) for absorbing the intermediate hydrogen atoms, which may greatly enhance the catalytic performance.

In the second part of the thesis, $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ and $\text{Ni}_3\text{Cr}_2\text{P}_2\text{Se}_9$ nanosheets were chosen as the target materials and the chemical Li-intercalation and exfoliation method was also used to exfoliate these materials into single- or few-layer nanosheets. From the material point of view, studying novel materials is usually an effective strategy to obtain some exciting results, such as the discovery of MoS_2 for HER and black phosphorous for FET device fabrication, which has led the hot research direction in the past decade. Currently, most of the research work on of metal chalcogenide nanosheet mainly focused on the binary compound, such as MoS_2 , MoSe_2 , WS_2 , WSe_2 etc., only a few results have reported on the multinary metal chalcogenide nanosheets. For instance, it has reported by our group that

the ternary Ta_2NiS_5 and Ta_2NiSe_5 nanosheets exfoliated from their bulk crystals exhibited extraordinary sensing ability on DNA detection, indicating that multinary metal chalcogenide nanosheets may also be an effective platform for construction of fluorescent sensors. Since $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ and $\text{Ni}_3\text{Cr}_2\text{P}_2\text{Se}_9$ have the similar layered structure like Ta_2NiS_5 and Ta_2NiSe_5 , it may also be able to be exfoliated into monolayer or few-layer nanomaterials.

From the method point of view, as presented literature review part, the chemical Li-intercalation and exfoliation method is effective for preparation of ternary Cu_2WS_4 nanosheets with high yield, which may be also suitable for preparation of $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ and $\text{Ni}_3\text{Cr}_2\text{P}_2\text{Se}_9$ nanosheets. Moreover, this method has showed great potential for preparation of ternary $\text{ReS}_{2x}\text{Se}_{2(1-x)}$ series alloyed TMD nanodots with high yield. Therefore, it is reasonable to believe that this method may be also useful for the preparation of monolayer or few-layer $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ and $\text{Ni}_3\text{Cr}_2\text{P}_2\text{Se}_9$ nanosheets from their bulk crystals, due to their similar multinary elemental composition and layered structure. From the application point of view, it has been confirmed that monolayer 1T-phase MoS_2 nanosheets are highly effective electrode material for fabrication of supercapacitor, owing to their intrinsic high electrical conductivity, hydrophilicity and the ability to accommodate ions in the restacked film. While for $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ and $\text{Ni}_3\text{Cr}_2\text{P}_2\text{Se}_9$ nanosheets, their bulk crystals have been proved to be metallic with high electrical conductivity. Therefore, it is believed that the restacked film consisting of $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ and $\text{Ni}_3\text{Cr}_2\text{P}_2\text{Se}_9$ nanosheets may also have great potential to be used to fabricate high performance supercapacitors.

3.2 Chemicals and Synthesis

3.2.1 Chemicals

Rhenium powder (~22 mesh, 99.999%, Puratronic[®]), sulfur pieces (99.999%, Puratronic[®]) and selenium shots (1-3 mm, 99.999%, Puratronic[®]), nickel powder (~325 mesh, 99.8%), chromium powder (~325 mesh, 99%), red phosphorus lump (99.999% (metal basis), Puratronic[®]), sulfur pieces (99.9995% (metal basis), Puratronic[®]) and/or selenium shots

(amorphous, 2-6 mm (0.08-0.2 in), 99.999%, Puratronic[®]) were purchased from Alfa Aesar (USA). The *n*-Butyllithium solution (~2.0 M in cyclohexane), *n*-hexane (anhydrous, 95%) and commercial Pt/C (10 wt.% loading, matrix activated carbon support) were purchased from Sigma-Aldrich (Germany). Ultrafiltration tubes (Millipore, 4.0 mL, 10KD) were purchased from Merck Pte Ltd (Singapore). All the chemicals were used as received without further purification. The Milli-Q water (Milli-Q System, Millipore) was used in all experiments.

3.2.2 Synthesis of $\text{ReS}_{2x}\text{Se}_{2(1-x)}$ Bulk Crystals

Chemical vapor transport (CVT) method was utilized to synthesize all the solid solutions of $\text{ReS}_{2x}\text{Se}_{2(1-x)}$ ($0 \leq x \leq 1$) layered bulk crystals based on the previous reports^[1-4] with slight modification. Halogens (I_2 or Br_2) were employed as the transport agent in the synthetic process. Stoichiometric amounts of rhenium, sulfur and/or selenium were vacuum-sealed in quartz ampoules with the internal pressure in the range of 10^{-5} to 10^{-6} Torr. In addition to the elemental constituents, iodine (2mg/cc) was also incorporated into the quartz ampoule as a transport agent. Iodine was sealed in a small capillary to avoid contamination of the vacuum pump. The sealed tubes were then subjected to two-zone horizontal tube furnace.

Initially, the source zone (T1) and the growth zone (T2) were kept at 900 °C and 1000 °C, respectively, for 120 h. It allows the constituents to completely react and prevents the back transport. Then, the temperature of source zone (T1) was increased to 1060 °C step by step, while that of growth zone (T2) remained at 1000 °C. It was kept for another 240 h. Then, the temperatures of both zones were lowered to room temperature. After the ampoules were taken out from the tube furnace, the well-grown compounds were collected for further characterizations and subsequent measurements.

3.2.3 Preparation of $\text{ReS}_{2x}\text{Se}_{2(1-x)}$ Nanodots

After performing the ball milling process of the grown bulk crystals, the corresponding ground powders were used to prepared ultrasmall and ultrathin $\text{ReS}_{2x}\text{Se}_{2(1-x)}$ nanodots via the chemical Li-intercalation method. Taking ReSSe as an example, 30 mg of ReSSe powder were intercalated with 3 mL of *n*-butyllithium solution (2.0 M in cyclohexane) for 72 h in a glove box under Ar atmosphere. After the reaction, the upper solution containing unreacted *n*-butyllithium was removed carefully with pipet. The Li-intercalated powder was then washed with *n*-hexane by centrifuge at 2,000 r.p.m for three times to the further removing of the excessive *n*-butyllithium, followed by sonication in 60 ml of water for 30 min to get a uniform solution with exfoliated products. The obtained suspension was further centrifuged with the speed of 14,800 r.p.m for another 30 min to remove the small-sized nanosheets and unreacted bulk crystals. The final product, i.e. ReSSe ND suspension, was collected after washing 3-4 times with Milli-Q water using Millipore ultrafiltration tubes.

3.2.4 Synthesis of $\text{Ni}_3\text{Cr}_2\text{P}_2\text{X}_9$ (X=S, Se) Bulk Crystals

Chemical vapor transport (CVT) technique is employed to obtain bulk single crystals of $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ and $\text{Ni}_3\text{Cr}_2\text{P}_2\text{Se}_9$ compounds. Seminal work with regards to the discovery of these compounds and their successful synthesis of single crystals was carried out by McGuire *et al.*^[5] Here in this work, the stoichiometric amounts of nickel powder (Alfa Aesar, ~325 mesh, 99.8%), chromium powder, red phosphorus lump, sulfur pieces and/or selenium shots were used. These chemicals were used as-received without further purification. These materials were sealed in an evacuated quartz tube (ampoule) with an inner pressure in the range of 10^{-5} - 10^{-6} Torr. In addition to the elemental constituents (Ni, Cr, P, and S/Se), a small amount (2mg/cc) of iodine spheres were added inside the ampoule to act as the transport agent. Sealed ampoules were then subjected to a two-zone horizontal tube furnace.

Initially, the source zone was kept at 650 °C and the growth zone at 750 °C for 48 hours. This was done to allow the constituents to react completely as well as prevent the back transport or formation of undesired additional phases. After this duration, the temperature

of source zone was slowly elevated to 750 °C and that of growth zone was lowered to 700 °C. This arrangement continued for next 120 hours. Further, the temperatures of both the zones were lowered down, and the plate-like crystals were subsequently obtained from the ampoule for further characterizations and measurements.

3.2.5 Preparation of $\text{Ni}_3\text{Cr}_2\text{P}_2\text{X}_9$ (X=S, Se) Nanosheets

The large scale $\text{Ni}_3\text{Cr}_2\text{P}_2\text{X}_9$ (X=S, Se) nanosheets were obtained by the well-developed chemical Li-intercalation and exfoliation method. Taking $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ as an example, 30 mg of $\text{Ni}_3\text{Cr}_2\text{P}_2\text{X}_9$ powder were intercalated with 3 mL of *n*-butyllithium solution (2.0 M in cyclohexane) for 48 h in a glove box under Ar atmosphere. After the reaction, the upper solution containing unreacted *n*-butyllithium was removed carefully with pipet. The Li-intercalated powder was then washed with *n*-hexane by centrifuge at 2,000 r.p.m for three times for the further removing of the excessive *n*-butyllithium, followed by sonication in 60 ml of water for 30 min to obtain a uniform solution with exfoliated $\text{Ni}_3\text{Cr}_2\text{P}_2\text{X}_9$ nanosheets. The obtained suspension was then centrifuged at the speed of 3,000 r.p.m for another 15 min to remove the unreacted bulk crystals. The final product, i.e. $\text{Ni}_3\text{Cr}_2\text{P}_2\text{X}_9$ nanosheets suspension, was then collected by centrifugation at the speed of 12,000 r.p.m. for 30 min.

3.3 Characterizations

After the successful preparation of ultrasmall metal chalcogenide nanodots and ultrathin metal chalcogenide nanosheets, it is critical to use suitable techniques to characterize these nanomaterials to reveal their structural characteristics including the crystal phases, morphology, chemical compositions, optical properties, electronic properties and surface properties. Since every technique has its own advantages and shortcomings, it is better to use the combination of different facilities to characterize the samples for the comprehensive understanding of the structural information and physiochemical properties of the samples. In addition, the optimal conditions on operating different techniques are usually dependent on the essential properties of the material. Hence, understanding the

suitable operating conditions on different samples are of fundamentally crucial to acquire high quality and reliable data. In this part, the characterization techniques used for the investigation of prepared layered ultrathin metal chalcogenide nanomaterials will be briefly introduced.

3.3.1 X-Ray Diffraction (XRD)

X-ray diffraction (XRD) is one of the most powerful techniques for the characterization of crystallographic information of the crystalline materials. In this thesis, a Bruker D8 diffractometer (German) with a Cu K α ($\lambda=1.54178$ Å) X-ray source was used to measure the powder X-ray diffraction (XRD) pattern of the bulk layered crystals of $\text{ReS}_{2x}\text{Se}_{2(1-x)}$ ($0 \leq x \leq 1$) and $\text{Ni}_3\text{Cr}_2\text{P}_2\text{X}_9$ ($\text{X}=\text{S}, \text{Se}$).

Specifically, all of the XRD patterns were measured in the range of 10° to 80° with an average interval of 0.05° and a dwell time of 1 second. The crystal phase of the layered bulk crystals of $\text{ReS}_{2x}\text{Se}_{2(1-x)}$ ($0 \leq x \leq 1$) and $\text{Ni}_3\text{Cr}_2\text{P}_2\text{X}_9$ ($\text{X}=\text{S}, \text{Se}$) were identify by the XRD. The corresponding crystals were ground into micro-sized powders before depositing on the XRD sample holders for the measurement. The experimental XRD pattern was then compared with reference and simulated XRD pattern to confirm the crystallinity and phase purity.

3.3.2 Scanning Electron Microscopy (SEM)

Field emission scanning electron microscopy (SEM) images and energy-dispersive x-ray spectra (EDS) were obtained using a field emission scanning electron microscope (FESEM, JSM7600F), equipped with Oxford EDS detector. In a typical SEM machine, the equipped electron gun is usually the source for releasing the electron beam, which will interact will the samples to emit a variety to signals, including the back-scattering electrons and the secondary electrons. Among them, the back-scattering electron signals are related to the atomic number of the elements, which can help to identify the elemental distribution on the materials. While for the secondary electron signals, they can give the detailed

information of the material surface. Therefore, SEM is a commonly used technique for the characterization of topology, surface structure and morphology of a solid sample. In addition, the EDS detector can roughly investigate the chemical composition of the samples. All these important features make SEM machine one of the most powerful techniques for material characterization.

For the SEM test, the secondary electrons were utilized as the signal to get detail surface morphology of the layered bulk crystals of $\text{ReS}_{2x}\text{Se}_{2(1-x)}$ ($0 \leq x \leq 1$) and $\text{Ni}_3\text{Cr}_2\text{P}_2\text{X}_9$ ($\text{X}=\text{S}, \text{Se}$). The SEM is operating at the accelerating voltage of 5 keV with the working distance of 4.5 cm and a probe current of 7 μA to acquire the SEM images of all the bulk crystals prepared by CVT method. Normally, their ground powder was directly placed on the conductive carbon tape for measurement. Furthermore, the exact elemental composition and precise ratios between different elements of the bulk crystals were identified by the EDS spectra. Typically, these EDS spectra were recorded at an accelerating voltage of 20 keV, a probe current of 10 μA and a working distance of 15 cm. Due to the high conductivity of all the bulk crystals, surface coating with gold is not necessary for all samples in this thesis. Meanwhile, the surface coating will also influence the accuracy of the EDS test results.

3.3.3 Transmission Electron Microscopy (TEM)

A transmission electron microscope (JEOL, JEM-2100F) coupled with energy dispersive X-ray spectroscopy (EDS) was used to collect the transmission electron microscopy (TEM) images, EDS spectra and elemental mappings. In general, the TEM samples were prepared by dip-coating of aqueous solutions containing corresponding $\text{ReS}_{2x}\text{Se}_{2(1-x)}$ nanodots or $\text{Ni}_3\text{Cr}_2\text{P}_2\text{X}_9$ ($\text{X}=\text{S}, \text{Se}$) nanosheets on ultrathin amorphous carbon film-coated copper grids, following by drying at room temperature in a vacuum oven for overnight. The accelerating voltage of 200 keV was used in all the TEM test. With the advance of science and technology, TEM technique has become one of the most powerful tools for material characterization. Generally, the converged electron beam is the most important factor in the whole system, which is generated by the field emission gun source with an extremely

high voltage. The generated electron beam will pass through the samples and interact with the sample after converged through a series of lenses. The signals of interaction of electrons transmitting through the sample will then be collected by the highly sensitive Gatan CCD camera to form visualized images. To make sure the good quality of formed TEM image, the thickness of the sample is required to be as thin as possible. Since the resolution of the TEM can reach as high as $\sim 1.9 \text{ \AA}$, we can study the particle size of the prepared ultrasmall nanodots and the lateral size of the prepared nanosheets using low magnification TEM images. Another thing worth pointing out is that the contrast of the samples under TEM test is dependent on the Z number of the elements in different materials, while for same materials, the contrast information can roughly reveal the thickness of sample, i.e., the darker the thicker. Therefore, it is used to roughly measure the thickness of the prepared $\text{ReS}_{2x}\text{Se}_{2(1-x)}$ ($0 \leq x \leq 1$) nanodots and $\text{Ni}_3\text{Cr}_2\text{P}_2\text{X}_9$ ($\text{X}=\text{S}, \text{Se}$) nanosheets.

Second, high-resolution TEM (HRTEM) image and selected area electron diffraction (SAED) pattern can be used to identify the crystal structure and preferred orientations. First, crystalline materials normally show obvious crystal lattice fringes, while amorphous materials don't have any crystal lattice fringes, which can be used as standard to distinguish them. The distance of crystal lattice fringes obtained from the HRTEM images usually can tell the exposed crystal facets of specific sample, because every material has the unique lattice fringes on different exposed facets. Furthermore, by utilizing SAED technique, the single-crystalline, polycrystalline and amorphous nature of a material could be readily confirmed. Because different types of materials will show different SAED patterns. While for single-crystalline material, the SAED pattern will be composed by individual bright spot due to the great periodicity of the well-defined crystal structure. On the other hand, the SAED pattern of a polycrystalline material normally display ring-like feature because the pattern comes from the average signals from various crystal domains. Note that amorphous material does not show any SAED pattern due to the lack of long periodicity. For the layered metal chalcogenide nanosheets in this thesis, the SAED pattern can give the information about the preferred crystal orientation.

Finally, yet importantly, the EDS spectra and corresponding elemental mapping are the important ways to study the precise elemental distribution and ratios of the prepared $\text{Ni}_3\text{Cr}_2\text{P}_2\text{X}_9$ ($\text{X}=\text{S}, \text{Se}$) nanosheets. It is also a critical technique to identify whether the prepared nanosheets is oxidized or not. More importantly, the elemental mapping can give accurate information about the elemental distribution across the whole nanosheets, which can help to understand the structure of the nanosheets.

3.3.4 Scanning Transmission Electron Microscopy (STEM)

The high angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) images were recorded on a JEOL ARM200F (JEOL, Tokyo, Japan) transmission electron microscope equipped with a cold field emission gun and double hexapole Cs correctors (CEOS GmbH, Heidelberg, Germany), operating at accelerating voltage of 200 kV. All the samples for HAADF-STEM characterizations were prepared by the same method mentioned in Section 3.3.3.

Since the HRTEM cannot distinguish different elemental atoms on the nanodots and nanosheets, the HAADF-STEM technique is another powerful supplementary technique used to acquire the clear and precise atomic distribution of the $\text{ReS}_{2x}\text{Se}_{2(1-x)}$ ($0 \leq x \leq 1$) nanodots and $\text{Ni}_3\text{Cr}_2\text{P}_2\text{X}_9$ ($\text{X}=\text{S}, \text{Se}$) nanosheets, respectively. The underlying principle is that under HAADF-STEM mode, the image contrast of different atom is highly correlated to the Z number of the elements, i.e., heavy atom (large Z number) shows brighter contrast compared to the light atom (small Z number).

3.3.5 UV-Vis Absorption Spectroscopy

The UV-Vis absorption spectra were measured by a Lambda 950 UV/Vis Spectrophotometer (PerkinElmer Inc., USA) at room temperature using QS-grade quartz cuvettes (111-QS, Hellma Analytics). In this thesis, the UV-Vis technique is used to study the absorption features of $\text{ReS}_{2x}\text{Se}_{2(1-x)}$ ($0 \leq x \leq 1$) nanodots and $\text{Ni}_3\text{Cr}_2\text{P}_2\text{X}_9$ ($\text{X}=\text{S}, \text{Se}$) nanosheets in the UV-Vis region. It is well-known that the UV-Vis absorption

characteristic of a material is closely related to the intrinsic bandgap. For $\text{ReS}_{2x}\text{Se}_{2(1-x)}$ ($0 \leq x \leq 1$) nanodots, the absorption spectra are not only dependent on the intrinsic bandgap, but also affected by the quantum effect, which appears with the size of material reduced to nanometer size. On the other hand, for $\text{Ni}_3\text{Cr}_2\text{P}_2\text{X}_9$ ($\text{X}=\text{S}, \text{Se}$) nanosheets, due to the metallic nature originated from the electronic structure, it is not expected to show any characteristic absorption peaks.

3.3.6 Atomic Force Microscopy (AFM)

The atomic force microscope (AFM) images were recorded on a Dimension 3100 AFM equipped with Nanoscope IIIa controller (Veeco, CA, USA) and an NSCRIPTOR system with a Si tip (resonance frequency: 320 kHz; spring constant: 42 N/m) in the tapping mode under ambient conditions. The scanning rate for image acquiring is 1 Hz. In this thesis, the AFM technique is mainly used for the measurement of the thickness of $\text{ReS}_{2x}\text{Se}_{2(1-x)}$ ($0 \leq x \leq 1$) nanodots and $\text{Ni}_3\text{Cr}_2\text{P}_2\text{X}_9$ ($\text{X}=\text{S}, \text{Se}$) nanosheets as well as the lateral size of the exfoliated $\text{Ni}_3\text{Cr}_2\text{P}_2\text{X}_9$ ($\text{X}=\text{S}, \text{Se}$) nanosheets. The thickness and layer numbers of the nanodots and nanosheets can be obtained by analysis of the height profiles collected from AFM test.

Before subjected to AFM test, the sample preparation is also important to get high-quality data. For $\text{ReS}_{2x}\text{Se}_{2(1-x)}$ nanodots, mica is selected as the substrate to deposit the ultrasmall size samples because of its ultra clean surface. Typically, the samples used for AFM test were prepared by dropping the diluted aqueous solutions containing $\text{ReS}_{2x}\text{Se}_{2(1-x)}$ NDs on the mechanically cleaved mica substrates, followed by drying in air prior to characterization. While for $\text{Ni}_3\text{Cr}_2\text{P}_2\text{X}_9$ ($\text{X}=\text{S}, \text{Se}$) nanosheets, due to the aggregation issue of 2D nanosheets after drying, some necessary processes were taken to make sure the accuracy of AFM measurements. Generally, the substrates were modified with APTES to make positive-charged surface for getting well-spread nanosheets on Si/SiO₂ substrates. First, the cleaned Si/SiO₂ (1×1 cm) substrates were immersed into an APTES water solution with the volume ratio 1:100 for 10 min, followed by the rinsing with DI water. Subsequently, the modified Si/SiO₂ substrates were dried at 100 °C for 2h to get the

positive-charged APTES-modified Si/SiO₂ substrates. After that, the diluted solution of Ni₃Cr₂P₂X₉ (X=S, Se) nanosheets was dropped onto the surface of these modified substrates. The solution will be kept for 10 min and then blew dry by N₂ gas flow. Due to the negative-charged surface of the metal chalcogenide nanosheets, the prepared Ni₃Cr₂P₂X₉ (X=S, Se) nanosheet can be tightly adsorbed on the surface by the electrostatic force with good dispersity, which were then adopted for the further AFM measurement.

3.3.7 X-Ray Photoelectron Spectroscopy (XPS)

X-Ray photoelectron spectroscopy (XPS) measurements were recorded on a VG ESCALAB 220i-XL instrument (base pressure < 5×10⁻¹⁰ mbar) equipped with a monochromatic Al K α (1486.7 eV) X-ray source. All XPS spectra were calibrated by the C 1s peak located at 284.6 eV as the reference. For the sample preparation of for XPS test, the concentrated sample solution containing ReS_{2x}Se_{2(1-x)} (0≤x≤1) nanodots or Ni₃Cr₂P₂X₉ (X=S, Se) nanosheets were dropped onto the clean Si substrate followed by the natural drying in vacuum oven overnight at room temperature.

XPS is an important technique to measure the chemical composition and elemental valance state of each element in a compound. Especially, when the valance states of the elements are related to the crystal structure of the compounds, it can be the critical data to determine the phase of the material. It is noteworthy that the detection limit of XPS on vertical dimension is less than 10 nm, which means that it can only be used to test the surface properties of a sample. However, due to the accuracy of the XPS techniques, it can usually be used to quantitatively determine the precise ratios between different elements in samples. In this thesis, all the XPS was primarily used to investigate the oxidation state of the elements in prepared ReS_{2x}Se_{2(1-x)} nanodots and Ni₃Cr₂P₂X₉ (X=S, Se) nanosheets, which can be used to analysis of the degrees of oxidation after the synthetic process. This is important for catalyst, because some catalysts are sensitive to surface oxidation.

3.3.8 Extended X-ray Absorption Spectra (XAS)

The X-ray absorption spectra technique is a state-of-the-art analytic tool to reveal the deep structural information of a material, such as coordination and valence state of a specific element as well as the bond length with surrounding elements. Currently, there are two types of XAS techniques, including extended X-ray absorption fine structure (EXAFS) and X-ray absorption near edge structure (XANES). In this thesis, the XAS technique was used to study the vacancy types in $\text{ReS}_{2x}\text{Se}_{2(1-x)}$ nanodots. The XANES and EXAFS measurements of Re L_3 -edge were conducted at the XAFCA beamline of Singapore Synchrotron Light Source (SSLS).^[6] The storage ring of SSLS operated at $E=700$ MeV and $I_{\text{max}}=250$ mA. The X-ray radiation was monochromatized by the Si (111) double-crystal monochromator. Re metal powder was used as a reference for the energy calibration, and all samples were tested in transmission mode at room temperature. Data processing and fitting were conducted using the Demeter software package.^[7]

3.4 Density Functional Theory Calculations

Density functional theory (DFT) calculation is one of the most powerful tools in theoretical computational chemistry, which can provide deep insight and fundamental principles behind the experimental results. In this thesis, the theoretical study was performed to investigate the mechanism why $\text{ReS}_{2x}\text{Se}_{2(1-x)}$ ($0 \leq x \leq 1$) nanodots can have such kind of enhanced electrocatalytic activity on HER. The Vienna *ab initio* simulation package (VASP) was used to carry out all the DFT calculations on the basis of the projector augmented wave (PAW) method.^[8, 9] Standard PAW potentials were used to explain the electron-ion interactions, with valence configurations of $5s^25p^66s^25d^5$ for Re (Re_svGW), $3s^23p^64s^23d^{10}4p^4$ for Se (Se-sv_GW), $3s^23p^4$ for S (S_GW) and $1s^1$ for H (H_GW). The smooth part of wave functions was expanded by the plane-wave basis set with a cut-off kinetic energy of 520 eV. The functions parameterized by the Perdew-Burke-Ernzerhof (PBE) was used to perform the whole calculations on the electron-electron exchange and correlation interactions,^[10] which is also a form of the general gradient approximation (GGA). The initial atomic structures of ReS_2 , ReSe_2 and ReSSe were built based on previous experimental results.^[11] All the geometry structures were optimized before analysing the electronic properties. Note that when the Hellmann-Feynman forces were

smaller than 0.01 eV/Å, all the atoms would stop relaxing. A value of 1.0×10^{-5} eV was set as the convergence criterion for the electronic self-consistent loop. The structural optimization of ReSSe and ReSe₂ was carried out by Brillouin-zone integrations based on a gamma-centered ($4 \times 4 \times 4$) k-point grid. Since the lattice constant c of ReS₂ is almost double as that of ReSe₂ and ReSSe, a smaller gamma-centered ($4 \times 4 \times 2$) k-point grid was adopted for the calculation of the bulk of ReS₂.

After that, the monolayers of ReS₂, ReSe₂ and ReSSe were investigated by isolating each layer by 10 Å. The edge was modelled by removing 4 units (each unit includes one Re atom) along the b direction in a (1×4) monolayer cell (there are totally 8 units before removing 4 units). The vacancy was modelled by removing one S or Se atoms from a (2×2) monolayer cell. There are two kinds of anions in terms of their height. Our DFT results suggest that the systems with the vacancies by removing anions with lower height are more stable. As a result, only the systems with this type of vacancies were investigated in the study.

Both anions and Re cations exposed at edges or vacancies were investigated as the active sites for the adsorption of H atoms. Our results demonstrate that the unsaturated coordinated Re atoms have stronger binding energy with the H atom. Therefore, only the Gibbs free energies (ΔG_{H^*}) on the Re site were provided here, which were calculated by the formula:

$$\Delta G_{H^*} = \Delta E_{H^*} + \Delta ZPE - T\Delta S$$

Where ΔZPE , ΔS and ΔE_{H^*} represent the zero-point energy change, entropy change and binding energy of H* adsorption, respectively. In addition, the ΔZPE and $T\Delta S$ are acquired via the theory proposed by Nørskov et al.^[12]

3.5 Applications

3.5.1 Fabrication and Performance Measurement of HER

Typically, $\text{ReS}_{2x}\text{Se}_{2(1-x)}$ ND suspension was coated onto a GCE used as the working electrode. Specifically, 5 μL of the catalyst aqueous suspension was dropped onto the pre-polished GCE (3 mm in diameter), followed by drying in air at the room temperature for 4 h. Then, 1.0 μL of 5% Nafion ethanol solution was dropped onto the surface of the catalyst-modified GCE followed by drying for another 2 h. The electrocatalytic performance for HER was tested by the linear sweep voltamperometry (LSV) at the scan rate of 5 mV s^{-1} in 0.5 M H_2SO_4 aqueous solution saturated by H_2 . The electrocatalytic stability tests of catalysts were measured by continuous CV scanning test in the potential window of -0.202~0 V (vs. RHE). Commercial 10% Pt/C catalyst was used as a reference for evaluating the HER performances of all the $\text{ReS}_{2x}\text{Se}_{2(1-x)}$ NDs.

All the electrochemical experiments were carried out on an electrochemical workstation (CHI 760C, CH Instruments Inc., USA). The electrochemical cell was assembled with a conventional three-electrode set-up using Ag/AgCl (3 M KCl), graphite rod and catalyst-modified glassy carbon electrode (GCE) as the reference electrode, counter electrode and working electrode, respectively. 0.5 M H_2SO_4 aqueous solution was utilized as electrolyte throughout all the experiments. Electrochemical impedance spectroscopy (EIS) was measured in 0.5 M H_2SO_4 aqueous solution using an alternating current (AC) voltage of 5 mV and direct current (DC) voltage of -0.50 V vs. Ag/AgCl within the frequency range from 100 kHz to 0.1 Hz.

The calibration of Ag/AgCl (3 M KCl) reference electrode was carried out with respect to the reversible hydrogen electrode (RHE). The calibration was performed in the pure H_2 -saturated electrolyte with the Pt wire as the working electrode through cyclic voltammetry (CV) at a scan rate of 1 mV s^{-1} . The thermodynamic potential for the hydrogen electrode reactions was determined by the average value of two measured potentials at which the current crossed zero. Therefore, in this thesis, the potential with respect to the RHE can be calculated as follow:

$$\text{Potential (vs. RHE)} = \text{Potential (vs. Ag/AgCl (3 M KCl))} + 0.248 \text{ V.}$$

3.5.2 Fabrication and Performance Measurement of Supercapacitor

Typically, the prepared ultrathin $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ nanosheets will be restacked by the vacuum and filtration method using an Anodic Aluminum Oxide (AAO) filter with 0.2 μm pore size. After filtration, the freestanding $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ film with the thickness of around 1.0 μm will be subjected to 24 h drying in a vacuum oven. Then, a piece of $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ film will be cut off from the dried freestanding film will for the supercapacitor performance test. The cut piece was then rinsed with DI water to make it wet to be able to attach on the conductive carbon paper, followed by another 4 h drying in air. Sequentially, the dried carbon paper attached with $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ film was dried at 40 $^{\circ}\text{C}$ in vacuum oven for overnight, which could be used in the supercapacitor performance test.

All the experiments were carried out on an electrochemical workstation (CHI 760C, CH Instruments Inc., USA). The electrochemical cell was assembled with a conventional three-electrode system using graphite rod, Ag/AgCl (3 M KCl) and the carbon paper attached with $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ film as the counter electrode, reference electrode and working electrode, respectively. The aqueous solution of 1.0 M H_2SO_4 was adopted as the electrolyte throughout the test.

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Chapter 4

ReS_{2-x}Se_{2(1-x)} Nanodots for Electrocatalytic Hydrogen Evolution Reaction

By combining the chemical Li-intercalation and CVT method, the ultrasmall 1T'-ReS_{2-x}Se_{2(1-x)} nanodots from the corresponding bulk powders can be prepared, which include ReS₂, ReS_{1.8}Se_{0.2}, ReS_{1.4}Se_{0.6}, ReSSe, ReS_{0.6}Se_{1.4}, ReS_{0.2}Se_{1.8}, and ReSe₂. Among them, the ReSSe nanodot with active low-site S vacancies and rich active edge sites showed the improved electrocatalytic performance for HER when compared with both of ReSe₂ and ReS₂ nanodots, which delivers a small Tafel slope of 50.1 mV dec⁻¹ and a low overpotential of 84 mV at the current density of 10 mA cm⁻², as well as the great long-term stability.

*This section published substantially as (Z. C. Lai, A. Chaturvedi, Y. Wang, T. H. Tran, X. Z. Liu, C. L. Tan, Z. M. Luo, B. Chen, Y. Huang, G.-H. Nam, Z. C. Zhang, Y. Chen, Z. N. Hu, B. Li, S. B. Xi, Q. H. Zhang, Y. Zong, L. Gu, C. Kloc, Y. H. Du, H. Zhang, *J. Am. Chem. Soc.* **2018**, 140, 8563-8568).

4.1 Introduction

To realize the sustainable hydrogen economy, rational design and preparation of highly efficient catalysts for electrocatalytic hydrogen evolution reaction (HER) are very important. For water splitting, there has been a lot of efforts devoting to the research of electrocatalysts with low energy consumption and high efficiency.^[1-16] The discovery of TMDs nanosheets, such as MoS₂,^[17] has raised the increasing research interest on TMDs catalysts due to their earth abundance compared with commercial Pt-based catalysts and high catalytic activities.^[18-24] It has been reported that the edge sites of 2H-phase TMDs and basal planes of 1T-phase TMDs are the active sites toward the electrocatalytic HER.^[17] Therefore, preparing small-sized and 1T-phase TMDs are the important ways to achieve high-performance HER activity.^[4, 18-19, 25-28] Furthermore, another efficient strategy to enhance the catalytic activities of TMD nanomaterials is the phase-engineering. For instance, it has been proved that 1T-TMD nanosheet are promising electrocatalysts for HER because of the high electrical conductivity, which can result in the fast charge transport behavior in the electrocatalytic reaction.^[10, 20, 27, 29-31] In addition, strain-induced catalytic activity enhancement on HER is also an important factor.^[22, 32-33] For instance, strained 1T-WS₂ nanosheet showed enhanced HER catalytic performance when compared with those without strains.^[22] Another important strategy is based on the defect engineering to enhance the HER performance of TMD electrocatalysts. For example, inducing S vacancies on the strained 2H-MoS₂ nanosheet can greatly enhance the electrocatalytic activity when compared with the strained 2H-MoS₂ nanosheets without S vacancies.^[33] This is also confirmed by the research on 1T-MoSSe nanodot and porous 1T-MoS₂ nanosheet, suggesting the importance of defect-engineering of TMDs for HER.^[19, 28] But, there is only one kind of anionic vacancies because of the symmetric trigonal prismatic 2H phase and octahedral 1T phase structures. On the other hand, the 1T'-phase TMDs have highly asymmetric structures which could produce different kinds of anionic vacancies, since there are different kinds of chalcogen atoms in the crystal structure, which is totally different from the 2H and 1T structures. Moreover, the synthesis of 1T'-TMDs still remains a big challenge, making it difficult to study the fundamental effect of the asymmetric

vacancy in 1T'-TMDs.^[34] Hence, the 1T'-phase ReS_{2-x}Se_{2(1-x)} may be ideal model catalysts to study the fundamental effect of asymmetric vacancies for electrocatalytic HER.

In this chapter, by combining the chemical Li-intercalation and the chemical vapor transport (CVT) method, the ultrasmall 1T'-ReS_{2-x}Se_{2(1-x)} nanodots can be prepared using the corresponding powder of bulk crystals, which include ReS₂, ReS_{1.8}Se_{0.2}, ReS_{1.4}Se_{0.6}, ReSSe, ReS_{0.6}Se_{1.4}, ReS_{0.2}Se_{1.8}, and ReSe₂. Among them, the ReSSe nanodots with active low site S vacancies as well as the rich active edge sites showed better electrocatalytic performance for HER than that of both ReSe₂ and ReS₂ nanodots. Significantly, the 1T'-phase ReSSe nanodots show the best water-splitting performance with a small Tafel slope of 50.1 mV dec⁻¹. Moreover, a low overpotential of 84 mV can be achieved at the current density of 10 mA cm⁻². The optimal hydrogen absorption energy of the active site is concluded to be the reason for the great hydrogen evolution performance, which is resulted from by the asymmetric S vacancy in the highly asymmetric 1T' structure.

4.2 Results and Discussions

4.2.1 Synthesis and Characterizations of 1T'-phase ReS_{2-x}Se_{2(1-x)} Nanodots

Generally, the combination of chemical Li-intercalation and CVT method were used to prepare ultrasmall ReS_{2-x}Se_{2(1-x)} NDs. As presented in the schematic diagram (**Figure 4.1**), the bulk crystals of ReS_{2-x}Se_{2(1-x)} ($x=0-1$), including ReS₂, ReS_{1.8}Se_{0.2}, ReS_{1.4}Se_{0.6}, ReSSe, ReS_{0.6}Se_{1.4}, ReS_{0.2}Se_{1.8} and ReSe₂, were synthesized by well-developed CVT method.

Figure 4.1 Schematic diagram of the CVT process for preparation of ReS_{2-x}Se_{2(1-x)} crystals.

As characterized by the scanning electron microscopy (SEM) (**Figure 4.2a,b**), the as-prepared ReSSe bulk crystals exhibited a small crystal sizes of few hundreds of nanometers. The prepared bulk crystals of ReSSe were then measured by the energy dispersive X-ray spectroscopy (EDS) to reveal the precise chemical composition (**Figure 4.2c**). The samples were then tested by X-ray diffraction (XRD) (**Figure 4.2d**), which also matched well with the reference XRD pattern of ReSe_2 and ReS_2 in the database.

Figure 4.2 (a, b) SEM images, (c) EDS spectrum and (d) XRD pattern of the ReSSe bulk crystals prepared by CVT method. Inset in (c): the elemental ratio of prepared ReSSe bulk crystals obtained from the EDS spectrum.

Before being subjected to the reaction with *n*-butyllithium solution, these prepared big crystal of $\text{ReS}_{2-x}\text{Se}_{2(1-x)}$ was treated with the ball-milling process to reduce the crystal size, which is helpful for the high-yield production. The reacted compounds were then sonicated in de-ionized (DI) water with ice bath (**Figure 4.3a**), followed by the high-speed centrifugation, leading to the ultrasmall and uniform $\text{ReS}_{2-x}\text{Se}_{2(1-x)}$ NDs solution.

Figure 4.3 Schematic diagram of the synthetic procedure and characterizations of ReSSe NDs. (a) Simulated structure of ReSSe and schematic diagram of the synthetic process of ReSSe NDs. (b) Low-magnification TEM image of the prepared ReSSe NDs. Inset: Size distribution of ReSSe NDs. (c) HRTEM image of the prepared ReSSe NDs. (d) HRTEM image of individual ReSSe nanodots. (e) HAADF-STEM image of a single ReSSe nanodot showing typical 1T' structure overlapped with the simulated structure. (f) EDS spectra of the prepared ReSSe NDs obtained under TEM mode. (g) UV-Vis spectra of the diluted solution of ReSSe NDs. Inset: Photograph of the ReSSe ND solution. (h) AFM image of the prepared ReSSe NDs. (i) Statistical analysis of the height of 110 ReSSe NDs measured from AFM images.

The particle size distribution of the as-prepared ReSSe NDs was then investigated by the transmission electron microscopy (TEM), which is demonstrated in **Figure 4.3b-c**, showing an average size of 1.7 ± 0.4 nm (inset in **Figure 4.3b**). As illustrated in **Figure 4.3d**, the crystal structure of ReSSe NDs was revealed by the high-resolution TEM (HRTEM) image, showing a clear d value of 0.26 nm close to the (002) plane of ReSSe. As illustrated in **Figure 4.3e**, the intrinsic distorted structure of the 1T'-ReSSe NDs was further investigated by the atomic-resolution high angle annular dark-field scanning TEM (HAADF-STEM).^[35] The chemical composition of the ReSSe NDs (**Figure 4.3f**) was

measured by the EDS under TEM mode, which showed obvious signals of S, Se and Re elements. In addition, the UV-Vis spectra of the prepared ReS_{2-x}Se_{2(1-x)} NDs aqueous solution showed similar features with the reported ReS₂ nanosheets, giving a smooth and flat line (**Figure 4.3g**).^[36] Furthermore, the Zeta potential test was used to reveal the negatively charged surface of these ReS_{2-x}Se_{2(1-x)} NDs, delivering the value of -29.7 mV, which is main reason for the stabilization of ReS_{2-x}Se_{2(1-x)} NDs in aqueous solution (inset in **Figure 4.3g**). As showed in **Figure 4.3h-i**, the thickness of these ReS_{2-x}Se_{2(1-x)} NDs was characterized by the atomic force microscopy (AFM), showing an average height of 1.2 ± 0.6 nm.

In addition, a series of ReS_{2-x}Se_{2(1-x)} NDs, such as ReS₂, ReS_{1.8}Se_{0.2}, ReS_{1.4}Se_{0.6}, ReS_{0.6}Se_{1.4}, ReS_{0.2}Se_{1.8} and ReSe₂, were obtained using the same method as well. The XRD patterns of all these obtained ReS_{2-x}Se_{2(1-x)} bulk crystals demonstrated that there is a gradual shift between ReSe₂ and ReS₂ in terms of the main peaks (**Figure 4.4**). This has been revealed by the reported results.^[37] Similar crystal size as that of ReS₂ crystals were also observed on the ground powder of ReS₂, ReS_{1.8}Se_{0.2}, ReS_{1.4}Se_{0.6}, ReS_{0.6}Se_{1.4}, ReS_{0.2}Se_{1.8}, and ReSe₂, which is showed in **Figure 4.5**. Moreover, as shown in the EDS results (see **Table 4.1**), the chemical composition of the prepared bulk crystal was close to designed stoichiometric ratios.

Figure 4.4 (a) XRD patterns of all ReS_{2-x}Se_{2(1-x)} bulk crystals prepared by CVT method. (b) The magnified XRD patterns of the dotted rectangle in (a), showing the gradual shift of the peak corresponding to (003) plane.

Figure 4.5 FESEM images of ReS_{2-x}Se_{2(1-x)} crystals prepared by CVT method followed by ball grinding: (a) ReS₂, (b) ReS_{1.8}Se_{0.2}, (c) ReS_{1.4}Se_{0.6}, (d) ReS_{0.6}Se_{1.4}, (e) ReS_{0.2}Se_{1.8} and (f) ReSe₂.

Table 4.1 EDS characterization of the bulk ReS_{2-x}Se_{2(1-x)} crystals prepared by CVT method.

Compound	Element	Calculated (Ideal)	Experimental (EDS)
ReS ₂	Re	33.33 %	35.42 %
	S	66.67 %	65.35 %
ReS _{1.8} Se _{0.2}	Re	33.33 %	35.53 %
	S	60.00 %	57.83 %
	Se	6.67 %	6.64 %
ReS _{1.4} Se _{0.6}	Re	33.33 %	34.80 %
	S	46.67 %	48.03%
	Se	20.00 %	17.17 %
ReS _{1.0} Se _{1.0}	Re	33.33 %	34.56 %
	S	33.33 %	34.21 %
	Se	33.34 %	31.23 %
ReS _{0.6} Se _{1.4}	Re	33.33 %	35.88 %
	S	20.00 %	20.67 %
	Se	46.67 %	43.45 %
ReS _{0.2} Se _{1.8}	Re	33.33 %	34.29 %
	S	6.67 %	7.33 %
	Se	60.00 %	58.38 %
ReSe ₂	Re	33.33 %	33.38 %
	Se	66.67%	66.62 %

As shown in **Figure 4.6**, the ReS₂, ReS_{1.8}Se_{0.2}, ReS_{1.4}Se_{0.6}, ReS_{0.6}Se_{1.4}, ReS_{0.2}Se_{1.8} and ReSe₂ series NDs were obtained by the same chemical Li-intercalation and exfoliation method as well. As illustrated in **Figure 4.7a-b**, due to the large contrast difference caused by the Z difference between S atoms and Re atoms, the Re atoms can be clearly visualized in the HAADF-STEM images of ReS₂ NDs. However, for the ReSe₂ NDs, both of Se and Re atoms are clearly observed in the HAADF-STEM images, because of the small Z difference between Se and Re atoms (**Figure 4.7c,d**).

Figure 4.6 TEM images of prepared ReS_{2-x}Se_{2(1-x)} NDs: (a) ReS₂, (b) ReS_{1.8}Se_{0.2}, (c) ReS_{1.4}Se_{0.6}, (d) ReS_{0.6}Se_{1.4}, (e) ReS_{0.2}Se_{1.8} and (f) ReSe₂ NDs.

Figure 4.7 (a) HAADF-STEM image of prepared ReS₂ NDs. (b) The high-resolution HAADF-STEM image obtained from the red square in (a). (c) HAADF-STEM image of prepared ReSe₂ NDs. (d) The high-resolution HAADF-STEM image obtained from the red square in (c).

Furthermore, the surface properties and structural characteristics of the prepared ReSSe NDs were studied by the X-ray photoelectron spectroscopy (XPS), extended X-ray absorption fine structure (EXAFS) and X-ray absorption near-edge structure (XANES). It is well known that the vigorous exfoliation process assisted by the Li-intercalation could cause various kinds of defects in TMDs, such as S vacancies.^[27-28] Clearly, as shown in the XPS spectra (**Figure 4.8a**), for ReSSe, the binding energy of Re 4f in nanodots was about 0.3 eV lower than that in the bulk crystals, which proved that Re atoms were reduced partially in the prepared nanodots. But, as regard of the binding energies of Se 3p and S 2p, there are almost no difference between the bulk crystals and nanodots (**Figure 4.8b**), indicating that some anionic vacancies, such as S and Se vacancies have been induced in the ReSSe NDs. The XANES and EXAFS tests were then performed to confirm the

primary kinds of vacancies in obtained ReSSe NDs. The clear difference between bulk crystals and prepared nanodots of ReSSe is revealed by the Re L₃-edge XANES spectra (**Figure 4.8c**) and the Fourier transformed EXAFS (FT-EXAFS) (**Figure 4.8d**). This is confirmed by the corresponding $k^3\chi(k)$ oscillation curves as well (**Figure 4.9**). The peak position of 2.15 Å in ReSSe NDs is 0.03 Å larger than that of the bulk crystals (2.12 Å), indicating the existence of more Re-Se bond in the ReSSe NDs, rather than Re-S bonds, because it belongs to the Re-S/Se coordination.

Figure 4.8 High-resolution XPS and X-ray absorption characterization of prepared ReSSe bulk crystals and NDs. (a, b) Re 4f (a) and S 2p and Se 3p spectra (b) of ReSSe bulk crystals and obtained ReSSe NDs. (c, d) XANES spectra (c) and Fourier transformed (FT) k^3 -weighted $\chi(k)$ -function of the EXAFS spectra (d) for Re L₃-edges of ReSSe bulk crystals and ReSSe NDs.

Figure 4.9 EXAFS oscillation function $k^3\chi(k)$ for Re L_3 -edges of the ReSSe bulk crystals and ReSSe NDs.

Moreover, there is a 50% peak intensity reduced on ReSSe NDs when compared with the bulk crystals, clearly revealing the size reduction and structural change of ReSSe NDs. The sum up of complete structural parameters are detailed in **Table 4.2**. Note that in ReSSe bulk crystals, the coordination number (N) of Re-Se and Re-S are both 3, while in ReSSe NDs, the N values of Re-Se and Re-S bonds are ~ 1.9 for Re-Se and ~ 1.4 for Re-S, respectively, revealing the unsaturated coordination in ReSSe NDs. It is concluded that various exposed unsaturated Re atoms at vacancy and edge sites were formed in ReSSe NDs, due to vigorous exfoliation induced structural distortion and unsaturated coordination in the ReSSe NDs. It was noteworthy that there is a much higher coordination number ($N \sim 1.9$) of Re-Se bond than that of Re-S bond ($N \sim 1.4$) in prepared ReSSe NDs, which implies that the S atom can be partially removed from prepared nanodots rather than Se atom after the Li-assisted exfoliation process. This can thus produce more S vacancy in the basal plane of ReSSe.

Table 4.2 Fourier transformed EXAFS curve-fitting results of ReS₂Se bulk crystals and prepared ReS₂Se NDs.

Sample	Path	N	R (Å)	σ^2 (10^{-3} Å ²)	R-factor
Bulk crystals	Re-S	3.0±0.3	2.34±0.02	9.4±1.0	0.0075
	Re-Se	3.0±0.3	2.49±0.02	5.2±0.5	
Nanodots	Re-S	1.4±0.2	2.36±0.02	10.0±1.0	0.0096
	Re-Se	1.9±0.2	2.51±0.03	6.7±0.7	

4.2.2 Electrocatalytic Activity of ReS_{2-x}Se_{2(1-x)} Nanodots on HER

As reported by previous studies, the 1T/1T' structure and the S vacancy play important role on high-performance electrocatalytic water splitting.^[10, 27, 29-30, 33] As a proof-of-concept application, the obtained 1T' phase ReS_{2-x}Se_{2(1-x)} NDs were utilized as electrocatalyst for HER. The electrochemical test was conducted using a standard three-electrode set-up in 0.5 M H₂SO₄ aqueous solution saturated with H₂, using Ag/AgCl (3 M KCl), graphite rod and catalyst-modified glassy carbon electrode (GCE) as the reference electrode, counter electrode and working electrode, respectively. Before test, the reference electrode is calibrated by conducting the LSV in the aqueous solution of 0.5 M H₂SO₄ using Pt as working and counter electrode (**Figure 4.10**).

Figure 4.10 Calibration curve of Ag/AgCl (3 M KCl) reference electrode relative to reversible hydrogen electrode. The potential is -0.248 V when the current is equal to 0 A.

As shown in **Figure 4.11a**, the linear sweep voltamperometry (LSV) curve of ReS₂, ReSSe and ReSe₂ NDs as well as the commercial 10% Pt/C catalyst with *iR*-correction were tested. Specifically, the onset potentials of ReS₂, ReSe₂ and ReSSe NDs were estimated to be -196, -72 and -32 mV, respectively. Importantly, a low overpotential of -84 mV can be measured on the prepared ReSSe NDs at the current densities of 10 mA cm⁻², which is much lower than that of ReSe₂ NDs (-123 mV) and ReS₂ NDs (-320 mV). The corresponding Tafel slopes were also calculated from the polarization curves, in which ReSSe NDs showed an impressive value as small as 50.1 mV dec⁻¹ which are illustrated in **Figure 4.11b**, indicating that the catalytic reaction was carried out based on the combining mechanism of Volmer-Tafel and Volmer-Heyrovsky. In addition, the Volmer reaction is considered as the rate-determining step. The electrode kinetics under HER process were investigated by the electrochemical impedance spectroscopy (**Figure 4.11**), giving the impedances the obtained nanodots of ReSe₂ (23.1 Ω), ReS₂ (678.8 Ω) and ReSSe (14.4 Ω) at the potential of -0.202 V (vs. RHE). This trend is similar to the order of their catalytic

performance, suggesting that a faster Faradic process may lead to a superior HER reaction kinetics. More impressively, even tested by more than 20,000 cycles, the ReSSe NDs still show high performance on HER, revealing its excellent long-time operating stability (Figure 4.11d).

Figure 4.11 Electrocatalytic HER performance of ReSSe NDs. (a) Polarization curves (iR -corrected) of the commercial 10% Pt/C, bulk ReSSe, and chemically exfoliated ReS₂, ReSSe and ReSe₂ NDs used as catalysts in 0.5 M H₂SO₄ aqueous solution. (b) The corresponding Tafel slopes of the catalysts derived from (a). (c) Nyquist plots of bulk ReSSe, ReS₂ NDs, ReSSe NDs, ReSe₂ NDs at working potential of -0.202 V (vs. RHE). Insets: (Bottom-left) the corresponding fitting equivalent circuit, where R_s represents the uncompensated resistance, R_p represents the charge transfer resistance, and CPE is the value of the argument of the constant phase element. (Top-right) the enlarged plot of the area indicated with a red dash square. (d) Durability test of ReSSe NDs. The polarization curves were recorded before and after 20000 potential cycles in 0.5 M H₂SO₄ aqueous solution from 0 to -0.202 V (vs. RHE).

As shown in **Figure 4.12a,b**, other compositions of ReS_{2-x}Se_{2(1-x)} NDs were also measured under the similar conditions for comparison, in which the ReSSe NDs exhibited the best

performance for electrocatalytic HER. In addition, the Nyquist plot delivers the electrochemical impedances of the prepared nanodots of ReS_{1.8}Se_{0.2} (398.7 Ω), ReS_{1.4}Se_{0.6} (55.4 Ω), ReS_{0.6}Se_{1.4} (46.9 Ω), and ReS_{0.2}Se_{1.8} (26.9 Ω) at potential of -0.202 V (vs. RHE), showing similar trend as the catalytic performance, because faster Faradic process can promote superior HER reaction kinetics.

Figure 4.12 Electrocatalytic HER performances of all exfoliated ReS_{2-x}Se_{2(1-x)} NDs. (a) Polarization curves (iR -corrected) of exfoliated ReS_{2-x}Se_{2(1-x)} NDs in 0.5 M H₂SO₄ electrolyte. (b) The corresponding Tafel slopes of the catalysts derived from (a). (c) Nyquist plots of ReS_{2-x}Se_{2(1-x)} NDs at the working potential of -0.202 V (vs. RHE). (d) The enlarged plots of the area shown in the red square in (c).

As showed in **Figure 4.12a-b**, TEM characterization was performed to study the tested ReSSe NDs, exhibiting similar crystallinity and dispersity with the original ReSSe NDs, confirming the stability of ReSSe NDs after stability test. Moreover, compared with most of the reported nanostructured TMD catalysts, the prepared ReSSe NDs still exhibited the superior catalytic performance (see **Table 4.3**).

Figure 4.12. (a) Low-magnification and (b) High-resolution TEM image of ReSSe NDs after long-term stability test.

Table 4.3 Comparison of electrocatalytic performances of TMD-based catalysts for HER.

Catalyst	Electrode	Onset potential (mV)	Tafel slope (mV dec ⁻¹)	η at $j = 10$ mA cm ⁻² (mV)	Catalyst loading	Reference
Ultrasmall 2H MoS ₂ nanoparticles	Au(111)	ca. -100	55-60	ca. 200	N.A.	17
MoS ₂ nanoparticles on graphene	Glassy carbon	ca. -100	41	ca. 155	0.28 mg cm ⁻²	18
Amorphous MoS ₃ film	Glassy carbon	ca. -120	40	ca. 190	N.A.	38
Double-gyroid MoS ₂	Fluorine-doped tin oxide	-(150-200)	50	~230	N.A.	19
Metallic 1T MoS ₂ nanosheets	Graphite	ca. -100	43	187	N.A.	20
Metallic 1T MoS ₂ nanosheets	Glassy carbon	ca. -100	40	ca. 200	~0.05 mg cm ⁻²	21

Strained 1T' metallic WS ₂ nanosheets	Glassy carbon	-(80-100)	55	ca. 220	6.5 $\mu\text{g cm}^{-2}$	22
Vertically aligned 1T MoS ₂ film	Glassy carbon	ca. -110	43-47	ca. 210	N.A.	39
Defect-rich MoS ₂ nanosheets	Glassy carbon	~-120	50	ca. 190	0.285 mg cm^{-2}	23
Oxygen-doped MoS ₂ nanosheets	Glassy carbon	~-120	55	ca. 180	0.285 mg cm^{-2}	24
1T' ReS ₂ nanosheets	Glassy carbon	ca. -175	75	ca. 300	N.A.	36
Expanded MoS ₂ nanosheets	Glassy carbon	-103	49	149	0.28 mg cm^{-2}	40
MoS _{1.04} Se _{0.96} nanoflakes	Glassy carbon	-(80-110)	48	ca. 165	0.28 mg cm^{-2}	41
Strained MoS ₂ nanosheets with S	Gold nanocone	ca. -60	60	~170	N.A.	33
Amorphous MoS _x Cl _y	Vertical graphene	-125	46	175	N.A.	9
Vertically-oriented lithiated ReS ₂	Au foil	~-100	84	ca. 200	N.A.	42
Pure metallic 1T MoS ₂ nanosheets	Glassy carbon	ca. -80	41	~175	43 $\mu\text{g cm}^{-2}$	31
Porous 1T MoS ₂ nanosheets	Glassy carbon	N.A.	43	~153	~0.14 mg cm^{-2}	27

CoMoS ₃ hollow prism	Glassy carbon	-75	56.9	171	0.285 mg cm ⁻²	11
MoS _{1.08} Se _{0.92} nanotubes	Glassy carbon	-101	55	219	0.32 mg cm ⁻²	43
Co-doped MoS ₂ foam	Glassy carbon	N.A.	74	156	0.5 mg cm ⁻²	44
1T MoS ₂ nanodots	Glassy carbon	-58	53	173	71 µg cm ⁻²	28
1T MoSSe nanodots	Glassy carbon	-49	40	140	71 µg cm ⁻²	28
1T' ReSe ₂ nanodots	Glassy carbon	-72	50.8	123	0.25 mg cm ⁻²	This work
1T' ReSSe nanodots	Glassy carbon	-32	50.1	84	0.25 mg cm ⁻²	This work

4.2.3 Mechanism for the Enhanced Catalytic Activity towards HER

As showed in **Figure 4.13**, The Gibbs free energies (ΔG_{H^*}) for adsorbing the intermediate hydrogen atoms (H^*) on the vacancy and edge sites of ReSSe, ReS₂ and ReSe₂ was systematically investigated via the extensive first principles calculations based on density functional theory (DFT), which is important to understand the origin of the high-performance of ReSSe catalysts (**Figure 4.14**). Since it has been confirmed by the XANES, FT-EXAFS and XPS test that S vacancies are dominant in the prepared ReSSe NDs rather than Se vacancies, S vacancy are considered as the main factor here. In addition, there are four types of vacancy site can be formed by losing the chalcogenide atom in two different paths, including high-site Se vacancy (H_{Se-v}), low-site Se vacancy (L_{Se-v}), high-site S vacancy (H_{S-v}) and low-site S vacancy (L_{S-v}), originating from the asymmetric nature of the 1T' phase structure (see **Figure 4.13**).

Figure 4.13 Simulated models of different type of S/Se vacancy of ReS₂, ReSe₂ and ReSSe.

Moreover, as shown in **Table 4.4**, the total energy on different kinds of vacancy-containing structures was calculated based on the DFT as well, which revealed the higher stability of ReS₂, ReSe₂ and ReSSe with low-site S/Se vacancy as compared with that of the high-site S/Se vacancy counterparts.

Table 4.4 Comparison of calculation ΔG_{H^*} and formed energy of different types of S/Se vacancies on ReS₂, ReSe₂ and ReSSe NDs.

Sample	Vacancy type	ΔG_{H^*} (eV)	Total energy E without H (eV)	Total energy with H (eV)	ZPE (zero point energy) of adsorbed H (eV)
ReS ₂	H _{S-v}	-0.33	-377.051	-380.763	0.163
	L _{S-v}	0.46	-377.952	-381.093	0.163
ReSe ₂	H _{Se-v}	-0.40	-349.851	-353.873	0.183
	L _{Se-v}	0.28	-350.710	-354.021	0.155
ReSSe	H _{S-v}	-0.37	-362.700	-366.691	0.187
	L _{S-v}	0.00	-363.763	-366.970	0.155

Hence, it is concluded that the edge site and the low-site S/Se vacancy could be the primary active sites for HER (**Figure 4.14a**). Based on the calculation results (**Figure 4.14b**), the ΔG_{H^*} values on the edge sites are estimated to be 0.43, 0.92 and 0.52 eV for ReSe₂, ReS₂ and ReSSe, respectively, indicating that the unsaturated coordinated Re atoms connected with Se atoms at the edge is more reactive rather than the S atoms. Moreover, the ΔG_{H^*} value can be further reduced in all systems when the H atom adsorbs on the vacancy. This is due to the fact that each H atom can only interact with one unsaturated coordinated Re

atom at the edge site, while with two unsaturated coordinated Re atoms when absorbed at the vacancy site. Therefore, the much different ΔG_{H^*} values can be observed on different kinds of vacancy and edge, exhibiting 0.00, 0.46 and 0.28 for ReSSe L_{S-V}, ReS₂ L_{S-V} and ReSe₂ L_{Se-V}, respectively (**Figure 4.14b**). As for comparison, the ΔG_{H^*} of ReSSe H_{S-V}, ReS₂ H_{S-V} and ReSe₂ H_{Se-V} were also calculated, showing the values of -0.37, -0.33 and -0.40 eV, respectively (**Figure 4.14b**). Due to the theory reported by Norskov and the coworkers, the ΔG_{H^*} of 0.00 eV is considered as the optimal value for electrocatalysts on HER (e.g., Pt).^[47] Same ΔG_{H^*} value was also observed on the H atoms bonded with the ReSSe L_{S-V} site exposed with unsaturated coordinated Re atoms, indicating its best catalytic performance for HER. Meanwhile, the highest ΔG_{H^*} value was observed on the unsaturated coordinated Re atoms in ReS₂, suggesting their lowest activity. These theoretical results are consistent with all the experimental observations. It also can be concluded that the synergistic effect originated from the alloying of S and Se atom in ReSSe may improve the catalytic performance for HER. This is also one of the reasons render ReSSe NDs for superior performance. On the basis of the analysis of experimental and calculation results, an important conclusion can be drawn that the excess of charge densities induced by the unsaturated coordinated Re atoms may significantly improve the electrocatalytic performance of prepared ReSSe ND. Moreover, the way used to create low-site S vacancy for the purpose of forming abundant active sites for electrocatalytic HER may also be applicable in other highly asymmetric 1T'-phase TMD nanomaterials.

Figure 4.14 Theoretical calculation results of ReS₂, ReSe₂ and ReSSe with different types of S/Se vacancies. (a) Simulated models of an H atom bonded with the ReS₂ edge, ReSe₂ edge, ReSSe edge, ReS₂ L_{S-V}, ReSe₂ L_{Se-V} and ReSSe L_{S-V}. (b) Calculated free energy (ΔG_{H^*}) versus the reaction coordinate of HER in the edge sites and vacancy sites of 1T'-ReS₂, 1T'-ReSe₂ and 1T'-ReSSe NDs.

Based on the obtained experimental and theoretical results, some simple ideas for the design and synthesis of highly efficient electrocatalysts toward HER can be concluded. First, the chemical Li-intercalation and exfoliation method not only can be used to prepare 2D nanosheets, but also can be used to prepared nanodots from the layered bulk materials. Second, the electrical conductivity of electrocatalyst is one of the most important factors in the catalytic reactions involving electron transfer. Because the catalytic reaction is happening on the surface of catalyst, a high electrical conductivity may lead to the faster electron transfer kinetic, which can promote the catalytic reaction. In our experiments, the improved electrical conductivity on the ReSSe nanodots is one of the reasons for the enhanced electrocatalytic activity. Third, in our experiments, the multinary components of ReS_{2-x}Se_{2(1-x)} give more possibility of creating defects, which is crucial for the defect-engineering of catalysts toward HER. In this case, introducing more components into traditional catalysts may be a good way to design new catalyst, such as heteroatom doping. Last but not least, we have proved that the asymmetric crystal structure is critical for the enhanced activity of 1T'-ReSSe nanodots. Therefore, the intrinsic symmetries on crystal structure of the materials can be one of the fundamental parameters to be considered, when we try to discover a new catalyst for specific catalytic reactions.

4.3 Conclusions

In conclusions, by combining the CVT and chemical Li-intercalation method, the ultrasmall 1T'-ReS_{2-x}Se_{2(1-x)} nanodots can be prepared using the corresponding powder of bulk crystals, which include ReS₂, ReS_{1.8}Se_{0.2}, ReS_{1.4}Se_{0.6}, ReSSe, ReS_{0.6}Se_{1.4}, ReS_{0.2}Se_{1.8}, and ReSe₂. Among them, the ReSSe nanodots with active low site S vacancies as well as the rich active edge sites showed better electrocatalytic performance for HER than that of both ReS₂ and ReSe₂ nanodots. Significantly, the 1T'-phase ReSSe nanodots show the best water-splitting performance with a small Tafel slope of 50.1 mV dec⁻¹ as well as the excellent long-term stability. Moreover, a low overpotential of 84 mV can be achieved at current density of 10 mA cm⁻². The optimal hydrogen absorption energy of the active site is concluded to the reason for the great hydrogen evolution performance, which is resulted

from by the asymmetric S vacancy in the highly asymmetric 1T' structure. This research could open a new direction to guide the design and preparation of 1T'-phase TMD electrocatalysts with high efficiency via the defect engineering down to the atomic level, and even extend to other catalysts with asymmetric structure.

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Chapter 5

Ultrathin $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9/\text{Ni}_3\text{Cr}_2\text{P}_2\text{Se}_9$ Nanosheets for Supercapacitor

Development of clean energy and highly efficient energy storage device is of importance for the sustainable economy and society. As one of the reliable energy storage devices, high-performance supercapacitors have been widely recognized and used in many application fields, especially for portable and wearable electronic devices. As the key component in supercapacitor, the electrode material is critical for fabrication of high-power density and long cyclic life supercapacitor device. Here, by the combination of chemical Li-intercalation and chemical vapor transport method, we have prepared the single- and few-layer $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ and $\text{Ni}_3\text{Cr}_2\text{P}_2\text{Se}_9$ nanosheets for the high-performance supercapacitor in acid electrolyte. When tested at the scan rate of 20 mV s^{-1} , the $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ nanosheet-based supercapacitor can deliver a specific capacitance as high as 160.7 mF cm^{-2} .

*This section will be submitted to Advanced Materials.

5.1 Introduction

Development of clean energy and high-efficient energy storage device is very important for the sustainable economy and society, which requires the development of renewable energy source as well as the high-efficiency energy storage and conversion devices, such like Lithium-ion batteries (LiBs),^[1-6] Sodium-ion batteries (SiBs)^[7-8] and supercapacitors.^[9-14] Among them, supercapacitor has become more and more widely recognized and been used in many fields, especially for portable and wearable electronic devices, because of its high energy density, great durability and fast charge/discharge process.^[15-19] Therefore, high-performance supercapacitor is always highly desired. As the key component in supercapacitor, the electrode material plays an important role on fabrication of high-power density and long cyclic life supercapacitor device. Herein, a number of functional electrode materials have been developed for fabrication of supercapacitors, including metal oxides,^[13, 20-21] carbon-based nanomaterials,^[22-23] conducting organic materials,^[24] graphene-based materials,^[18, 25-27] transition metal chalcogenide materials,^[9, 11, 14, 28] etc. Among all the reported electrode materials, the exfoliated transition metal chalcogenide nanosheets have been considered as one of the most promising candidates for fabrication of high-performance supercapacitors because of their high hydrophilicity and the great ability to dynamically accommodate and release various ions between the restacked layers.^[9-10, 14-15, 29] For example, the Manish group has reported that the exfoliated 1T-MoS₂ nanosheets can be used as electrode materials for fabrication of high-performance supercapacitors operated in inorganic and organic electrolytes.^[14] Similar phenomenon has also been reported on 1T'-MoTe₂ and WTe₂.^[9, 11] However, because of the mixed phase of exfoliated 1T-MoS₂ nanosheet, the conductivity of the restacked 1T-MoS₂ film is restricted, which hampers their performance in supercapacitors. Therefore, developing new transition metal chalcogenide nanomaterials with high conductivity are highly desirable for enhanced performance in supercapacitors.

In this chapter, monolayer and few-layer quaternary $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ and $\text{Ni}_3\text{Cr}_2\text{P}_2\text{Se}_9$ nanosheets are exfoliated from their layered bulk crystals obtained from the chemical vapor transport (CVT) method, using the chemical Li-assisted exfoliation method. The obtained

$\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ nanosheets are then restacked by using vacuum filtration method to form a film, which can be attached to the conductive carbon paper. The performance of the supercapacitor based on the conductive carbon paper attached with the $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ thin film is investigated in 1.0 M H_2SO_4 aqueous solution.

5.2 Results and Discussions

5.2.1 Synthesis and Characterizations of $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ Nanosheets

The synthesis of layered crystals of $\text{Ni}_3\text{Cr}_2\text{P}_2\text{X}_9$ (X=S, Se) was first reported on 2007 by Michael and Francis as the new quaternary transition metal chalcogenide materials. As shown in **Figure 5.1**, individual layer of the $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ consists of a few octahedra, in which the transition metal atoms (Ni or Cr) positioned at the octahedra and the chalcogenide atoms seating at the vertices. These octahedra are connected in pairs by sharing the face along *c* direction. As shown in **Figure 5.1a**, the layer distance of $\text{Ni}_3\text{Cr}_2\text{P}_2\text{X}_9$ is around 9.24 Å, making it possible to be exfoliated by lithium intercalation.

Figure 5.1 Simulated structure model of the layered $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$. (a) Side view of the single crystal unit of $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ with a layer distance of 9.24 Å. (b) Top view of the single crystal unit of $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ through *c* direction.

The ultrathin $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ nanosheets were prepared by combining the CVT and chemical Li-intercalation method, which is similar to the method we used in chapter 4. The

$\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ bulk crystal was first synthesized by using the previously reported CVT method,^[30] which were then reacted with butyllithium solution, followed by the 30 min sonication process in DI water. The single-layer $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ nanosheets were collected by 15 min centrifugation at the speed of 3000 r.p.m., followed by another centrifugation at 12,000 r.p.m. for 30 min. The as-prepared $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ bulk crystals were characterized by SEM (**Figure 5.2a-b**), revealing a crystal size of a few tens of micrometers and a clear layered structure. As showed in **Figure 5.2c-d**, the exact compositions of the obtained $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ bulk crystals were measured by EDS, exhibiting the high accuracy with designed stoichiometric ratio of Ni, Cr, P and S. The structure of the prepared $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ bulk crystals were further confirmed by the XRD (**Figure 5.3**), in which the experimental result is consistent with the simulated XRD pattern of $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$.

Figure 5.2 Morphology and chemical composition characterization of the $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ bulk crystals prepared by CVT method. (a, b) the SEM images of the prepared $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ bulk crystals. (c) EDS spectrum of the $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ bulk crystals. (d) The exact ratio of different elements of the prepared $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ bulk crystals.

Figure 5.3 XRD pattern of the $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ bulk crystals prepared by CVT method.

TEM images (**Figure 5.4a-b**) clearly revealed that the lateral size of the obtained $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ nanosheets can be as large as a few micrometers. The low contrast also confirms their ultrathin thickness. The structure and crystallinity of exfoliated $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ nanosheets are confirmed by HRTEM measurement. As illustrated in **Figure 5.4c**, the d value of 0.17 nm can be assigned to the (303) plane of $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$. The corresponding fast Fourier transform (FFT) pattern also revealed the crystalline nature of the obtained nanosheets. Furthermore, the SAED pattern obtained from a single $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ nanosheet (**Figure 5.4d**) perfectly matched the simulated SAED pattern viewing from c direction (inset in **Figure 5.4d**), revealing that c plane is exposed crystal plane on exfoliated $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ nanosheet. The elemental mapping of a single $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ clearly revealed the existence of Ni, Cr, P and S elements in the prepared $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ nanosheets (**Figure 5.4e-i**), further proving the successful exfoliation of $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ nanosheets. The chemical composition of obtained $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ nanosheets is also investigated by EDS spectra (**Figure 5.5**), which is consistent with the elemental mapping result.

Figure 5.4 Structure and composition analysis of the exfoliated $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ nanosheets. (a) Low magnification TEM image of the prepared $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ nanosheets. (b) TEM image of a single $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ nanosheet. (c) HRTEM image of a single $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ nanosheet. Inset in (c): the corresponding FFT pattern. (d) SAED pattern of a single $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ nanosheet. Inset in (d): the simulated SAED pattern viewed from **c** direction. (e) The dark-field STEM image of a single $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ nanosheet. (f-i) The elemental mapping of the $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ nanosheet in (e): (f) Ni k, (g) Cr k, (h) P k, (i) S k.

Figure 5.5 EDS spectra of the prepared $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ nanosheets obtained under TEM mode.

Moreover, the UV-Vis spectrum of the brown aqueous solution of prepared $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ nanosheets gives a smooth line with a shoulder peak at wavelength of 750 nm, which is similar to the reported $\text{Ti}_x\text{Ta}_{1-x}\text{O}_5\text{S}_y$ nanosheets (**Figure 5.6**). The atomic force microscopy (AFM) characterization was performed to reveal thickness of prepared $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ nanosheet. As shown in **Figure 5.7**, the average height of $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ nanosheets 1.4 ± 0.2 nm, which is equivalent to 1~2 layers of $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$. The SEM images obtained from the AFM samples are consistent with TEM and AFM result (**Figure 5.8**).

Figure 5.6 UV-Vis spectra of the diluted solution of exfoliated $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ nanosheets.

Figure 5.7 AFM characterization of exfoliated $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ nanosheets. (a) AFM image of the prepared $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ nanosheets. (b) Statistical analysis of the height of 100 $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ nanosheets measured from AFM images.

Figure 5.8 SEM characterization of exfoliated $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ nanosheets deposited on Si/SiO_2 substrate. (a, b) Low magnification SEM images of the exfoliated $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ nanosheets. (c, d) High magnification SEM images of the exfoliated $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ nanosheets.

Moreover, the X-ray photoelectron spectroscopy (XPS) was conducted to study the detailed surface property and structural characteristics of the obtained $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ nanosheets. It is well known that the Li-intercalation of transition metal chalcogenide bulk crystals can produce many defects and oxidations. Obviously, compared with the bulk crystals, the exfoliated $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ nanosheets showed clear O 1s signal from the XPS survey spectra (**Figure 5.9**). As demonstrated in the high-resolution XPS spectra of Cr 2p obtained from $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ nanosheets, a 2.2 eV higher binding energy was measured as compared with the bulk crystal (**Figure 5.10a**), which may be induced by oxidation of Cr^{3+} into higher valence state. As showed in **Figure 5.10b**, there is also a new peak appearing in the XPS spectra of P 2p at 133.4 eV, which can be ascribed to the P-O bonding, further confirming the partial oxidation in the $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ nanosheets. However, the binding energy of Ni 2p and S 2p were almost unchanged in both $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ nanosheets and bulk crystals (**Figure 5.10c-d**), which is due to the fact that Ni and S have more stable valence state as compared to Cr and P.

Figure 5.9 Comparison of XPS survey spectrum of prepared $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ bulk crystals exfoliated $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ nanosheets.

Figure 5.10 Comparison of high-resolution XPS spectrum of prepared $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ bulk crystals exfoliated $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ nanosheets. (a) Cr 2p. (b) P 2p. (c) Ni 2p. (d) S 2p.

5.2.2 Synthesis and Characterizations of $\text{Ni}_3\text{Cr}_2\text{P}_2\text{Se}_9$ Nanosheets

Besides the $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ nanosheets, the $\text{Ni}_3\text{Cr}_2\text{P}_2\text{Se}_9$ nanosheet has been obtained using the same method. As demonstrated in **Figure 5.11a-b**, the obtained $\text{Ni}_3\text{Cr}_2\text{P}_2\text{Se}_9$ bulk crystals exhibited similar crystal size as that of $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ crystal. The precise chemical compositions of the as-obtained bulk crystal were further measured by EDS (**Figure 5.11c-d**), showing high accuracy with the designed stoichiometric ratios. The experimental XRD pattern of prepared $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ bulk crystal exhibited high consistency with the simulated XRD patterns (**Figure 5.12**), indicating the successful preparation of $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ bulk crystals.

Figure 5.11 Morphology and chemical composition characterization of the $\text{Ni}_3\text{Cr}_2\text{P}_2\text{Se}_9$ bulk crystals prepared by CVT method. (a), (b) the SEM images of the prepared $\text{Ni}_3\text{Cr}_2\text{P}_2\text{Se}_9$ bulk crystals. (c) EDS spectrum of the $\text{Ni}_3\text{Cr}_2\text{P}_2\text{Se}_9$ bulk crystals. (d) The exact ratio of different elements of the prepared $\text{Ni}_3\text{Cr}_2\text{P}_2\text{Se}_9$ bulk crystals.

Figure 5.12 XRD pattern of the $\text{Ni}_3\text{Cr}_2\text{P}_2\text{Se}_9$ bulk crystals prepared by CVT method.

Furthermore, using the similar chemical Li-intercalation and exfoliation method, the large-scale ultrathin $\text{Ni}_3\text{Cr}_2\text{P}_2\text{Se}_9$ nanosheets could also be prepared. As shown in **Figure 5.13a-b**, these prepared $\text{Ni}_3\text{Cr}_2\text{P}_2\text{Se}_9$ nanosheets also have the big lateral size of a few micrometers and ultrathin thickness. The crystal lattice fringe of 0.27 nm obtained from the HRTEM image (**Figure 5.13c**) is consistent with the (202) plane of $\text{Ni}_3\text{Cr}_2\text{P}_2\text{Se}_9$. The FFT pattern obtained from HRTEM images show similar pattern with that of $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ nanosheet (inset in **Figure 5.13c**). The SAED characterization was also conducted to further reveal the structure of exfoliated $\text{Ni}_3\text{Cr}_2\text{P}_2\text{Se}_9$ nanosheets, showing great consistency with that of $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$.

Figure 5.13 Structure analysis of the exfoliated $\text{Ni}_3\text{Cr}_2\text{P}_2\text{Se}_9$ nanosheets. (a) Low magnification TEM image of the exfoliated $\text{Ni}_3\text{Cr}_2\text{P}_2\text{Se}_9$ nanosheets. (b) TEM image of an individual $\text{Ni}_3\text{Cr}_2\text{P}_2\text{Se}_9$ nanosheet. (c) HRTEM image of a $\text{Ni}_3\text{Cr}_2\text{P}_2\text{Se}_9$ nanosheet. Inset in (c): the corresponding FFT pattern. (d) The SAED pattern of a $\text{Ni}_3\text{Cr}_2\text{P}_2\text{Se}_9$ nanosheet.

5.2.3 Supercapacitor Performance Test of $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ Nanosheets

Previous studies demonstrated that the exfoliated transition metal chalcogenide nanosheets have great potential for the fabrication of supercapacitors. As a proof-of-concept application, our prepared $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ nanosheets were also used as electrode material for the fabrication of supercapacitor. The prepared $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ nanosheets restacked film was examined in a three-electrode set-up using Ag/AgCl (3 M KCl), graphite rod and the carbon paper attached with $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ film as the reference electrode, counter electrode and working electrode, respectively. The aqueous solution of 1.0 M H_2SO_4 is used as electrolyte. The electrochemical performance of the fabricated device was characterized by cyclic voltammograms (CV) and galvanostatic charge/discharge measurements. The

restacked $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ film was first tested in two different voltage range to determine the suitable operating voltage windows. As showed in **Figure 5.14a**, it is clear that during the voltage range of $-0.6 \sim 0.4$ V, the supercapacitor can deliver better performance as compared to the voltage range of $-0.75 \sim 0.25$ V. Because when the applied voltage goes beyond -0.6 V, the HER reaction will happen, which will decompose the electrolyte during the operating process. Therefore, all the performance tests were performed the voltage window of $-0.6 \sim 0.4$ V. Furthermore, as shown in **Figure 5.14b**, the CV curves did not show significant distortions with the increase of scan rate, indicating a good rate capability of the restacked $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ film-based device. Specifically, the fabricated device delivered the specific capacitance (C_s) of 160.7, 94.1, 81.0, 35.9 mF cm^{-2} at the scan rate of 20, 50, 100, 200, 500 mV s^{-1} , respectively (**Figure 5.14c**). In addition, **Figure 5.14d** shows the galvanostatic charge/discharge tests of the fabricated device at a broad current-density range from 0.9 to 4.5 mA cm^{-2} . Impressively, a specific capacitance of as high as 51.3 mF cm^{-2} can be obtained at the current density of 0.9 mA cm^{-2} .

Figure 5.14 Supercapacitor performance test of restacked film based on $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ nanosheets. (a) Cyclic voltammograms (CV) at different voltage range. (b) CVs collected at scan rate ranging from 20 to 500 mV s^{-1} . (c) Plot of specific capacitance (C_s) vs. scan rate. (d) Galvanostatic discharge curves collected at current density of 0.9, 2.25 and 4.5 mA cm^{-2} .

Based on the obtained experimental results, some basic rules for design and synthesis of electrode materials for fabrication of supercapacitors are summarized. First, the chemical Li-intercalation and exfoliation method not only can be used exfoliate multinary layered metal chalcogenide materials with suitable layer distance. Second, the exfoliated 2D nanosheets may inherit the physical properties from the bulk crystals. For example, the exfoliated $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ nanosheets possess the high electrical conductivity as that of the bulk crystals, which is critical for the application in supercapacitors. Third, in our experiments, $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ nanosheets showed better stability as compared with the $\text{Ni}_3\text{Cr}_2\text{P}_2\text{Se}_9$ nanosheets, which may provide the guidance for the searching of new electrode materials for supercapacitor application. In this case, for the same family of layered metal chalcogenide materials, the sulfates will be more promising than the selenide counterparts to be exfoliated for supercapacitor application. Last but not least, it is necessary to develop new synthetic method for the preparation of multinary 2D nanosheets to avoid the oxidation during the synthetic process. Because we can clearly observe the oxidation from the exfoliated nanosheets, which may be detrimental to the operating stability of the supercapacitors operated in acid electrolyte.

5.3 Conclusions

In summary, by combining chemical Li-intercalation and CVT method, the single-layer $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ and $\text{Ni}_3\text{Cr}_2\text{P}_2\text{Se}_9$ nanosheets have been obtained from the corresponding elemental powders. The restacked $\text{Ni}_3\text{Cr}_2\text{P}_2\text{Se}_9$ film showed great performance for supercapacitor, exhibiting a high specific capacitance of 160.7 and 51.3 mF cm^{-2} , at a scan rate of 20 mV s^{-1} and a current density of 0.9 mA cm^{-2} , respectively. The galvanostatic charge/discharge measurements also reveal the good rate capacity of the fabricated device based on restacked $\text{Ni}_3\text{Cr}_2\text{P}_2\text{Se}_9$ film. Our work could provide a new approach for the design and preparation of transition metal chalcogenide electrode materials for the fabrication of supercapacitors with high performance.

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Chapter 6

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. First, a facile synthetic strategy combining the chemical Li-intercalation and chemical vapor transport method was developed to prepare a series of the ultrasmall $1T'$ - $\text{ReS}_{2x}\text{Se}_{2(1-x)}$ nanodots, including ReS_2 , $\text{ReS}_{1.8}\text{Se}_{0.2}$, $\text{ReS}_{1.4}\text{Se}_{0.6}$, ReSSe , $\text{ReS}_{0.6}\text{Se}_{1.4}$, $\text{ReS}_{0.2}\text{Se}_{1.8}$, and ReSe_2 . As a result, the ReSSe nanodots exhibited the best performance with highest HER activity and excellent long-term operating stability. Comprehensive structural characterizations and analysis as well as the DFT calculations revealed that the asymmetric S vacancy plays an important role in the enhancement of HER performance. Second, a new series of layered metal chalcogenide nanosheets, i.e., the single- and few-layer $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ and $\text{Ni}_3\text{Cr}_2\text{P}_2\text{Se}_9$ nanosheets, were prepared by combining the chemical Li-intercalation and chemical vapor transport method. It was found that the prepared $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ nanosheets could be restacked by the vacuum filtration method to form a film with high conductivity, which showed great potential in fabrication of supercapacitors. Based on the current research status, the future work that can be focused on in the near future is also discussed.

6.1 General Discussion

In this thesis, I am focusing on the synthesis and structure engineering of a series of $\text{ReS}_{2x}\text{Se}_{2(1-x)}$ nanodots with unique sulfur vacancies, and a new family of quaternary ultrathin 2D metal chalcogenide nanosheets, i.e. $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ and $\text{Ni}_3\text{Cr}_2\text{P}_2\text{Se}_9$ nanosheets with high conductivity. Simultaneously, I also investigated these prepared layered metal chalcogenide nanomaterials for some potential applications, including electrocatalytic HER and supercapacitor.

6.1.1 Discussion on the Defect Engineering of $\text{ReS}_{2x}\text{Se}_{2(1-x)}$ Nanodots

First, a series of alloyed $\text{ReS}_{2x}\text{Se}_{2(1-x)}$ bulk crystals were synthesized by the CVT method from the corresponding elementary powders. All the alloyed bulk crystals were then subjected to chemical Li-intercalation and exfoliation process to produce a series of $\text{ReS}_{2x}\text{Se}_{2(1-x)}$ nanodots with ultrasmall size and ultrathin thickness. These obtained nanodots were characterized by XPS and XANES, showing unique structure characteristics induced by S and/or Se defects. For the first time, it was found that there were various types of defects in different alloyed $\text{ReS}_{2x}\text{Se}_{2(1-x)}$ materials can be produced during the violent exfoliation process. Different from the 2H and 1T phase TMD materials, the 1T'-phase $\text{ReS}_{2x}\text{Se}_{2(1-x)}$ materials intrinsically comes with possibility of producing asymmetric chalcogenide vacancies, resulting from their parent asymmetric 1T' structure. However, based on the DFT calculations of the Gibbs free energy on the absorption of intermediate hydrogen atoms, $\text{ReS}_{2x}\text{Se}_{2(1-x)}$ nanodots with different vacancies were expected to showed totally different electrocatalytic HER activity in acid medium. The ReSSe nanodots with low site asymmetric S vacancy exhibited the best values of Gibbs free energy similar to that of Pt catalyst. Therefore, it was used as the highly efficient electrocatalyst toward HER. Owing to the unique structural characteristics, this ReSSe nanodot-based catalyst also showed great long-term durability. Since there is a big family of 1T'-phase TMDs, this synthetic strategy may also be fulfilled on other 1T'-phase TMD materials, such as 1T'- MoS_2 .

6.1.2 Discussion on the Preparation of $\text{Ni}_3\text{Cr}_2\text{P}_2\text{X}_9$ ($\text{X} = \text{S}, \text{Se}$) Nanosheets

Second, ultrathin single- and few-layer quaternary metal chalcogenide nanosheets, i.e. $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ and $\text{Ni}_3\text{Cr}_2\text{P}_2\text{Se}_9$ nanosheet, was prepared by the exfoliation of their bulk crystals. Similarly, the bulk crystal was first obtained by the CVT method and then exfoliated by the chemical Li-assisted exfoliation method. The produced $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ nanosheets exhibited high hydrophilicity and high electrical conductivity and could be facilely restacked by the vacuum and filtration method to form a freestanding film. More importantly, the restacked film remained stable at a wide range sweeping voltage window of $-0.6 \sim 0.4$ V, with a great ability to be dynamically expanded and intercalated by various ions. Thus, the restacked freestanding film was used as the efficient electrode material for the fabrication of supercapacitor when supported on the conductive carbon paper substrate. Because of its high hydrophilicity and electrical conductivity, the fabricated supercapacitor device can deliver a good rate capability and high specific capacitance. This is also the first time for the demonstration of exfoliation of a new-layered quaternary transition metal chalcogenide family into single-layer dimension, further confirming the generality of the chemical Li-assisted intercalation and exfoliation method. In addition, since it is the first time for the successful preparation of $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$ and $\text{Ni}_3\text{Cr}_2\text{P}_2\text{Se}_9$ nanosheets, the potential of these single-layer nanosheets in other application filed may need further investigation, such as sensor and catalysis.

6.2 Reconnaissance Work not Included in Main Chapters

Although some achievements have been acquired during my PhD study, there are still a great number of opportunities for us to explore in this research direction. On the basis of the current progress discussed in this thesis, I will also give some suggestions on the potential future works, which can be carried out in the future.

First, previous studies have showed that ultrasmall size and ultrathin layered transition metal chalcogenide nanodots are highly desired for electrocatalytic water splitting in acid medium, such as $1\text{T-MoSSe}^{[1]}$ and the $1\text{T}'\text{-ReSSe}^{[2]}$ nanodots. Thus, size engineering of

layered metal chalcogenide materials could be the effective strategy for construction of highly efficient electrocatalysts, since there are tons of layered metal chalcogenide to be explored.^[3] Furthermore, defect engineering of layered TMD materials is another important method for preparation of high-performance electrocatalysts for HER. For example, it has been proved that the porous 1T-MoS₂ nanosheets with defects showed enhanced activity compared to the ones without defect.^[4] This is also confirmed by the 1T-MoSSe with Se vacancy and the 1T'-ReSSe with S vacancy.^[1-2] However, different from 1T and 2H phase TMDs, the 1T'-TMDs can produce more kinds of defects due to their highly asymmetric 1T' structure.^[5] Therefore, another potential research direction can be the introduction of asymmetric defects into the 1T' TMD nanomaterials, such as 1T'-MoS₂, WS₂, MoTe₂ and WTe₂. Moreover, in principle, this concept can be fulfilled with any kind of materials having asymmetric crystal structure, which may extend our method to more research fields. In addition, the asymmetric vacancy induced enhancement on catalytic activity may also be found in other applications, which calls for urgent study.

Second, the exploration of new materials with novel physicochemical properties is always an effective way to solve specific problems for various applications. Our attempts on the preparation of Ni₃Cr₂P₂S₉ and Ni₃Cr₂P₂Se₉ bulk crystals proved that the new quaternary layered metal chalcogenide materials also can be successful. More importantly, the restacked Ni₃Cr₂P₂S₉ film showed great potential in fabrication of supercapacitor. Hence, the exploration of the exfoliation of new layered metal chalcogenide materials using the well-developed chemical Li-intercalation method can be another possible future direction. Furthermore, exploration of the new properties of new metal chalcogenide nanosheets can also develop new potential application of the prepared materials. For example, by studying the properties of prepared single-layer Ni₃Cr₂P₂S₉ film nanosheets, the aqueous solution of Ni₃Cr₂P₂S₉ nanosheets showed strong absorption on the wavelength of 750 nm, which may be potentially used as photothermal agent for killing cancer cells. Similar phenomenon on layered metal chalcogenide materials has been reported on Ti_xTa_{1-x}S_yO_z nanosheets,^[6] enabling the possibility for utilizing of Ni₃Cr₂P₂S₉ and Ni₃Cr₂P₂Se₉ nanosheets in this field.

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