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**ELECTROCHEMISTRY OF LAYERED MATERIALS FOR
ENERGY APPLICATIONS**

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SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

2019

ELECTROCHEMISTRY OF LAYERED MATERIALS FOR ENERGY APPLICATIONS

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SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

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

2019

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research done by me except where otherwise stated in this thesis. The thesis work has not been submitted for a degree or professional qualification to any other university or institution. I declare that this thesis is written by myself and is free of plagiarism and of sufficient grammatical clarity to be examined. 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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A handwritten signature in black ink that reads "Wang Yong". The signature is written in a cursive, flowing style. The first name "Wang" is written in a larger, more prominent script, and the second name "Yong" is written in a slightly smaller, more compact script. The signature is placed on a light gray rectangular background.

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Wang Yong

Supervisor Declaration Statement

I have reviewed the content and presentation style of this thesis and declare it of sufficient grammatical clarity to be examined. To the best of my knowledge, the thesis is free of plagiarism and the research and writing are those of the candidate's 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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..... *J. England*
Jason England

Authorship Attribution Statement

This thesis contains material from 7 papers published in the following peer-reviewed journals in which I am listed as an author.

Chapter 4 is published as Luxa, J.; Wang, Y.; Sofer, Z.; Pumera, M.*, Layered Post-Transition-Metal Dichalcogenides (X-M-M-X) and Their Properties. *Chem. Eur. J.* **2016**, 22, 18810-18816.

The contributions of the co-authors are as follows:

- Prof Martin provided the project area and guidance as well as helped to edit the manuscript.
- I prepared the manuscript. Prof Sofer, Dr Jan Luxa and Prof Martin revised the manuscript.
- I performed the experiments to investigate and analyze the electrochemical properties of materials.
- All electrochemical measurements, and the materials characterization with SEM and XPS were conducted by me to observe the electrochemical properties.
- Dr Jan Luxa assisted to characterize the materials with XRD, Raman spectroscopy, photoluminescence spectra.

Chapter 5 is published as Wang, Y.; Szökölóvá, K.; Nasir, M. Z. M.; Sofer, Z.; Pumera, M.*, Electrochemistry of Layered Semiconducting A^{III}B^{VI} Chalcogenides: Indium Monochalcogenides (InS, InSe, InTe). *ChemCatChem*. **2019**, 11, 2634-2642.

The contributions of the co-authors are as follows:

- Prof Martin recommended the research direction and helped to revise and edit the manuscript.
- I analyzed the data and wrote the manuscript; Dr Zafir, Prof Sofer together with Prof Martin revised the manuscript.
- Katerina Szökölóvá and Prof Sofer performed the materials synthesis, and characterized the materials by TEM, XRD, Raman spectroscopy and photoluminescence spectra.

- I performed the materials characterization, conducted the SEM, XPS and all the electrochemical measurements, and conducted data evaluation.

Chapter 6 is published as Wang, Y.; Sofer, Z.; Luxa, J.; Pumera, M.*, Lithium Exfoliated Vanadium Dichalcogenides (VS₂, VSe₂, VTe₂) Exhibit Dramatically Different Properties from Their Bulk Counterparts. *Adv. Mater. Interfaces*, **2016**, 23, 1600433.

The contributions of the co-authors are as follows:

- Prof Martin provided materials area and helped to edit and revise the manuscript.
- I analyze the data and prepare the draft. Dr. Jan Luxa, Prof Sofer and Prof Martin revised the manuscript.
- Dr. Jan Luxa and Prof Sofer synthesized all the materials and characterized the materials by XRD and STEM.
- I performed the SEM and XPS to analysis the materials and all the electrochemical measurements to evaluate the electrochemical performance of the materials.

Chapter 7 is published as Wang, Y.; Szokolova, K.; Nasir, M. Z. M.; Sofer, Z.; Pumera, M.*, Layered Crystalline and Amorphous Platinum Disulfide (PtS₂): Contrasting Electrochemistry. *Chem. Eur. J.*, **2019**, 25, 7330-7338.

The contributions of the co-authors are as follows:

- Prof Martin suggested the research direction and provided the guidance.
- I wrote the manuscript. Dr. Zafir, Prof Sofer and Prof Martin helped to edit and revise the manuscript.
- Katerina Szokolova and Prof Sofer performed the materials synthesis and conducted the XRD, TEM for materials analysis
- I collected the SEM and XPS data as well as all the electrochemical signals and analyzed the data.

Chapter 8 is published as Wang, Y.; Sofer, Z.; Luxa, J.; Chia, X.; Pumera, M.*, Graphene/Group 5 Transition Metal Dichalcogenide Composites for Electrochemical Applications. *Chem. Eur. J.*, **2017**, 23, 10430-10437.

The contributions of the co-authors are as follows:

- Prof Martin provided the idea for the project and necessary guidance.
- I wrote the manuscript. Dr. Xinyi Chia, Prof Sofer and Prof Martin helped to revised and edited the manuscript.
- Dr. Jan Luxa and Prof Sofer synthesized the materials and collected the corresponding XRD data.
- I performed the materials characterization by SEM and XPS, and conducted data evaluation.
- I conducted all the electrochemical measurements to analysis the electrochemical properties and data analysis.

Chapter 9 is published as Wang, Y.; Mayorga-Martinez, C. C.; Chia, X.; Sofer, Z.; Pumera, M.*, Nonconductive layered hexagonal boron nitride exfoliation by bipolar electrochemistry. *Nanoscale*, **2018**, 10, 7298-7303.

The contributions of the co-authors are as follows:

- Prof Martin recommended the research area and provided the materials and guidance.
- I analyzed the data wrote the drafts. Dr. Carmen, Dr. Xinyi Chia and Prof Martin helped to revise the manuscript.
- Prof Sofer performed TEM for material analysis
- I performed all the materials exfoliation, collected XPS, AFM, SEM and STEM data; and conducted data evaluation.
- I performed the electrochemical measurement to analyze the electrochemical properties.

Chapter 10 is published as Wang, Y.; Mayorga-Martinez, C. C.; Chia, X.; Sofer, Z. k.; Mohamad Latiff, N.; Pumera, M.*, Bipolar Electrochemistry as a Simple Synthetic

Route towards Nanoscale Transition of Mo_2B_5 and W_2B_5 for Enhanced Hydrogen Evolution Reaction. **2019**, 7, 12148-12159.

The contributions of the co-authors are as follows:

- Prof Martin suggested the materials area for project and provided the guidance.
- The manuscript was prepared by me and further revised and edited by Dr. Xinyi, Dr. Carmen and Prof Martin.
- I performed all the experiments to prepare the materials, collected XPS, SEM and STEM data, and conducted the electrochemical experiments to obtain the electrochemical performances, and conducted the data analysis.
- Dr. Carmen and Prof Sofer assisted to perform XRD and TEM to characterize the materials.

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Wang Yong

Abstract

It is critical and important to search for the renewable and clean fuel alternatives due to the limited supply of fossil fuel, CO₂ emission and increasing world energy demand. Advanced energy storage devices and carriers such as hydrogen, supercapacitors, fuel cells and batteries has been regarded as the clean, efficient and renewable energy supplier to meet the future world energy demand. Therefore, searching for good electrode materials is of importance for the implementation of sustainable energy devices and energy carriers. Transition metal dichalcogenides (TMDs) as well as other layered materials have been used as the electrode materials in various electrochemical applications due to the intriguing optical, electrical and electrochemical properties. Especially, TMDs such as MoS₂ and WS₂ have been reported to be highly active towards electrochemical hydrogen evolution reaction (HER). Therefore following this line of thinking, this thesis investigated a spectrum of TMDs and layered materials to reveal their electrochemical properties and their potential as the electrocatalyst toward HER. Layered post-transition metal chalcogenides like gallium chalcogenides and indium chalcogenides as well as the Group 5 TMDs have been comprehensively studied to reveal their fundamental electrochemical properties and electrocatalytic activity. Furthermore, novel strategies including exfoliation of TMDs, phase engineering and TMD hybrids with conductive graphene have been utilized to tune and improve the electrocatalytic activity toward HER. Moreover, electrochemical concept of bipolar electrochemistry was adopted to exfoliate and downsize the layered materials for electrochemical applications with improved HER performance. These findings and knowledge of the electrochemical properties of layered materials are beneficial for the practical sustainable energy applications.

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Chapter 1

Objectives of the Thesis

The increasing world energy demand has been driving us to produce the renewable fuels to meet the future need. Advanced electrochemical water splitting is such a promising technology to produce the hydrogen fuel. Hydrogen fuel can be used to generate the electricity and power vehicle in fuel cells. However, electrochemical hydrogen production requires electrocatalysts to promote the reaction kinetic and decrease the overpotential required for HER. The state-of-the-art electrocatalyst toward electrochemical hydrogen production is noble metal Pt. Noble Pt is expensive and low abundant on earth, which limits the industrial applications. Therefore, searching for the electrocatalysts with earth abundant elements is significant. TMDs have been investigated as the potential electrocatalysts for the electrochemical hydrogen production. In order to find the suitable electrocatalysts, this thesis entitled *“Electrochemistry of Layered Materials for Energy Applications”* studies the electrochemistry of several types of layered materials as well as their potential as the electrocatalysts. The world energy crisis and the importance of HER as well as the challenges are discussed in **Chapter 2**. Three aspects are then investigated in this thesis; **Part I** comprehensively studies the electrochemical properties of layered material, **Part II** adopts novel methods to tune the electrocatalytic activity of layered materials, and in **Part III**, bipolar electrochemical method is used to exfoliate and downsize the layered materials for electrochemical applications. The background and literature review on electrochemical energy applications as well as the novel strategies to optimize the electrocatalytic activity are presented in **Chapter 3**.

Part I investigates the fundamental electrochemical and electrocatalytic properties of layered semiconducting post-transition metal chalcogenides which has been overlooked. **Chapter 4** investigates the electrochemistry of layered gallium chalcogenides (GaS, GaSe and GaTe) as well as the indium selenides while **Chapter 5** comparatively explores the electrochemistry of layered indium chalcogenides.

Subsequently, **Part II** presents the factors affecting the electrocatalytic performance of TMDs toward HER. **Chapter 6** studies and compares the electrocatalytic performance of bulk and exfoliated vanadium dichalcogenides (VS_2 , VSe_2 and VTe_2). Following, **Chapter 7** explores effect of phase engineering on HER by studying the electrochemistry of crystalline and amorphous PtS_2 . Lastly, **Chapter 8** presents the effect of conductive support on the electrocatalytic activity by nanocomposites of graphene with Group 5 TMDs (VS_2 , NbS_2 and TaS_2).

Lastly, **Part III** focuses on bipolar electrochemistry as the novel electrochemical method for exfoliation and downsizing the layered materials. In **Chapter 9**, hexagonal boron nitride is exfoliated into few layers by bipolar electrochemistry. In **Chapter 10**, bipolar electrochemistry is used to downsize the Mo_2B_5 and W_2B_5 into nanoparticles with enhanced electrochemical hydrogen production performance.

Finally, the thesis ends with **Chapter 11**, which presents the conclusion and discusses the future direction of the field.

Chapter 2

Introduction

- 2.1 The Global Energy Crisis
- 2.2 Hydrogen Economy and Hydrogen Production
- 2.3 Layered Metal Chalcogenides Families
 - 2.3.1 Transition Metal Dichalcogenides
 - 2.3.2 Post-transition Metal Chalcogenides

2.1 The global Energy Crisis

Global energy crisis is the most concerning issue faced by human in the 21st century. The energy crisis stems from the limited supply of natural energy sources which cannot meet the world's energy demand due to increasing energy consumption, population growth and economic developments.¹⁻³ Besides, these natural fossil fuels have limited supplies and are non-renewable as they take millions of years to form. From the long-term perspective of global energy production (Figure 2.1),⁴ the transformation, changing demands and increased consumption of various energy sources has been obviously presented. In the 1800s, energy was mainly produced from the burning of biofuels and coal was just starting to provide an alternative energy source. Subsequently, oil was used from the 1870s. The early 1900s saw the transition to alternative energy sources of natural gas and hydroelectric energy. The emergence of nuclear technology led to the exploitation of nuclear power as a novel energy source in the 1960s. The 1980s saw the increased awareness on the limitations of non-renewable sources and development in energy-related technologies which harnessed energy from renewable wind and solar. However, their contribution to world energy consumption remains small to date. Even till today, non-renewable sources still play dominant roles in global energy production.

Figure 2.1 World energy consumption measured in terawatt-hours (TWh) per year from 1800s to 2017. Reproduced from Ref. 4.

Combustion of fossil fuels raises greater concerns which greatly affect global environmental balance. Burning of fossil fuels releases greenhouse gases into the atmosphere, which play significant roles in global warming. According to the research, carbon dioxide (CO₂), water vapor, methane, nitrous oxide as well as tropospheric ozone in atmosphere are regarded as the greenhouse gases. These gases trap and capture heat from the sun which eventually causes greenhouse effect.⁵ The greenhouse gas carbon CO₂ comes primarily from the burning of carbonaceous fuels (coal, oil and natural gas) for electricity, heat, and transportation. Figure 2.2 shows the changes in levels of atmospheric CO₂ from over the past 800,000 years.⁶ It was found that atmospheric CO₂ concentrations steadily stayed lower than 300 ppm before the modern industrialization. However, the start of industrial revolution saw levels of atmospheric CO₂ to accelerate significantly (1958 to 2018) with a 40% increase to reach the highest CO₂ level of 408 ppm.⁷ The increase in CO₂ concentration poses a global warming issue resulting in increasing global temperatures and rapid climate changes. It is believed that global average temperature increase will reach 2 °C (3.6 °F) by 2060⁸ which will dramatically change ecosystems and affect the diversity in Earth.

CO₂ emissions for global energy supply has reached a high level of 33.1 Gt in 2018 and about 80% comes from fossil fuels combustion.⁹ To address the energy crisis and reduce CO₂ emissions, it is crucial to explore and develop alternative renewable clean energy sources to meet the ever increasing demand. Moving forward, global energy production from non-renewable sources should also transit to renewable alternatives which would add lesser strain on their limited supply.

Figure 2.2 Atmospheric carbon dioxide concentrations over duration of 800,000 years.

Reproduced from Ref. 6.

2.2 Hydrogen Economy and Hydrogen Production

Hydrogen is regarded as a highly promising alternative to non-renewable fossil fuels in many aspects. Hydrogen as an energy carrier has high energy density and clean byproduct, water.¹⁰ Hydrogen is able to release energy by reaction with oxygen gas in fuel cells to generate electricity.¹¹ Besides that, elemental hydrogen is abundant in Earth where it exists in the forms of water and hydrocarbons. Although hydrogen is widely available, hydrogen gas is not naturally available and needs to be chemically retrieved from water or hydrocarbon sources. Hydrogen gas generation is largely produced from steam reforming of fossil fuels (96% of the total capacity) and additionally from electrolysis (4%).^{12, 13} However, this production process is still highly reliant on non-renewable fossil fuels and still releases CO₂ into the environment. To access the hydrogen economy, few challenges need to be overcome.¹³ The first challenge is to develop low-cost and efficient technologies to generate hydrogen gas from renewable sources such as water. Following that, these technologies should achieve high efficiency energy conversion of fuel-cell-hybrid vehicles for the oxidation of hydrogen. Lastly, there should be measures and engineering practices in place for the safe operation and storage of hydrogen gas produced.¹³ Figure 2.3 provides a schematic on a possible model of the hydrogen economy development.¹⁴ Recently, tremendous research has been devoted toward

optimizing electrolysis of water to obtain hydrogen gas, namely focusing on electrochemical HER. HER takes place at the cathode while the oxygen evolution reaction (OER) occurs at the anode in a water splitting process displayed in equations (1) and (2).

Due to the sluggish reaction rate, water splitting needs electrocatalysts to lower energy required and enhance the efficiency for both HER and OER.¹⁵⁻¹⁹ The well-known electrocatalysts to date for both HER and OER is Pt with good electrocatalytic performance and negligible overpotential. However, Pt is very expensive which is not favorable for industrial use and applications. Therefore, it is essential and important to explore other alternative electrocatalysts to replace the precious Pt. To date, Transition metal chalcogenides, phosphides, carbides, borides, nitrides and other non-metal based electrocatalysts have thus far been reported to be efficient electrocatalysts for HER.^{18, 20-}

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Figure 2.3 Schematic illustration of the possible model of hydrogen economy development including H₂ production and H₂ utilization. Reproduced from Ref. 14.

2.3 Layered Metal Chalcogenides Families

The discovery of layered graphene in 2004 with extraordinary electronic, optical and physical properties has driven the scientific field to explore other two dimensional materials.²⁵ In particular, layered metal chalcogenides have attracted immense attention to study their intriguing properties. Due to the different types of metal groups, the different layered metal chalcogenides family can be classified as TMDs, Group III chalcogenides, Group IV chalcogenides, and topological insulator as shown in Figure 2.4. Further discussion of TMDs and Group III chalcogenides will be presented in the thesis.

The figure shows a periodic table with several elements highlighted in colored boxes and labeled with red text and arrows:

- Transition Metal Dichalcogenides:** A red box encompasses transition metals from Groups 4 to 10 (Ti, V, Cr, Mn, Fe, Co, Ni, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Hf, Ta, W, Re, Os, Ir, Pt) and chalcogenides S, Se, and Te.
- Group III Chalcogenides:** A red box and arrow point to Al, Ga, In, and Tl.
- Group IV Chalcogenides:** A red box and arrow point to Si, Ge, Sn, and Pb.
- Topological Insulators:** A red box and arrow point to Sb, Bi, As, Te, Se, and S.

Figure 2.4 Layered metal chalcogenides including TMDs, post-transition metal chalcogenide (group III chalcogenides and group IV chalcogenides) and topological insulators.

2.3.1 Transition Metal Dichalcogenides

TMDs represent a type of interesting layered materials. In general, TMDs have a formula of MX₂, where M is the transition metal from Groups 4-10 and X is the chalcogen atoms. Each TMD layer is composed of one layer of M atoms and two layers of X atoms to form an X-M-X motif. These motifs are stacked by weak van der Waals forces to form the

three dimensional counterparts, which makes it possible to delaminate/exfoliate to single or few layers. Depending on the atomic arrangement and stacking sequence of layers, TMDs can exist as three different polytype phases which are 1T, 2H and 3R as shown in Figure 2.5.²⁶ 2H phase refer to the trigonal prismatic coordination (D_{3h}) in single TMDs layers while 1T phase has an octahedral coordination (O_h). 3R phase has the same trigonal prismatic coordination as 2H, but presents different stacking sequence (AbA CaC BcB) as compared to 2H (AbA BaB). Various TMDs show different polymorph forms based on the metal groups attached. For example, Group VI TMDs (MoS_2 and WS_2) exists with 2H phase in its natural form while Group IV TMDs (Ti and Zr) adopt the 1T phase instead. Interestingly, 2H and 1T polymorph TMDs show distinctively different properties with potentially wide spectra and variety of applications. Taking MoS_2 as an example, MoS_2 in 2H phase is semiconducting with an indirect bandgap of 1.29 eV.²⁷ Besides that, 2H phase MoS_2 is stable and chemically inert, which has interesting optical properties.²⁸ However, 1T phase MoS_2 is metastable and metallic, and is more efficient electrocatalyst towards electrochemical hydrogen production.^{29, 30} Phase transition from 2H MoS_2 to 1T MoS_2 was achieved by chemical exfoliation by lithium intercalation.²⁹

Figure 2.5 The TMD metal coordination as well as the stacking sequence of TMD layers.

Reproduced from Ref. 26.

The weak interlayer forces and the development of several exfoliation methodologies render it possible to delaminate the layered TMDs to single or few layer sheets. Single layered TMDs not only inherit the original properties of the bulk counterparts, but inherit additional unique optical and electronic properties due to confinement effects. Developing efficient, feasible, low cost methods of preparing the high quality TMDs nanosheets in large scale is essential and important to fulfill their potential in numerous applications. The earliest reported exfoliations of MoS₂ were conducted using adhesive tape (mechanical cleavage) or lithium intercalation.^{31, 32} Up to date, the efficient and extensively used methods for mass production of TMDs nanosheets are liquid exfoliation and chemical exfoliation by lithium intercalation.^{26, 33-35} Liquid exfoliation usually requires the use of organic solvents like *N*-methyl pyrrolidone or dimethylformamide to downsize TMDs by sonication method. Sonication is adopted to help overcome and break the interlayer forces while the organic solvents stabilize the resultant TMD nanosheets formed. Chemical exfoliation by lithium intercalation aids in the exfoliation of TMDs by intercalating lithium ions between the layers thus occupying the interlayer spaces and separate the sheets. The resultant products lead to the formation of lithium intercalated compounds. TMDs suspension is refluxed in butyllithium for several hours followed by sonication in water. Other bottom-up processes reported require the use of reactive precursors for the synthesis of ultrathin TMDs such as chemical vapor deposition (CVD) and hydrothermal synthesis.^{36, 37}

2.3.2 Post-transition Metal chalcogenides

Although TMDs have been widely studied to explore their electrochemical properties and various applications, few studies investigate the properties of post-transition metal dichalcogenides, especially Group III chalcogenides. Group III chalcogenides, such as gallium (GaS, GaSe, GaTe) and indium chalcogenides (InS, InSe), represent a class of

interesting semiconductors with band gap energies ranging from near-infrared (NIR) to UV region. Most of Group III chalcogenides are layered compounds. The general formula of Group III chalcogenides is MX , where M is the metal (Ga, In) and X is the chalcogen (S, Se, Te). These compounds may exist in other stoichiometry such as M_2X_3 and M_2X . However, such compounds do not exhibit layered state.^{38, 39} Each layer consists of two metal atoms and two chalcogen atoms in the X-M-M-X sequence shown in Figure 2.6, different from that of TMDs.⁴⁰ Similar to TMDs, These layers are stacked by van der Waals forces. Group III chalcogenides have been reported to applied in many applications in transistor, photodetector, photocatalysis, and electrocatalysis owing to their moderate bandgaps, defined charge carrier properties and high carrier mobility.⁴¹⁻⁴⁶

Figure 2.6 Atomic structures of semiconducting GaS, GaSe, GaTe and InSe. Reproduced from the Ref 40.

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Chapter 3

Background and Literature Review

- 3.1 Electrochemical Energy Conversion and Storage
 - 3.1.1 Hydrogen and Oxygen Evolution Reactions
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3.1 Electrochemical Energy Conversion and Storage

Advanced electrochemical energy technologies, including electrolysis of water, fuel cells, batteries and supercapacitors, have been attracting numerous attention with increasing environmental degradation issues and depleting supply of non-renewable energy sources. The electrolysis of water splits water molecules into hydrogen and oxygen gases *via* two half reactions: HER at the cathode and OER at the anode. Electrochemical splitting of water is a strongly thermodynamic uphill reaction which requires large energy inputs to promote the reactions. Besides, supercapacitors as energy storage devices is also critical in the development of sustainable energy technologies. Supercapacitors are able to store energy by electrostatic charge accumulation or Faradic processes. In view of the large-scale potential uses of these sustainable energy conversion and storage devices, it is of vital to explore efficient, low cost and superior electrocatalysts or electrode materials for water electrolysis and supercapacitor applications.

3.1.1 Hydrogen and Oxygen Evolution Reactions

Electrolysis of water is regarded as an efficient non-polluting method for the mass production of H₂ of high purity. In a water electrolytic cell, HER occurs at the cathode to generate H₂ while OER takes place at the anode to release O₂, as illustrated in Figure 3.1.¹ The chemical equations for HER and OER are shown below:

Electrolysis of water requires an energy input of 237.2 kJ mol⁻¹ to drive the cathodic HER and anodic OER process. Theoretically, the minimum potential required for electrolytic water splitting is 1.23 V. However, a much higher potential is required to oxidize water in practical applications.^{2, 3} This additional potential which exceeds the theoretical potential values is termed as overpotential. Therefore, potential electrocatalysts should

be exploited to decrease overpotential values of both HER and OER to make the electrolytic device more energy-efficient.

Figure 3.1 Schematic illustration of an electrochemical water electrolysis cell.

Reproduced from Ref. 1.

HER involves the reduction of protons by an electron to generate H_2 under acidic condition. The possible reaction mechanisms for HER are shown as the following: ⁴

The process of HER are summarized into two pathways. The first step is the Volmer adsorption reaction (Equation 1), which involves an electron transfer to reduce a proton forming an absorbed hydrogen atom (H_{ads}) at the electrocatalyst surface. The Tafel value (b) for this reaction is about 120 mV dec^{-1} at room temperature. The following is either a desorption Heyrovsky or Tafel reaction. At lower H_{ads} coverage, a Heyrovsky process (Equation 2) takes place where a H_{ads} reacts with a proton and electron to produce H_2 . The Tafel value for Heyrovsky reaction is about 40 mV dec^{-1} . On the contrary, two H_{ads} could combine to form H_2 when the H_{ads} coverage is high. This process is defined as the Tafel step with Tafel value of 30 mV dev^{-1} (Equation 3). Tafel slope value is the intrinsic

property of an electrocatalyst and provides information of the favored HER mechanism. A smaller Tafel slope value indicates faster current density increase with overpotential. Tafel slope can be experimentally obtained by plotting the linear range of the Tafel equation of $\eta = a + b \log |j|$. For example, noble metal Pt has a Tafel slope value of 30 mV dec⁻¹, indicating Volmer-Tafel mechanism with the rate-determining Tafel step.

The reduction potential for HER is theoretically 0 V. However, additional potential is required to drive HER in real conditions resulting from the polarization of electrodes which is defined as overpotential. Implementation of electrocatalysts for HER is able to reduce overpotential thus promoting reaction rates and device efficiency by being more energy efficient. The highly efficient electrocatalyst for HER is Pt with low overpotential and Tafel slope value. However, the cost of Pt is very high, which hinders the applications of Pt as electrocatalyst. As a result, it is of importance to look for the alternative low-cost electrocatalysts with comparable HER performance as substitutes.

The optimal and ideal electrocatalyst should have hydrogen adsorption energy close to zero ($\Delta G_H = 0$), which means the hydrogen atom is binding to electrocatalyst active sites neither too strongly nor weakly.⁵ Figure 3.2 shows the volcano type relationship, which shows the exchange current density (i_0) as a function of hydrogen adsorption free energy (ΔG_H).⁶ It is clearly observed that platinum has excellent HER performance with ΔG_H close to zero. Additionally, molybdenum disulfide (MoS₂) is determined to have ΔG_H of +0.08 eV which is close to zero. Therefore, MoS₂ is believed to be an efficient electrocatalyst for HER, which has been experimentally demonstrated.⁶ To date, several classes of alternative HER electrocatalysts, such as transition metal chalcogenides, phosphides, borides, carbides as well as nitrides have been attracting interest.⁷

Figure 3.2 The HER exchange current densities as a functional of hydrogen adsorption energies. Reproduced from Ref. 6.

OER occurring at the anode involves the oxidation of water to generate O₂ which is a critical half-cell reaction for water electrolysis and fuel cells. Due to the sluggish reaction kinetics of OER, water electrolysis are highly limited in practical applications. Unlike HER, which is a two electrons transfer reaction, OER is a four electrons-one proton reaction. Therefore, OER would require higher energy inputs than HER to initiate the reaction. The possible mechanisms of OER have been widely studied in both acidic and alkaline electrolytes which are shown below:⁸

Proposed OER mechanisms in acidic electrolyte:

Or

Proposed OER mechanisms in alkaline electrolyte:

Or

Where M represents surface metal cation.

In both acidic and alkaline conditions, intermediates species (MO or MOOH) are formed. Based on studies reported, there are two possible pathways of O₂ formation. The first proposed pathway involves the combination of two absorbed oxygen atoms (MO) to produce O₂ (Equations 6 and 11). The alternative proposed pathway suggests that MO reacts with H₂O under acidic condition or OH⁻ in alkaline electrolyte to generate an MOOH intermediate, followed by decomposition to form O₂ (Equations 7, 8 and 12, 13). Studies on OER mechanisms show that interactions between the intermediates species (MO, MOH or MOOH) and the electrode surface are critical to the performance of an electrocatalyst. Optimal OER electrocatalysts should have neither too weak nor too strong M-O bonds.

High energy input and sluggish reaction kinetics for OER make it necessary to use electrocatalysts to reduce the overpotential and facilitate the process. Precious metal oxides like RuO₂ and IrO₂ are demonstrated to be active for OER.⁹ However, both RuO₂ and IrO₂ suffer from long term instability and high cost which limits practical applications. RuO₂ oxidises to RuO₄ at high positive potential which gets dissolved in the electrolyte.¹⁰ In a similar manner, IrO₂ gets oxidized to IrO₃ which subsequently dissolves during the experiment.^{11, 12} Other classes of electrocatalysts for OER including perovskites, layered metal hydroxides as well as non-oxide electrocatalysts like metal chalcogenides and metal pnictides, have also been studied to be suitable for OER. These OER electrocatalysts are low cost, relatively stable and earth abundant. Similar to HER, the

parameters containing i_0 , overpotential, onset potential and Tafel slope are also utilized to evaluate OER electrocatalytic performances.⁸

3.1.2 Supercapacitor

Supercapacitor, also known as ultra-capacitor, is regarded as the promising energy storage and conversion technologies for sustainable development to meet the increasing world energy demand. The concept of supercapacitor was first conceptualized by Hermann von Helmholtz in 1853 and porous carbon based supercapacitor was patented for the first time in 1957.¹³ The first double layer capacitor was developed in 1982 using metal oxide. Supercapacitors are capable of storing larger energy than the conventional supercapacitor and applied in energy management, consumer electronics and heavy hybrid vehicles.¹⁴ Although supercapacitors have lower energy density than batteries, higher power density, longer stability with unlimited cycle life and faster charging/discharging processes also favor the practical applications.

Supercapacitors based on energy storage mechanism can be divided into two types: electrochemical double layer capacitor (EDLC) and pseudocapacitor. The storage mechanism of EDLC is the accumulation of electrostatic charge at the electrode materials surface. Therefore, electrode materials with high specific area and accessible nanopores such as graphene, carbon nanotube and activated carbon are beneficial for EDLC. Several models have been proposed to illustrate the mechanisms and ion behavior in EDLC (Figure 3.3).¹⁵ Helmholtz model is the fundamental preliminary theory put forth which describes the formation of a single layer of corresponding oppositely ions in the electrolyte onto the electrode surface to neutralize the charges of the solid electronic conductor.¹⁶ The distance d between the two layers is calculated from the electrode surface to the centre of ions. Helmholtz model was further modified and developed by Gouy and Chapman. The proposed model took into consideration the diffusion tendencies

of ions in liquid electrolyte and state that ions concentrations at the electrode surface follow the Boltzmann's distribution. However, this model is unable to accurately obtain the diffusion distance. In consideration of the deficiencies both of Helmholtz and diffusion models, Stern proposed a new model which involves the formation of two layers of ions defined as inner Stern layer and outer diffusion layer shown in Figure 3.3 c. The inner Stern layer, also called compact layer, is used to describe ions which are adsorbed at the electrode material surface. At the Stern layer, the specifically adsorbed ions exist which is the inner Helmholtz plane (IHP). At the same Stern layer, there are non-specifically adsorbed ions which form the outer Helmholtz plane. Understanding the Stern model and ions behaviors, capacitance from EDLC comes from the compact and diffusion layers capacitance. On the other hand, pseudocapacitors depend on the reversible redox behaviors of active species on electrode materials like metal oxides and conducting polymers which often afford higher capacitance than EDLC.¹⁷

The developments and advancements in synthesis technology have enabled fabrication of improved nanocomposite electrode materials for supercapacitors. Rational design of composite electrode materials has not only enhanced specific capacitance, but also show improved cycle stability and rate capability. The nanocomposites of conducting polyaniline (PANI) with graphene or TMDs have been studied to show higher specific capacitance values. For example, PANI/MoS₂ hybrid synthesized by *in situ* polymerization shows good capacitive performance of 575 F g⁻¹ at 1 A g⁻¹ as a result of its unique structure.¹⁸ Furthermore, the hybrid electrode of PANI nanowire arrays grown on 3D tubular MoS₂ showed the high capacitance of 552 F g⁻¹ at 0.5 A g⁻¹ with long cycle life and excellent rate capability due to the unique architecture and synergistic effects.¹⁹

Figure 3.3 The various proposed models of electrochemical double layer capacitor: (a) Helmholtz model, (b) Gouy–Chapman model or diffuse model, and (c) Stern model. IHP refers to the inner Helmholtz plane, OHP represents the outer Helmholtz plane while d is the distance from the electrode surface to the centre of ions. Reproduced from Ref. 15.

3.2. Electrochemical Properties of Layered Metal Chalcogenides

3.2.1 Inherent Electrochemistry

Inadequate electrochemical studies on layered metal chalcogenides make it essential and interesting to investigate their electrochemical properties for potential applications ranging from electrocatalysis to electrochemical sensing. Although electrochemical energy conversion and storage like HER of layered metal chalcogenides has been widely studied, few studies have been reported about their inherent electrochemical properties. Inherent electrochemistry refers to the intrinsic redox behaviors which take place at the surface of layered metal chalcogenides under applied potential. This redox behaviors correlates with the electrolyte used and additionally influenced by pH and potentials applied. It is necessary and critical to understand the inherent electrochemical properties of layered metal chalcogenides as the performing potential window can be limited by the inherent electrochemistry. The first study of inherent electrochemical properties was

reported to reveal the oxidation peaks of carbon supported MoS₂ nanoparticles starting at the potential of +0.6 V to +0.98 V vs NHE shown in Figure 3.4 a.²⁰ This oxidation peak was chemically irreversible and disappeared in the subsequent scan which resulted in poorer HER performance. From the inset in Figure 3.4 a, two anodic peaks were observed, a conspicuous peak centered at the potential of about +0.98 V and a minor peak located at +0.7 V. Considering that the edges of MoS₂ are more susceptible to oxidation than the basal plane, the two peaks are related to the edges (+0.7 V) and basal plane (+0.98 V) oxidations. By performing XPS to investigate the surface chemical composition and bonding information, it is concluded that MoS₂ is oxidized to SO₄²⁻, S₂²⁻ and MoO₃. More studies were then performed to understand the inherent electrochemical properties of single layered MoS₂. Cyclic voltammetry of MoS₂ nanosheets were conducted at a potential range of +1.1 to -1.1 V in a N₂ saturated aqueous electrolyte as shown in Figure 3.4 b.²¹ An irreversible reduction peak located at -0.71 V was observed, which disappeared in subsequent scans. From the XPS analysis, this reduction peak may be due to phase transition from 1T to 2H of MoS₂. It is interesting to note that this reduced single layered MoS₂ showed faster electron transfer rate and better conductivity than untreated counterpart which is applied in electrochemical glucose detection.

Figure 3.4 a) CV profiles of two consecutive scans of MoS₂ at 2 mV s⁻¹. Conditions: N₂ saturated, 0.5 M H₂SO₄. Reproduced from Ref. 20. b) Three consecutive CV scans of

single layered MoS₂ at -1.1 V to +1.1 V in N₂ saturated 0.5 M NaCl electrolyte at 50 mV s⁻¹. Reproduced from the Ref. 21.

Having recognized the oxidative and reductive behaviors of MoS₂ nanoparticles and single layered MoS₂, the effect of chemical exfoliation on the inherent electrochemistry of MoS₂ was further studied by using three different organic intercalants which are methyl lithium (Me-Li), *n*-butyllithium (*n*-Bu-Li) and *tert*-butyllithium (*t*-Bu-Li).²² It is observed that *n*-Bu-Li and *t*-Bu-Li resulted in greater extents of exfoliation of MoS₂ as compared to Me-Li. The exfoliated MoS₂, as well as the bulk counterparts, were observed to show an oxidation peak at +1.3 V as well as a reduction peak centered at -1.0 V shown in Figures 3.5 a-d. These oxidation and reduction peaks subsequently diminished in heights in the following scans. However, *n*-Bu-Li and *t*-Bu-Li exfoliated MoS₂ displayed larger peak current densities as compared to bulk and Me-Li exfoliated MoS₂. This may be due to the larger surface area from the efficient chemical exfoliation of MoS₂ by *n*-Bu-Li and *t*-Bu-Li. Through careful analysis, it was inferred that the oxidation peak is generated by oxidation of Mo⁴⁺ to Mo⁶⁺ while Mo⁶⁺ is reduced to Mo⁴⁺ giving rise to reductive peak observed. The inherent electrochemistry study was then extended to other TMDs beyond MoS₂. Three different TMDs including MoSe₂, WS₂ and WSe₂ were electrochemically exfoliated and their electrochemical activities were studied.²³ It is observed that the characteristic inherent electroactivities were dependent on the compositions of the TMDs as shown in Figure 3.5 e-m. Among the various TMDs, a general increasing trend of the oxidation potential was observed in the order WSe₂ < MoSe₂ < WS₂ < MoS₂. Post-transition metal chalcogenides such as IIIA–VIA and IVA–VIA layered semiconducting materials were also studied as interesting classes of semiconductors. Although the synthesis strategies, optical and electronic properties of these post-transition metal chalcogenides have been researched in the past several

decades, their intriguing electrochemical properties remain unrevealed. GaSe and GeS, belonging to IIIA–VIA and IVA–VIA materials, respectively, have been selected to investigate the inherent electrochemistry shown in Figure 3.5 n-q.²⁴ GaSe showed no apparent oxidation and reduction peaks except for a small anodic current signal at potential between + 0.5 to + 1.0 V. It was found that the passivation of the generated Ga₂O₃ layer prohibited further electrochemical oxidation at higher anodic potentials. GeS was revealed to display both oxidation and reduction peaks which was ascribed to redox behaviors of Ge²⁺/Ge⁴⁺.

Figure 3.5 (a-d) CV curves of bulk the exfoliated forms of MoS₂. Conditions: 0.1 M KCl electrolyte at 100 mV s⁻¹ with start potential of 0 V. Reproduced from Ref. 22. (e-m) CV profiles of bulk and exfoliated MoSe₂, WS₂ and WSe₂. Conditions: 50 mM PBS solution electrolyte (pH 7.2) at 100 mV s⁻¹ with start potential of 0 V. Reproduced from Ref. 23.

(n-q) CV profiles of layered metal chalcogenides (GaSe and GeS) at Conditions: 50 mM PBS (pH 7.2) as the background electrolyte at 100 mV s^{-1} with start potential of 0 V. Reproduced from Ref. 24. These arrows inserted in figures indicate the scan direction. Considering the electrochemical redox reactions occurring on the electrode material surface, XPS has demonstrated to be a suitable method to study the surface composition changes upon electrochemical treatments. Besides, potential–pH or Pourbaix diagrams shown in Figure 3.6 can also provide insights into the products of the inherent redox reactions upon electrochemical treatment at various pH values.²⁵ At high anodic potential, the chalcogens S and Se exist in the form of HSO_4^- , HSeO_4^- under acidic condition or SO_4^{2-} , SeO_4^{2-} under basic condition. MoS_2 undergoes oxidation at anodic potential to form soluble MoO_3 while WS_2 is predicted to generate the less soluble WO_3 under neutral pH, which is in agreement with reported research.^{20, 22, 26} However, identifying the inherent redox behaviors of these TMDs and the products is still a challenge.

Figure 3.6 Potential–pH diagrams describing the thermodynamic stability of a) Mo-S-O-H, b) W-O-H-S, c) S-O-H and d) Se-O-H system. Reproduced from Ref. 25.

3.2.2 Heterogeneous Electron Transfer

Heterogeneous electron transfer (HET) kinetics is the fundamental study providing the preliminary information on the electron transfer efficiency between the solid electrode material surface and aqueous analytes. Semiconducting TMDs have been investigated for their electron transfer processes using surface sensitive redox probes including $[\text{Ru}(\text{NH}_3)_6]^{2+/3+}$, $\text{Fe}(\text{CN})_6^{3-/4-}$, $\text{Fe}^{2+/3+}$, $\text{Cu}^{+/2+}$ and $\text{V}^{3+/2+}$. TMDs possess two distinct planes: basal plane and edge surface, due to the layered conformation shown in Figure 3.7 a. Studies have shown that these two planes have significantly different electron transfer capabilities. Gerischer *et al.* studied the HET properties at the two distinct planes of MoS_2 in the presence of $\text{Cu}(\text{NH}_3)_6^{2+/1+}$, $\text{Fe}(\text{CN})_6^{3-/4-}$ and $\text{Fe}^{3+/2+}$ and found that edge surfaces displayed higher HET rates than basal surface.²⁷ Tan *et al.* experimentally demonstrated that MoS_2 edge surfaces displayed a higher HET rates (k_{obs}^0 : $4.96 \times 10^{-5} \text{ cm s}^{-1}$) than that of basal plane (k_{obs}^0 : about zero) toward $\text{Fe}(\text{CN})_6^{3-/4-}$ redox probe shown in Figure 3.7 b.²⁸ In addition, it was found that mechanical damage on the basal plane of MoS_2 crystals promoted the electrochemical signal, demonstrating that the edge surface dominates the electrochemistry as shown in Figure 3.7 c. Exfoliation into single/few layers and electrochemical pretreatment have also determined to influence the electron transfer of TMDs. Furthermore, Zhang *et al.* prepared the single-layer MoS_2 by electrochemical lithium intercalation followed by ultrasonication in water. Interestingly, electrochemically reduced MoS_2 exhibited a pair of characteristic redox peaks toward $\text{Fe}(\text{CN})_6^{3-/4-}$ and $[\text{Ru}(\text{NH}_3)_6]^{2+/3+}$ redox probes while untreated MoS_2 had no obvious electrochemical signal, suggesting good conductivity and higher electron transfer rate of electrochemically reduced MoS_2 .²¹ This enhanced electron transfer may be due to the

phase transition from 2H to 1T resulted from the electrochemical reduction. Similar research on lithium exfoliated MoS₂ also identified that electrochemical pretreatment (oxidation and reduction) could tune the electron transfer rates shown in Figure 3.7 d-f.²⁹ Electrochemical reduction pretreatment was found to effectively accelerate the HET rates of bulk and exfoliated MoS₂. Theoretical insights provided by density functional theory calculation revealed that reduction pretreatment contributed to stabilize the 1T phase by electron doping, which resulted in enhanced HET rates. This electrochemical activation of the HET rates upon electrochemical reduction pretreatment was also observed in exfoliated MoSe₂, WS₂ and WSe₂.³⁰ Furthermore, a comprehensive study was conducted to study and compare HET rates of bulk TMDs (MoSe₂, WS₂ and WSe₂) with their few layered counterparts exfoliated by different lithium intercalants.²³ It is worthy to note that the electrochemical signals from the inherent electrochemistry of TMDs overlap with the characteristic redox in the first scan, making it unreliable to obtain the HET from the first scan. Therefore, subsequent scan was record to display a pair of redox peaks towards Fe(CN)₆^{3-/4-} probe. MoSe₂ and WS₂ were observed to show improved HET rates upon exfoliation while exfoliated WSe₂ had a decreased HET rate. Bu-Li exfoliated MoSe₂ showed the highest HET rates ($9.17 \times 10^{-4} \text{ cm s}^{-1}$) because of the higher conductivity and larger surface area arising from few layered state, which can be potentially used as sensing applications. Besides the TMDs, Tan *et al.* studied the HET of post-transition metal chalcogenide including semiconducting GaSe and GeS.²⁴ HET rates at GaSe modified electrode toward Fe(CN)₆^{3-/4-} was found to be equivalent to bare glassy carbon electrode ($k_{obs}^0 : 1.1 \times 10^{-3} \text{ cm s}^{-1}$) while GeS yielded a poorer HET rates ($k_{obs}^0 : 1.5 \times 10^{-5} \text{ cm s}^{-1}$).

Figure 3.7 a) Schematic illustration of basal and edge planes of MoS₂ crystal. CV profiles of b) basal and edge plane of MoS₂ crystal, c) basal plane of MoS₂ in the forms of pristine basal plane, mechanically damaged basal plane and cleaved basal plane in 10 mM Fe(CN)₆^{3-/4-}. Conditions: 0.1 M KCl solution as electrolyte at 100 mV s⁻¹. Reproduced from Ref. 28. (d, e) CV curves of bulk and exfoliated MoS₂ as well as the electrochemically reduced or oxidized counterparts. Conditions: 5 mM Fe(CN)₆^{3-/4-} at 100 mV s⁻¹. (f) Histogram of peak to peak separation along with their error bars. Reproduced from Ref. 29.

3.3 Layered Metal Chalcogenides for Hydrogen Evolution Reaction

Numerous studies have been devoted to study the electrocatalytic activities of different TMDs toward HER as well as strategies to improve their HER performances. During the last decades, various strategies including edge, structure, defect and phase engineering, doping as well as increasing their conductivity by incorporation of conductive substrates have been adopted to improve the catalytic activity.

It is crucial to understand the active sites of TMDs for HER. It has been demonstrated that the edge sites of MoS₂ are active for HER instead of basal plane. Hinnemann *et al.* used DFT calculation to elucidate that the edge structure of MoS₂ is active for HER and experimentally demonstrated that MoS₂ nanoparticles was a good electrocatalyst toward

HER with an overpotential of +0.1-0.2 V for HER shown in Figure 3.8 a.³¹ It was found that the ΔG_H of MoS₂ edge sites was around thermos-neutral, which was close to that of Pt and hydrogenase model.³¹ Following, Bonde *et al.* calculated the ΔG_H of S-edge and Mo/W-edge of MoS₂ and WS₂ by DFT shown in Figure 3.8 b.²⁰ Both S-edge and transition metal-edge had similar ΔG_H close to zero, indicating MoS₂ and WS₂ were good HER electrocatalysts. Besides, cobalt-incorporated MoS₂ and WS₂ was expected to show enhanced HER performance as the ΔG_H at S-edge was reduced by cobalt incorporation. Experimental identification of active sites of MoS₂ nanoparticles was obtained by Jaramillo and co-workers who investigated that the i_0 was linearly proportional to the edge length instead of MoS₂ area coverage, suggesting MoS₂ edge sites is active for HER (Figure 3.8 c, d).³² Furthermore, Tan *et al.* also reported that edge plane of macroscopic MoS₂ crystal showed superior HER performance while basal plane of MoS₂ crystal had negligible HER performance, which was in agreement with previous study.²⁸

Figure 3.8 a) DFT based calculations of hydrogen adsorption energy diagram for HER. Reproduced from Ref. 31. b) Crystal structure of MoS₂ and WS₂ as well as the hydrogen adsorption energies. Reproduced from Ref. 20. Plot of i_0 against MoS₂ c) area coverages and d) edge lengths. Reproduced from Ref. 32.

By understanding the intrinsic activity and active sites of MoS₂ toward HER, studies was then extended to other TMDs. Theoretical insights into the intrinsic HER activity of various TMDs beyond MoS₂ were provided using DFT calculations.³³ It was determined that the basal plane of MoSe₂ had high ΔG_H of 2.13 eV while both Mo-edge and S-edge displayed thermos-neutral ΔG_H , indicating that edge sites are catalytically active rather than basal plane. As for WSe₂, the basal plane is not active for HER as it had large ΔG_H of 2.31 eV. The Se-edge of WSe₂ is considered to be the active sites for HER because it had a thermos-neutral energy of -0.05 eV, which is lower than that of W-edge (0.17 eV). Furthermore, Tsai *et al.* continued to study the activity and stability of 26 TMDs toward HER by calculating ΔG_H and free energy of H–X adsorption (X=S or Se).³⁴ Considering the crystal structure (1T, 2H), surface termination and basal plane, all the ΔG_H and HX adsorption free energies of TMDs were summarized in Table 3.1. It was found that the stability of the TMDs highly influenced the activity toward HER regardless of the composition and structure of TMDs. In general, basal plane has inferior activity than edge sites toward HER. Interestingly, 1T-MoS₂ exceptionally has both active basal plane and edge sites. Besides, the metallic transition metal sulfides were calculated to have ΔG_H of around 0 eV and expected to show HER high activities. Overall, understanding the intrinsic activities of TMDs would help to develop novel strategies to improve the HER performances of TMDs.

Table 3.1 Summary of the hydrogen adsorption energies and HX adsorption free energies (ΔG_{HX} , X=S/Se) values for various TMD catalysts. Reproduced from Ref. 34.

Compound	2H						1T			
	Basal		M-edge		X-edge		Basal		Edge	
	ΔG_{HX}	ΔG_H	ΔG_{HX}	ΔG_H	ΔG_{HX}	ΔG_H	ΔG_{HX}	ΔG_H	ΔG_{HX}	ΔG_H
TiS ₂	–	–	–	–	–	–	–0.09	0.38	–0.33	0.15
VS ₂	–0.08	0.12	–0.92	0.38	–0.20	0.01	0.21	0.05	–0.20	0.01
NbS ₂	–0.90	0.12	–0.45	–0.19	0.09	0.13	–0.27	0.19	–0.56	0.08
TaS ₂	–1.02	0.29	–0.66	–0.06	0.03	–0.15	–0.91	0.24	–1.04	0.38
MoS ₂	–0.55	1.92	–0.69	0.06	–0.05	–0.45	–0.42	0.12	–1.09	0.12
WS ₂	–0.68	2.23	–0.96	–0.04	–0.76	–0.06	–0.83	0.25	–1.37	0.12
PdS ₂	–	–	–	–	–	–	0.41	0.71	–0.25	–0.39
PtS ₂	–	–	–	–	–	–	0.34	1.35	–0.84	–0.08
TiSe ₂	–	–	–	–	–	–	–0.20	0.81	–0.25	0.04
VSe ₂	–0.57	0.62	–0.81	0.61	–0.17	0.25	–0.21	0.39	–0.17	0.25
NbSe ₂	–0.93	0.54	–0.36	0.18	–0.44	–0.28	–0.33	0.48	–0.66	0.07
TaSe ₂	–0.85	0.65	–0.47	–0.16	0.00	–0.10	–0.83	0.67	–0.96	0.30
MoSe ₂	–0.31	2.13	–0.66	0.02	–0.56	–0.05	–0.76	0.66	–1.09	0.48
WSe ₂	–0.13	2.31	–0.88	0.17	–0.71	–0.05	–0.90	0.85	–1.35	0.49
PdSe ₂	–	–	–	–	–	–	–0.04	0.89	–0.44	–0.03
PtSe ₂	–	–	–	–	–	–	–0.18	1.44	–0.93	–0.02

The edge sites of MoS₂ are catalytically active toward HER, leading to strategies to improve catalytic performances by exposing more edge sites. This strategy aims to increase more active sites by surface engineering to expose more edge sites or introduce defects into TMDs nanosheets.⁷ Chen *et al.* fabricated the core-shell MoO₃-MoS₂ nanowires by sulfidization of MoO₃ nanowires.³⁵ The as-obtained electrocatalyst towards HER showed the low onset overpotential of 150-200 mV and stability in acid condition as the vertically aligned MoO₃-MoS₂ nanowires had a high aspect ratio, facile charge transport and high surface area with edge exposed MoS₂ shown in Figure 3.9 a-c. Furthermore, double-gyroid MoS₂ bicontinuous network was fabricated by electrodeposition of Mo into the silica template followed by sulfidization shown in Figure 3.9 d.³⁶ This unique MoS₂ structure exposed most of the edge sites due to the high surface curvature, resulting in superior HER performance. Additionally, Sung *et al.* prepared nano-assembled MoS₂ spheres through aggregation of MoS₂ nanoflakes.³⁷ These assembled nanospheres retained large fractions of edge sites, leading to better HER performances than bulk and single-layer MoS₂ nanosheets. Interestingly, Xie *et al.* reported the controllable preparation of defect-rich MoS₂ nanosheets by simply adjusting precursors' concentrations.³⁸ In order to prepare the defect-rich MoS₂, excess thiourea was added since thiourea could adsorb onto the surface of MoS₂ thus inhibiting crystal growth and forming defects shown in Figure 3.9 e. On the contrary, high concentration of precursors without excess thiourea was the requirement to fabricate defect-free MoS₂ nanosheets. The defect-rich MoS₂ nanosheets showed excellent HER performance reflected by the small HER onset overpotential (120 mV) shown in Figure 3.9 f. Furthermore, Wang *et al.* reported the use of Ar or O₂ plasma to generate defects on MoS₂ nanosheets, which could activate the basal plane and facilitate HER.³⁹

Figure 3.9 SEM of a) MoO₃ nanowires before sulfidization and b) core-shell MoO₃-MoS₂ nanowires sulfidized at 200 °C, c) HER performance of core-shell MoO₃-MoS₂ nanowires. Reproduced from Ref. 35. d) Schematic illustration of the synthesis of double-gyroid MoS₂. Reproduced from Ref. 36. e) Synthetic pathway of the defect-rich and defect-free MoS₂ and f) their corresponding HER performances as well as the Tafel slopes. Reproduced from Ref. 38.

Amorphous phase TMDs are also regarded as potential electrocatalysts toward HER due to the porous morphology with high fraction of unsaturated active sites. Few examples have been reported to reveal the catalytic activities of amorphous TMDs. Hu *et al.* reported the synthesis of amorphous molybdenum sulfide films by simple electropolymerization to be efficient electrocatalysts for electrochemical hydrogen production.⁴⁰ It was revealed that amorphous MoS₃ became amorphous MoS₂ prior to HER by XPS analysis, suggesting that amorphous MoS₂ was the real active form for HER. Besides, a facile and feasible chemical method was reported to synthesize amorphous MoS₃

particles.⁴¹ The HER performance was obtained from the amorphous MoS₃ deposited electrodes and excellent activity towards HER was identified. A pre-activation process prior to HER involving the partial reduction of MoS₃ to MoS₂ resulted in the formation of MoS_x with the existence of the S₂²⁻ ligand, different from the case of amorphous MoS₃ film. Studies on the origin of catalytic activity of amorphous molybdenum was carried out on chemically synthesized amorphous MoS₃.⁴² It was observed that amorphous MoS₃ was partially reduced to MoS₂ during the reaction condition resulting in the improved electrocatalytic activity, which is in agreement with amorphous MoS₃ particles. Furthermore, electrochemical measurements performed to obtain the active surface area of the catalyst film indicated that rough, nanostructured morphologies of electrocatalysts also facilitate electrocatalytic activities.

Electronic structure also affects the catalytic activities of layered TMDs. Therefore, the catalytic efficiency of TMDs can be increased by tuning the electronic structure, as evidenced by the phase transition from 2H to 1T of exfoliated MoS₂ and WS₂ with improved HER performances.⁷ Metallic 1T MoS₂ was chemically prepared from semiconducting 2H MoS₂ by lithium intercalation and exfoliation in water. The phase transition was caused by electron transfer between the intercalated lithium ions and MoS₂ nanosheets thus leading to the favorable octahedral coordination of Mo atoms.⁴³ These 1T MoS₂ nanosheets presented dramatically improved HER performances compared to semiconducting 2H MoS₂ shown in Figure 3.10 a, b. Electrochemical measurements revealed that metallic conductivity and increased active sites of 1T MoS₂ led to the superior HER activity. Following, Chhowalla *et al.* reported the synthesis of few layered MoS₂ nanosheets with a high fraction of metallic phase using LiBH₄ as the intercalant.⁴⁴ By removing the excess negative charges on nanosheets' surfaces, metallic MoS₂ showed superior HER performance than 2H MoS₂ in Figure 3.10 c, d. Electrochemical

measurements of edge oxidized 2H MoS₂ presented an inferior HER performance, while edge oxidation had no influence on the catalytic efficiency of metallic MoS₂. Therefore, the active sites toward HER of 1T MoS₂ are mainly basal plane, which is in agreement with DFT calculations of ΔG_H on basal plane of metallic TMDs.³⁴ They further investigated the HER performance of exfoliated WS₂ nanosheets by lithium intercalation.⁴⁵ Characterization revealed that the exfoliated WS₂ nanosheets contained high concentrations of strained 1T phase with disordered superlattice ($2a_0 \times a_0$) regions. It was found that exfoliated WS₂ was intrinsically active and exhibited excellent HER performance, resulting in the lower overpotential and Tafel slope value. Besides, both concentration and strain of metallic 1T phase affected the catalytic activity of exfoliated WS₂ because i_0 gradually decreased during annealing which increased 2H phase and reduced strain shown in Figure 3.10 e. DFT calculations showed that ΔG_H of 1T WS₂ depended on the strain. When the applied strain was in the range of 2.0 to 3.0%, ΔG_H decreased from 0.28 eV to reach thermos-neutral as tensile strain enhanced the density of states below the Fermi level as shown in Figure 3.10 f. Martin *et al.* comprehensively studied the efficiency of phase transition of four different TMDs (MoS₂, MoSe₂, WS₂ and WSe₂) during lithium intercalation.⁴⁶ From XPS analysis, the phase transition by lithium intercalation is more favorable towards WS₂ and MoSe₂ as compared to MoS₂ and WSe₂, leading to higher concentrations of metallic phase, which in turn resulted in higher electrocatalytic activity toward HER.

Figure 3.10 a) Linear sweep voltammetry showing HER performances of exfoliated and as-grown MoS₂ b) with the corresponding Tafel slopes. Reproduced from Ref. 43. (c) Linear sweep voltammetry showing HER of 2H and 1T MoS₂ as well as the edge oxidized counterparts d) with their corresponding Tafel slopes. Dashed lines represent the iR-corrected 1T and 2H MoS₂ HER curves. Reproduced from Ref. 44. e) Plot of HER i_0 as a function of 1T phase concentration annealed at different temperatures. f) DFT calculations of free hydrogen adsorption energies on metallic WS₂ nanosheets with the various applied strain. Reproduced from Ref. 45.

The heteroatom doping of 2D TMDs nanosheets could disturb the basal plane, resulting in expanded interlayer distances and modified d-band electronic properties of metal atoms, thereby improving the electrocatalytic activities by tuning the ΔG_H . This is similar to graphene doped with nitrogen, boron, sulfur, and phosphorus atoms showed enhanced catalytic activities.⁴⁷ Heteroatom-doped TMDs can be divided into nonmetal-doped and metal-doped TMDs. In the case of nonmetal-doped TMDs, Xiang and coworkers fabricated MoS_{2(1-x)}Se_{2x} alloy by CVD at various ratios ($x = 0, 0.11, 0.39, 0.51, 0.61, 1$).⁴⁸ It was found that the bandgap of MoS_{2(1-x)}Se_{2x} monolayer can be modulated by controlling the Se concentration. Higher contents of Se resulted in decreased bandgaps and higher

conductivities, which is beneficial for HER. The introduction of Se adjusted the ΔG_H of single-layer $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ to a thermos-neutral value, leading to enhanced HER performances compared with the MoS_2 and MoSe_2 as shown in Figure 3.11 a and b. Monolayer $\text{WS}_{2(1-x)}\text{Se}_2$ alloy was also synthesized to tune the bandgap by varying Se content.⁴⁹ Through the introduction of Se, distortion occurred on the basal plane induced by the larger radius of Se atoms leading to a polarized electric field. Therefore, the adsorbed reactants can be polarized and oriented in the presence of the electric field, which favored bond cleavage of the absorbed molecules on the basal surface. As a result, monolayer $\text{WS}_{2(1-x)}\text{Se}_2$ exhibited improved HER performance with lower onset potential than WS_2 and WSe_2 . In addition, H, O, N, S and P doped TMDs has also been reported. By controlling the disorder to expose more active sites and incorporation with oxygen to increase the conductivity, Xie *et al.* reported optimized MoS_2 electrocatalysts with remarkable HER performances (onset overpotential of 120 mV) shown in Figure 3.11 c and d.⁵⁰ Yan *et al.* obtained enhanced HER performance from S-doped MoSe_2 nanosheets as a result of increased unsaturated active sites and electrical conductivity by S incorporation shown in Figure 3.11 e and f.⁵¹ Nonmetal P was also used as dopant to significantly enhance the HER performance of MoS_2 shown in Figure 3.11 g and h. The P dopant not only acted as the new active sites, but reduced the ΔG_H for neighboring S atoms, thereby activating the basal plane.⁵² Xue *et al.* also reported that N-doped WS_2 is active towards HER.⁵³ Furthermore, P-doped CoS_2 , P-doped 2H MoS_2 and H-incorporated TiS_2 were reported to be highly advanced electrocatalysts toward HER.⁵⁴⁻⁵⁶

Figure 3.11 a) Schematic illustration of HER of $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ monolayer, b) HER of single layered $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ with various ratios. Reproduced from Ref. 48. c) Illustration of the electron transfer process of oxygen incorporated MoS_2 , d) HER performance of oxygen incorporated MoS_2 . Reproduced from Ref. 50. e) Electrocatalytic performance toward HER of S-doped MoSe_2 nanosheets, MoSe_2 and Pt as well as f) the corresponding Tafel slopes. Reproduced from Ref. 51. g) HER performances and h) Tafel slopes of pure and P-doped MoS_2 nanosheets. Reproduced from Ref. 52.

Metal atoms have also been introduced into TMDs nanosheets to enhance HER performances. Previous experiments and DFT calculations revealed that Co incorporated MoS_2 and WS_2 nanoparticles had promotion effect toward HER.²⁰ Besides, DFT calculations suggested that doping MoS_2 with six different metals (Ru, Rh, Co, Fe, Mn, Ta) would lower ΔG_{H} close to thermo-neutral and display enhanced HER performances than pristine MoS_2 (Figure 3.12 a).⁵⁷ Vanadium doped MoS_2 was also synthesized *via* a solid state reaction and found to be a good catalyst towards HER.⁵⁸ Through the incorporation of vanadium, semiconducting 2H MoS_2 was transformed to a semi-metallic 2D material with increased in-plane conductivity and higher carrier concentration. Therefore, V-doped MoS_2 is more appropriate for HER (overpotential value of 0.13 V) than intrinsic MoS_2 shown in Figure 3.12 b. He *et al.* reported a novel and simple method to prepare Co incorporated WS_2 without the formation of Co_9S_8 as the side product.⁵⁹ The

as-obtained $\text{Co}_x\text{W}_{(1-x)}\text{S}_2$ was measured to show superior catalytic activity toward HER due to the modified electronic structure by doping shown in Figure 3.12 c and d. In addition, Mn-doped CoSe_2 and Ti-doped VS_2 also possessed improved HER performances.^{60, 61}

Figure 3.12 a) Hydrogen adsorption energies of S edge sites of different metal doped MoS₂. Reproduced from Ref. 57. b) HER of vanadium doped MoS₂. Reproduced from Ref. 58. Electrochemical measurements of Co incorporated WS₂: a) HER polarization, b) corresponding Tafel slopes. Reproduced from Ref. 59.

Electrical conductivity is critical to influence the electrocatalytic activity of TMDs as higher conductivities facilitate electron transfer, which is beneficial for HER process. Previously we have discussed the phase transition of MoS₂ and WS₂ from semiconducting phase to metallic phase resulted in improved HER performance in the 1T phase with higher conductivity.^{43, 45} Furthermore, the introduction of dopant atoms into TMDs intra-layer also enhanced the intrinsic conductivities.⁵⁸ Given the high catalytic activity of TMDs limited by electrical resistance, synergetic composites with conductive substrates were developed to promote electron transfer during HER. Dai *et al.* reported the synthesis

of MoS₂ nanoparticles grown on reduced graphene oxides (rGO) by hydrothermal reaction as an advanced electrocatalyst toward HER.⁶² Reduced graphene oxide not only provided the substrate for uniform distribution of MoS₂ nanoparticles without aggregation, it also promoted electron transport during HER. As shown in Figure 3.13 a-c, MoS₂/rGO composite exhibited superior HER performance compared to MoS₂ nanoparticles. WS₂/rGO hybrid was also prepared by Yang and coworkers by hydrothermal synthesis.⁶³ Benefiting from the enhanced electron transfer kinetics, WS₂/rGO hybrid presented better HER performance than pure WS₂ nanosheets shown in Figure 3.13 d-f. Other carbon materials including doped graphene, carbon nanotube and carbon fiber were also exploited as the conductive substrates to incorporate TMDs and fabrication of superior electrocatalysts toward HER. Li reported a simple chemical fabrication of hybrid electrocatalyst with amorphous MoS_x grown on vertical N-doped carbon nanotube (NCNT) shown in Figure 3.13 g-i.⁶⁴ The resultant hybrid catalyst attained an excellent HER performance due to the proliferation of the active sites from the amorphous phase and promoted charge transfer kinetic along carbon nanotubes. Besides, a 3D electrocatalyst of MoS₂ nanoparticles uniformly grown on mesoporous graphene foam was constructed by a facile solvothermal method. Benefiting from the exposed active sites, rapid mass diffusion and electron transfer, MoS₂/MGF exhibited higher catalytic activity than pure MoS₂.⁶⁵ Intrinsic metallic TMDs with higher in-plane conductivities such as TaSe₂, VS₂ and VSe₂ have enhanced HER performances due to the rapid electron transfer observed.^{66, 67} Metallic VS₂ nanosheets were obtained by CVD and demonstrated excellent HER performance with low overpotential 68 mV at the -10 mA cm⁻², and small Tafel slope value of 34 mV dec⁻¹.⁶⁸

Figure 3.13 a) Schematic illustration of HER on MoS₂/rGO composites, b) HER performances and c) Tafel slopes. Reproduced from Ref. 62. d) Diagrammatic view of the HER process, e) HER performances and f) Tafel slopes of WS₂/rGO (blue curve). Reproduced from Ref. 63. g) Schematic illustration, h) HER performance and i) Tafel slopes of MoS_x-NCNT (N-doped carbon nanotube). Reproduced from Ref. 64.

3.4 Bipolar Electrochemistry for Downsizing Layered Materials

Bipolar electrochemistry is a facile electrochemical method applied to exfoliate and downsize layered materials. In a bipolar electrochemical setup (Figure 3.14),⁶⁹ two Pt electrodes termed as driving electrodes are inserted into an electrolyte solution between the well suspended layered materials of interest. The suspended layered materials are generally conductive and regarded as the bipolar electrode (BPE). When a constant DC potential is applied to the driving electrodes, a uniform electric field is generated across the solution and BPEs are immediately polarized. Due to the potential difference between BPE and electrolyte solution, electrochemical reactions of water electrolysis are driven to occur at the two poles of BPEs, leading to the fragmentation or exfoliation of layered materials to nanoparticles. Bipolar electrochemistry has been used as electrochemical reactors, batteries and fluidized bed electrodes since the 1970s. In the past decades, bipolar electrochemistry has been developed to be use in photo-electrochemical cells,

electronic devices, electrochemical sensing and optical detection.⁷⁰ In this part, we focused on bipolar electrochemistry for exfoliation and downsizing of layered materials. Our group has reported the use of bipolar electrochemistry for the preparation of the TMDs and black phosphorus nanoparticles for biosensing. WS₂ nanoparticles were obtained from chemically exfoliated WS₂ nanosheets using bipolar electrochemistry treatment.⁷¹ The WS₂ nanoparticles were then applied as nanolabels for protein detection. Follow up research are devoted to fabricate MoSe₂, WSe₂ and black phosphorus nanoparticles for applications in electrochemical immunoassays.⁷²⁻⁷⁴ Interestingly, phase transition from 2H to 1T is observed from bipolar electrochemically exfoliated WS₂ nanosheets.⁷⁵

Figure 3.14 Schematic illustration of bipolar electrochemistry set-up. Reproduced from Ref. 69.

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Chapter 4

Electrochemistry of Layered Gallium Chalcogenides

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4.1 Introduction

Layered transition-metal dichalcogenides (TMDs) have been attracting great interest due to the unusual properties they exhibit when exfoliated down to mono- or few-layered material.^{1, 2, 3-6} In addition to TMDs, there is a family of $A^{III}B^{VI}$ layered chalcogenides that also exhibit a layered two-dimensional structure, which gives rise to intriguing properties. The compounds are semiconductors with band gap energies that go from the UV region up to the near-infrared (NIR) region. GaS has a band gap energy of 3.05 eV, whereas InSe has a band gap energy of 1.25 eV. These compounds have the general formula of MX, in which M represents gallium and indium and X stands for sulfur, selenium, and tellurium. Compounds with M_2X_3 stoichiometry and the same composition also exist, but do not generally exhibit layered structures.^{7, 8} Unlike TMDs, in which one metal and two chalcogen atoms form one layer, $A^{III}B^{VI}$ semiconductors have layers composed of two metal and two chalcogen atoms, giving rise to a X–M–M–X motif. The exception is GaTe, in which the presence of a large anion leads to a reduction in symmetry from hexagonal to monoclinic. Similar to the case of TMDs, these motifs are stacked by weak van der Waals forces to create three-dimensional structures.⁹⁻¹²

Numerous publications concerning the potential applications of these compounds have been published. For example, gallium sulfide coupled with carbon nanotubes can be used as a high-performance anode in a lithium-ion battery.¹³ GaS also allowed for the construction of highly responsive photodetectors on both rigid and flexible substrates.¹⁴⁻¹⁶ The preparation of promising electrocatalysts for the HER from GaS has also been demonstrated.¹¹ Last, but not least, the construction of ultrathin GaS transistors has also been demonstrated.¹⁷ Similarly, GaSe was studied quite extensively. Numerous papers concern its use as a transistor,¹⁷ photodetector,¹⁸ part of nonlinear optics,¹⁹ terahertz

radiation source,²⁰ and many more applications. The catalytic properties of GaSe have also been studied previously.¹²

Unlike gallium sulfide and selenide, gallium telluride remains relatively unexplored. Most reports are on the synthesis^{21, 22} or optical properties,^{22, 23} with no reports on the electrochemistry or catalytic properties of GaTe. Similarly, the investigation of indium selenide remains limited to applications in electronics, such as high-mobility field-effect transistors (FETs)^{24, 25} and optoelectronics as image sensors.²⁶

Although a number of papers have studied the properties of $A^{III}B^{VI}$ layered chalcogenides and their possible applications, there is a lack of comparative study of the properties of IIIA group chalcogenides, namely, GaS, GaSe, GaTe, and InSe, from the viewpoint of electrocatalysis. Upon considering promising results of gallium sulfide towards the HER,¹¹ it is of high importance to explore the HER performance of $A^{III}B^{VI}$ layered chalcogenides in more detail. Therefore, herein we fundamentally explore the electrochemical properties of $A^{III}B^{VI}$ layered chalcogenides and their HER catalytic performances.

4.2 Results and Discussion

4.2.1 Material Characterization

Herein, we investigated the electrochemical properties of $A^{III}B^{VI}$ layered chalcogenides, namely, GaS, GaSe, GaTe, and InSe. The structure of these compounds is displayed in Figure 4.1, showing the X-M-M-X arrangement, which can be seen for the hexagonal structure of GaS and InSe with $P6_3/mmc$ symmetry and GaSe with $P-6m2$ symmetry. The differences in point group only originate from different stacking methods of individual layers. GaTe has significantly lower symmetry, with a monoclinic structure (space group

B2m). Optical images of the corresponding synthesized samples are shown in Figure 4.1 together with the structures.

Figure 4.1 Structures of GaS, GaSe, GaTe, and InSe. Blue dots correspond to the metal and yellow dot corresponds to the chalcogen. Optical images of the corresponding synthesized materials are also shown. Scale bar: 1 cm.

The surface morphology of prepared $A^{III}B^{VI}$ layered chalcogenides was examined by means of SEM. Figure 4.2 presents the scanning electron micrographs of GaS, GaSe, GaTe, and InSe. The layered structure with no clear delamination, as expected for bulk material, is clearly observed. Furthermore, we performed energy-dispersive X-ray spectroscopy (EDS) to analyze the elemental composition. Results in Figure 4.S1 and Table 4.S1 in the Supporting Information showcase the homogeneous distribution of elements together with the chalcogen to metal ratio close to one, which indicates the successful synthesis of bulk GaS, GaSe, GaTe, and InSe.

Figure 4.2 Scanning electron microscopy (SEM) images of (a) GaS. (b) GaSe. (c) GaTe. (d) InSe. Scale bars are 1 μm .

More information about the base and edge plane morphology was acquired through AFM measurements (Figure 4.S2 in the Supporting Information). Base planes with steps varying from several nanometers to several hundred nanometers are clearly observable in the base plane figures. The edge plane measurements revealed a much more random distribution of individual sheets. This distribution is attributed to the damage caused during the preparation of samples, during which crystals were cut in perpendicular to the base plane.

XRD analysis was performed to confirm the phase composition. The diffractograms are displayed in Figure 4.3. Analysis has revealed pure gallium chalcogenides (GaS PDF# 01-071-0009; GaSe PDF# 01-080-2271; GaTe PDF# 01-071-0620) and pure InSe (PDF# 00-034-1431). No other phases, including oxides, were detected. The sharp profile of the reflections indicates very good crystallinity and strong preferential orientation due to the layered structure. The (00l) preferential orientation is observed for layered chalcogenides with hexagonal symmetry (GaS, GaSe, and InSe), whereas for monoclinic GaTe preferential orientation in the (*h*00) direction is observed. These results are in good

agreement with the morphology observed by SEM and other analytical methods (see below).

Figure 4.3 Diffractograms of GaS, GaSe, GaTe, and InSe. Small lines at the bottom of the spectra represent reference data taken from the PDF database.

Raman spectroscopy was then used to obtain further structural information about the prepared chalcogenides (Figure 4.4). For GaS and InSe, which have D_{6h}^4 symmetry, and GaSe with D_{3h} symmetry (slightly different layer stacking), several vibrational modes are visible.²⁷⁻²⁹ These vibration modes represent both intra- (E_{2g} , E_{1g}) and interlayer (A_{1g}^1 , A_{2g}^2) interactions and are in good agreement with the literature.²⁷⁻²⁹ GaTe has a richer Raman spectrum because of its less symmetrical point group $B2m$. The results are nevertheless still in good agreement with the literature and indicate the successful synthesis of bulk GaTe crystals.³⁰ Together with the Raman-active phonon modes (several A_g , A_u , B_g , and B_u modes), three optically active A_u modes can be seen also at 130, 143, and 200 cm^{-1} .

Figure 4.4 Raman spectra of GaS, GaSe, GaTe, and InSe.

Photoluminescence spectra were measured by using a $\lambda=532$ nm laser to showcase the band structure of prepared chalcogenides. GaSe shows a strong band at about 2.01 eV ($\lambda=618$ nm), which is in an excellent agreement with previous reports on bulk GaSe crystals.¹⁸ Similarly, GaTe exhibits photoluminescence with a maximum centered at $\lambda=747$ nm (1.66 eV) and is in good agreement with reports from the literature.³¹ Finally, for the InSe bulk crystals, we obtained a maximum centered at $\lambda=995$ nm (1.25 eV), which was also in good agreement with the literature.²⁹ The increase in the full-width at half-maximum (FWHM) of the luminescence peaks for GaTe and InSe indicates increasing amount of defects, as well as the effect of temperature on photoluminescence peak broadening with band gap reduction. The reported band gap value of GaS is 3.05 eV;³² however, excitation at $\lambda=532$ nm leads to only a small peak at $\lambda=694$ nm (1.79 eV), which indicates the presence of deep levels within the GaS band gap associated with impurities or defects in the structure, such as vacancies or interstitial atoms. The results of photoluminescence measurements with excitation at $\lambda=532$ nm are shown in Figure 4.5. The photoluminescence of GaS was further measured by using a He–Cd UV laser ($\lambda=325$ nm). The absence of a luminescence signal at 3.05 eV ($\lambda=406$

nm) originates from the fact that this direct transition is located about 0.45 eV above the indirect transition.³³ The broad and weak luminescence maxima at $\lambda \approx 620$ and 780 nm originate from indirect band and deep level transitions, which are typically nonradiative recombinations and are accompanied only by extremely low photoluminescence yields. Results are shown in Figure 4.S3 in the Supporting Information.

Figure 4.5 Photoluminescence spectra of GaS, GaSe, GaTe and InSe measured using 532 nm laser with 0.5 mW excitation power.

Further information about the surface chemical composition and bonding information was obtained by X-ray photoelectron spectroscopy (XPS). First, wide scan spectra were recorded (Figure 4.S4 in the Supporting Information). The presence of oxygen and carbon in the materials is ascribed to adsorbed oxygen/moisture and adventitious carbon. From the survey spectra, the chalcogen to metal ratio was evaluated and the results are shown in Table 4.S1 in the Supporting Information. These results show a discrepancy with the results obtained by EDS. The reasons for different ratios are due to the high surface sensitivity of the XPS method. Moreover, GaS exhibits a metal-deficient surface, whereas GaSe, GaTe, and InSe exhibit a metal-rich surface. High-resolution core-level spectra of Ga 3d and In 3d are shown in Figure 4.6. The deconvolution of Ga 3d revealed two pairs

of peaks originating from gallium sulfide and gallium oxides. The first pair is located at about 19.5 and 19.9 eV and corresponds to the Ga–S bond, whereas the other pair is located at about 21.46 and 21.91 eV. Comparison with the literature revealed that Ga₂O₃ had a pair located at (20.4±0.2) and (20.8±0.2) eV.³⁴ This lead us to conclude that this pair does not originate from Ga₂O₃.³⁴ In the case of GaSe, only one pair of peaks at about 19.54 and 19.94 eV is observed and attributed to the Ga–Se bond. One distinct peak of GaTe is found at about 19.8 and 20.2 eV and attributed to the Ga–Te bond. The other pair present in the spectrum originates from Ga₂O₃ located at about 20.6 and 21.05 eV, respectively. The presence of gallium oxide is due to the surface hydrolysis of chalcogenide and its subsequent oxidation in air. Furthermore, two In 3d pairs with spin-orbit split doublets at 444.16 and 451.76 eV and 444.20 and 451.80 eV ($\Delta E=7.6$ eV), originating from In–Se and In–O, respectively, were obtained after deconvolution.¹⁰ Also, some indium in the indium (0) oxidation state was detected. This may indicate partial surface disproportionation of In²⁺ in InSe into In³⁺ and In⁰.

Figure 4.6 High-resolution X-ray photoelectron spectra of Ga 3 d and In 3 d of GaS, GaSe, GaTe, and InSe. C 1 s peaks at about 284.5 eV are used as a calibration reference.

4.2.2 Inherent electrochemistry and electrocatalytic properties

The potential window at which individual materials may operate is always limited due to their inherent electrochemistry or solvent-related electrochemical reactions.³⁵ At present, fundamental electrochemical studies of A^{III}B^{VI} layered chalcogenides and their inherent electrochemistry are not adequate.¹² To further investigate the nature of processes that occur when external voltage is applied, we conducted cyclic voltammetry (CV) in both anodic and cathodic scan directions over the range of -1.8 to $+1.8$ V in a 0.05 M solution of phosphate-buffered saline (PBS; pH 7.2). Three consecutive scans were performed to reveal the electrochemistry of the material's surface. Figure 4.7 and Figure 4.S5 in the Supporting Information display the cyclic voltammograms of GaS, GaSe, GaTe, and InSe in both anodic and cathodic scan directions. All gallium chalcogenides show an inconspicuous peak at about -0.6 V (Figure 4.S5 in the Supporting Information). From measurements of Ga₂O₃ in PBS shown in Figure S6 in the Supporting Information, we can conclude that this process is likely to be related to the reduction of Ga₂O₃ on the surface of Ga chalcogenides. This is also very well supported by the fact that this reduction peak only appears after cycling to anodic potentials, at which a small oxidation peak at about $+1.3$ V can be seen; this may lead to oxidation of the material's surface to moieties such as Ga₂O₃ (Figure 4.S5 in the Supporting Information). CV data also indicate that repetitive cycling makes the surface more electrochemically active, as documented by the increase in current during subsequent scans. In addition, GaTe shows an oxidation peak at about $+0.3$ V, which shifts to slightly lower potentials in subsequent scans in both anodic and cathodic directions. A very slight peak at about -1.0 V, which is much more pronounced in the cathodic scan direction, can also be seen in Figure 4.S5 in the

Supporting Information. Because no similar peaks were detected in the CV curves of GaS and GaSe, it is unlikely that these peaks originate from Ga compounds (also in good agreement with XPS, for which no or very little Ga oxides were detected), so we suggest that these peaks are related to redox processes of Te. Finally, InSe exhibits a reduction peak at about -1.6 V during cathodic scanning. The absence of this peak during anodic scanning suggests that anodic scanning deactivates this reducible moiety at the material's surface. By comparison with data obtained from the measurement of In_2O_3 (Figure 4.S6 in the Supporting Information), we conclude that this process is related to the reduction of In_2O_3 , leading to the formation of insoluble products that inhibit the further course of this reaction. Also, an inconspicuous peak located at about $+1.3$ V emerges during the anodic scan. Interestingly, this oxidation process inhibits the reduction of In_2O_3 previously described, but gives rise to a new reduction peak located at about -0.6 V in subsequent scans. Unfortunately, due to a lack of data on this topic in the literature, precise determination of these redox processes was not possible.

Figure 4.7 Cyclic voltammograms of GaS during the a) anodic and b) cathodic scans, GaSe during the c) anodic and b) cathodic scans, GaTe during the e) anodic and f) cathodic scans, and InSe during the g) anodic and h) cathodic scans. Arrows represent the scan direction. Conditions: 0.5 M PBS (pH 7.2) as a supporting electrolyte; scan rate, 100 mV s^{-1} .

Previous research into layered materials has revealed their excellent performance in electrocatalysis. For example, 2D MoS_2 and WS_2 are very efficient for the HER.³⁶⁻

³⁹ Some papers reported $\text{A}^{\text{III}}\text{B}^{\text{VI}}$ layered chalcogenides as excellent HER catalysts. GaS nanosheets obtained by liquid exfoliation show much better HER performance with smaller nanosheets than that with larger nanosheets, which suggests that the catalytic site

of GaS for the HER is located at the edge of the sheets.¹¹ Other work has investigated the performance of bulk GaSe towards the oxygen evolution reaction (OER), oxygen reduction reaction (ORR), and the HER, revealing that electrochemical pretreatment could enhance the HER catalytic activity.¹² Currently, there is a lack of knowledge about the catalytic activity of $A^{III}B^{VI}$ layered chalcogenides, which makes them attractive for further research.

The HER performance of bulk GaS, GaSe, GaTe, and InSe is shown in Figure 4.8 and Figure 4.S7 in the Supporting Information. It is clear that all four materials show poorer HER performances than bare GC. It has been reported that active sites for the HER are at the edge of materials with X–M–M–X structures.^{11, 12, 40} Therefore, the reason for the poor HER performance is mainly due to low conductivity and less active sites being present in the bulk state. Although these materials exhibit low catalytic activity towards the HER, it is of interest to compare the HER performance in detail. As shown in Figure 4.8 a and c, the best performing electrocatalyst for the HER is GaSe followed by GaS and GaTe. XPS analysis revealed no gallium oxide on the surface of GaSe, which may substantially contribute to the better HER performance.¹² Furthermore, InSe shows a peak at about -1.0 V versus RHE during the initial scan, which disappears in subsequent scans in Figure 4.8 b. This peak originates from the inherent electrochemistry of InSe and was discussed above. The shift in potential can be caused by different pH values compared with inherent electrochemistry measurements. Subsequent scans were also performed that revealed, for gallium chalcogenides, the overpotential became slightly lower, which indicated activation of the material's surface (Figure 4.S7 in the Supporting Information). On the contrary, InSe shows the opposite trend. This is likely to be caused by insoluble products formed on the surface of InSe during electrochemical reduction observed in the first HER cycle.

Figure 4.8 a) and b) Polarization curves for the HER on GaS, GaSe, GaTe, and InSe. GC=glassy carbon, RHE=reversible hydrogen electrode. c) Overpotential of three consecutive scans at -10 mA cm^{-2} . d) Tafel slope values of three consecutive scans. Conditions: scan rate of 2 mV s^{-1} , $0.5 \text{ M H}_2\text{SO}_4$ as the electrolyte.

Another way to measure the catalytic activity of HER catalysts is the Tafel slope value. The results of Tafel slope analysis are shown in Figure 4.8 d. The Tafel slope values can be used to determine the rate-limiting step for the HER. Generally, the rate-limiting steps are those given by Equations (1)–(3):^{37, 41, 42}

1. Adsorption step (Volmer): $\text{H}_3\text{O}^+ + \text{e}^- \rightarrow \text{H}_{\text{ads}} + \text{H}_2\text{O}$; $b \approx 120 \text{ mV/dec}$
2. Desorption step (Heyrovsky): $\text{H}_{\text{ads}} + \text{H}_3\text{O}^+ + \text{e}^- \rightarrow \text{H}_2 + \text{H}_2\text{O}$; $b \approx 40 \text{ mV/dec}$
3. Desorption step (Tafel): $\text{H}_{\text{ads}} + \text{H}_{\text{ads}} \rightarrow \text{H}_2$; $b \approx 30 \text{ mV/dec}$

The values of the Tafel slopes indicate that the Volmer adsorption step [Eq. (1)] is the rate-limiting step for all of the materials. Similarly to overpotential, the Tafel slope value decreases for GaS, GaSe, and GaTe with subsequent scans; this indicates their activation. For InSe, the Tafel slope value increases gradually, in good agreement with previous discussions.

4.3 Conclusion

We have successfully prepared single-phase $A^{III}B^{VI}$ layered chalcogenides (GaS, GaSe, GaTe, and InSe). The synthesized materials were characterized in detail by means of XRD, XPS, EDS, Raman spectroscopy, and photoluminescence spectroscopy. The layered structure is clearly visible in SEM images. All of these materials exhibit negligible inherent electrochemistry; this is related to surface oxidation originating from either natural oxidation or anodic potential sweeping. Energy-related research into $A^{III}B^{VI}$ layered chalcogenides towards the HER shows their relatively low HER performance due to lower conductivity and fewer active sites in the bulk state. Further HER investigation after exfoliation has to be performed in the future. We believe that these findings of their electrochemical properties will contribute to finding possible applications in the future.

4.4 Experimental Section

4.4.1 Materials

Gallium (99.999 %), indium (99.999 %), and sulfur (99.999 %) were obtained from STREM (Germany). Selenium (99.999 %) and tellurium (99.999 %) were obtained from Chempur (Germany). Sulfuric acid, potassium chloride, potassium phosphate dibasic, sodium chloride, and sodium phosphate monobasic were purchased from Sigma–Aldrich, Singapore. GC electrodes, Ag/AgCl reference electrodes, and Pt working electrodes were purchased from CH Instrument, USA. Deionized water with an electrical resistivity of 18.4 MΩ cm was used to prepare suspensions and electrolytes.

4.4.2 Apparatus

SEM was performed by using a JEOL 7600F field-emission scanning electron microscope (JEOL, Japan), at a voltage of 2 KV. EDS data were recorded at an accelerating voltage of 15 KV. XPS measurements were carried out by utilizing a $\text{MgK}\alpha$ source (SPECS, Germany) at 1253 eV, as well as a Phibos 100 spectrometer. Wide-scan and high-resolution spectra of Ga 3 d, In 3 d, S 2 p, Se 3 d, C 1 s, and O 1 s were obtained to analyze the surface composition and metal-to-chalcogen ratio of the materials. The 284.5 eV peak of C 1 s was used for calibration. Powder XRD data were collected at room temperature with a Bruker D8 Discoverer powder diffractometer with parafocusing Bragg–Brentano geometry by using $\text{CuK}\alpha$ radiation ($\lambda=0.15418$ nm, $U=40$ kV, $I=40$ mA). Data were scanned with an ultrafast detector (Lynxeye XE) over the angular range $2\theta=10\text{--}80^\circ$ with a step size of 0.02° (2θ). Data evaluation was performed in the software package Eva. An inVia Raman microscope (Renishaw, England) with a charge-coupled device (CCD) detector was used for Raman spectroscopy in back-scattering geometry. A Nd-YAG laser ($\lambda=532$ nm, 50 mW) with a $50\times$ magnification objective was used for measurements. Instrument calibration was performed with a silicon reference that gave a peak center at 520 cm^{-1} and a resolution of less than 1 cm^{-1} . To avoid radiation damage, the laser power output used for these measurements was kept at 5 mW. The photoluminescence measurements were performed by using a Nd-YAG laser ($\lambda=532$ nm, 50 mW) with a $50\times$ magnification objective and $\lambda=325$ nm He–Cd laser (22 mW) with a $40\times$ magnification UV objective. For measurements with Nd-YAG and He–Cd lasers, laser powers of 0.5 and 2.2 mW, respectively, were used. Characterization by AFM was performed on a NT-MDT Ntegra spectrometer from NT-MDT in tapping mode. The measurements were performed on freshly cleaved basal planes. Edge planes were prepared for measurements by cutting and polishing crystals perpendicularly to the basal plane. The electrochemical measurements were conducted by using a μ Autolab III

electrochemical analyzer (Eco Chemie, The Netherlands) with the NOVA version 1.8 software.

4.4.3 Syntheses of GaS, GaSe, GaTe, and InSe

Stoichiometric amounts of metal and chalcogen corresponding to 10 g of synthesized material were placed in a quartz glass ampoule with inner dimensions of 20×140 mm. The ampoule was evacuated with a pressure below 2×10^{-3} Pa and melt sealed by using an oxygen–hydrogen torch. For the synthesis of layered chalcogenides, in all experiments, a heating rate of $5\text{ }^{\circ}\text{C min}^{-1}$ and a cooling rate $1\text{ }^{\circ}\text{C min}^{-1}$ with a dwell-on temperature for 60 min were used. The synthesis of GaSe was performed at $960\text{ }^{\circ}\text{C}$, GaTe at $860\text{ }^{\circ}\text{C}$, and InSe at $700\text{ }^{\circ}\text{C}$. All syntheses were performed in a muffle furnace. For the synthesis of GaS, a quartz ampoule 25×250 mm size was used; this was placed in a tube furnace. The part containing gallium was heated on $980\text{ }^{\circ}\text{C}$, whereas the second part of ampoule was kept at $650\text{ }^{\circ}\text{C}$ to avoid bursting of the ampoule due to a high pressure of sulfur. The heating profile was similar to that used for other chalcogenides.

4.4.4 Electrochemical Procedures

Suspensions (1 mg mL^{-1}) of GaS, GaSe, GaTe, and InSe were prepared by using deionized water, followed by sonication for 1 h to obtain homogeneous suspensions. An aliquot ($4\text{ }\mu\text{L}$) of the suspension was drop-casted on the GC surface, and GC could be renewed by polishing with $0.05\text{ }\mu\text{m}$ alumina particles on a polishing pad after each measurement. Deionized water was evaporated at room temperature to give randomly distributed materials. CV and linear sweep voltammetry (LSV) measurements were conducted by using a three-electrode system: modified GC, Pt, and Ag/AgCl as working, counter, and reference electrodes. PBS (50 mM, pH 7.2) was used as a background electrolyte for CV measurements at a scan rate of 100 mV S^{-1} , whereas 0.5 M sulfuric acid was utilized as an electrolyte for LSV experiments at a scan rate of 2 mV S^{-1} .

4.5 Supporting Information

Figure 4.S1 EDS elemental mapping of GaS, GaSe, GaTe, InSe.

Table 4.S1 The XPS and EDS data of surface composition of GaS, GaSe, GaTe, InSe

TMD Materials	Chalcogen/Metal ratio(XPS)	Chalcogen/Metal ratio(EDS)
GaS	4.013	1.010
GaSe	0.338	0.922
GaTe	0.741	1.108
InSe	0.830	0.825

Figure 4.S2 Base plane AFM images of a) GaS, b) GaSe, c) GaTe, d) InSe and edge plane AFM images of e) GaS, f) GaSe, g) GaTe, h) InSe

Figure 4.S3 Photoluminescence spectrum of GaS using He-Cd UV laser (325 nm).

Figure 4.S4 Wide scan X-ray photoelectron spectrum of GaS, GaSe, GaTe, InSe.

Figure 4.S5 Cyclic Voltammograms of (a) GaS during anodic scan and (b) cathodic scan, (c) GaSe during anodic scan and (d) cathodic scan, (e) GaTe during anodic scan and (f) cathodic scan, (g) InSe during anodic scan and (h) cathodic scan. Arrow represents the scan direction. Conditions: 0.5 M PBS, PH 7.2 acts as supporting electrolyte, scan rate, 100 mV/s.

Figure 4.S6 Three consecutive polarization curves of inherent electrochemistry measurements on Ga₂O₃ and In₂O₃. Cathodic scans are shown only. Anodic scans led to the same results.

Figure 4.S7 Three consecutive polarization curves for HER on GaS, GaSe, GaTe and InSe. Conditions: scan rate of 2 mV/s, 0.5 M H₂SO₄ as electrolyte.

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Chapter 5

Electrochemistry of Layered Indium Chalcogenides

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5.1 Introduction

The exploration and discovery of new two-dimensional (2D) materials have actively driven scientific research in the fields of materials research ever since the discovery of graphene in 2004.¹ Transition metal dichalcogenides (TMDs) have been extensively studied attributing to their unique properties in single or few layers structures.²⁻⁵ These studies are herein extended to post transition metal chalcogenides which are often overlooked. The class of $A^{III}B^{VI}$ chalcogenides represents a family of layered semiconductors which have attracted immense attention due to their unique electronic structures and optoelectronic properties.⁶⁻⁸ These layered materials have a general chemical formula of MX ($M=Ga$ or In , $X=S$, Se or Te) unlike TMDs. Other forms, such as M_2X and M_2X_3 , do not display layered structures.^{9, 10} Indium monochalcogenides (InS , $InSe$, $InTe$) are an upcoming class of $A^{III}B^{VI}$ chalcogenides which have been attracting interest due to their intriguing electronic properties. InS displays an orthorhombic structure belonging to the $Pnnm$ space group with their ethane-like S_3InInS_3 motifs. These S_3InInS_3 motifs are mutually linked by sharing S atoms to form a three dimensional network structure. InS has an indirect band gap of about 1.90 eV at room temperature.¹¹ Layered $InSe$ shows a rhombohedral structure belonging to $P6_3/mmc$ space group with an energy gap of 1.24 eV at room temperature. Each layer comprises of two metal and two chalcogen atoms in a $X-M-M-X$ sequence. These layers are predominantly stacked with weak interlayer Van der Waals forces and covalent intra-layer bonds. However, $InTe$ is a mixed-valence compound belonging to tetragonal $I4/mcm$ space group which can be represented by the chemical formula of $In^+In^{3+}Te_2^{2-}$. In^{3+} and In^+ cations occupy two different crystallographic positions with different chemical bonding environments. Each In^{3+} cation is tetrahedrally coordinated to four Te^{2-} anions thus exhibiting a $In^{3+}Te_4^{2-}$ substructure. However, In^+ cations display distorted square anti-prismatic coordination

with eight surrounding Te^{2-} ions. These In^+ cation chains are linked to the $\text{In}^{3+}\text{Te}_4^{2-}$ substructure by weak electrostatic interactions.¹²

$\text{A}^{\text{III}}\text{B}^{\text{VI}}$ chalcogenides hold great potentials in various applications in electronics, optoelectronics and catalysis due to their moderate bandgaps, high carrier mobility and defined charge carrier properties.¹³ For example, InSe field effect transistors (FETs) show high electron mobility exceeding $10^3 \text{ cm}^2 (\text{Vs})^{-1}$, outperforming their TMD counterparts.^{8,14} Besides that, few-layers InSe photodetector displayed great performance from visible to near-infrared light region with fast response time and long-term stability in photoswitching.⁷ Single-layer $\text{A}^{\text{III}}\text{B}^{\text{VI}}$ monochalcogenides were computationally calculated to be potential photocatalysts for water splitting,^{6, 15} whereby InSe coupled with TiO_2 was reported as excellent photocatalyst for visible light H_2 production.¹⁶ Most research on InS and InTe were focused on their synthesis, optical and electrical properties.^{11, 17-21}

Recently, numerous studies have investigated the possible applications of layered $\text{A}^{\text{III}}\text{B}^{\text{VI}}$ chalcogenides with some reports on their electrocatalytic properties.²²⁻²⁴ In addition, fundamental electrochemical properties and behaviours of indium monochalcogenides remain predominately unexplored. Therefore, it is essential and imperative to investigate the electrochemical as well as electrocatalytic performances towards HER, oxygen evolution reaction (OER) and oxygen reduction reaction (ORR) of indium monochalcogenides. The differences in performances of chalcogen atoms will also be compared between the indium monochalcogenides. Herein, we synthesized, characterized and investigated the fundamental electrochemical properties of indium monochalcogenides (InS, InSe, InTe). They were also characterized by scanning electron microscopy (SEM), transmission electron microscope (TEM), X-ray diffraction (XRD),

Raman spectroscopy, photoluminescence spectra and X-ray photoelectron spectroscopy (XPS).

5.2 Results and Discussion

5.2.1 Material Characterization

Figure 5.1 Scanning electron micrographs (left) and corresponding elemental mappings of (a) InS, (b) InSe, and (c) InTe obtained by energy-dispersive X-ray spectroscopy (EDS).

Characterization studies were first performed to understand the morphological features of the synthesised indium monochalcogenides. Scanning electron microscopy (SEM) was performed in order to reveal their surface morphologies. Figure 5.1 shows SEM images of InS, InSe and InTe where their layered structures were observed. The layers are stacked together indicating the bulk state of these materials. Elemental mappings by energy-dispersive X-ray spectroscopy (EDS) in Figure 5.1 showcased the homogeneous distribution of elements In, S, Se and Te for the respective materials. The chalcogen to metal ratios of InS, InSe and InTe obtained from EDS were 1.11, 0.77 and 0.91 respectively. These values are close to the theoretical chemical ratio of 1 which suggests the successful synthesis of the respective indium monochalcogenides.

Figure 5.2 Transmission electron micrographs (left and centre), and high-resolution TEM images (right) of (a) InS, (b) InSe and (c) InTe. The inset images in the left are the SAED of corresponding indium monochalcogenides. Scale bars for the HR-TEM images represent 5 nm.

The morphology of indium monochalcogenides was further investigated by transmission electron microscope (TEM). Figure 5.2 shows the layered flakes of indium monochalcogenides with a high degree of crystallinity. The detail image of SAED with indexing of diffraction pattern is shown on Figure 5.S1. The elemental mappings obtained from the TEM in Figure 5.S2 indicate the homogeneous distribution of elements of In, S, Se and Te. X-Ray diffraction (XRD) was then conducted to study the crystallinity and phase composition of indium monochalcogenides shown in Figure 5.S3. Diffractograms revealed the single phase of InS, InSe and InTe. InSe and InTe with layered structure exhibited preferential orientation due to its high anisotropy.

Figure 5.3 Raman spectra of (a) InS, (b) InSe and (c) InTe.

Raman spectroscopy was subsequently performed to understand the structural features of indium monochalcogenides. Figure 5.3 shows the Raman spectra of InS, InSe and InTe obtained using green laser with wavelength of 532 nm. From the Raman spectrum of InS in Figure 5.3 a, characteristic peaks with frequency values of 59.8 (A_g^3), 150.7(A_g^1), 224.8 (A_g^4), and 318.2 cm^{-1} (A_g^3) were identified. These Raman peaks are consistent with the reported Raman spectrum of InS.²⁵ A_g^1 and A_g^2 modes are due to the intra-layer stretching vibrations while A_g^3 and A_g^4 modes corresponding to the intra-layer bending vibrations.²⁵ In the case of InSe (Figure 5.3 b), the spectrum displayed prominent peaks at frequency values of 117.5 (A'_1), 179.5 (E''), 201.7 ($E'(TO)$) and 228.6 (A'_1) cm^{-1} , which were determined to originate from the InSe.²⁶ As for InTe, the Raman spectrum reveals two peaks located at 122.0 and 138.8 cm^{-1} (Figure 5.3 c), which corresponds to A_{1g} and E_g vibrational modes respectively.^{27,28}

Figure 5.4 Photoluminescence spectra of InS, InSe and InTe obtained using a laser (532 nm) with 0.5 mW excitation power.

Photoluminescence spectra of indium monochalcogenides were obtained using laser with a wavelength of 532 nm to study their band structure (Figure 5.4). InS showed two photoluminescence peaks. The peak located at about 650 nm (1.98 eV) can be attributed to the band-edge transition and the second peak at lower energy centred at 870 nm (1.51 eV) originated from deep level transitions (associated with defect and impurities) to the defect and deep levels within the band-gap. These results are in good agreement with reported literature.²⁹ For InSe, the photoluminescence peak centred at 995 nm (1.25 eV) associated with band-edge transition can be clearly observed.^{24, 26} InTe did not show any photoluminescence peak in the measured range, since its bandgap is reported to be 1.44 eV.³⁰

Figure 5.5 High-resolution X-ray photoelectron spectra of InS, InSe and InTe. C 1s peak at ca. 284.5 eV is used as calibration reference.

X-ray photoelectron spectroscopy (XPS) was then conducted to examine the surface elemental composition and bonding information of the indium monochalcogenides. From the survey scans obtained (Figure 5.S4), characteristic peaks of C 1s at 284.5 eV, O 1s at 531.1 eV, In 3d at 444.4 eV, S 2p at 162.1 eV, Se 3d at 54.9 eV and Te 3d at around 575.4 eV were identified. Due to the limited information from the survey scan, high resolution XPS core-level spectra of In 3d, S 2p, Se 3d and Te 3d were investigated in Figure 5.5. These spectra were calibrated to the adventitious C 1s at 284.5 eV. For InS (Figure 5.5 a), the deconvolution of In 3d revealed spin-orbit split doublets located at 443.9, 451.5 eV and 444.3, 451.9 eV ($\Delta E=7.6$ eV), which originate from In (0) and In-S.³¹ The S 2p spectrum is well fitted to one spectral component, with binding energy of 161.2 and 162.3 eV corresponding to sulfide (Figure 5.5 b). In the case of InSe, two pairs of peaks at 444.1, 451.7 eV and 444.8, 452.4 eV ($\Delta E=7.6$ eV) were obtained by deconvolution (Figure 5.5 c) and assigned to In-Se and In-O.³² In addition, the deconvolution of the Se 3d indicated metal selenide centred at binding energies of 55.7 and 54.9 eV (Figure 5.5 d).³² As for InTe, Figure 5.5 e shows two distinct pairs of peaks at 443.8, 451.39 eV and 444.8, 452.4 eV ($\Delta E=7.6$ eV). These peaks were in agreement with reported binding energies assigned to In (0) and In-Te.³³ Te 3d spectrum was deconvoluted into two pairs of peaks located at 572.3, 582.7 eV and 576.4, 586.7 eV which lie close to the reported values of In-Te and TeO₂ (Figure 5.5 f).³³ From the XPS spectra obtained, it affirms the synthesis of indium monochalcogenides with the small presence of the oxidised counterparts which were inherently formed during the synthesis procedures.

5.2.2 Electrochemical Properties

Figure 5.6 Cyclic voltammograms (vs. Ag/AgCl) of InS (a) anodic and (b) cathodic scan, InSe (c) anodic and (d) cathodic scan, InTe (e) anodic and (f) cathodic scan. Insets show (a-d) reduction, and (e-f) oxidation peaks observed. Arrows indicate the direction of scans starting at scan potential of 0 V. Conditions: 0.5 M PBS at pH 7.2 as electrolyte; scan rate of 100 mV s^{-1} .

Having analysed the structural morphologies and compositions of the indium monochalcogenides, we next proceed to analyse their electrochemical characteristics, namely their inherent electrochemical properties. The operating potential window of materials is limited by the inherent electrochemistry^{34,35} or solvent-related electrochemical reactions.³⁶ Inherent electrochemistry refers to the redox behaviours of electrode materials stemmed from the surface electroactive components when an electrochemical potential is applied.⁵ Three consecutive cyclic voltammetry (CV) scans in both anodic and cathodic directions were performed to investigate their inherent electrochemical behaviours. CV measurements were performed over a potential range of -1.8 V to +1.8 V in phosphate buffered saline (PBS) of pH 7.2. Figure 5.6 shows the cyclic voltammogram of indium monochalcogenides. For the sake of clarity, the electrochemical potentials in this work were reported with reference to Ag/AgCl electrode unless otherwise indicated. As illustrated in Figure 5.6, all CV profiles in both anodic and cathodic scan directions show an inconspicuous reduction peak at about -0.6 V. Upon comparing with CVs obtained with bare glassy carbon (Figure 5.S5), this signal

was attributed to the intrinsic behaviour of glassy carbon. Considering the CV scans for InS in both anodic and cathodic direction in Figure 5.6 a and b, the absence of additional peaks would indicate that InS is electrochemically inert without any conspicuous redox properties. On the other hand, CVs with InSe displayed a sharp reduction signal at around -1.6 V in the cathodic scan. The signal was ascribed to the reduction of indium oxide (In_2O_3) as reported.²⁴ This is consistent with the XPS study which showed the presence of In_2O_3 on the surface of InSe. However, this reduction peak was absent during the anodic scan which suggests the deactivation of this reducible moiety by positive potentials. In the anodic scan direction (Figure 5.6 e), InTe exhibited an oxidative peak at about 0.3 V which shifted to a lower potential (0.2 V) at subsequent consecutive scans. However, no oxidation peak was observed in the first scan for cathodic direction (Figure 5.6 f) but appeared in the subsequent two scans centred at 0.2 V. Comparison of the first scans for InTe in both anodic and cathodic directions, an initial oxidation scan is a prerequisite for the appearance of the oxidation peak. Since no similar oxidation peaks were spotted in the CV profiles of InS and InSe, we can rationally assign these oxidation peaks to the inherent oxidation of tellurium. Similar oxidative peaks were also identified for GaTe,²⁴ VTe₂,^{37, 38} PdTe₂ and PtTe₂.³⁹ The anodic signal at about 0.2 V is due to the oxidation of Te (0) to Te(II) while the signal at about 0.3 V may correspond to the oxidation of Te (0) to Te(IV).³⁹⁻⁴¹ The inherent oxidation signals obtained could potentially hinder the performance of InTe as a sensing platform for the detection of analytes with low oxidation potentials. The electrochemical signals from the target analyte might get overlapped and masked.

Figure 5.7 (a) Cyclic voltammograms (vs. Ag/AgCl) of indium monochalcogenides with 5 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$. (b) Peak-to-peak separations of indium monochalcogenides along with their error bars. Conditions: 0.1 M KCl as electrolyte; scan rate of 100 mV s⁻¹.

Having understood the intrinsic electrochemical behaviours of these materials, we proceed to analyse their electrochemical efficiencies. HET rate is preliminarily measured to examine the suitability of materials for electrochemical sensing applications. The ideal electrode material for electrochemical sensing possesses innately rapid HET rate in order to lower the overpotential required for an electrochemical reaction to take place. In this study, we examine the HET rates of indium monochalcogenides in the presence of $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox probe using cyclic voltammetry. The peak-to-peak separation (ΔE) between the oxidation and reduction peaks correlates with the HET rate constant, k_{obs}^0 obtained by Nicholson's method, where wider ΔE can be interpreted as slower HET and smaller k_{obs}^0 value.⁴² The electrochemical measurements of $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox probe were performed from -0.6 V to 1.0 V to minimise interference from the inherent electrochemical signals of indium monochalcogenides. Figure 5.7 shows the voltammetric profiles of indium monochalcogenide-modified electrodes and histogram of experimentally observed ΔE . From Figure 5.7 a, both bare glassy carbon (GC) and indium monochalcogenides showed a pair of reversible redox peaks at about +0.15 V and +0.28 V. It is worth to note that the observed inherent oxidation peak for InSe at 0.6 V vs. Ag/AgCl did not totally overlap with the redox peak of $[\text{Fe}(\text{CN})_6]^{3-/4-}$ probe and had no significant influence on the measurement of HET rate. The k_{obs}^0 of InS, InSe, InTe

and GC were calculated to be $9.3 \times 10^{-4} \text{ cm s}^{-1}$ ($\Delta E = 0.21 \text{ V}$), $3.1 \times 10^{-3} \text{ cm s}^{-1}$ ($\Delta E = 0.12 \text{ V}$), $3.7 \times 10^{-3} \text{ cm s}^{-1}$ ($\Delta E = 0.11$) and $3.8 \times 10^{-3} \text{ cm s}^{-1}$ ($\Delta E = 0.11$), respectively. InS showed the poorest HET performance with an order of magnitude lower than that of InSe and InTe, while InTe displayed the best HET performance. However, the HET performance of InTe was very comparable to that of bare GC. Comparing the indium monochalcogenides, InSe and InTe would be preferred over InS for electrochemical sensing applications if required. We subsequently studied the electrocatalytic performances of InS, InSe and InTe towards HER, oxygen evolution reaction (OER) and oxygen reduction reaction (ORR), which are of importance for energy harvesting applications^{43, 44} and fuel cells.⁴⁵ Previous literature reported the electrochemical properties of InSe for HE.²⁴ Therefore, it would be essential to extend and compare the research scope to InS and InTe.

Figure 5.8 (a) Polarization curves (vs. RHE) for HER of InS, InSe and InTe. (b) Polarization curves (vs. RHE) of the successive second scan of InS, InSe and InTe. (c) Overpotential values obtained at -10 mA cm^{-2} from (b). (d) Tafel slope values of InS, InSe and InTe from (b). Conditions: 0.5 M sulfuric acid as electrolyte; scan rate of 2 mV s^{-1} .

The HER performances of InS, InSe and InTe were measured in 0.5 M H₂SO₄ at a scan rate of 2 mV s⁻¹. Figure 5.8 a shows the HER polarization curves of indium monochalcogenides as well as bare GC for comparison. It was observed that all indium monochalcogenides exhibited an inherent reduction peaks in the acidic electrolyte used. The inherent reduction peaks of InS, InSe and InTe at -0.97 V vs. RHE during the first scan were due to the reduction of indium oxide in 0.5 M H₂SO₄.²⁴ Furthermore, the additional reduction peak at -1.10 V vs. RHE for InTe was attributed to the reduction of Te as previously described. A consecutive second measurement was performed where the inherent peaks were observed to disappear as shown in Figure 5.8 b. No conducting binders was used for the subsequent HER measurement. The respective overpotential and Tafel slope values were presented in Figure 5.8 c and d. Comparing with the electrocatalytic performance of bare GC (0.95 V), InS, InSe and InTe showed negligible HER catalytic performance with overpotential of 0.92 V, 1.32 V and 1.31 V at -10 mA cm⁻². The reasons for the poor HER performances are mainly due to their semiconducting properties with lower conductivity and less active sites at bulk state. Tafel slope is another parameter to evaluate the HER performance that can be used to elucidate the HER electrochemical mechanism. In general, the HER pathway can be expressed as the following steps:

1. Adsorption step (Volmer): $\text{H}_3\text{O}^+ + \text{e}^- \rightarrow \text{H}_{\text{ads}} + \text{H}_2\text{O}$; $b \approx 120 \text{ mV dec}^{-1}$
2. Desorption step (Heyrovsky): $\text{H}_{\text{ads}} + \text{H}_3\text{O}^+ + \text{e}^- \rightarrow \text{H}_2 + \text{H}_2\text{O}$; $b \approx 40 \text{ mV dec}^{-1}$
3. Desorption step (Tafel): $\text{H}_{\text{ads}} + \text{H}_{\text{ads}} \rightarrow \text{H}_2$; $b \approx 30 \text{ mV dec}^{-1}$

From Figure 5.8 d, InS showed the smallest Tafel slope value of 75.7 mV dec⁻¹ and is inferred to undergo a fast Volmer step followed by the rate limiting step of Heyrovsky step. It is followed by InSe (115.7 mV dec⁻¹) with the rate limiting step of Volmer step.

InTe presented the biggest Tafel slope value of $197.5 \text{ mV dec}^{-1}$. The HER limiting step of InTe is postulated to be Volmer adsorption step as the value is close to 120 mV dec^{-1} . We then examined the electrocatalytic performance of InS, InSe and InTe towards oxygen evolution (OER) and oxygen reduction reaction (ORR) in 1.0 M KOH solution as presented in Figure 5.S6. The mechanism of OER requires the extraction of four protons and four electrons for the production of each molecule O_2 .⁴⁶ From Figure 5.S6 a, InS, InSe and InTe are regarded as weak catalyst towards OER with high onset potentials of about 2 V *vs.* RHE which is very comparable to bare GC. The possible reasons for this negligible enhancement in performance may be due to unfavourable free energies of OOH^* and OH^* intermediates and the instability of the materials at high anode potential.⁴⁷ Subsequently, we studied the electrocatalytic performances of indium monochalcogenides towards ORR (Figure 5.S6 b). All materials displayed cathodic peaks at about -0.4 V *vs.* Ag/AgCl which was ascribed to the reduction of O_2 . Onset potential is usually adopted as a parameter to evaluate the electrocatalytic activity for ORR. As observed in Figure 5.S6 b, InS and InTe displayed similar onset potentials of about -0.22 V *vs.* Ag/AgCl. However, the ORR performance of InSe interfered with the inherent electrochemical performance, making it difficult to obtain the onset potential. Overall, InS, InSe and InTe are not ideal electrocatalysts for ORR due to the low current response and relatively high onset potential.

5.3 Conclusion

We have synthesised and investigated the electrochemical properties of indium monochalcogenides. Indium monochalcogenides were characterized by SEM, TEM, XRD, Raman spectroscopy, photoluminescence spectroscopy and XPS. The results indicate that InSe and InTe exhibit inherent electrochemical activities while InS is electrochemically inert. InSe showed a reduction peak ascribed to indium oxide at -1.6 V

and InTe got oxidised at 0.2 V due to the oxidation of tellurium. Further studies were made to reveal the electrochemical activities of indium monochalcogenides towards HER, OER and ORR. All indium monochalcogenides exhibit negligible HER, OER and ORR performances when compared to bare glassy carbon. This is attributed to their semiconducting properties with lower conductivity and less active sites at bulk state. These fundamental findings provide insights into the comprehensive electrochemical attributes of layered $A^{III}B^{VI}$ indium chalcogenides which can be useful for future applications.

5.4 Experimental Section

5.4.1 Materials

Sulfur, selenium, tellurium and indium of 99.999% purity were obtained from Alfa Aesar. Potassium hydroxide, sulfuric acid, sodium phosphate monobasic, sodium chloride, potassium phosphate dibasic, potassium hexacyanoferrate(III), potassium chloride, potassium hexacyanoferrate(II) trihydrate and platinum on carbon were purchased from Sigma-Aldrich, Singapore. Working glassy carbon (GC), counter platinum and reference Ag/AgCl electrodes were obtained from CH Instruments, Texas, USA. The glassy carbon electrode used has a diameter of 3 mm. Ultrapure water (Milli-Q) was utilized for the preparation of background electrolytes.

5.4.2 Synthesis of Indium Chalcogenides

The materials were prepared by direct reaction of elements in quartz glass ampoules under high vacuum. Stoichiometric amount of indium and respective chalcogens corresponding to 10 g of respective monochalcogenides were placed in quartz glass ampoule and melt sealed under high vacuum (1×10^{-3} Pa) using oxygen-hydrogen torch. InS was prepared by heating of ampoule with In and S at 800 °C for 24 h using heating and cooling rates of 10 °C min⁻¹. Subsequently, the ampoule with InS was heated at

540 °C for 100 h. InSe was prepared by heating of ampoule with In and Se at 850 °C for 12 hours. The heating rate was 5 °C min⁻¹ and the cooling rate was 0.5 °C min⁻¹. InTe was prepared by heating of ampoule with In and Te at 800 °C for 12 h using heating rate of 5 °C min⁻¹ and cooling rate of 0.5 °C min⁻¹.

5.4.3 Apparatus

Scanning electron microscopy (SEM) was performed using a JEOL 7600F field-emission SEM (JEOL, Japan) at the voltage of 5 kV. Besides, Energy dispersive X-ray spectroscopy (EDS) was conducted at an acceleration voltage of 20 kV.

X-ray powder diffraction was conducted on Bruker D8 Discoverer (Bruker, Germany) powder diffractometer, and Bragg–Brentano geometry was focused using CuK_α radiation ($\lambda = 0.15418$ nm, U = 40 kV, I = 40 mA) at room temperature. The data were scanned over an angular range of 10 – 80° (2 θ) with a step size of 0.016° (2 θ). Data evaluation was performed in the software package EVA.

Raman spectroscopy was collected using a Raman microscope (Renishaw, England) in a backscattering geometry with a CCD detector. Measurements were made using a DPSS laser (532 nm, 50 mW) with an applied power of 5 mW and a 50x magnification objective. Silicon wafer reference was used to calibrate the instrument which has a peak position at 520 cm⁻¹ and a resolution of less than 1 cm⁻¹. The sample was suspended in deionized water (1 mg ml⁻¹) and sonicated for 10 min prior to the deposition of the suspension on a small piece of silicon wafer.

The photoluminescence spectrum was obtained by using Nd-YAG laser (532 nm, 50 mW). Spectra were collected with a TE cooled CCD camera and a 50x objective lens. The samples were suspended in deionized water with the concentration of 1mg ml⁻¹ and treated by sonication for 10 min. Then the suspensions were deposited on a small silicon wafer and dried before the measurements.

High resolution transmission electron microscopy (HR-TEM) was conducted by using an EFTEM Jeol 2200FS microscope (Jeol, Japan) at the accelerated voltage of 200 KeV. Element maps were obtained using the SDD detector X-MaxN 80 TS from Oxford Instruments (England). The samples were prepared by dropping suspension (1 mg mL^{-1} aqueous solution) on a TEM grid (Cu; 200 mesh; Formvar / carbon) and drying at 60°C for 12 h.

X-ray photoelectron spectroscopy (XPS) was performed by using monochromatic Mg K α source (SPECS, Germany) at 1253 eV and a multi-channel energy analyser (SPECS Phoibos 100 MCD-5). Wide scan and high resolution core level spectra for analysis were collected and C 1s at 284.5 eV was used for calibration.

Electrochemical measurement of cyclic voltammetry (CV) and linear sweep voltammetry (LSV) were conducted with a μ Autolab type III electrochemical analyser (Eco Chemie, The Netherlands) using NOVA 1.10 software.

5.4.4 Electrochemical Procedure

5 mg mL^{-1} of indium monochalcogenides suspensions were prepared in ultrapure water by sonication for 1 h to obtain the homogeneous suspensions. $4 \text{ }\mu\text{L}$ of the suspensions were drop-casted on glassy carbon and dried at room temperature. Glassy carbon was renewed by polishing with 0.05 mm alumina particles and rinsed with ultrapure water. Cyclic voltammetry was used to study the inherent electrochemical properties and heterogeneous electron transfer (HET) of indium chalcogenides in a three-electrode system where modified glassy carbon, Ag/AgCl, and Pt electrode as working, reference, and counter electrode. 5 mL of phosphate buffer solution (PBS) (50 mM, pH = 7.2) electrolyte was used for inherent electrochemical studies and $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox probe in 0.1 M KCl for HET measurements. $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox probe was prepared by mixing equal volumes of 2.5 mM $\text{Fe}(\text{CN})_6^{3-}$ and 2.5 mM $\text{Fe}(\text{CN})_6^{4-}$. The HET rate constants (k_{bs}^0)

were calculated using Nicholson's method, which correlates the peak-to-peak separation (ΔE_p) to a dimensionless parameter Ψ and in turn to k_{0bs}^0 . The roughness factor was not taken into consideration. The diffusion coefficient used for calculation is $D = 7.26 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ in 0.1 M KCl. Electrocatalytic measurements towards hydrogen evolution, oxygen evolution and oxygen reduction reaction was performed in a three-electrode system. 5 mL of 0.5 M H_2SO_4 was used for HER measurements and 1.0 M KOH was used for OER and ORR.

5.5 Supporting Information

Figure 5.S1 The detail of SAED of InS, InSe and InTe with indexed diffraction pattern.

Figure 5.S2 Elemental mappings of (a) InS, (b) InSe and (c) InTe obtained from the transmission electron microscopy (TEM).

Figure 5.S3 X-Ray diffraction (XRD) of (a) InS, (b) InSe and (c) InTe. Red lines at the bottom of the spectra represent reference data taken from the PDF database.

Figure 5.S4 XPS survey scans of (a) InS, (b) InSe and (c) InTe. All spectra are calibrated to adventitious C 1s at 284.5 eV.

Figure 5.S5 Cyclic voltammograms (vs. Ag/AgCl) of bare glassy carbon in (a) anodic and (b) cathodic scan direction. Inset shows the inherent reduction peak obtained in both cathodic and anodic scans. Conditions: 0.5 M sulfuric acid as electrolyte; scan rate, 2 mV s⁻¹.

Figure 5.S6 Linear sweep voltammograms for (a) oxygen evolution reaction (OER) and (b) oxygen reduction reaction (ORR) for InS, InSe and InTe. Conditions: 1.0 M KOH as electrolyte; scan rates of (a) 5 mV s⁻¹ and (b) 10 mV s⁻¹ respectively.

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Chapter 6

Lithium Exfoliated Vanadium Dichalcogenides

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6.1 Introduction

The discovery of the ultrathin two-dimensional nanomaterial graphene in 2004 has attracted a lot of interest, due to its remarkable electronic, optical and mechanical properties.¹ These unique properties of graphene spurred on the exploration to other 2D materials. Most of the research is focused on the transition metal dichalcogenides (TMDs) because of their unusual properties in monolayer or few layers state.²⁻⁴ Similarly to graphite, TMDs are layered compounds with each layer composed of a metal layer sandwiched between two layers of chalcogen atoms, stacked by weak van der Waals forces.

Bulk TMDs have been widely studied for the use as lubricants⁵ and battery materials.⁶ However, some exciting physical properties arise when the bulk material is exfoliated down into mono or few layers. One of these properties is the transition from indirect to direct bandgap, which is observed with the decreasing of the thickness and arises from the quantum confinement effects.⁷⁻¹⁰ The efficient catalytic activity towards hydrogen evolution reaction of these ultrathin 2D materials has been revealed because of the enhanced concentration of active sites - edges. The activity of S site in MoS₂ towards HER has been demonstrated by the linear correlation between HER reaction rate and the number of S edge sites.¹¹ Furthermore, the catalytic activity of inert basal planes of MoS₂ can be triggered by introducing Pt, Co and Ni atoms, which was proved by density functional theory (DFT) calculations and experiments.¹²

Hydrogen, which is considered as a renewable fuel, possessing high energy density¹³ and clean products, can be used as an alternative fuel in the future. The universal technology for hydrogen production is water splitting catalyzed by platinum. The high-cost and low abundance of Pt hinders its prevalence in industry. Therefore, it is necessary and urgent to find low-cost and earth-abundant alternative catalysts. Two dimensional TMDs, such

as MoX_2 and WX_2 , have been demonstrated to exhibit potential as an active HER electrocatalysts¹⁴⁻¹⁶ and photocatalysts.^{17,18} A lot of efforts have been made to optimize the HER catalytic ability of TMDs. For example, the HER activity of TMD nanosheets can be significantly promoted by introducing defects during the preparation process¹⁴ and doping by metal atoms (Pt, Co and Ni) which can arouse the catalytic activity of inert plane.¹² Moreover, the phase transition from 2H to 1T MoS_2 endows 1T MoS_2 enhanced HER catalytic activity.¹⁹

Group five dichalcogenides, namely vanadium disulfide (VS_2), vanadium diselenide (VSe_2) and vanadium ditelluride (VTe_2) belong to layered TMDs, with one layer of V atoms sandwiched between two layers of chalcogen atoms, stacked together by weak van der Waals forces. VS_2 , VSe_2 and VTe_2 possess metallic behavior without a band gap in their electronic structure.^{2, 20, 21} VS_2 and VSe_2 monolayer exhibit ferromagnetic properties^{20, 22} and VSe_2 also shows charge-density-wave behavior.²¹ The hexagonal 1T VS_2 prepared by chemical vapor deposition has been demonstrated to be highly active towards HER.²³ 1T VS_2 can be used as an in-plane supercapacitor,²⁴ battery material^{25, 26} and moisture sensor.²⁷ To the best of our knowledge, there has been no research devoted to the catalytic properties of VSe_2 and VTe_2 towards HER. In this study, we fundamentally study the inherent electrochemistry and HER behavior of bulk and exfoliated vanadium dichalcogenides. Bulk vanadium dichalcogenides were synthesized from elements in quartz ampoules and the exfoliation of materials was performed using n-butyllithium, in a similar manner as it is carried out for exfoliating group 6 TMDs. Characterization of bulk and exfoliated TMD materials was conducted using X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and scanning transmission electron microscopy (STEM). Inherent electrochemistry and electrocatalytic activity towards hydrogen evolution

reaction (HER) was examined by cyclic voltammetry (CV) and linear sweep voltammetry (LSV).

6.2 Results and Discussion

6.2.1 Characterization of the Bulk and Exfoliated Vanadium Dichalcogenides

In this study, the properties of Li exfoliated vanadium dichalcogenides as well as their bulk counterparts are studied. The electrochemical behavior of transition metal dichalcogenides (bulk and exfoliated VS₂, VSe₂, VTe₂) is investigated in terms of inherent electrochemistry and hydrogen evolution reaction. The surface morphology and composition of bulk and exfoliated VS₂, VSe₂, VTe₂ was examined using scanning electron microscopy (SEM) and scanning transmission electron microscopy (STEM). Composition was examined by X-ray diffraction (XRD), energy-dispersive X-ray spectroscopy (EDS), and X-ray photoelectron spectroscopy (XPS). Electrochemical properties were investigated by means of cyclic voltammetry (CV) and linear sweep voltammetry (LSV).

Figure 6.1 Morphological Characterization: SEM images of (a) Exfoliated VS₂. (b) Exfoliated VSe₂. (c) Exfoliated VTe₂. (d) Bulk VS₂. (e) Bulk VSe₂. (f) Bulk VTe₂.

In order to investigate the structure differences between bulk and exfoliated materials, we examined the surface morphologies of the TMDs by SEM. Figure 6.1 displays the electronic micrographs of the bulk and exfoliated materials. The layered structure of TMDs can be clearly observed. From Figure 6.1 d-f, the large polygonal stacks of bulk TMDs without any signs of delamination are visible. After exfoliation, shown in Figure 6.1 a-c, the resulting materials exhibit decreased thickness of layers due to greater expansion between flakes. Scanning transmission electron microscopy (STEM) images (Figure 6.S4) were also taken for further morphology investigation. Based on the STEM images the degree of exfoliation follows the EX-VS₂ > EX-VSe₂ > EX-VTe₂ order. In the case of EX-VS₂, exfoliation led to formation of sheets with few-layer thickness with majority of them being sub-micron sized. Sheet thickness of EX-VSe₂ is similar to that of EX-VS₂, but most of the sheets have larger lateral size (> 1 μm). Finally EX-VTe₂ is composed of sheets with relatively large thickness (no longer transparent). Further discussion of relation between degree of exfoliation and electrocatalytic activity towards HER will be discussed in the following parts. The elemental analysis of bulk and exfoliated VS₂, VSe₂ and VTe₂ were conducted using EDS, showing the roughly homogeneous distribution of the vanadium and chalcogen in Figure 6.S3. It is essential to note that the elemental distribution of S and Se in exfoliated VS₂ and VSe₂ is uneven (Figure 6.S3). The chalcogen-to-metal ratio obtained from EDS shown in Table 6.S1 indicates the exfoliated materials are highly enriched with vanadium, which is in good agreement with XPS data (Table 6.S1) as well as X-ray diffraction (Figure 6.2). For clarity, concentrations of all elements are shown in Table 6.S2.

The X-ray diffraction showed significant changes in the composition of the material after exfoliation. Due to the strong affinity of vanadium towards oxygen, exfoliated materials with large surface area undergo fast oxidation process. This phenomenon could not be avoided despite the fact that exfoliation process was executed in an inert argon atmosphere and prior to analysis, all the samples were stored in a vial filled with argon. Persisting chalcogenide phase can be seen only in the case of vanadium sulphide. Layered V_5S_8 as well as hydrated vanadium oxides ($V_5O_{12}.6H_2O$), elemental sulphur and intercalated vanadium sulphide ($Li_{0.33}VS_2$) was observed in the EX- VS_2 sample. In the case of other chalcogenides, the oxidation is preannounced even more. The presence of elemental selenium together with vanadium oxide (V_2O_3) and lithium vanadate ($Li_{1.11}V_3O_{7.89}$) was detected in EX- VSe_2 sample. EX- VTe_2 sample also undergoes oxidation and lithium vanadates ($Li_{1.11}V_3O_{7.89}$ and $Li_4V_{10}O_{27}$) together with elemental tellurium were observed. Interestingly the oxidation proceeds in a topochemical way and the materials retain their layered morphology; however the dichalcogenide phases were strongly affected by the oxidation of exfoliated material. The results of X-ray diffraction are shown in Figure 6.2. The XRD analysis of starting materials revealed impurity free, single phase of vanadium dichalcogenides only (Figure 6.S1). These results suggest that the oxidation observed for exfoliated samples is indeed caused by the increased surface area introduced during exfoliation.

Figure 6.2 X-ray diffractograms of exfoliated vanadium dichalcogenides.

To further understand the surface elemental composition and bonding information, XPS analysis was performed. As presented in Figure 6.S2, the characteristic peaks of C 1s at *ca.* 284 eV, O 1s at *ca.* 530 eV, V 2p at *ca.* 516 eV, S 2p at *ca.* 161 eV, Se 3p at *ca.* 161 eV and Te pair at *ca.* 575 and 586 eV were identified in the survey scan XPS spectra of exfoliated and bulk VS₂, VSe₂, and VTe₂. The high resolution XPS core-level spectra (Figure 6.3) of vanadium were investigated because of the limited information obtained from the survey scans. The surface elemental composition of bulk and exfoliated materials can be found in Table 6.S1 and Table 6.S3. The oxygen and carbon concentration at material's surface as high as 80% can be attributed to the surface-adsorbed oxygen, metal oxides and adventitious carbon species, which will be discussed further on. The chalcogen-to-metal ratio from XPS data is in good agreement with EDS data illustrated in Table 6.S1. While the chalcogen-to-metal ratio of exfoliated materials is a lot lower than 2 (which would be expected for a stoichiometric compound), the chalcogen-to-metal ratio of bulk materials is 2 or close to 2. These results suggest that the composition of exfoliated samples is complicated and are in good agreement with results mentioned above.

Figure 6.3 High resolution X-ray photoelectron spectra of the V 2p and O 1s regions of (a) exfoliated and (b) bulk VS₂, VSe₂, and VTe₂.

Deconvoluted core-level spectra of V 2p and O 1s are shown in Figure 6.3. Because of the Shirley background contribution, the O 1s portion is also included. The V 2p_{1/2} peak is broader compared to the V 2p_{3/2} peak owing to the Coster–Kronig effect.²⁸ This effect is defined as a form of Auger process in which the core hole in a shell with a certain principle quantum number is filled by an electron from a higher energy shell of the same principle quantum number. In general, such processes result in broad-peak shapes.²⁹ The deconvolution itself revealed that a mixture of species is present at the surface of prepared materials. Two peaks located at 516.82 eV and 524.22 eV of exfoliated VS₂ are attributed to V (IV) 2p_{3/2} and V (IV) 2p_{1/2}. Similarly, the peaks of bulk VS₂ observed at 516.68 eV and 524.08 eV are also ascribed to V (IV) 2p_{3/2} and V (IV) 2p_{1/2}.³⁰ Presence of peaks at the same binding energies of the rest of vanadium chalcogenides also indicates the presence V (IV) oxidation state. Furthermore, the peaks located at 517.3 eV and 524.63 eV are ascribed to V (V) 2p_{3/2} and V (V) 2p_{1/2}, respectively.³¹ suggesting the oxidation of the materials from V (IV) to V (V) oxidation state. Deconvolution also revealed a pair of oxygen peaks originating from two distinct oxygen environments. The first peak of O 1s appears at 529-530 eV and corresponds to metal oxides, indicating the presence of the vanadium oxides (see XRD discussion). The oxygen peak at 531-532 eV corresponds to other oxygen forms such as adsorbed moisture and CO₂. The high resolution X-ray photoelectron spectra of chalcogen (Figure 6.S5) suggest that both Se and Te are present in the form of V-Se and V-Te bonds only, while sulphur is present in two oxidation states. One conspicuous peak at 169 eV in the S 2p high-resolution spectra of bulk and exfoliated VS₂ is ascribed to the oxidized S (IV) state, while the other one located at 164 eV originates from V-S bonds.³²

Figure 6.4 Cyclic voltammograms of (a) bulk VS₂ during anodic scan and (b) cathodic scan, (c) bulk VSe₂ during anodic scan and (d) cathodic scan, (e) bulk VTe₂ during anodic scan and (f) cathodic scan. Arrows indicate the starting scan direction. First scan is marked in blue, with second scan in saffron and third scan in gray. Conditions: supporting electrolyte, 0.5 M PBS at pH 7.2; scan rate, 100 mV/s.

6.2.2 Inherent Electrochemistry of Bulk and Exfoliated Vanadium Dichalcogenides

The inherent electrochemistry originating from the electroactive moieties of the material always restricts their operating potential window and application. The inadequate fundamental knowledge of the inherent electrochemistry of bulk and exfoliated VS₂, VSe₂ and VTe₂ makes it essential to investigate their inherent electrochemical properties. Therefore, we conducted a cyclic voltammetric experiments in anodic and cathodic scan directions over the range of ± 1.8 V in the absence of the depolarizer. The cyclic voltammograms of bulk and exfoliated VS₂, VSe₂ and VTe₂ in two scan directions are displayed in Figure 6.4 and Figure 6.5. Some differences in inherent electrochemistry of

bulk and exfoliated materials can be seen. The anodic scan of bulk VS₂ does not show any redox peaks (Figure 6.4 a). However, the exfoliated VS₂ shows a broad oxidation peak at *ca.* +1.41 V and a reduction peak at *ca.* -1.40 V during the initial anodic sweep as well as a small oxidation peak at *ca.* +1.4 V in the subsequent scans (Figure 6.5 a). The cathodic scan of bulk VS₂ also does not possess any conspicuous redox peak. In comparison with bulk VS₂, exfoliated VS₂ shows an oxidation peak at *ca.* +1.40 V and reduction peaks at *ca.* -1.36 V during the cathodic scan direction. It is worth noting that the reduction peak in the second and third scan emerges only after the oxidation process of exfoliated VS₂ (Figure 6.5 b). This suggests that the electroactive moieties in exfoliated VS₂ are in reduced state and have to be activated by an oxidative treatment. As for bulk and exfoliated VSe₂, there are no obvious peaks during the anodic scan of bulk VSe₂ and the cathodic scan of exfoliated VSe₂ (Figure 6.4 c and Figure 6.5 d). As illustrated in Figure 6.4 d, one reduction peak is materialized at *ca.* -1.45 V during the first cathodic scan of bulk VSe₂. A faint reduction peak at *ca.* -1.3 V in the initial anodic sweep of the exfoliated VSe₂ is also observed (Figure 6.5 c). Two oxidation peaks of bulk VTe₂ are plotted at *ca.* +0.23 V and +0.19 V during the first two anodic scans shown in Figure 6.4 e. The first scan of bulk VTe₂ in the cathodic direction also results in a reductive peak at *ca.* -1.0 V and an oxidation peak at *ca.* +0.21 V. The absence of reduction peak in Figure 6.4 e suggests that the initial oxidation of bulk VTe₂ prohibits the further reaction of electrochemical active substance. After the exfoliation, the anodic and cathodic scans of exfoliated VTe₂ do not show any obvious peak except two inconspicuous reduction peaks at *ca.* -0.8 V and -1.25 V during the first anodic scan (Figure 6.5 e and f).

As shown in Figure 6.5 a and b, during the anodic and cathodic scans, the current of oxidative and reductive peaks of initial scan decreases or even disappear in the subsequent scan. The decrease in current of the peaks indicates the decrease or depletion

of the electroactive moieties during the first scan, suggesting these processes are irreversible. As illustrated in Figure 6.4 a, b and Figure 6.5 a, b, EX-VS₂ shows the additional oxidation and reduction peaks during first anodic scan compared to bulk VS₂, which implies that EX-VS₂ has additional electroactive moieties. Unlike VS₂, the oxidation and reduction peaks of bulk VTe₂ during the first anodic and cathodic scan are absent when VTe₂ is exfoliated.

Thus, we find that all the TMDs studied here exhibit unique redox peaks, although some of them are inconspicuous. These peaks are inherent to different TMDs and each represents their specific characteristics. Due to the different inherent electrochemical performance of bulk and exfoliated VS₂, VSe₂ and VTe₂, we can postulate that the exfoliation of materials has influence on the inherent electrochemical properties of VS₂, VSe₂ and VTe₂.

Figure 6.5 Cyclic voltammograms of (a) exfoliated VS₂ during anodic scan and (b) cathodic scan, (c) exfoliated VSe₂ during anodic scan and (d) cathodic scan, (e))

exfoliated VTe₂ during anodic scan and (f) cathodic scan. Arrows indicate the starting scan direction. First scan is marked in blue, with second scan in saffron and third scan in gray. Conditions: supporting electrolyte, 0.5M PBS at PH 7.2; scan rate, 100 mV/s.

6.2.3 Hydrogen Evolution of the Bulk and Exfoliated Vanadium Dichalcogenides

Research on TMDs for the application in electrocatalysis has gained considerable interest. Here we investigated the electrocatalytic performance towards hydrogen evolution reaction (HER) of bulk and exfoliated VS₂, VSe₂ and VTe₂ using linear sweep voltammetry (LSV). The prepared TMDs suspension were deposited on a glassy carbon (GC) electrode followed by LSV measurements in 0.5 M H₂SO₄. Figure 6.6 shows the HER polarization curves of the TMDs including the HER performance of bulk and exfoliated materials. Polarization curve of GC is also demonstrated for reference.

Figure 6.6 Electrocatalytic hydrogen evolution reaction performance of TMDs in acidic electrolyte. Polarization curves for HER on (a) exfoliated VS₂, VSe₂ and VTe₂, (b) bulk VS₂, VSe₂ and VTe₂. Conditions: 0.5 M H₂SO₄ electrolyte; scan rate, 2 mV/s.

The HER catalytic activity trend of bulk materials is VTe₂>VSe₂>VS₂ while the trend for exfoliated materials is VS₂>VSe₂>VTe₂. The total reversal of HER catalytic activity trend between bulk and exfoliated materials suggests that the exfoliation process has dramatically changed the surface composition of TMDs, leading to different HER performance. From the surface composition analyses shown in Table 6.S1, a sharp decrease in chalcogen-to-metal ratio after exfoliation was observed. Also the deconvolution of core-level spectra of V 2p and O 1s and XRD analysis revealed the

presence of vanadium oxides and lithium vanadates. We can infer that the change of trend from bulk $\text{VTe}_2 > \text{bulk VSe}_2 > \text{bulk VS}_2$ to $\text{EX-VS}_2 > \text{EX-VSe}_2 > \text{VTe}_2$ can be attributed to the decrease of chalcogen-to-metal ratio after exfoliation, as well as the presence of vanadium oxides and lithium vanadates, which can highly influence the HER performance as their presence most likely leads to a reduction of conductivity and availability of catalytically active sites. Also the degree of exfoliation (STEM images), which is in good agreement with HER performance, has to be taken into consideration. Compared to GC, we found that all the TMDs have similar or higher overpotential at -10 mA cm^{-2} than GC except bulk VTe_2 . In contrast, reports in literature reveal that the VS_2 prepared by chemical vapor deposition was reported to be highly efficient for HER with overpotential necessary for -10 mA cm^{-2} as low as 68 mV.²³ On the other hand, The VS_2 nanosheets obtained by hydrothermal method exhibit overpotential of 500 to 450 mV vs. RHE, and VS_2/rGO shows overpotential of 350 mV vs. RHE,³³ indicating relatively low HER activity of VS_2 prepared by these methods. Because of the substantial signal originating from inherent electrochemistry observed for VTe_2 at *ca.* -0.8 V (Figure 6.S6 f), during the HER measurement, we performed three consecutive scans of LSV (Figure 6.S6). Deeper look into the consecutive LSV measurements revealed that such a low overpotential of bulk VTe_2 is most likely not related to HER but inherent electrochemistry instead. The slight shift in the peak potential may be caused by the different pH of electrolyte used for LSV and CV measurements, but is, nevertheless, in good agreement with the fact that this peak is absent in the second and third scans. On the basis of these results we suggest that the activity in second and third LSV scans of bulk VTe_2 should be taken as a comparative value instead of the value obtained during the first scan. Moreover the activity of bulk VTe_2 in the second and third scan remains the same indicating that no activation/deactivation of bulk VTe_2 takes place in subsequent cycling. No obvious trend

can be seen for both EX-VS₂ and bulk VS₂ making the conclusion about activation/deactivation of VS₂ impossible. EX-VSe₂, bulk VSe₂ and EX-VTe₂ on the other hand all exhibit slight shift of overpotential to lower values. This suggests that their HER performance can be slightly tuned with repeated cycling.

6.3 Conclusion

We have prepared bulk and exfoliated VS₂, VSe₂, and VTe₂, and investigated their electrochemical properties. The results show that both bulk and exfoliated VS₂, VSe₂, VTe₂ possess inherent electrochemical activity, which can limit their application for electrocatalysts and electrode materials. The lithium exfoliation route using *n*-butyllithium leads to strikingly different degrees of exfoliation following the VS₂ > VSe₂ > VTe₂ order. Additionally vanadium oxides and lithium vanadates are formed during the process of exfoliation. This contributes to the observed opposite trends of the electrocatalytic effect of bulk and exfoliated 5 group transition metal dichalcogenides.

6.4 Experiment Section

6.4.1 Materials

Sodium Phosphate monobasic, potassium phosphate dibasic, potassium chloride and sodium chloride and platinum on carbon were purchased from Sigma-Aldrich. Pt, Ag/AgCl reference electrode and glassy carbon electrode were purchased from CH Instruments, Texas, USA. Vanadium (99.5%; -325 mesh) and sulphur (99.999%) was obtained from STREM (Germany). Selenium (99.999%) and tellurium (99.999%) were obtained from Chempur (Germany). Butyllithium (2.5 M in hexanes) was obtained from Sigma-Aldrich (Czech Republic). Hexane was obtained from Penta, Czech Republic.

6.4.2 Apparatus

Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) were performed with a JEOL 7600F field emission SEM (JEOL, Japan). SEM and EDS

data were obtained at an acceleration voltage of 2 kV and 15 kV respectively. X-ray photoelectron spectroscopy (XPS) was conducted using a monochromatic Mg K α source (SPECS, Germany) at 1253 eV. Survey scan and high resolution spectra of V 2p, O 1s, S 2p, Se 3d, Te 3d and C 1s were obtained. The relative sensitivity factors were used to calculate the chalcogen-to-metal ratios of various materials. X-ray powder diffraction data were collected at room temperature with an Bruker D8 Discoverer θ - θ powder diffractometer with parafocusing Bragg–Brentano geometry using Cu K α radiation (λ = 0.15418 nm, U = 40 kV, I = 40 mA). Data were scanned with an LYNXEYE XE detector over the angular range 5 - 80° (2 θ) with a step size of 0.019° (2 θ) and a counting time of 5 s step⁻¹. Data evaluation was performed in the software package HighScore Plus 3.0e. Voltammetric measurements of cyclic voltammetry (CV) and linear sweep voltammetry (LSV) were recorded on a μ Autolab type III electrochemical analyzer (Eco Chemie, The Netherlands) using NOVA 1.8 software.

6.4.3 Synthesis of Vanadium Dichalcogenides

Bulk chalcogenides were synthesized from elements in quartz ampoules. The stoichiometric amount of vanadium and chalcogen (2 wt.% excess of chalcogen) corresponding to 10 g of vanadium dichalcogenides were placed in a quartz glass ampoule and evacuated to the base pressure below 2×10^{-3} Pa. The ampoule was melt sealed under high vacuum using hydrogen-oxygen torch. The ampoules were placed in muffle furnace and heated to 400 °C for 24 hours, subsequently to 600 °C for 24 hours and for 48 hours to 800 °C. The heating and cooling rate was 5 °C/min.

6.4.4 Exfoliation of Vanadium dichalcogenides

The intercalation of vanadium dichalcogenides was performed using n-butyllithium in glovebox under argon atmosphere. 10 mmol of dichalcogenides was placed in flask and dispersed in 10 mL of dry hexane. 10 mL of 2.5M butyllithium was added to the reaction

mixture and stirred for 24 hours. The intercalated vanadium dichalcogenides were separated by suction filtration and repeatedly washed with hexane. 5 mL of water under argon atmosphere was slowly added to the intercalation for the exfoliation 2. The exfoliated dichalcogenides were diluted on 100 mL and purified by dialysis. Finally the exfoliated product was separated by suction filtration and dried in vacuum oven at 50 °C for 48 hours.

6.4.5 Electrochemical Procedure

1 mg ml⁻¹ concentration of bulk and exfoliated VS₂, VSe₂ and VTe₂ were prepared in ultrapure water and ultrasonicated for 1 h in order to obtain homogeneous suspension. The glassy carbon electrode surface was renewed by polishing with a 0.05 μm alumina particle slurry on a polishing pad and then washed with ultrapure water and dried. After sonication for 5 minutes, the 4 μL aliquot of material suspension was dropcasted on the electrode's surface. The electrodes were dried at room temperature in order to get randomly distributed materials on the GC surface. Cyclic voltammetry measurement was performed using phosphate buffer solution (PBS, 0.5 mM, pH 7.2) as background electrolyte in a three-electrode configuration, with modified GC, Pt and Ag/AgCl electrodes as working, counter and reference electrode. All cyclic voltammetry measurements were carried at 100 mV.s⁻¹. For hydrogen evolution reaction, linear sweep voltammetry (LSV) measurements were conducted using 0.5 M sulfuric acid solution as electrolyte at a scan rate of 2 mV s⁻¹.

6.5 Supporting Information

Figure 6.S1 The X-ray diffractograms of vanadium dichalcogenides used for exfoliation.

Figure 6.S2 Survey scan X-ray photoelectron spectrum of (a) exfoliated, (b) bulk VS_2 , VSe_2 , and VTe_2 .

Figure 6.S3 EDS elemental mappings of exfoliated and bulk VS_2 , VSe_2 and VTe_2

Table 6.S1 The XPS and EDS data of surface composition of bulk and exfoliated VS₂, VSe₂ and VTe₂.

TMD materials	Chalcogen metal ratio(XPS)	Chalcogen metal ratio(EDS)	Atom (%) composition of C(XPS)	Atom (%) composition of O(XPS)
EX-VS ₂	0.165	0.273	33.64	50.47
EX-VSe ₂	0.542	0.822	50.84	28.44
EX-VTe ₂	0.693	0.156	38.55	44.32
Bulk VS ₂	1.736	1.53	43.16	34.07
Bulk VSe ₂	2.094	2.001	41.19	29.20
Bulk VTe ₂	2.449	1.823	37.45	42.89

Table 6.S2 Elemental composition of bulk and exfoliated VS₂, VSe₂ and VTe₂ obtained from EDS.

TMD materials	Atom (%) composition of carbon	Atom (%) composition of oxygen	Atom (%) composition of vanadium	Atom (%) composition of chalcogen
EX-VS ₂	5.97	63.62	23.89	6.52
EX-VSe ₂	20.71	49.44	16.38	13.47
EX-VTe ₂	8.49	50.01	35.62	5.57
Bulk VS ₂	23.88	34.30	16.49	25.33
Bulk VSe ₂	22.27	27.97	16.58	33.18
Bulk VTe ₂	27.94	25.42	16.52	30.12

Table 6.S3 Elemental composition of bulk and exfoliated VS₂, VSe₂ and VTe₂ obtained from XPS survey spectra.

TMD materials	Atom (%) composition of carbon	Atom (%) composition of oxygen	Atom (%) composition of vanadium	Atom (%) composition of chalcogen
EX-VS ₂	33.64	50.47	14.95	0.94
EX-VSe ₂	50.84	28.44	13.43	7.28
EX-VTe ₂	38.55	44.32	10.00	7.12
Bulk VS ₂	43.16	34.07	8.32	14.45
Bulk VSe ₂	41.19	29.20	9.57	20.04
Bulk VTe ₂	37.45	42.89	5.49	14.17

Figure 6.S4 STEM images of a) EX-VS₂, b) EX-VSe₂ and c) EX-VTe₂. Scale bars correspond to 1 μm.

Figure 6.S5 High resolution X-ray photoelectron spectra of the chalcogen of exfoliated and bulk VS_2 , VSe_2 and VTe_2 .

Figure 6.S6 Electrocatalytic hydrogen evolution reaction performance of TMDs in acidic electrolyte. Polarization curves of the successive three scans of (a)exfoliated VS_2 , (b) exfoliated VSe_2 , (c) exfoliated VSe_2 , (d) bulk VS_2 , (e) bulk VTe_2 and (f) bulk VTe_2 . Conditions: 0.5 M sulfuric acid works as electrolyte; scan rate, 2 mV/s.

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Chapter 7

Electrochemistry of Layered Crystalline and Amorphous PtS₂

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7.1 Introduction

Layered materials have been at the forefront of research since the discovery of the graphene in 2004.¹ Graphene is a single layer of graphite comprising of hexagonal honeycomb carbon lattice.² With extraordinary electronic properties and excellent thermal conductivity,³ graphene has varied applications in biosensor systems,⁴ energy harvesting,^{5, 6} and electronic devices.^{7, 8} These findings have generated renewed interest into other layered materials, such as transition metal dichalcogenides (TMDs), due to their interesting layered structure. TMDs have a general formula of MX_2 where M is a transition metal atom from Group 4 to 10, and X is the chalcogen atom (S, Se or Te).^{9, 10} Each TMD layer comprises of a transition metal atom layer sandwiched between two chalcogen atom layers. These TMD layers are held together by weak Van der Waals forces in its bulk form. Group 6 TMDs (MoS_2 , WS_2) have been extensively studied and reported to have potential applications in electronics, energy harvesting and sensing systems.¹¹⁻¹⁷ Thus, there is the need to expand studies to other TMD materials beyond Group 6, such as platinum dichalcogenides to explore viable alternatives in electrocatalytic applications such as hydrogen gas production and reduction of water. Hydrogen is a renewable fuel source with high energy density¹⁸ and ‘clean’ by-products. It is regarded as a viable alternative to carbon-based fuels and has been used in fuel cells to generate electricity and power vehicles.^{19, 20} Hydrogen fuel can be produced from both non-renewable (natural gas, coal) and renewable (hydro, wind, solar) energy sources.²⁰ Recently, tremendous attention has been devoted to generate hydrogen through the electrochemical reduction of water. One of the technological barriers faced by hydrogen economy is to develop low cost, efficient and sustainable hydrogen production. Water splitting, including electrolysis and photo-electrolysis, offers the potential for economical hydrogen production. To date, the best electrocatalyst is platinum, but its scarcity and

high cost hinder wide-scale applications. Therefore, it is necessary to search for alternative electrocatalysts. TMDs, mainly MoS₂ and WS₂, have demonstrated to be highly catalytic for HER.^{13, 21-25} As such, it would be beneficial to expand studies to other TMDs, namely platinum-based dichalcogenides, as potential alternatives to elemental platinum in electrocatalytic applications such as hydrogen gas production.

The lattice structures of compounds (crystalline vs. amorphous) were also reported to influence the electrochemical performances of TMDs. Amorphous materials, also known as glassy materials, are non-equilibrium materials with no long-range periodicity in the atomic arrangement. These materials have been actively researched on and are reported to have high density of active sites from the porous, rough and nanostructured morphology which results in better HER performance.²⁶ Amorphous forms of molybdenum sulfide,²⁶⁻²⁹ tungsten phosphide nanoparticles³⁰ and cobalt boride³¹ have displayed efficient performances as electrocatalysts for HER. Furthermore, amorphous materials are also the best active candidates for high performance supercapacitors due to the unique porous structure which generates high surface area.³² It would thus be advantageous to understand the differing capabilities of TMD with differencing lattice structures.

Herein, crystalline and amorphous platinum disulfide (PtS₂) were synthesized and their fundamental electrochemical characteristics including inherent properties, heterogeneous electron transfers (HET), oxygen reduction reaction (ORR) and hydrogen evolution reaction (HER) were studied. These studies aimed to compare the varying electrochemical and electrocatalytic properties of crystalline and amorphous PtS₂. Additionally, previous studies have shown that electrochemical pre-treatment is capable of tuning the catalytic performances of layered metal dichalcogenides.^{33, 34} Hence, the effects of electrochemical reduction pre-treatment on the electrocatalytic properties of

crystalline and amorphous PtS₂ were also investigated. These two materials were characterized by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), transmission electron microscope (TEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS).

7.2 Results and Discussion

7.2.1 Material Characterization

Figure 7.1 Scanning electron microscopy (SEM) images of a) crystalline and b) amorphous PtS₂.

Scanning electron microscopy (SEM) was first performed to observe the morphological differences of crystalline and amorphous PtS₂. From Figure 7.1 a, the layered structure of crystalline PtS₂ is clearly evident and these layers are closely stacked in the bulk state. In contrast, amorphous PtS₂ appear to form clusters with rough nanostructure surface without any apparent indication of layered structure (Figure 7.1 b). Elemental mapping of both materials by energy dispersive X-ray spectroscopy (EDS) shows the homogeneous element distribution of C, O, S, Pt for both materials (Figure 7.S1). The chalcogen to metal ratios of crystalline and amorphous PtS₂ obtained from EDS are 1.83 and 1.50 respectively, which are close to the stoichiometric ratio of 2. The chemical compositions were further investigated by XPS and the chalcogen to metal ratios of PtS₂ crystal and amorphous PtS₂ are 1.92 and 1.83, which is in close agreement with EDS data.

Figure 7.2 Transmission electron micrographs (left and centre), and high-resolution TEM images (right) of (a) crystalline and (b) amorphous PtS₂. The inset image is the SAED of amorphous PtS₂. Scale bars represent 5 nm for the HR-TEM images.

The crystallinity of both PtS₂ materials were further investigated by transmission electron microscope (TEM) and X-ray diffraction (XRD). TEM micrographs of crystalline PtS₂ (Figure 7.2 a) showed layered structure with particle size of up to 2 μm. However, TEM micrographs of amorphous PtS₂ showed nanoclusters formation with no apparent layer character (Figure 7.2 b). The elemental mappings by TEM in Figure 7.S2 indicated that Pt and S atoms were homogeneously distributed. The phase composition of PtS₂ was further examined by XRD (Figure 7.S3). PtS₂ has a hexagonal crystal system belonging to the *P-3m1* space group. XRD showed the single phase purity of crystalline PtS₂ (Figure 7.S3 a) and amorphous PtS₂ (Figure 7.S3 b). Crystalline PtS₂ crystal showed diffraction reflections at 17.6°, 35.6° and 54.6° corresponding to the (001), (002) and (003) planes indicating preferential orientation.³⁵ On the contrary, the lack of the characteristic XRD peaks of amorphous PtS₂ provided evidence of its amorphous state. Hence, it can be

ascertained that the respective synthesised PtS₂ materials were crystalline and amorphous in nature.

7.2.2 Electrochemical Properties

Figure 7.3 Cyclic voltammograms of crystalline PtS₂ during a) anodic, and b) cathodic scan, amorphous PtS₂ during c) anodic, and d) cathodic scan. Conditions: 0.5 M PBS solution as electrolyte (pH 7.2), scan rate of 100 mV s⁻¹. Arrows indicate the direction of scans starting at scan potential of 0 V. The glassy carbon electrode used has a diameter of 0.3 cm.

The inherent electrochemical properties of the synthesised crystalline and amorphous PtS₂ were first investigated. The operating electrochemical potential window of electrode materials is always limited by their inherent electrochemical activities and reaction with electrolyte used.³⁶⁻³⁸ Inherent electrochemistry stems from the redox behaviours of electroactive moieties on materials surfaces when an electrochemical potential is applied.³⁹ The increasing attention on noble metal dichalcogenides for various electrochemical applications drive us to study the inherent electrochemical properties of both crystalline and amorphous PtS₂.^{34, 40} Cyclic voltammetry (CV) in both anodic and

cathodic scan directions were herein performed to examine the inherent electrochemical properties of crystalline and amorphous PtS₂.

CV measurements of crystalline and amorphous PtS₂ shown in Figure 7.3 were performed at the potential range of -1.8 to + 1.8 V starting at a potential of 0 V in phosphate buffer saline electrolyte of pH 7.2. It was noted that both crystalline and amorphous PtS₂ showed similar inherent electrochemical signals where a broad reduction peak was observed at around -1.3 V vs. Ag/AgCl in the first scan in both the anodic and cathodic scans. The peak disappeared for crystalline PtS₂ at subsequent scans while it became diminished for amorphous PtS₂ for both directions scans. Considering the reducible Pt element in both crystalline and amorphous PtS₂, this peak is assigned to the reduction of the Pt from Pt (IV) to Pt (II) or Pt (0).³⁴ It would be beneficial for both states of PtS₂ to undergo an electrochemical reduction step before use in sensing applications at high negative potentials. Besides that, both crystalline and amorphous PtS₂ exhibited broad oxidation peak between +0.6 V to +1.1 V vs. Ag/AgCl in the cathodic scan direction. This corresponds to the oxidation of the chalcogen atom S, with the oxidation state of -2, to HSO₄⁻ and SO₄²⁻.³⁴ Amorphous PtS₂ showed a very broad oxidation peak which could be attributed to the oxidation of intermediate oxidation states of Pt in the material which overlaps with the oxidation of the chalcogen atoms. From the inherent electrochemistry study, it was observed that both forms of PtS₂ displayed limited operating potential due to their inherent redox activities. As such, it would greatly limit the capability of the materials in electrochemical sensing applications without prior pre-treatment process.

Figure 7.4 a) Cyclic voltammograms of 5 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ on bare glassy carbon, crystalline and amorphous PtS_2 . Scan rate of 100 mV s^{-1} . b) Peak-to-peak separations of bare glassy carbon, crystalline and amorphous PtS_2 . Error bars representing standard deviations obtained from three measurements.

We next set forth to analyse the electron transfer performance of crystalline and amorphous PtS_2 . Heterogeneous electron transfer (HET) rate is usually adopted as it provides a preliminary representation on the efficiency of electron transfer between the analyte and electrode surface. Typically, faster HET rates correspond to lower overpotentials required for electrochemical reactions to take place. In this study, we utilized surface sensitive ferro/ferricyanide ($[\text{Fe}(\text{CN})_6]^{3-/4-}$) redox probe to study the HET rates of the crystalline and amorphous PtS_2 by CV. The wider peak-to-peak separation (ΔE) between the redox peaks can be interpreted as a representation of slower HET rates in accordance to Nicholson's method.⁴¹ This study enables us to investigate and understand the differences in HET rates of crystalline and amorphous PtS_2 .

Figure 7.4 a shows the CV curves of bare glassy carbon, crystalline and amorphous PtS_2 . Both materials exhibit reversible redox peaks corresponding to $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox probe

and no interference from the inherent electrochemistry was observed. From Figure 7.4 b, it was noted that amorphous PtS₂ has smaller ΔE as compared to its crystalline counterpart. Crystalline PtS₂ displayed almost similar ΔE to bare glassy carbon. It can be inferred that amorphous PtS₂ possessed a faster HET rate than crystalline PtS₂. HET rate constants (k_{obs}^0) of crystalline and amorphous PtS₂ were calculated to be $9.50 \times 10^{-4} \text{ cm s}^{-1}$ and $3.74 \times 10^{-3} \text{ cm s}^{-1}$, respectively. Amorphous PtS₂ displayed better electron transfer properties as evident from the higher k_{obs}^0 value obtained. This would suggest that the amorphous form of TMDs might display better electrochemical response than their crystalline counterparts. Amorphous PtS₂ would thus be more favourable for electrochemical sensing applications than its crystalline counterpart due to its more efficient electron transfer abilities.

Previous studies have demonstrated that inherent electrochemistry impacts the electrochemical properties of materials.^{33, 34, 42} By recognizing the inherent redox peaks of crystalline and amorphous PtS₂, a suitable potential of -1.5 V, beyond the characteristic reduction peak, was selected for electrochemical pre-treatment. X-ray photoelectron spectroscopy (XPS) was performed to investigate the surface chemical composition before and after electrochemical pre-treatment to analyse the effect on both crystalline and amorphous PtS₂.

Figure 7.5 High resolution X-ray photoelectron spectra of Pt 4f region of a) crystalline, c) amorphous PtS₂, and (b, d) their electrochemically reduced forms at a potential of -1.5 V. These spectra were calibrated to the adventitious C 1s peak at 284.5 eV.

The survey scan XPS spectra of crystalline and amorphous PtS₂, along with their electrochemically pre-treated counterparts (Figure 7.S4) displayed characteristic peaks of C 1s at 284.5 eV, O 1s at 530.9 eV, S 2p at 163.0 eV and Pt 4f at 72.9 eV. High resolution XPS core level spectra of Pt 4f and S 2p bonding modes were recorded in Figures 7.5 and 7.6 respectively. From Figure 7.5 a, the deconvolution of peaks for Pt 4f for crystalline PtS₂ revealed the predominance of Pt (IV) oxidation state at binding energies of 73.4 and 76.7 eV for 4f_{7/2} and 4f_{5/2} bonding modes respectively. A minor doublet peak for Pt (0) was observed at binding energies of 71.6 and 75.0 eV for 4f_{7/2} and 4f_{5/2} binding modes.^{34,}

⁴³ On the contrary, the deconvolution of peaks for amorphous PtS₂ showed the additional presence of Pt (II) oxidation state with binding energies of 72.6 and 75.9 eV for 4f_{7/2} and 4f_{5/2} binding modes (Figure 7.5 c). In addition, smaller peaks were obtained for Pt (IV) and Pt (0) oxidation states. The differences in synthesis procedures (see Experimental Section) could have attributed to the presence of intermediate oxidation state of Pt in amorphous PtS₂ which could have an impact on its electrochemical performance as well. Both crystalline and amorphous PtS₂ were then subjected to electrochemical reduction pre-treatment where their surface elemental compositions were analysed and compared with their untreated counterparts. The principle Pt 4f signals of electrochemically pre-treated crystalline and amorphous PtS₂ do not show any significant shift in binding energies. From Figure 7.5 b, the Pt 4f peak of electrochemically reduced crystalline PtS₂ was deconvoluted into two pairs of peaks corresponding to Pt (IV) and Pt (0) at the same binding energies as the untreated form. Surface element composition analysis indicated that electrochemical reduction pre-treatment resulted in the decreased contribution of Pt

(IV) from 92.2% to 76.1% and increased percentage of Pt (0) from 7.8% to 23.9% (Table 7.S1). Therefore, electrochemical reduction pre-treatment involved the reduction of Pt (IV) to Pt (0) on the surface of crystalline PtS₂. Likewise, electrochemically reduced amorphous PtS₂ was deconvoluted into three pairs of peaks of Pt (0), Pt (II) and Pt (IV) which were at similar binding energies with untreated amorphous PtS₂ (Figure 7.5 d). From Table 7.S1, it was found that electrochemical pre-treatment led to the increased proportion of Pt (0) from 2.8% to 7.3% and Pt (IV) from 22.1% to 25.1%. At the same time, Pt (II) contribution dropped from 75.1% to 67.6%. The minor increase of Pt (IV) may due to the removal of sulfate layer and expose of beneath PtS₂.

Figure 7.6 High resolution X-ray photoelectron spectra of S 2p region of a) crystalline, c) amorphous PtS₂, and (b, d) their electrochemically reduced forms at a potential of -1.5 V. These spectra were calibrated to the adventitious C 1s peak at 284.5 eV.

The surface elemental composition of the chalcogen atoms was next analysed. From Figure 7.6 a, a small broad peak for S (IV) oxidation state was detected which would suggest the presence of very low amounts of oxidised sulfur groups (SO₄²⁻) in crystalline PtS₂. This would also affirm the absence of Pt (II) oxidation state in crystalline PtS₂ as observed in Figure 7.5 a. Conversely, there is a significant presence of S (IV) oxidation

state in amorphous PtS₂ at binding energy of 168.7 eV (Figure 7.6 c).³⁴ The presence of SO₄²⁻ and Pt (II) oxidation state would suggest the formation of PtSO₄ within amorphous PtS₂. The characteristic peaks of S²⁻ were obtained at binding energies of 161.4 and 162.6 eV for 2p_{3/2} and 2p_{1/2} binding modes in both crystalline and amorphous PtS₂.³⁴ Moving on to the XPS spectra of the electrochemically reduced counterparts, deconvolution analysis revealed peaks corresponding to S²⁻ and SO₄²⁻ for reduced amorphous PtS₂ (Figure 7.6 d) whereas only S²⁻ peak in reduced crystalline PtS₂ was observed (Figure 7.6 b). From Table 7.S1, electrochemical pre-treatment of amorphous PtS₂ caused a surge in the proportion of S²⁻ from 25.6% to 81.8% and significant decrease in SO₄²⁻ from 74.4% to 18.2%. Furthermore, there was an absence of SO₄²⁻ signal for reduced crystalline PtS₂. On the whole, electrochemical reduction pre-treatment on both crystalline and amorphous PtS₂ contributed to the removal of oxidized sulfate groups and increased the proportion of Pt (0) which might be beneficial for energy harvesting applications.

7.2.3 Energy Related Electrochemical Reactions

Having understood the morphological and electrochemical properties of the materials, we next investigated the electrocatalytic performances of both crystalline and amorphous PtS₂ as well as their electrochemically reduced forms towards oxygen reduction reaction (ORR) and hydrogen evolution reaction (HER). In this part, we explored the electrocatalytic performances of as-synthesised crystalline and amorphous PtS₂. Previous studies have demonstrated the feasibility of tuning the electrochemical properties of transition metal dichalcogenides through electrochemical pre-treatment.^{33, 34, 40} Following this approach, the influence of electrochemical reduction pre-treatment on crystalline and amorphous PtS₂ was also explored.

Figure 7.7 Linear sweep voltammograms for oxygen reduction reaction (ORR) on crystalline, amorphous PtS₂ and their electrochemically reduced forms. Conditions: 0.1 M KOH as electrolyte, scan rate of 10 mV s⁻¹.

ORR is highly important for the implementation of clean and sustainable energy conversion and storage technology, especially for alkaline fuel cells.⁴⁴ Previous study showed that PtTe₂ exhibited similar ORR performance to Pt/C.⁴⁵ It would thus suggest that PtS₂ would display similar performance to its tellurium chalcogen counterpart. The electrocatalytic performances of crystalline and amorphous PtS₂ towards ORR were investigated in 0.1 M KOH solution at scan rate of 10 mV s⁻¹. Figure 7.7 shows the ORR polarization curves obtained. Onset potential was used to evaluate and compare the ORR performances of the different materials which was obtained at current value of -7 μA (current density: -1 mA cm⁻²). Bare GC showed the highest onset potential of -371 mV *vs.* Ag/AgCl. It was interesting to note that crystalline PtS₂ showed similar ORR performance with an onset potential of -374 mV *vs.* Ag/AgCl. The onset potential of amorphous PtS₂ occurred earlier at -331 mV *vs.* Ag/AgCl, which saw a shift of +43 mV as compared to its crystalline counterpart. Upon electrochemical reduction pre-treatment, there was no significant change to the onset potential of crystalline PtS₂ (-379 mV *vs.* Ag/AgCl). On the contrary, amorphous PtS₂ displayed enhanced performance with a larger decrease of onset potential to -241 mV *vs.* Ag/AgCl. These results demonstrated that amorphous PtS₂ showed superior electrocatalytic capacity towards ORR than

crystalline PtS_2 . Moreover, amorphous PtS_2 is more sensitive to electrochemical reduction pre-treatment which led to the substantially improved ORR performance observed. Our findings further corroborate with previous studies on the enhanced performance of amorphous materials in electrochemical applications.

Figure 7.8 a) Linear sweep voltammograms for hydrogen evolution reaction (HER) on crystalline, amorphous PtS_2 and their electrochemically reduced forms. b) Overpotential values obtained at -10 mA cm^{-2} . c) Tafel slope values obtained for respective materials. Conditions: 0.5 M H_2SO_4 as electrolyte, scan rate of 2 mV s^{-1} .

Moving on to HER, linear sweep voltammetry was performed in 0.5 M H_2SO_4 to analyse the electrocatalytic performances of crystalline and amorphous PtS_2 , as well as the

electrochemically reduced forms. The HER polarization curves were plotted in Figure 7.8 a while the corresponding overpotential values obtained at -10 mA cm^{-2} and Tafel slope values were presented in Figures 7.8 b and Figure 7.8 c respectively. The HER performances of bare GC and Pt/C were also included for reference. Overpotential values obtained at -10 mA cm^{-2} was used to assess the efficiency of the HER performances. Lower overpotential values would translate to better performance of the material towards HER. As expected, Pt/C showed superior HER electrocatalytic performance with the lowest overpotential value of 84.9 mV vs. RHE at -10 mA cm^{-2} . The HER polarization curves of the untreated PtS_2 revealed amorphous PtS_2 to be the more superior electrocatalyst than crystalline PtS_2 . The overpotential values at -10 mA cm^{-2} for amorphous and crystalline PtS_2 were 0.30 V and 0.70 V vs. RHE , respectively. Therefore, amorphous PtS_2 demonstrated higher HER efficiency in comparison to its crystalline counterpart. To probe this variation, electrochemically active surface area of crystalline and amorphous PtS_2 were obtained by capacitance of non-faradic current as shown in Figure 7.9.²⁶ The non-faradic current is a result of the electrochemical double layer capacitance (C_{dl}) which is proportional to the electrochemically active surface area and scan rates applied. The potential window of 0.15 V to 0.35 V vs. RHE was selected for the CV measurements as there were no obvious faradic current contributions in this range (Figures 7.9 a and b). Corresponding scan rate dependence of the current density at given potential of 0.3 V vs. RHE was plotted (Figure 7.9 c) to analyse the linear relationship of both crystalline and amorphous PtS_2 . The double layer capacitance, which is proportional to the surface area, can be obtained from the slope of plot. The C_{dl} of amorphous PtS_2 was calculated to be 4.6 mF cm^{-2} , which was two orders of magnitude higher than that of crystalline PtS_2 (0.08 mF cm^{-2}). This increase in double layer capacitance can be translated to the proliferation of active sites for HER as electrochemically active surface

area is proportional to the available active sites for HER, thus contributing to the improved HER performance observed (Figure 7.8 a). Electrochemical reduction pre-treatment was able to tune the electrocatalytic behaviour of both crystalline and amorphous PtS₂. Electrochemically reduced amorphous PtS₂ displayed enhanced electrocatalytic performance to attain a lower overpotential of 0.17 V *vs.* RHE at -10 mA cm⁻². Besides that, the electrocatalytic performance of crystalline PtS₂ was also activated by electrochemical pre-treatment to give overpotential of 0.31 V *vs.* RHE at current density of -10 mA cm⁻². It had thus been demonstrated that both amorphous and crystalline PtS₂ can be activated by electrochemical reduction pre-treatment for HER.

In addition to overpotential values, Tafel slope calculations can also provide insights into the predominant HER mechanism.⁴⁶ By plotting the linear range fitted to the Tafel equation of $\eta = a + b \log |j|$, Tafel slope b can be obtained (Figure 7.8 c).²² Tafel slope is determined by the rate limiting steps of HER involved. The rate limiting steps are as follows:^{22, 47, 48}

1. Adsorption step (Volmer): $\text{H}_3\text{O}^+ + \text{e}^- \rightarrow \text{H}_{\text{ads}} + \text{H}_2\text{O}$; $b \approx 120 \text{ mV/dec}$
 2. Desorption step (Heyrovsky): $\text{H}_{\text{ads}} + \text{H}_3\text{O}^+ + \text{e}^- \rightarrow \text{H}_2 + \text{H}_2\text{O}$; $b \approx 40 \text{ mV/dec}$
- Or Desorption step (Tafel): $\text{H}_{\text{ads}} + \text{H}_{\text{ads}} \rightarrow \text{H}_2$; $b \approx 30 \text{ mV/dec}$

HER mechanism firstly undergoes the essential adsorption Volmer step to produce the hydrogen atoms, followed by either desorption Heyrovsky or Tafel step. Among all the materials, Pt/C yielded the lowest Tafel slope value of 34.3 mV/dec which corresponds to the Volmer-Tafel mechanism consistent with reported literature.^{22, 49} Before electrochemical pre-treatment, amorphous PtS₂ exhibited a moderate Tafel slope value of 96.9 mV/dec whereas crystalline PtS₂ had a large Tafel slope of 160 mV/dec. These Tafel slope values suggested that both amorphous and crystalline PtS₂ were limited by the discharging Volmer step.³⁴ Electrochemical reduction pre-treatment was able to activate

both PtS₂ materials for HER as evident from the lower overpotential values obtained which concurrently led to the lower Tafel slope values in comparison with the untreated forms (64.5 mV/dec for reduced amorphous PtS₂ and 81.1 mV/dec for reduced crystalline PtS₂). The Tafel slope of reduced amorphous PtS₂ was similar to that of reported MoP, which suggested the HER mechanism undergoes a fast Volmer step followed by the rate-limiting Heyrovsky desorption step.^{50, 51} However, the Tafel slope of reduced crystalline PtS₂ did not match any activation controlled HER mechanisms^{49, 52, 53} and a more complex HER mechanism with mass transport limitation may be involved.

It was also essential to affirm that external sources of Pt, such as the counter electrode, did not contribute negatively to the observations made. Previous study had reported the negative effect of using Pt as counter electrode for measurement of HER performance where the re-deposition of electrochemically or chemically dissolved Pt onto the working electrode can significantly boost the HER performance thus affecting the measurements obtained.⁵⁴ Regarding to this defect, we conducted comparison experiments using glassy carbon as the counter electrode to study the effect of Pt counter electrode on the HER performance of amorphous PtS₂. The HER results with amorphous PtS₂ using either GC or Pt as counter electrode showed no significant difference in their performances (Figure 7.S5). Therefore, the use of Pt counter electrode had no significant influence on the HER performances in this work.

Figure 7.9 Cyclic voltammograms of a) crystalline and b) amorphous PtS₂ measured in 0.5 M H₂SO₄ at the scan rates from 10 to 320 mV s⁻¹. c) Current density measured at 0.30 V vs. RHE plotted with variable scan rates applied to estimate relative electrochemically active surface area.

7.3 Conclusion

We have synthesized and characterized both crystalline and amorphous PtS₂. Crystalline PtS₂ displayed uniform layered morphology while amorphous PtS₂ showed formation of nanoclusters with no apparent layered structure. Both crystalline and amorphous PtS₂ were found to exhibit inherent electroactivities where electrochemical reduction peak at around -1.3 V vs. Ag/AgCl was ascribed to the reduction of Pt from Pt (IV) to Pt (II) or Pt (0) and a broad oxidation peak of chalcogen S are observed. Amorphous PtS₂ would display greater performance in electrochemical sensing applications with greater electron

transfer abilities due to its higher HET rate constants ($3.74 \times 10^{-3} \text{ cm s}^{-1}$) than crystalline PtS₂ ($9.50 \times 10^{-4} \text{ cm s}^{-1}$). Amorphous PtS₂ also exhibited better ORR and HER performances than crystalline PtS₂ attributed higher electrochemically active surface area. Both crystalline and amorphous PtS₂ showed enhanced ORR and HER electrocatalytic performances upon electrochemical reduction pre-treatment. These findings provide insights into the electrochemical and electrocatalytic performances of both crystalline and amorphous PtS₂, which will be useful for the further applications. It was also evident that electrochemical reduction pre-treatment significantly enhances the electrocatalytic performances of materials with the removal of oxidised sulphur groups and formation of Pt (0).

7.4 Experimental Section

7.4.1 Materials

Hexachloroplatinic (IV) acid hexahydrate and Pt sponge were obtained from Safina, Czech Republic. Sulfur (99.999%) was obtained from STREM, Germany and H₂S from SIAD, Czech Republic. Sulfuric acid, potassium hydroxide, sodium phosphate monobasic, potassium phosphate dibasic, sodium chloride, potassium chloride, potassium hexacyanoferrate (III), potassium hexacyanoferrate (II) trihydrate and platinum on carbon were purchased from Sigma-Aldrich, Singapore. Glassy carbon (GC), platinum and Ag/AgCl reference electrodes were obtained from CH Instruments, Texas, USA. Milli-Q water was utilized for the preparation of background electrolytes.

7.4.2 Apparatus

Scanning electron microscopy (SEM) was performed using a JEOL 7600F field-emission SEM (JEOL, Japan) at the voltage of 5 kV. Energy dispersive X-ray spectroscopy (EDS) was conducted at an acceleration voltage of 20 kV.

Transmission electron microscopy (TEM), high resolution transmission electron microscopy (HR-TEM) and selected area electron diffraction (SAED) were executed using EFTEM JEOL 2200 FS microscope (JEOL, Japan) at an acceleration voltage of 200 keV. The samples were prepared by drop-casting the material suspensions on a TEM Cu grid and dried at 60 °C for 12 h. Elemental maps of EDS by TEM were obtained with SDD detector X-MaxN 80 T S from Oxford Instruments, England.

Powder X-ray diffraction (XRD) was performed at room temperature with an Bruker D8 Discoverer powder diffractometer and parafocusing Bragg–Brentano geometry, using Cu K α radiation (λ =0.15418 nm, U=40 kV, I=40 mA). XRD data were obtained with an ultrafast Lynxeye XE detector over the angular range 10°–80° (2 θ). XRD data evaluation was carried out with HighScore Plus 3.0e software.

X-ray photoelectron spectroscopy (XPS) was carried out by using a monochromatic Mg K α source (SPECS, Germany) at 1253 eV and a multichannel energy analyser (SPECS Phoibos 100 MCD-5). Wide scan and high resolution core-level spectra were obtained for analysis and C 1s at 284.5 eV for calibration.

Electrochemical measurement of cyclic voltammetry (CV) and linear sweep voltammetry (LSV) were performed with μ Autolab type III electrochemical analyser (Eco Chemie, The Netherlands) using NOVA 1.10 software.

7.4.3 Synthesis of Crystalline and Amorphous PtS₂

Amorphous PtS₂ was made by reaction of H₂PtCl₆ with H₂S. 2 g of H₂PtCl₆.6H₂O was dissolved in 100 mL water and H₂S was bubbled through the solution (100 mL min⁻¹) for 6 h. Subsequently, formed PtS₂ was separated by suction filtration, washed with deionized water and dried in vacuum oven (50 °C for 48 h). Crystalline PtS₂ was made by direct reaction of Pt and S in quartz glass ampoule. Platinum sponge and sulphur, with molar ration of 1:3, was placed in quartz glass ampoule (15x100 mm), evacuated on the

pressure 1×10^{-3} Pa and melt sealed. The ampoule was heated on 800 °C for 90 days. The heating and cooling rate were 5 °C/min. Excess of sulfur was removed by heating of PtS₂ on 150 °C in high vacuum for 5 hours.

7.4.4 Electrochemical Procedures

Crystalline and amorphous PtS₂ suspensions with the concentration of 5 mg mL⁻¹ were prepared in ultrapure water and sonicated for 2 h to obtain well-dispersed suspensions. 4 µL of suspension was drop-casted on a glassy carbon electrode and dried at room temperature in order to obtain a random distribution of material on the GC surface. The GC surface was renewed by polishing with 0.05 mm alumina particles on a polishing pad, and rinsed with deionized water. Cyclic voltammetry (CV) for the measurement of inherent electrochemical properties and heterogeneous electron transfer was performed in 5 mL electrolyte using a three electrode system where modified glassy carbon, Ag/AgCl, and Pt electrode as working, reference, and counter electrode respectively. Phosphate buffer solution (PBS, 50 mM, pH 7.2) was used as the electrolyte for inherent electrochemistry studies, and [Fe(CN)₆]^{3-/4-} redox probe for HET measurements. [Fe(CN)₆]^{3-/4-} redox probe was prepared by mixing equal volume of 2.5 mM Fe(CN)₆³⁻ and 2.5 mM Fe(CN)₆⁴⁻. The HET rate constants (k_{obs}^0) were calculated using Nicholson's method,⁴¹ which correlates the peak-to-peak separation (ΔE) to a dimensionless parameter Ψ , and subsequently to k_{obs}^0 . The roughness factor was not taken into consideration. The diffusion coefficient used for calculation is $D = 7.26 \times 10^{-6}$ cm² s⁻¹ in 0.1 M KCl.⁵⁵

7.5 Supporting Information

Figure 7.S1 Elemental mappings of a) crystalline and b) amorphous PtS_2 obtained by energy-dispersive X-ray spectroscopy (EDS) based on scanning electron microscopy (SEM).

Figure 7.S2 Elemental mappings of a) crystalline and b) amorphous PtS_2 obtained by EDS based on transmission electron microscopy (TEM).

Figure 7.S3 X-ray diffractograms of a) crystalline and b) amorphous PtS_2 .

Figure 7.S4 Survey scan of X-ray photoelectron spectra of crystalline, amorphous PtS_2 and their electrochemically reduced forms. The survey spectra were calibrated to the adventitious C 1s peak at 284.5 eV.

Table 7.S1 Elemental compositions of crystalline and amorphous PtS_2 and the chalcogen/metal ratio before and after electrochemical pre-treatment.

Sample	Pt(0) %	Pt(II) %	Pt(IV) %	S(II) %	S(IV) %	Chalcogen/ Metal Ratio
Crystalline PtS_2	7.77	0	92.24	78.79	21.21	1.92
Crystalline PtS_2 -Red	23.94	0	76.06	100	0	1.83
Amorphous PtS_2	2.82	75.08	22.09	25.6	74.41	1.83
Amorphous PtS_2 -Red	7.32	67.58	25.11	81.78	18.25	1.25

Figure 7.S5 Hydrogen evolution reaction (HER) performances of amorphous PtS₂ and electrochemically reduced form with Pt and bare GC counter electrodes. Conditions: 0.5 M H₂SO₄ as electrolyte, scan rate of 2 mV s⁻¹.

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Chapter 8

Electrochemistry of Graphene/Group 5 TMDs Composites

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8.1 Introduction

The discovery of graphene has drawn considerable attention due its remarkable electronic, optical and mechanical properties.¹⁻³ These unique properties of graphene have inspired researchers to explore other 2D materials, such as transition metal dichalcogenides (TMDs),⁴ C₃N₄,^{5, 6} graphyne,⁷ black phosphorus⁸ and so on. It is reported that more than twenty 2D materials have been studied.⁹⁻¹² Interestingly, most of them could be exfoliated down to stable mono/few layers with unique properties different from their bulk counterparts. Among these layered materials, TMDs, especially single layered TMDs, have attracted tremendous interest due to their versatile nature which enable them to be adopted for wide-ranging applications including electrocatalysts,^{13, 14} photocatalysts,^{15, 16} sensor,^{17, 18} super-capacitors,¹⁹ and batteries²⁰.

Due to the depletion of non-renewable fossil fuels and environmental degradation, it is of paramount importance to search for renewable and clean fuel. In particular, the TMDs have been found to be promising in clean energy electrocatalysis, with emphasis on hydrogen production.^{21, 22} Hydrogen is considered as a renewable fuel with high energy density²³ and can be produced by electrocatalyzed or photocatalyzed water splitting to give a clean byproduct. In order to decrease the overpotential, hydrogen evolution reaction (HER) requires an electrocatalyst to facilitate this reaction. Platinum is the best electrocatalyst at present. However, the rarity of this precious metal drives up costs and necessitates the quest for alternative electrocatalysts that are earth-abundant – the TMDs. TMDs such as MoS₂ and WS₂ have been demonstrated to be highly efficient for HER when exfoliated to a monolayer or few layers as a result of 2H to 1T phase transformation and the presence of more active sites.¹⁴

Interestingly, when TMDs are hybridized with other materials such as graphene and carbon nanotube, the strong coupling between the TMD and carbon material further

improves their HER performance.²⁴ Methods for optimizing the electrocatalytic activity of TMDs are to increase the number of active sites for HER and improve the electrical conductivity by growing TMDs on the conductive substrates. For example, MoS₂ nanoparticles grown on graphene have been reported to show highly exposed active site and promoted electrical conductivity with graphene, resulting in the excellent HER performance with overpotential of approximately 0.1 V.²⁵ So far, Group 6 TMDs have been investigated as hybrid electrocatalysts for HER and there are few papers on the nanocomposites of graphene/Group 5 TMDs for electrocatalysts application. It is also potentially attractive to employ Group 5 TMDs for hybrid materials. Based on density functional theory calculation,^{26, 27} Group 5 TMDs are pointed out to be favorable for HER, especially VS₂ which shows the best HER performance. This prediction has been demonstrated by the VS₂ nanosheet prepared by chemical vapor deposition for highly efficient HER.²⁸ However, vanadium dichalcogenide nanosheets, which were obtained by lithium exfoliation method established for MoS₂ and WS₂, exhibited relatively mediocre performance for HER.²⁹ The suppressed HER performance of exfoliated vanadium dichalcogenides was caused by the presence of non-stoichiometric vanadium oxide and lithium vanadates formed during the exfoliation process, leading to the reduction of conductivity and availability of active sites.

Herein, we report our study on the nanocomposites of graphene and Group 5 TMDs, namely VS₂, NbS₂ and TaS₂ for HER. In this fundamental research, the MS₂/graphene nanocomposites (M= V, Nb or Ta) were prepared by thermal exfoliation of graphene oxide/TMD precursors in H₂S atmosphere. As a control, thermal exfoliation of graphene with the Group 5 transition metal precursors were also performed in the H₂ atmosphere, to yield a composite of graphene and the Group 5 metal oxides. In this paper, MS₂/graphene composites and M oxides/graphene composites are denoted as TRG-M-

H₂S and TRG-M-H₂ respectively. Graphene oxide was prepared by Hummers method while vanadium tetrachloride, niobium pentachloride and tantalum pentachloride were utilized as TMD precursors. The resulting hybrids were characterized in terms of morphology and composition by scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD) and X-ray photoelectron spectra (XPS). Additionally, we measured the electrocatalytic viability of these hybrid materials towards HER and their supercapacitor performance.

8.2 Results and Discussion

8.2.1 Material Characterization

The synthesis of graphene composites is related to the synthesis of sulfur doped thermally reduced graphene oxide with additional step of transition metal doping. Graphene oxide dispersion is ultrasonicated with transition metal halide in isopropanol and subsequent evaporation of solvent. In the final step is performed thermal exfoliation in the hydrogen sulphide atmosphere. These are standard procedures which can be also performed in industrial scale (Scheme 8.1). Prior to the electrochemical application measurements, we characterize the hybrid materials. The surface morphologies of these prepared hybrids are examined using SEM. Figure 8.1 shows the scanning electron micrographs of the composite of graphene with Group 5 TMDs. All samples exhibit exfoliated structure with a wrinkled surface, which is the typical feature of reduced graphene oxide. Besides, we clearly observe the nanoparticles in the sample of TRG-Ta-H₂ and TRG-Ta-H₂S, which can be regarded as tantalum oxide and tantalum sulfide. No nanoparticle is found in other samples. Subsequently, SEM-EDS spectra were used to analyze the surface composition. The elemental mappings in Figure 8.S1 show roughly homogeneous distribution of C, O, S, and metals (V, Nb or Ta). Furthermore, the atomic percentage of each individual element obtained using EDS is summarized in Table 8.1. In general, all three TMD-

graphene composites are chalcogenide deficient. Unlike the expected, the chalcogenide to metal ratios of these composites are less than 2. The specific chalcogenide to metal ratios based on EDS data of these three samples are TRG-VS_{0.76}, TRG-NbS_{1.68} and TRG-TaS_{0.76}, respectively.

Scheme 8.1 Synthesis procedure of graphene/Group 5 TMD composites.

Figure 8.1 Scanning electron micrographs of the composite of graphene with Group 5 TMDs. (a) TRG-V-H₂, (b) TRG-V-H₂S, (c) TRG-Nb-H₂, (d) TRG-Nb-H₂S, (e) TRG-Ta-H₂ and (f) TRG-Ta-H₂S.

Table 8.1 Elemental composition (%) of the composites obtained from EDS

Elemental composition (%) of the composites obtained from EDS					
Samples	C	O	M	S	Other atomic (K,Mn)
TRG-V-H ₂	83.5	14.37	2.09	-	0.04
TRG-V-H ₂ S	86.83	11.05	1.17	0.89	0.06
TRG-Nb-H ₂	92.81	6.7	0.43	-	0.06
TRG-Nb-H ₂ S	93.02	4.52	0.88	1.48	0.09
TRG-Ta-H ₂	91.75	7.34	0.77	-	0.14
TRG-Ta-H ₂ S	90.74	7.46	0.96	0.73	0.11

In order to reveal more information, XRD was performed to confirm the phase composition of these composites. Obviously, all samples show a reflection at about 25° corresponding to TRGO (002),³⁰ which indicate the successful synthesis of TRGO. According to the XRD patterns, on one hand, all three resulting nanocomposites which are reduced in H₂ atmosphere contains metal oxide as well as metal carbide (Figure 8.2 a, c and e). No TMD was formed during the reduction process as there was no chalcogen source. On the other hand, three nanocomposites reduced in H₂S atmosphere exhibit the peaks of corresponding metal sulfide, indicating the successful synthesis of graphene/TMDs composites. More specifically, in the case of TRG-V-H₂S (Figure 8.2 b), nonstoichiometric vanadium sulfide, namely V_{0.87}S, and vanadium dioxide were detected using XRD. As for TRG-Nb-H₂S (Figure 8.2 d), the peaks of nonstoichiometric Nb_{1.06}S₂ and Nb₂S₃ were found. Similarly, TRG-Ta-H₂S (Figure 8.2 f) also shows the reflections of TaS₂ and Ta₂O₅. Therefore, SEM-EDS and XRD results suggest the successful synthesis of graphene/TMD nanocomposites with TMDs homogeneously distributed on the graphene templates.

To further study the surface elemental composition and bonding information, XPS was utilized to obtain the survey scan and high resolution of C 1s, V 2p, Nb 3d and Ta 4f spectra of these hybrid materials. From the survey scan in Figure 8.S2, the characteristic peaks of C 1s at *ca.* 284 eV, O 1s at *ca.* 530 eV, S 2p at *ca.* 164 eV, V 2p_{3/2} at *ca.* 516 eV, Nb 3d_{5/2} and 3d_{3/2} paired peaks at *ca.* 208 and 210 eV, Ta 4f_{7/2} and 4f_{5/2} pair at about *ca.* 28 and 30 eV are identified, confirming the composite materials that we obtained.

Figure 8.2 XRD pattern of the composite of graphene with 5th group of transition metals. (“X” in each panel represents the characteristic peak of TRGO)

Figure 8.3 shows the high resolution spectra of C 1s and the concentration of components are summarized in Table 8.2 after deconvolution into six types. TRGO prepared without TMD precursor is also included for clarification (Figure 8.S3). A relatively low

concentration of oxygen functionalities (< 20%) for all six samples reduced in H₂ or H₂S atmosphere indicates that the graphene oxides underwent a reduction process to graphene. TRGO prepared without TMD precursors reduced in H₂ atmosphere shows slightly higher oxygen functionalities concentration in comparison with other six samples (Table 8.2), indicating that the presence of TMD precursors has no impact on the reduction of graphene oxides. The C 1s high resolution XPS spectra of TRGO is shown in Figure 8.S3. The high resolution XPS spectra of V 2p, Nb 3d and Ta 4f regions are also presented in Figure 8.4. The surface elemental composition on the basis of XPS measurements are also displayed in Table 8.3. For three nanocomposites reduced in H₂ atmosphere, we find that no metal-sulfur bond exists and only metal oxides were detected. Deconvolution results reveal that TRG-V-H₂ (Figure 8.4 a) is a mix of species with the dominant components originating from V (IV) and V (V) states evident in V 2p_{3/2} and 2p_{1/2} binding energies of 516.7 eV and 524.1 eV;³¹ and 517.1 eV and 524.5 eV.^{29, 32} Similarly, TRG-Nb-H₂ also shows the primary Nb 3d signal which is deconvoluted into Nb (V) species as manifested in 3d_{5/2} and 3d_{3/2} binding energies of *ca.* 207.8 eV and 210.5 eV, respectively. This binding energies lie close to the published values of Nb₂O₅ at 3d_{5/2} and 3d_{3/2} binding energies at 207.7 eV and 210.4 eV.³³ In addition, less prominent signals in TRG-Nb-H₂ belonging to Nb (IV) located at *ca.* 207.2 eV and 209.9 eV are also observed. These signals can be attributed to the binding energies of NbO₂.³⁴ Furthermore, in the case of TRG-Ta-H₂, one pair of peaks at *ca.* 27.4 eV and 29.3 eV lies in good agreement with the reported binding energies of Ta₂O₅.^{33, 35} Besides, TaO₂ may also contribute to part of the Ta (IV) signal at 4f_{7/2} and 4f_{5/2} binding energies of 26.0 eV and 27.9 eV.³⁶

Table 8.2 Concentration (%) of remaining oxygen functionalities after thermal reduction as obtained from the deconvolution high resolution XPS C 1s spectra.

Concentration (%) of remaining oxygen functionalities after thermal reduction as obtained from the deconvolution high resolution XPS C 1s spectra.						
Sample	C=C	C-C	C-O	C=O	O-C=O	π - π
TRG-V-H ₂	62.5	14	12.1	6.5	0.7	4.2
TRG-V-H ₂ S	61.3	15.9	11.5	5.9	0.4	4.9
TRG-Nb-H ₂	57.3	19.1	12.4	5.9	0.5	4.8
TRG-Nb-H ₂ S	60.6	20.6	9.4	5	0.7	3.7
TRG-Ta-H ₂	54.4	21.6	12.7	6.2	0.7	4.4
TRG-Ta-H ₂ S	58.5	20.6	11.8	4.5	1.1	3.5
TRGO	54.4	12.9	15	6.3	0.7	10.6

Figure 8.3 High resolution X-ray photoelectron spectra of C 1s region of the composite of graphene with 5th group of transition metals. Individual components are as follows: C=C at *ca.* 284.5 eV, C-C at *ca.* 285.5 eV, C-O at *ca.* 286.2 eV, C=O at *ca.* 287.4 eV, O-C=O at *ca.* 288.5 eV and π - π at *ca.* 290.1 eV. All spectra are calibrated to the C 1s at 284.5 eV.

The surface composition from XPS (Table 8.3) indicates that TRG-Nb-H₂S and TRG Ta-H₂S are sulfur deficient while TRG-V-H₂S has excess sulfur, which is not in good agreement with EDS results. The reasons for this discrepancy between XPS and EDS results are attributed to high sensitivity of the XPS method and differences in the depth and area of analysis of the two methods. The deconvolution results of three samples demonstrate the successful synthesis of TMDs as their characteristic signals were found (Figure 8.4). The fitted peaks of TRG-V-H₂S exhibit V(IV) and V(V) as the dominant components which are located at 2p_{3/2} binding energies of 516.3 eV and 517.1 eV, respectively, similar to the signals observed for TRG-V-H₂. These are consistent with reported literature values of VS₂ and V₂O₅.^{29, 33} It is reported that pentavalent state is the most stable oxidation state for niobium and tantalum.³⁷ This explains the substantial contribution of Nb (V) or Ta (V) in the TRG-Nb-H₂S and TRG-Ta-H₂S. The noticeable peaks of TRG-Nb-H₂S at *ca.* 207.8 eV and 210.6 eV are identical with the Nb 3d_{5/2} and Nb 3d_{3/2} binding energies of Nb₂O₅. Apart from the prominent peaks of Nb (V), a nearer pair from Nb (IV) at approximately Nb (IV) 3d_{5/2} 206.8 eV and Nb (IV) 3d_{3/2} 209.5 eV is also found. This paired signals lie very close to the reported value of Nb 3d_{5/2} at near 206.7 eV originating from trigonal NbS₂.³⁸ Similarly, for the Ta 4f spectra of TRG-Ta-H₂S, two pairs of peaks suggest the major presence of Ta(V), at *ca.* 27.4 eV and 29.3 eV (Ta 4f_{7/2} and 4f_{5/2}), due to Ta₂O₅.^{33, 35} and less prominent signals of Ta(IV) at *ca.* 26.1 eV and 28.0 eV (Ta 4f_{7/2} and 4f_{5/2}) corresponding to TaS₂.³³ In addition, Figure 8.S4 shows

the high resolution spectra of S 2p. It is worthy to note that the indistinctive peak at approximately *ca.* 169 eV is contributed by S (VI) in the form of sulfate.³⁹

Figure 8.4 High resolution X-ray photoelectron spectra of V 2p, Nb 3d and Ta 4f regions of the composite of graphene with 5th group of transition metals. All spectra are calibrated to the C 1s at 284.5 eV.

Table 8.3 Surface elemental composition (%) of these nano-composites on the basis of XPS measurements.

Surface elemental composition (%) of these nano-composites on the basis of XPS measurements.						
Sample	C 1s	O 1s	V 2p	Nb 3d	Ta 4f	S 2p
TRG-V-H ₂	88.3	9.8	1.9	-	-	-
TRG-V-H ₂ S	87.5	7.5	1.3	-	-	3.7
TRG-Nb-H ₂	89.6	8.6	-	1.8	-	-
TRG-Nb-H ₂ S	88.8	6.8	-	1.6	-	2.8
TRG-Ta-H ₂	85.2	11.3	-	-	3.5	-
TRG-Ta-H ₂ S	88.1	8.2	-	-	1.9	1.8

8.2.2 Electrochemical Hydrogen Evolution

The electrocatalytic performance of these nanocomposites was measured by linear sweep voltammetry (LSV) in 0.5 M H₂SO₄ acid solution with a three-electrode setup, in which glassy carbon (GC), Ag/AgCl and Pt are used as working electrode, reference electrode and counter electrode, respectively. Figure 8.5 a depicts the linear voltammograms of GC modified with different nanocomposites. For comparison, the polarization curves of TRGO sample and bare GC are also demonstrated for reference. It should be noted that the inherent electrochemistry of TRG-Nb-H₂S strongly interferes with the HER performance and hence we omitted this in discussion (Figure 8.S5). The parameters for comparing HER activities of all samples include the overpotential at the current density of -10 mA cm⁻² and the Tafel slope. These results are summarized in Figure 8.5 b, c. It is clear that all samples are more catalytic for HER than bare GC. The GC manifests highest overpotential of 0.95 V at the current density of -10 mA cm⁻².

Across all HER polarization curves, we observe that all nanocomposites exhibit superior HER performance in comparison with TRGO at a current density of -2 mA cm⁻². Thus,

we can conclude that the enhanced HER performance of these nanocomposites arises from the existence of metal oxides or TMDs. Further inspection of their overpotential at the current density of -10 mA cm^{-2} reveals that TRG-V-H₂S exhibits the lowest overpotential of near 0.77 V followed by very similar HER performance of TRG-Ta-H₂ and TRG-Nb-H₂ with the overpotential of approximately 0.79 V. Our group has reported that bulk VS₂ has the overpotential of 1.1 V at the current density of -10 mA cm^{-2} ,^{29, 33} which highlights the stimulative effect of graphene on enhanced HER performance of TRG-V-H₂S. In addition, TRG-V-H₂ and TRG-Ta-H₂S display higher overpotential at the current density of -10 mA cm^{-2} than TRGO. However, at a current density of -2 mA cm^{-2} , both TRG-V-H₂ and TRG-Ta-H₂S required a lower HER overpotential relative to TRGO. This discrepancy in overpotential at different current densities could be attributed to their higher Tafel slopes than TRGO that is associated to the slower HER kinetics despite requiring lower activation energy to spark the HER process. Interestingly, it is worth to note that TRG-Ta-H₂ (overpotential: 0.79 V) shows better HER than TRG-Ta-H₂S (overpotential: 0.86 V). Previous papers have reported that the reaction associated to the principal cathodic current peak in the cyclic voltammetry (CV) curves of tantalum oxide (TaO₂) is the reduction of protons.⁴⁰ which means that TaO₂ has catalytic ability towards HER. Awaludin *et al.* also studied that the electrochemically reduced TaO_x showed high activity to propel HER and oxygen reduction reaction.³⁶ From the surface composition analysis obtained from XPS (Table 8.3), it is observed that a certain amount of tantalum in TRG-Ta-H₂ is present in the form of TaO₂, which could be the reason for the better HER performance of TRG-Ta-H₂.

Apart from the overpotential, Tafel slope is the other important parameter that is used to evaluate the HER electrocatalytic ability, which usually can be used to identify the rate-

determining step of HER. Tafel slopes of all samples are shown in Figure 8.5 c. In general, the rate-determining steps that may take place during the HER process as follows:^{25, 41}

1. Adsorption step of Volmer process: $\text{H}_3\text{O}^+ + \text{e}^- \rightarrow \text{H}_{\text{ads}} + \text{H}_2\text{O}$; $b \approx 120 \text{ mV/dec}$
2. Desorption step of Heyrovsky process: $\text{H}_{\text{ads}} + \text{H}_3\text{O}^+ + \text{e}^- \rightarrow \text{H}_2 + \text{H}_2\text{O}$; $b \approx 40 \text{ mV/dec}$
3. Desorption step of Tafel process: $\text{H}_{\text{ads}} + \text{H}_{\text{ads}} \rightarrow \text{H}_2$; $b \approx 30 \text{ mV/dec}$

Firstly, the mechanism begins with the Volmer process of the reduction of hydrogen ion to adsorbed hydrogen atom followed by either the desorption step of Heyrovsky process or desorption step of Tafel process. As we discussed previously, The Tafel slope of TRG-V-H₂ and TRG-Ta-H₂S are the largest of all with a value beyond 200 mV dec⁻¹, which is coincident with their relatively poor HER performance. Compared to other processes, the Tafel slope lies closest to the Volmer process. Thus, the adsorption step is proposed to be the rate-limiting step. Out of all these samples, TRG-V-H₂S shows the lowest Tafel slope of 106 mV dec⁻¹ which is in agreement with the fact that TRG-V-H₂S shows the best HER activity. Similarly, the other samples of TRG-Nb-H₂, TRG-Ta-H₂, TRGO and GC are respectively found to have the Tafel slope of 152 mV dec⁻¹, 134 mV dec⁻¹, 141 mV dec⁻¹ and 130 mV dec⁻¹. All there Tafel slopes are closest to 120 mV dec⁻¹ and the HER processes on the surfaces of these materials are likely limited by the Volmer process. The summary of the key aspects of related TMDs, graphene and composites involving synthesis, characterization and HER performance comparison is displayed in Table 8.S1. Compared with reported HER performance of these related materials, we found our graphene/Groups 5 TMD composites show enhanced catalytic ability to HER than bulk counterparts due to the exposed active sites and enhanced electrical conductivity. However, these improved performance is inferior in terms of the excellent HER performance of VS₂ crystals prepared by CVD.²⁸

Figure 8.5 Electrocatalytic hydrogen evolution reaction performance of (a) various nanocomposites in 0.5 M H₂SO₄ acidic electrolyte. (b) Overpotential at -10 mA cm⁻² and Tafel slope (c) of nanocomposites. (d) Capacitance performance of these hybrids obtained from cyclic voltammetry measurements in PBS solution.

8.2.3 Capacitance Performance

Graphene with high specific area, high electrical conductivity, and physical strength is an outstanding electrode material for supercapacitor application. Besides, metallic few-layered VS₂ has been reported to show high capacitance for in-plane supercapacitors.⁴²

Thus we continue to perform the cyclic voltammetry (CV) measurements to investigate their capacitance performance in PBS solution with the three-electrode system. All the capacitance values are displayed Figure 8.5 d and CV curves at different scan rates are shown in Figure 8.S6. The capacitance of TRGO is the highest of all samples with a value of 30.6 F g^{-1} . None of the nanocomposites shows enhanced or comparable capacitance performance in comparison with TRGO except for TRG-V-H₂ with the capacitance value of 22.1 F g^{-1} . Since none of the nanocomposites show a capacitive performance that surpass that of unmodified TRGO, hybrid materials are unable to improve the capacitive performance even with the presence of Group 5 TMDs.

Previously, our group studied the heterogeneous electron transfer (HET) of Group 5 TMDs, which is used to evaluate the potential of these materials in electrochemical applications.³³ Among the Group 5 TMDs, we found that TaS₂ demonstrates highest HET rate of $3.4 \times 10^{-3} \text{ cm s}^{-1}$. This fast electron transfer enables TaS₂ to be favorable for electrochemical applications. For example, TaS₂ has been reported in another work as sensing platforms for fluorescent detection of DNA.⁴³ Besides, a sensitive and selective aptasensor based on layered VS₂/graphene composite was constructed for platelet-derived growth factor BB (PDGF-BB) detection.⁴⁴ Given the high surface area and good conductivity of graphene/Group 5 TMD composites, we envision that these composites can be applied as electrochemical sensors.

8.3 Conclusion

Composites of graphene with Group 5 TMDs namely VS₂, NbS₂ and TaS₂ were successfully synthesized through thermal reduction of graphene oxide along with TMD precursors in H₂S atmosphere as well as in H₂ atmosphere as a control. These hybrid materials were then characterized by SEM/EDS, XRD and XPS in detail. SEM/EDS showed the homogeneous distribution of resulting metal sulfide over the graphene surface.

Furthermore, XRD and XPS were respectively used to identify the phase and surface composition of these nanocomposites, which revealed that the dominant component in resulting materials is present in the form of metal oxide as well as a small amount of metal sulfide. HER measurements revealed that all these samples exhibited better catalytic activity than TRGO at the current density of 2 mA cm^{-2} . Although all those nanocomposites show higher HER performance due to the exposed active sites and enhanced electrical conductivity, the performance is not comparable to superior electrocatalyst MoS_2 . This fundamental study sheds light on the potential of Group 5 TMDs as hybrid electrocatalysts for hydrogen evolution reaction.

8.4 Experimental Section

8.4.1 Materials

Sodium phosphate monobasic, potassium phosphate dibasic, potassium chloride and sodium chloride were purchased from Sigma-Aldrich. Platinum, Ag/AgCl reference electrode and glassy carbon electrode were purchased from CH Instruments, Texas, USA. Graphite microparticles (2-15 μm , 99.9995%) were obtained from Alfa Aesar, Germany. Sulfuric acid, potassium permanganate (98%), sodium nitrate (99.5%), hydrogen peroxide (30%), hydrochloric acid (37%), barium nitrate (>99%), isopropanol (99.9%) were obtained from Penta, Czech Republic. Vanadium tetrachloride, niobium pentachloride and tantalum pentachloride were obtained from STREM, Germany. Deionized water with electrical resistivity of $18.4 \text{ M}\Omega \text{ cm}$ was utilized to prepare material suspensions and electrolytes for measurements.

8.4.2 Apparatus

Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) were done using a JEOL 7600F field emission SEM (JEOL, Japan). SEM and EDS data were obtained at a voltage of 2 kV and an accelerating voltage of 15 kV respectively.

Powder X-ray powder diffraction were recorded at room temperature with an Bruker D8 Discoverer powder diffractometer with parafocusing Bragg-Brentano geometry using $\text{CuK}\alpha$ radiation ($\lambda = 0.15418 \text{ nm}$, $U = 40 \text{ kV}$, $I = 40 \text{ mA}$). XRD data were scanned with an ultrafast detector Lynxeye XE over the angular range $10\text{--}80^\circ$ (2θ) with a step size of 0.02° (2θ). Data evaluation process was carried out with the software package HighScore Plus 3.0e. X-ray photoelectron spectroscopy (XPS) was performed by using a monochromatic $\text{Mg K}\alpha$ source (SPECS, Germany) at 1253 eV . Wide scan and high resolution spectra of V 2p, Nb 3d, Ta 4f, O 1s, S 2p, and C 1s were obtained for surface composition analysis. The C 1s signal at 284.5 eV was used to calibrate all spectra. Voltammetric measurements of linear sweep voltammetry (LSV) and cyclic voltammetry (CV) for recording the HER and capacitance performance of these nanocomposites were performed with a μ Autolab type III electrochemical analyzer (Eco Chemie, The Netherlands) using NOVA 1.8 software.

8.4.3 Synthesis of Nanocomposites

The composite of graphene with 5th group of transition metals were prepared by thermal exfoliation of graphene oxide composite precursors in controlled atmosphere. Graphene oxide was prepared by Hummers method.

Graphene oxide preparation with the Hummers method (HUGO). 5 g of graphite and 2.5 g of sodium nitrate were stirred with 115 mL of sulfuric acid (98%). The mixture was then cooled in an ice bath. With vigorous stirring, 15 g of potassium permanganate was then added over a period of two hours. In the subsequent four hours, the reaction mixture was allowed to reach room temperature before being heated to 35°C for 30 min. The reaction mixture was then poured into a flask containing 250 mL of deionized water and further heated to 70°C . After holding the temperature constant for 15 min, the mixture was then poured into 1 L of deionized water. The unreacted potassium permanganate and

manganese dioxide were removed by the addition of 3% hydrogen peroxide. The reaction mixture was then allowed to settle and decanted. The graphene oxide obtained was then purified by repeated centrifugation and re-dispersing in deionized water until a negative reaction on sulfate ions (with $\text{Ba}(\text{NO}_3)_2$) was achieved. Graphene oxide slurry was then dried in a vacuum oven at 60 °C for 48 h before use.

100 mg of graphene oxide was dispersed in 25 mL of isopropanol by ultrasonication. Under argon atmosphere was added to the graphene oxide suspension vanadium in the form of vanadium tetrachloride (37.8 mg), niobium in form of niobium pentachloride (29.1 mg) and tantalum in the form of tantalum pentachloride (19.8 mg) corresponding to 10 wt.% of metal to graphene oxide. Reaction mixture was stirred under argon atmosphere for 2 hours and subsequently ultrasonicated for 15 minutes. Finally was isopropanol removed by vacuum evaporation using rotary evaporator.

For the thermal exfoliation/reduction was precursors placed in porous quartz glass capsule connected to magnetic manipulator. Before exfoliation the quartz glass reactor was three times evacuated and refilled with nitrogen. Finally reactor was filled with atmosphere used for exfoliation. The exfoliation was performed in hydrogen sulfide atmosphere (250 mL/min) at 1000 °C for 12 minutes and in hydrogen atmosphere (250 mL/min) at 1000 °C for 12 minutes. The sample was removed from hot zone of the reactor after 12 minutes and cooled in reactive atmosphere before flushing of reactor with nitrogen.

8.4.4 Electrochemical Procedure

5 $\mu\text{g mL}^{-1}$ suspension of various nanocomposites and TRGO were prepared by utilizing deionized water with electrical resistivity of 18.4 M Ω cm. Then these suspensions were sonicated for 60 min to get the homogeneous suspensions. An aliquot of 1 μl suspension was dropcasted on the clean glassy carbon substrates and glassy carbon could be renewed

by polishing with 0.05 μm alumina particles on a polishing pad and then washing with deionized water after each measurements. Prior to electrical measurements, glassy carbon modified with suspension was dried at room temperature in order to obtain the randomly distributed materials on the electrode surface. Voltammetric measurements of linear sweep voltammetry (LSV) for recording HER performance were obtained by using 0.5 M H_2SO_4 as background electrolyte in a three-electrode configuration, with modified glassy carbon, Ag/AgCl and Pt electrode as working, reference and counter electrode at a scan rate of 2 mV s^{-1} . In addition, voltammetric measurements of cyclic voltammetry (CV) for capacitance analysis were carried out in a three-electrode system using phosphate buffer solution (PBS, 0.5 mM, pH 7.2) as electrolyte, in which Ag/AgCl and Pt worked as reference electrode and counter electrode.

8.5 Supporting Information

Figure 8.S1 SEM/EDS map of scanning electron micrograph and elemental distribution of the composite of graphene with group 5 TMDs. (a) TRG-V-H₂, (b) TRG-V-H₂S, (c) TRG-Nb-H₂, (d) TRG-Nb-H₂S, (e) TRG-Ta-H₂ and (f) TRG-Ta-H₂S. Scale bars represent 10 μm .

Figure 8.S2 XPS survey scan of the composite of graphene with group 5 TMDs. (a) TRG-V-H₂, (b) TRG-V-H₂S, (c) TRG-Nb-H₂, (d) TRG-Nb-H₂S, (e) TRG-Ta-H₂ and (f) TRG-Ta-H₂S. All spectra are calibrated to the C 1s at 284.5 eV.

Figure 8.S3 High resolution X-ray photoelectron spectra of C 1s region of TRGO. C 1s at 284.5 eV is used as the calibration reference.

Figure 8.S4 High resolution XPS spectra of S 2p of the composite of graphene with group 5 TMDs. All spectra are calibrated to the C 1s at 284.5 eV.

Figure 8.S5 Electrocatalytic hydrogen evolution reaction measurement of TRG-Nb-H₂S and TRG-Nb-H₂ in 0.5 M H₂SO₄ acidic electrolyte.

Figure 8.S6 Cyclic voltammograms curves of hybrid materials at different scan rates of 0.025, 0.05, 0.1, 0.2, 0.5 V s^{-1} .

Table 8.S1 Summary of the key aspects of related TMDs, graphene and composites involving synthesis, characterization and HER performance comparison.

Samples	Synthesis	Characterization by XPS (respect to M ⁴⁺)	HER performance a: Overpotential at -10 mA cm ⁻² b: Tafel slope
TRG-V-H ₂ S (This paper)	Thermal exfoliation with TMD precursor	V 2p _{3/2} : 516.3 eV, V 2p _{1/2} : 523.7 eV S 2p: 163.8 eV	0.77 V ^a , 106 mV/dec ^b
VS ₂ / rGO ⁵¹	Annealing of VS ₄ /rGO	V 2p _{3/2} : 516.3 eV S 2p _{3/2} : 160.6 eV, S 2p _{1/2} : 161.8 eV	Onset potential: 0.35 V 150 mV/dec ^b
Exfoliated VS ₂ ⁵²	Lithium intercalation	V 2p _{3/2} : 516.8 eV, V 2p _{1/2} : 524.2 eV S 2p: 164.0 eV	0.96 V ^a
VS ₂ Nanoplate Arrays ⁵³	Hydrothermal method	V 2p _{3/2} : 516.3 eV, V 2p _{1/2} : 523.7 eV S 2p: 162.7 eV, 163.9 eV	0.042 V ^a , 36 mV/dec
Bulk VS ₂ ⁵⁴	Solid state reaction	V 2p _{3/2} : 516.0 eV, V 2p _{1/2} : 523.4 eV S 2p _{3/2} : 160.8 eV, S 2p _{1/2} : 162.0 eV	1.0 eV ^a , 159 mV/dec
VS ₂ crystal ⁵⁵	CVD	Not applicable	0.068 V ^a , 34 mV/dec ^b
TRG-Nb-H ₂ S (This paper)	Thermal exfoliation with TMD precursor	Nb 3d _{5/2} : 206.8 eV, Nb 3d _{3/2} : 209.5 eV S 2p: 164.0 eV	Not applicable
Bulk NbS ₂ ⁵⁴	Solid state reaction	Nb 3d _{5/2} : 206.2 eV, Nb 3d _{3/2} : 209.0 eV S 2p _{3/2} : 160.8, S 2p _{1/2} : 162.0 eV	~1.0 V ^a , ~180 mV/dec ^b
TRG-Ta-H ₂ S (This paper)	Thermal exfoliation with TMD precursor	Ta 4f _{7/2} : 26.3 eV, Ta 4f _{5/2} : 28.0 eV S 2p: 164.2 eV	0.86 V ^a , 134 mV/dec ^b
Bulk TaS ₂ ⁵⁴	Solid state reaction	Ta 4f _{7/2} : 26.3 eV, Ta 4f _{5/2} : 28.2 eV S 2p _{3/2} : 160.8 eV, S 2p _{1/2} : 162.0 eV	~0.98 V ^a , ~180 mV/dec ^b
TRG (This paper)	Thermol exfoliation	Not applicable	0.85 V ^a , 140.0 mV/dec ^b

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Chapter 9

Exfoliation of Layered *h*-BN by Bipolar Electrochemistry

- 9.1 Introduction
- 9.2 Results and Discussion
 - 9.2.1 Electrochemical Exfoliation
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- 9.3 Conclusion
- 9.4 Experimental Section
 - 9.4.1 Materials
 - 9.4.2 Apparatus
 - 9.4.3 Electrochemical Exfoliation of *h*-BN
 - 9.4.4 Electrochemical Measurement of Inherent Electrochemistry
- 9.5 Supporting Information

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9.1 Introduction

The discovery of remarkable chemical and physical properties of graphene spurred on scientists to explore other two dimensional (2D) materials and their applications.¹⁻⁸ Beyond graphene, one example of a 2D material that has garnered tremendous attention is hexagonal boron nitride (*h*-BN). It is commonly described as an isoelectronic analogue of graphite, consisting of an equal number of boron and nitrogen atoms that are covalently bonded. The stacking of *h*-BN layers yields bulk graphitic *h*-BN structures. Between *h*-BN sheets, the interactions comprise both van der Waals forces and the electrostatic interaction. The electrostatic interaction arises from the electronegativity difference between boron and nitrogen atoms.⁹ With this structure, *h*-BN powder has been utilized as a lubricant for a long time. Besides, due to the unique properties of *h*-BN like high mechanical strength, chemical stability and low dielectric constant, it has been utilized as an inert flat substrate for graphene electronic devices,^{10, 11} which improves device performance. More attempts have been devoted to study the potential of *h*-BN as an electrocatalyst in the oxygen evolution reaction (ORR). It was found that *h*-BN nanosheet modified gold electrodes and *h*-BN nanosheet modified screen-printed graphitic electrodes (SPEs) reduced the overpotential for ORR.^{12, 13} To date, the preparation of few-layered *h*-BN nanosheets could be mainly summarized into two strategies: bottom-up and top-down approaches. Chemical vapour deposition (CVD), which is a bottom-up method, is usually adopted to prepare *h*-BN nanosheets/films whereby volatile precursors react or decompose on the substrate surface to produce thin *h*-BN films.¹⁴ Despite attaining high quality *h*-BN thin films with uniform thickness and large lateral size, the high cost and low yield circumscribe its large-scale and practical use. The top-down approach involves the direct exfoliation of bulk *h*-BN powder into a few layers or a single layer. Solution-based exfoliation of *h*-BN is a typical top-down method where the solvent prevents the re-stacking of *h*-BN nanosheets given a compatible surface tension component

between the solvent and *h*-BN nanosheets. Among suitable solvent choices identified for exfoliation, isopropyl alcohol (IPA)¹⁵ and *N,N*-dimethylformamide (DMF)^{16, 17} are able to downsize bulk *h*-BN powder and obtain a stable *h*-BN nanosheet suspension. Pure water, which is an economical choice of solvent, also effectively exfoliates *h*-BN when subjected to sonication.^{18, 19} The oxygen atom in a water molecule may attack the boron–nitrogen bond near intrinsic defect sites. This defect propagates to the *h*-BN edge to result in smaller *h*-BN sheets. The smaller *h*-BN sheets further exfoliate to form mono-layered and few-layered nanosheets when mechanically agitated upon sonication and assisted by the solvent polarity effect.¹⁸ Although this method is beneficial for the effective and scalable exfoliation of bulk *h*-BN, the long duration of the experiment, spanning up to 10 hours, is a major disadvantage. Hence, alternative top-down methods have been developed to obtain *h*-BN nanosheets, comprising mixture solvent exfoliation (mainly organic and water),^{20, 21} surface functionalization-assisted exfoliation,^{22–24} ball-milling,^{25–27} water freezing expansion exfoliation²⁸ and ion intercalation.²⁹ These methods can be used to prepare *h*-BN nanosheets in a high yield and scalable manner, which are critical for further applications.

Here we present a top-down approach to exfoliate *h*-BN using bipolar electrochemistry. This bipolar electrochemical exfoliation method is touted to be user-friendly given the facile operation, along with the advantage of low cost and efficiency. This method was, in the past, applied to the exfoliation of graphite,³⁰ transition metal dichalcogenides³¹ and layered black phosphorus.³² It has not been applied to insulators, and it has been assumed to be an impossible task. Here, we report the utility of bipolar electrochemistry for the exfoliation of insulators. Using two platinum electrodes an external electric field was applied to the bulk *h*-BN particles dispersed in solution; the particles become polarised and remain so even when the direct electric contact is absent. Opposite redox reactions can occur at the two extremities of the *h*-BN particles.³³ This concept of bipolar electrochemistry has been implemented to downsize

WS₂,^{31, 34} MoSe₂,³⁵ and black phosphorus³⁶ for biosensor applications by our group. Similarly, as we set forth to demonstrate in this work, the electrochemical exfoliation method can be extended to exfoliate *h*-BN into nanosheets as confirmed by a series of characterization techniques consisting of X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, scanning transmission electron microscopy (STEM), transmission electron microscopy (TEM) and atomic force microscopy (AFM). The resultant few-layered *h*-BN nanosheets show an average lateral size of $1.27\ \mu\text{m} \pm 0.48\ \mu\text{m}$ and a mean flake thickness of $8.4\ \text{nm} \pm 3.3\ \text{nm}$.

9.2 Results and Discussion

9.2.1 Electrochemical Exfoliation

In this work, *h*-BN nanosheets were prepared by a novel bipolar electrochemical exfoliation method by applying a constant DC potential of 10 V across the two Pt driving electrodes to a solution that contains well dispersed bulk *h*-BN particles in 0.5 M sodium sulfate.³¹ The purpose of adding sodium sulfate is to act as a support electrolyte, since the current should pass through the solution, where BN particles are dissolved. A higher concentration of the support electrolyte increases current excessively and damages the chemical structure of *h*-BN, whereas a lower concentration of the support electrolyte decreases the current and is insufficient for the efficient exfoliation to take place. Other supported electrolytes such as KCl and NaCl were tried but the exfoliation was found to be not efficient. The conditions for the bipolar electrochemical exfoliation were optimized in previous publications where we exfoliated TMDs and black phosphorus using this method.^{31, 34–36} A possible mechanism for exfoliation of bulk *h*-BN by bipolar electrochemistry (BE) is explained by the polarization of conducting or semiconducting materials that act as a bipolar electrode in electric field between two electrodes which we call driving electrodes. In the BE electrochemical reactions are promoted at its extremities (poles) even in the absence of a direct ohmic contact in the opposite

polarity of the driving electrodes.^{31, 34, 37} The mechanisms are shown in Schemes 9.1 A and B. The obtained few-layered *h*-BN suspension is milky white in color while the pristine bulk *h*-BN solution is white (Schemes 9.1 D and C). The *h*-BN nanosheet suspension was then centrifuged to remove Na₂SO₄ and the exfoliated sediment products were retrieved for further characterization.

Scheme 9.1 (A) Schematic representation of bipolar electrochemical exfoliation of *h*-BN. (B) The setup of bipolar electrochemical exfoliation of bulk *h*-BN. (C) Pristine bulk *h*-BN solution with the concentration of 5 mg ml⁻¹. (D) *h*-BN nanosheet suspension obtained from bipolar electrochemical exfoliation.

9.2.2 Material Characterization

The morphology of starting bulk *h*-BN was observed by SEM as shown in Figure 9.S1. The pristine *h*-BN appears in layered structures with a smooth surface. In order to confirm the successful exfoliation of bulk *h*-BN, the morphology of the obtained few-layered *h*-BN nanosheets was examined by STEM and TEM. Figure 9.1 A shows that bulk *h*-BN is exfoliated and downsized to thinner layers. TEM analyses captured in Figure 9.1 B and C showcase the few-layered structure of exfoliated *h*-BN nanosheets. The inset images of the periodic selective area electron diffraction (SAED) patterns and high resolution atomic TEM

of the *h*-BN nanosheets reveal a high degree of crystallinity. The uniform elemental map distribution of B and N elements in the few-layered *h*-BN nanosheets corresponds to *h*-BN as illustrated in the energy dispersive spectrometry (EDS) maps (Figure 9.1 D).

Figure 9.1 (A) STEM image of *h*-BN nanosheets. (B) Low magnification TEM image of *h*-BN nanosheets; the inset is the SAED pattern of few-layered *h*-BN. (C) Image of few-layered *h*-BN nanosheets from TEM; the inset is the high resolution atomic TEM image of the *h*-BN nanosheets. (D) EDS maps of *h*-BN nanosheets.

XPS was performed to acquire surface elemental composition and bond information in order to reveal the chemical change before and after exfoliation. The survey scans of bulk *h*-BN and few layered *h*-BN nanosheets are presented in Figure 9.2 A and D. From Figure 9.2 A and D, the characteristic peak of the B 1s signal centers at 190.5 eV whereas the N 1s signal is detected at 397.5 eV in both survey scans of bulk *h*-BN and *h*-BN nanosheets. The high resolution XPS spectra of the B 1s and N 1s regions of bulk *h*-BN and *h*-BN nanosheets are compared in Figure 9.2. The deconvolution of the B 1s spectrum of bulk *h*-BN (Figure 9.2 B) reveals a dominant peak located at 190.6 eV that is attributed to the B-N bond^{14, 38} whereas the two

modest peaks observed at 189.0 and 191.9 eV are ascribed to the B–C and B–O bonds.³⁸

³⁹ The deconvolution of the N 1s spectrum indicates prevalent sp^2 B–N bonding and mild C–N/C=N bonding centered at 397.7 and 399.5 eV, respectively (Figure 9.2 C).³⁹ Then, deconvolution analyses (Figure 9.2 E and F) of the *h*-BN nanosheets exhibit B 1s and N 1s binding energies identical to those of bulk *h*-BN. Therefore, it is suggested that bipolar electrochemical exfoliation of bulk *h*-BN did not lead to the oxidation of *h*-BN nanosheets. Furthermore, no chemical change in the exfoliated *h*-BN nanosheets had been detected.

Figure 9.2 Survey scan and high resolution XPS photoelectron spectra of bulk *h*-BN and *h*-BN nanosheets. (A) Survey scan of bulk *h*-BN. (B, C) High resolution XPS photoelectron spectra of the B 1s and N 1s regions of bulk *h*-BN. (D) Survey scan of *h*-BN nanosheets. (E, F) High resolution XPS photoelectron spectra of the B 1s and N 1s regions of *h*-BN nanosheets.

The Raman spectrum was recorded to analyse the vibration modes of bulk *h*-BN and *h*-BN nanosheets, which originate from the stretching of the bonds between the nitrogen and boron atoms. Raman samples are prepared by drop-casting the exfoliated and bulk *h*-BN suspensions on silicon wafer. Figure 9.3 A shows the Raman spectra of the bulk *h*-BN and *h*-BN

nanosheets using a green laser with $\lambda = 514.5$ nm. From Figure 9.3 A, bulk *h*-BN shows only a characteristic peak of the Raman G band located at 1366.7 cm^{-1} corresponding to the E_{2g} phonon mode.⁴⁰ The peak intensity becomes weaker when bulk *h*-BN is exfoliated to the *h*-BN nanosheets under the same conditions as the peak intensity is proportional to the number of *h*-BN layers.⁴⁰ Besides, the Raman peak of the *h*-BN nanosheets shifts to 1365.7 cm^{-1} due to the strain-induced red shifts in the case of stretching.⁴⁰ This Raman peak of the *h*-BN nanosheets is in agreement with previous literature,^{40, 41} which confirms the obtained *h*-BN nanosheets with the treatment of bipolar electrochemical exfoliation. The lateral size distribution of the *h*-BN nanosheets was further collected by STEM measurements of exfoliated *h*-BN shown in Figure 9.3 B. The results revealed that the *h*-BN nanosheets have a lateral size in the range of $0.35\text{ }\mu\text{m}$ to $2.89\text{ }\mu\text{m}$ with an average size of $1.27\text{ }\mu\text{m} \pm 0.48\text{ }\mu\text{m}$.

Figure 9.3 (A) Raman spectra of bulk *h*-BN and *h*-BN nanosheets. (B) The nanosheet size distribution data collected by STEM measurements of exfoliated *h*-BN.

AFM was performed in order to measure the thickness of the *h*-BN nanosheets. Figure 9.4 displays optical AFM images and histograms of the thickness distribution of electrochemically exfoliated *h*-BN nanosheets. The obtained thickness of the *h*-BN nanosheets varies in the range of 2.0 nm to 18.0 nm with the mean flake thickness of $8.4 \text{ nm} \pm 3.3 \text{ nm}$, which suggests effective exfoliation of the *h*-BN to few-layered sheets.

Figure 9.4 (A) AFM images ($1.0 \times 1.0 \mu\text{m}^2$) of electrochemically exfoliated *h*-BN nanosheets. (B) Height profiles of *h*-BN nanosheets which were taken along the black arrows in the AFM images. (C) Histograms of the thickness distribution of exfoliated *h*-BN.

Inherent electrochemistry originating from the redox reactions of electroactive moieties of the materials restricts their operating potential window and limits their use in electrochemical applications.^{42, 43} Previous literature has reported the applications of the *h*-BN nanosheet as a platform to develop electrochemical biosensors. For example, *h*-BN nanosheets functionalized with gold nanoclusters and antibody conjugates were used as fluorescent and electrochemical probes.⁴⁴ Furthermore, *h*-BN was utilized as a platform for the immobilization of catalase for the electrochemical detection of forchlorfenuron *via* the inhibition behaviour of forchlorfenuron to catalase.⁴⁵ In consideration of potential biomedical

applications of *h*-BN,⁴⁶ cyclic voltammetry (CV) was performed to study the inherent electrochemistry of bulk *h*-BN and *h*-BN nanosheets in the PBS electrolyte at pH 7.2 (Figure 9.5). Initially, *h*-BN is perceived to be electrochemically inert given that no obvious redox peaks are observed in the CV curves of bulk *h*-BN. Nevertheless, an inconspicuous peak in both anodic and cathodic scans of bulk *h*-BN is found at the potential of around -1.6 V. Interestingly, exfoliation of the bulk *h*-BN to *h*-BN nanosheets shows an apparent reduction peak in both scan directions which shifts to a relatively positive potential of -1.4 V compared to bulk *h*-BN. This result suggests that the *h*-BN nanosheets exhibit a limited cathodic potential window due to inherent electroactivity. Previous inherent electrochemistry studies of graphene have reported the reduction peak of chemically reduced graphene oxide (CRGO) at around -1.4 V, which originates from the reducible oxygen groups.⁴⁷ In contrast, graphite which is the bulk counterpart exhibits no peak.⁴⁷ As an isoelectronic analogue of graphite, we infer that the reduction peak of *h*-BN nanosheets may be due to the reducible oxygen groups. The higher peak current intensity after electrochemical exfoliation of bulk *h*-BN is likely due to the increased surface area once exfoliated. This observation is consistent with an electrochemical study on the extent of exfoliation in layered MoS₂ using various organolithium intercalants whereby the most efficient exfoliation, that is MoS₂ that has been *n*-butyllithium exfoliated, shows the highest inherent electrochemical peak intensity resulting from the larger specific surface area.⁴⁸

Figure 9.5 Cyclic voltammograms of glassy carbon, bulk *h*-BN and *h*-BN nanosheets. (A) Cyclic voltammograms of anodic scans and (B) cyclic voltammograms of cathodic scans. The

inset is the cathodic scan of bulk *h*-BN. Conditions: supporting electrolyte, 0.5 M PBS at pH 7.2; scan rate, 100 mV s⁻¹.

9.3 Conclusion

In summary, *h*-BN nanosheets were successfully synthesized directly from bulk *h*-BN using a bipolar electrochemistry method. Characterization with STEM, TEM, XPS, Raman and AFM confirmed the good exfoliation of *h*-BN to *h*-BN nanosheets. The as-obtained *h*-BN nanosheet shows an average lateral size of 1.27 $\mu\text{m} \pm 0.48 \mu\text{m}$ and a mean flake thickness of 8.4 nm ± 3.3 nm. An inherent electrochemistry study by cyclic voltammograms revealed the reductive property of bulk *h*-BN and few-layered *h*-BN nanosheets. With this method, *h*-BN nanosheets can be prepared in an efficient, scalable and environmentally friendly method for prospective uses. This scalable electrochemical method was proved in this article to be applicable not only to conducting materials, but to insulators as well, which is a breakthrough in the field. This paves the way for the scalable water-based electrochemical exfoliation of any layered insulator to few layered sheets for a wide spectrum of applications.

9.4 Experimental Section

9.4.1 Materials

Boron nitride was purchased from Merck (USA). Sodium sulfate, sodium phosphate monobasic, potassium phosphate dibasic, potassium chloride and sodium chloride were purchased from Sigma-Aldrich. Pt, Ag/AgCl reference, and glassy carbon electrodes were purchased from CH instruments, Texas, USA. Deionized water was used in the preparation of solutions.

9.4.2 Apparatus

Transmission electron microscopy (TEM), selected area electron diffraction (SAED) and high resolution transmission electron microscopy (HR-TEM) were performed using

EFTEM Jeol 2200 FS microscope (Jeol, Japan), a 200 keV acceleration voltage was used for measurement. Sample preparation was attained by drop casting the suspension (1 mg mL⁻¹ in water) on a TEM grid (Cu; 200 mesh; Formvar/carbon) and dried at 60 °C for 12 h. Elemental maps and energy dispersive spectrometer (EDS) spectra were acquired with SDD detector X-MaxN 80 T S from Oxford Instruments (England). Scanning electron microscopy and scanning transmission electron microscopy (STEM) were performed with a JEOL 7600F field emission SEM (JEOL, Japan). SEM and STEM images were obtained at an acceleration voltage of 2 KV and 30 kV, respectively. X-ray photoelectron spectroscopy (XPS) was conducted using an X-ray photoelectron Phoibos 100 spectrometer (SPECS, Germany), equipped with a monochromatic Mg K α X-ray radiation source at 1253 eV. Graphite was added to XPS measurement in order to obtain C 1s peak for calibration. Raman spectra were obtained by using a confocal micro-Raman LabRam HR instrument (HORIBA Scientific) in backscattering geometry with a CCD detector, a 514.5 nm Ar laser and a 100X objective attached to an Olympus optical microscope. Atomic force microscopy (AFM) conducted on NaioAFM microscope (Liestal, Switzerland) fitted with an ACL-A cantilever tip (AppNano, CSInstruments, France) with the following dimensions: length, 225 μ m; width, 43 μ m; tip radius, 6 nm. The NaioAFM microscope was connected to a computer with Nanosurf, Naio control software (version 3.8.0.8) and Nanosurf, easyScan 2 control software. The AFM images were obtained when the microscope was operated under dynamic force at vibration amplitude of 200 mV. The AFM image size of 1.0 μ m by 1.0 μ m was acquired. The AFM is mounted on an airtable TS-150 (Herzan, California, USA) for all measurements. Electrochemical experiments were carried out at room temperature by using an AutoLab PGSTAT 101 electrochemical analyzer (Eco Chemie, Utrecht, The Netherlands), controlled with a NOVA version 1.10 software (Eco Chemie).

9.4.3 Electrochemical Exfoliation of *h*-BN

Exfoliation of *h*-BN was conducted following the same protocol established by our group.²⁷ 5.0 mg ml⁻¹ of aqueous suspension of *h*-BN was prepared in deionized water by sonication for 3 hours. This homogeneous *h*-BN suspension was diluted to 0.5 mg ml⁻¹ by adding deionized water and 0.5 M Na₂SO₄ with the total volume of 4 ml and placed into an electrochemical cell. Two platinum driver electrodes were immersed into the electrochemical cell and 10 V potential was supplied for 30 min. After that, the suspensions were left to settle for a minimum of 48 h, and the solution was then centrifuged with the speed of 14000 rpm for 15 min and washed with deionized water for several times in order to remove Na₂SO₄ for characterization.

9.4.4 Electrochemical Measurement of Inherent Electrochemistry

0.5 mg mL⁻¹ concentration of bulk *h*-BN and *h*-BN nanosheet was prepared in deionized water. Glassy carbon electrode was renewed by polishing with a 0.05 μm alumina particle slurry on a polishing pad for 1min and then rinsed with deionized water and dried. Next, 4 μL aliquot of material suspension was drop casted on the electrode surface, which are dried at room temperature in order to get homogeneously distributed materials on the electrode surface. Cyclic voltammetry measurements was performed in a three electrode system where Pt, Ag/AgCl and glassy carbon as counter, reference and working electrode. Phosphate buffer solution (PBS, 0.5X10⁻³ M, pH 7.2) was utilized as background electrolyte which was purged with N₂ gas for 15 minutes and all cyclic voltammetry was performed at 100 mV s⁻¹.

9.5 Supporting Information

Figure 9.S1. Morphological characterization: SEM image of bulk *h*-BN.

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Chapter 10

Bipolar Electrochemistry for Enhanced Electrocatalytic Activity

- 10.1 Introduction
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 - 10.2.2 Electrochemical Hydrogen Evolution
- 10.3 Conclusion
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 - 10.4.1 Materials
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 - 10.4.3 Bipolar Electrochemistry Treatment
 - 10.4.4 Electrochemical Measurement
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10. 1 Introduction

With worldwide attention directed at environmental issues related to increasing carbon emissions and rapid depletion of non-renewable resources of energy, it is important for us to propel possible solutions to address this concern. Hydrogen is one of the most promising clean energy available due to its high energy density and it can be produced from a wide variety of resources ranging from water, biomass, natural gas, or coal.¹⁻⁵ Electrochemical splitting of water to produce hydrogen lies at the forefront of the energy conversion and storage research.⁶⁻⁹ This method is efficient, clean and viable to generate hydrogen with high purity. However, this technique requires electrocatalysts to decrease the activation barrier required for hydrogen evolution reaction (HER) to occur. State-of-the-art electrocatalysts for HER include precious metals, such as Pt, that are expensive and limited in supply, thus restricting their widespread applications. Therefore, there is a need to replace Pt with earth-abundant and low-cost alternative materials as HER electrocatalysts. Efforts have been made to explore and develop these non-precious transition metals based electrocatalysts for HER.¹⁰⁻¹⁴

In the past few years, transition metal molybdenum based materials have emerged as promising electrocatalysts for HER. Studies revealed that molybdenum phosphide,¹⁵⁻¹⁸ molybdenum carbide,¹⁹⁻²² molybdenum chalcogenide²³⁻²⁵ and molybdenum nitride¹⁹ can catalyze HER in an efficient manner. More recently, binary molybdenum borides have been reported to display excellent HER performance. A pioneer work had demonstrated commercial α -MoB to have good HER activity in both acidic and alkaline electrolyte.²² In another example, α -MoB₂ consisting of borophene subunits is able to efficiently catalyze HER even at large current densities due to its high conductivity, large density of highly active electrocatalytic sites and good mass transport properties.²⁶ Subsequent

works investigated several binary molybdenum borides and discovered that β -MoB, MoB₂ and Mo₂B₄ are efficient HER electrocatalysts while boron-deficient Mo₂B is less efficient, thus suggesting the boron-dependency of molybdenum borides with regards to HER activity.^{27,28} To further optimize its HER performance, ultrathin hexagonal Mo₃B films and Mo₂B nanoparticles were synthesized which yielded enhanced HER performance with lower onset potential and better Tafel slope values (Mo₂B nanoparticles: overpotential of 154 mV vs RHE at 10 mA cm⁻², Tafel slope of 49 mV dec⁻¹; ultrathin Mo₃B film: overpotential of 249 mV vs RHE at 20 mA cm⁻², Tafel slope of 52 mV dec⁻¹).^{27,29,30} In the case of MoB/g-C₃N₄, which functions as a Schottky catalyst, good HER performance is seen originating from n-type semiconducting g-C₃N₄ that generates a charge transfer across the Schottky junction and enhances the local electron density on MoB.³¹

Besides molybdenum, tungsten based materials are also widely studied for HER applications.^{19,32-34} Interestingly, from our literature search, the HER activity of tungsten borides have not yet been reported. One work had demonstrated transition metal-boron alloy Co-W-B as an active HER electrocatalyst with low overpotential and good stability in alkaline solution.³⁵ However, tungsten borides containing only W and B elements has not been explored. In view of the superior HER performance of binary molybdenum boride, tungsten borides are also anticipated to exhibit electrocatalytic properties.

Herein, we study the HER activity of bulk commercial Mo₂B₅ and W₂B₅ as well as report the use of bipolar electrochemical treatment to downsize the materials and enhance their HER performance. Bipolar electrochemistry (BP) treatment is conducted by applying a constant DC potential across two Pt driving electrodes to the electrolyte solution where target materials (Mo₂B₅ and W₂B₅) are suspended. When a potential is applied, the

extremes of these suspended particles become polarized and remain as such even when

the direct electric contact is absent. Opposite redox reactions occur at the two extremities of these bipolar electrode particles because of the potential difference between bipolar electrode particles and the solution.³⁶ This BP technique requires no direct contact with the Pt driving electrodes and is carried out in the solution. This concept has been adopted to exfoliate boron nitride (*h*-BN),³⁷ transition metal dichalcogenides³⁸ and layered black phosphorus³⁹ by our group. It is worth to note that Mo₂B₅ and W₂B₅ are non-layered, three-dimensional materials which are unable to be exfoliated. However, BP treatment was found to be successful in downsizing the Mo₂B₅ and W₂B₅ to smaller and thinner particles. More importantly, BP-treated Mo₂B₅ and W₂B₅ show better HER catalysis compared to their bulk untreated counterparts. Impedance studies reveal that the BP-treated Mo₂B₅ and W₂B₅ particles exhibit improved electron transfer capability relative to the untreated materials. This bipolar electrochemical downsizing method presents an alternative strategy to enhance HER electrocatalysis and can be extended to other transition metal based materials including carbides, phosphides and nitrides.

10.2 Results and Discussion

10.2.1 Material Characterization

In this work, we downsized commercial Mo₂B₅ and W₂B₅ using bipolar electrochemistry treatment. In this method, two Pt electrodes referred as “driving electrodes”, are inserted in a sodium sulfate (0.5 M) solution containing well dispersed Mo₂B₅ or W₂B₅ particles and a constant DC potential is applied over a specified duration across the two driving electrodes as illustrated in Scheme 10.1. When the DC potential is applied, the extremities/poles of Mo₂B₅ or W₂B₅ particles are immediately polarized therefore promoting electrochemical reactions that cause their fragmentation into smaller particles. This process happens even in the absence of a direct ohmic contact between the materials and driving electrodes (Scheme 10.1).

Scheme 10.1 Schematic representation of bipolar electrochemical treatment of M_2B_5 ($M = Mo$ or W) and the corresponding effect on their electrochemical performance.

For optimization of the bipolar electrochemistry method, various applied potentials and time duration were studied. The optimized parameters were found to be applied DC potential of 3 V for 1800s. BP-treated suspensions of Mo_2B_5 and W_2B_5 were then centrifuged and the products were retrieved for further characterization.

Firstly, we conducted several techniques to characterize commercial Mo_2B_5 and W_2B_5 and BP-treated Mo_2B_5 and W_2B_5 . Scanning electron microscope (SEM) images of bulk Mo_2B_5 and W_2B_5 as well as the transition electron microscopy (TEM) images of Mo_2B_5 and W_2B_5 after BP treatment are shown in Figure 10.1 to observe their morphology. SEM revealed bulk Mo_2B_5 as large crystals with lateral sizes up to tens of micrometer whereas TEM images of BP-treated Mo_2B_5 showed particles with lateral sizes of few micrometers. The corresponding SEM and TEM elemental mapping (energy dispersive X-ray spectroscopy, EDS) for bulk and BP-treated Mo_2B_5 are also included in Figure 10.1 a. EDS analysis show the homogeneous distribution of elements in the materials. For its tungsten counterpart, the SEM, TEM and EDS images of bulk and BP-treated W_2B_5 are presented in Figure 10.1 b with similar observations. The SEM images of bulk W_2B_5 reveal large stones of large lateral sizes while TEM images of BP-treated W_2B_5 show

smaller structures. Also, their respective EDS analysis display homogenous surface distribution of W and B.

Figure 10.1 SEM images of bulk (a) Mo_2B_5 and (b) W_2B_5 as well as their corresponding TEM images after bipolar electrochemical treatment. The EDS maps of bulk Mo_2B_5 , W_2B_5 and after BP treatments are also presented.

Additionally, scanning transmission electron microscopy (STEM) images of bulk and BP-treated Mo_2B_5 and W_2B_5 were also obtained (Figure 10.2). These images confirm the successful reduction in lateral size and thickness of Mo_2B_5 and W_2B_5 bulk materials through bipolar electrochemistry treatment. The lateral size was observed to decrease from the micrometer to the nanometer range after BP-treatment. For better comparison, STEM images of bulk Mo_2B_5 and W_2B_5 before the bipolar electrochemistry treatment are also shown in Figure 10.2 (left panels). Besides lateral size, the treatment also reduces

thickness of the materials (Figure 10.2 central and right panels). Between the two materials, these STEM images suggest that Mo_2B_5 became thinner compared to W_2B_5 particles after BP treatment. For more STEM images of BP-treated Mo_2B_5 and W_2B_5 , readers can refer to Figure 10.S1 and 10.S2 in the supporting information. As a result, bipolar electrochemistry can efficiently downsize Mo_2B_5 and W_2B_5 to smaller and thinner particles.

Figure 10.2 STEM images of (a) Mo_2B_5 and (b) W_2B_5 before and after bipolar electrochemistry at 3 V for 1800s.

To further verify the morphology and crystal structure of BP-treated Mo_2B_5 and W_2B_5 particles, TEM, high resolution transmission electron microscope (HR-TEM) and selected area electron diffraction (SAED) were conducted (Figure 10.3). These images supports that Mo_2B_5 and W_2B_5 were indeed downsized to smaller and thinner particles in agreement with the STEM results. The inset images of SAED shows the hexagonal symmetry of Mo_2B_5 and W_2B_5 phases.

Figure 10.3 TEM and HR-TEM images of BP-treated (a-c) Mo_2B_5 and (d-f) W_2B_5 . Inset images are the SAED pattern of Mo_2B_5 and W_2B_5 respectively.

The phase composition was also analyzed by X-ray diffraction (XRD) and the corresponding diffractograms of bulk and BP treated Mo_2B_5 , W_2B_5 are shown in Figure 10.4. XRD data shows phase purity that matches rhombohedral Mo_2B_5 and W_2B_5 ^{40,41} in bulk and BP treated materials. In the BP treated materials, Na_2SO_4 is observed because this salt was used as the supporting electrolyte and traces of it may have remained after the washing steps. Figure 10.4 e presents the crystal structure of Mo_2B_5 and W_2B_5 , which includes the existence of two types of boron layers, one graphene-like (red balls) and the other puckered layer (green balls). One layer of metal (blue balls) is sandwiched between these two types of boron layers.

Figure 10.4 X-ray diffraction patterns of (a) bulk Mo_2B_5 , (b) BP treated Mo_2B_5 and (c) bulk W_2B_5 , (d) BP treated W_2B_5 . (e) Crystal structure of Mo_2B_5 and W_2B_5 .

High resolution X-ray photoelectron spectroscopy (HR-XPS) was further performed to acquire surface elemental composition and bond information of bulk Mo_2B_5 (Figure 10.5), bulk W_2B_5 (Figure 10.6) and their BP treated forms. From the deconvolution analysis of high resolution spectra of bulk Mo_2B_5 in Figure 10.5 a, the Mo 3d region shows Mo^{4+} and Mo^{6+} doublet peaks which are located at around 230.2, 234.0 eV and 232.9, 236.1 eV, respectively.^{27,30} Furthermore, high resolution spectrum of B 1s was deconvoluted to two

distinct peaks at 191.6, and 194.2 eV, which can be assigned to boron oxide and boron species respectively.^{29,30} The XPS results of Mo₂B₅ suggest presence of surface oxidation in the sample. This is in agreement with previous reports where oxidation had also been observed in molybdenum boride materials even though they may have been freshly prepared.^{22,27,30} On the other hand, the high resolution spectrum of Mo 3d region of Mo₂B₅ (Figure 10.5 b) treated by bipolar electrochemistry at 3 V for 1800s was deconvoluted to Mo⁰ (228.3, 231.7 eV) and molybdenum oxides i.e. Mo⁴⁺ (229.0, 232.4 eV), Mo⁵⁺ (231.8, 235.0 eV) and Mo⁶⁺ (232.8, 235.9 eV).^{27,30,42} The deconvoluted peaks of B 1s spectrum of BP-treated Mo₂B₅ in Figure 10.5 b indicate two different boron environments; a deconvoluted peak at lower binding energy of 188.7 eV shows presence of B⁰ in molybdenum boride while another peak at higher binding energy of 193.4 eV originates from boron oxide.^{27,30} The presence of Mo⁰ and B⁰ suggests that BP-treatment exposes new surfaces of Mo₂B₅ or removes the oxidized surface contaminants.

Figure 10.5 High resolution XPS spectra of Mo 3d and B 1s regions for (a) bulk Mo₂B₅ and (b) BP-treated Mo₂B₅ at 3 V for 1800s.

The corresponding HR-XPS data for bulk and BP-treated W₂B₅ are shown in Figure 10.6. The deconvolution of peaks observed at the W 4f region of bulk W₂B₅ (Figure 10.6 a)

reveals W^{4+} peaks positioned at 33.2 and 35.29 eV.^{43,44} Apart from the W^{4+} peaks, a pair of greater W oxidation state located at higher binding energy of 37.1, 39.3 eV are observed. The deconvolution analysis for the high resolution B 1s spectrum of bulk W_2B_5 shows the presence of boron oxide and boron species at 194.1 and 190.6 eV, respectively.³⁰ From these XPS results, we found that W_2B_5 also undergoes surface oxidation similar to Mo_2B_5 . A study on aged molybdenum phosphide had also reported mere surface oxidation only detected by XPS while its crystallized phase remain well-retained.¹⁷ For BP-treated W_2B_5 particles, the XPS data is shown in Figure 10.6 b. The XPS deconvolution of W 4f shows presence of BP-induced oxidation arising from the treatment at 3 V for 1800s, where W^{5+} peak (34.7, 37.0 eV) and W^{6+} peak at (35.9, 38.1 eV) are seen (Figure 10.6 b). Interestingly, the B 1s peak (188.3 eV) remains unchanged in the B^0 state despite the oxidation of W (Figure 10.6 b).^{27,30}

Figure 10.6 High resolution XPS spectra of W 4f and B 1s regions for (a) bulk W_2B_5 and (b) BP-treated W_2B_5 at 3 V for 1800s.

10.2.2 Electrochemical Hydrogen Evolution

Following material characterizations, we investigated the electrocatalytic activity of the materials towards HER in 0.5 M H_2SO_4 electrolyte via linear sweep voltammetry (LSV)

measured at a scan rate of 2 mV s^{-1} . Figure 10.7 a shows the polarization curves of bulk and BP-treated Mo_2B_5 and W_2B_5 , together with Pt/C and bare glassy carbon electrode (GC) as controls for comparison. From the electrochemical analysis, GC shows negligible HER activity while Pt/C exhibits the best HER performance with an overpotential of 84.9 mV *versus* the reversible hydrogen electrode (RHE) at -10 mA cm^{-2} current density. Meanwhile, bulk Mo_2B_5 and W_2B_5 are slightly active towards HER with overpotential values of 0.74 V and 0.68 V respectively. Interestingly, both BP-treated Mo_2B_5 and W_2B_5 display enhanced HER performance compared to their original bulk counterparts with overpotential values of 0.54 V and 0.21 V respectively. This superior HER performance is comparable to other non-noble metal based electrocatalysts as shown in Table 10.S1. A possible reason for the improvement of HER performance after BP treatment is the generation of more active sites produced from the downsizing process. Moreover, this is further supported by our HR-XPS (Figures 10.5 and 10.6) and XRD (Figure 10.4) results which suggest that the BP treatment enables formation of new species in both Mo_2B_5 and W_2B_5 materials. It is possible that these new species formed after BP treatment have contributed to enhance the HER as well.

Figure 10.7 Hydrogen evolution reaction of bulk and BP-treated Mo₂B₅ and W₂B₅ tested in 0.5 M H₂SO₄ at the scan rate of 2 mV s⁻¹: (a) HER polarization curves of the bulk and BP-treated Mo₂B₅ and W₂B₅, Pt/C and bare glassy carbon electrode, (b) bar chart comparison of their HER overpotentials measured at -10 mA cm⁻² current density, (c) their corresponding Tafel plots, and (d) bar chart comparison of their obtained Tafel slope values.

Tafel slope values of tested materials were determined and presented in Figure 10.7 c,d to elucidate the HER mechanism. The possible rate determining steps (RDS) of HER are as follow: ⁴⁵⁻⁴⁷

1. Adsorption step (Volmer): $\text{H}_3\text{O}^+ + \text{e}^- \rightarrow \text{H}_{\text{ads}} + \text{H}_2\text{O}$; Tafel slope ≈ 120 mV/dec
2. Desorption step (Heyrovsky): $\text{H}_{\text{ads}} + \text{H}_3\text{O}^+ + \text{e}^- \rightarrow \text{H}_2 + \text{H}_2\text{O}$; Tafel slope ≈ 40 mV/dec
3. Desorption step (Tafel): $\text{H}_{\text{ads}} + \text{H}_{\text{ads}} \rightarrow \text{H}_2$; Tafel slope ≈ 30 mV/dec

The Tafel slope determines the rate limiting step for HER. As shown in Figure 10.7 c and d, the obtained Tafel slope value of Pt/C is 34.3 mV dec⁻¹ with the Tafel desorption step as the RDS step, similar to reported literature.^{17,28,45} For bulk Mo₂B₅ and W₂B₅, their Tafel slope values are calculated to be 118.4 and 115.0 mV dec⁻¹ respectively. These two Tafel slope values suggest that the HER mechanism for both bulk Mo₂B₅ and W₂B₅ materials are limited by the adsorption Volmer step. After BP treatment, the Tafel slope of Mo₂B₅ decreases to 101.0 mV dec⁻¹ indicating no alteration of its rate limiting step. However for BP-treated W₂B₅, this value significantly lowers to 62.2 mV dec⁻¹ which is similar to the reported Tafel slope values of MoP and MoB,^{17,22} where the HER process was inferred to undergo a fast Volmer step followed by a rate limiting Heyrovsky desorption step. Therefore, a similar HER mechanism can be deduced for BP-treated W₂B₅. It was reported that Tafel slope is strongly dependent on the particle size, which means that the same material with different particle sizes can result in different Tafel

slope values.²⁷ For example, larger commercial Mo₂C particles possess Tafel slope value that is twice that of synthesized Mo₂C.⁴⁸ Hence, the transformation of HER mechanism for W₂B₅ before and after BP treatment as observed from the drastic change in Tafel slope value may similarly occur due to its change in size. Other possible reasons for this observation also include its lower oxidative surface contamination as well as different surface atom terminations that may also influence the rate limiting step.

The effect of the different applied potentials on the HER performance of Mo₂B₅ (Figure 10.8 a-c) and W₂B₅ (Figure 10.8 d-f) was also investigated in the range of 0 to 10 V and their HER performance including the polarization curves, HER overpotential measured at -10 mA cm⁻² and Tafel slope values are presented in Figure 10.8. Diverse potentials ranging from 0 to 10 V were applied to Mo₂B₅ and W₂B₅ for 1800s in order to identify the best performing conditions for HER. From Figure 10.8 a-c, Mo₂B₅ was treated with potentials of 3, 5, 8 and 10 V for 1800s, giving rise to HER overpotentials of 0.54, 0.63, 0.58 and 0.62 V and Tafel slope values of 101.0, 134.7, 96.2 and 122.8 mV dec⁻¹ respectively. These results suggest that 3 V is the optimal potential for the bipolar electrochemistry treatment of Mo₂B₅ for HER application. Similarly, the same experimental parameters were examined for W₂B₅ (Figure 10.8 d-f) and an applied potential of 3 V was identified to acquire the best HER performance with an overpotential of 0.21 V measured at -10 mA cm⁻² and Tafel slope of 62.2 mV dec⁻¹ compared to the 2 V (0.47 V, 79.8 mV dec⁻¹), 5 V (0.37 V, 108.5 mV dec⁻¹), 8 V (0.38 V, 106.6 mV dec⁻¹) and 10 V (0.36 V, 79.1 mV dec⁻¹).

Figure 10.8 Linear scan voltammetry (LSV) measurements of the BP-treated Mo₂B₅ and W₂B₅ at different applied potentials and duration: (a-c) HER polarization curves, overpotential at -10 mA cm⁻² and Tafel slope of bulk Mo₂B₅ and BP-treated Mo₂B₅ at 1800s for various potentials, (d-f) HER performances, overpotential at -10 mA cm⁻² and Tafel slope of bulk W₂B₅ and BP-treated W₂B₅ at 1800s for different potentials, and (g-i) HER curves, overpotential at -10 mA cm⁻² and Tafel slope of original W₂B₅ and BP-treated W₂B₅ at 3 V for various time.

On the other hand, various treatment periods have been studied for W₂B₅ as this material shows more promising HER performance compared to Mo₂B₅. As shown in Figure 10.8 g-i, shorter electrolysis time of 900s and longer electrolysis time of 2400s at 3 V of W₂B₅ result in poorer HER performance. As such, we determined 1800s to be the suitable electrolysis time duration for BP treatment which is similar to other works.³⁸

Additionally, XPS and STEM were conducted to study the bonding information and size of BP-treated Mo₂B₅ and W₂B₅ particles at 10 V for 1800s in order to make a comparison with materials prepared at 3 V for 1800s. From the XPS measurements shown in Figure 10.S3, only oxidative deconvoluted peaks i.e. Mo⁶⁺ (233.8, 236.9 eV) and W⁶⁺ (35.6, 37.8

eV) are found (Figure 10.S3 b and e), suggesting that a high voltage applied of 10 V results in the oxidation of both Mo₂B₅ and W₂B₅. For the deconvolution of B 1s spectra, BP-treated Mo₂B₅ and W₂B₅ at 10 V shows that the boron oxide peaks located at around 193.5 eV (Figure 10.S3 c and f), which is different from those seen previously for BP-treated Mo₂B₅ and W₂B₅ at 3 V (Figure 10.6 b and d). This indicates that BP-treatment induced oxidation of boron at higher voltage. This oxidation may be the reason for the poorer HER performance observed for BP-treated materials at 10 V. STEM micrographs for BP-treated Mo₂B₅ and W₂B₅ at 10 V (Figure 10.S4 and 10.S5) confirm the successful downsizing effect produced from bulk to smaller and thinner particles, consistent with that seen previously after the BP treatment at 3 V.

Subsequently, we performed stability test of the BP treated Mo₂B₅ and W₂B₅ in 0.5 M H₂SO₄ by running 100 cyclic voltammetry (CV) 100 cycles at a scan rate of 100 mV/s (see Figure 10.9 a and d) at their respective HER onset potential window where the current density reaches at least -0.1 mA/cm^2 . The polarization curves of BP-treated Mo₂B₅ remained unchanged with comparison to its initial measurement, suggesting that this material is stable in acidic media. On the other hand, BP-treated W₂B₅ shows a negative shift in overpotential by 30 mV after the CV cycling. To investigate these further, long-term stability tests were performed by applying a continuous potential to the materials over 2 hours (shown in Figure 10.9 b and e). The potential chosen for each material corresponds to their overpotential. The corresponding HER LSVs before and after the long-term stability tests are recorded in Figure 10.9 c and f. For both materials, a negative shift in overpotential of 27 mV for W₂B₅ and 34 mV for Mo₂B₅ was observed. These results demonstrate the high stabilities of BP-treated W₂B₅ and Mo₂B₅ for HER applications. Note that there is a slight shift in overpotential of BP-treated W₂B₅ as nafion

was added in the material suspensions for the long-term stability tests to avoid the release of materials into the solution during the measurement.

Figure 10.9 Electrochemical stability tests of BP-treated Mo_2B_5 and W_2B_5 . HER polarization curves before and after 100 cyclic voltammetry cycles for (a) Mo_2B_5 and (d) W_2B_5 respectively. Long-term stability test conducted by applying -0.52 V vs. Ag/AgCl and -0.41 V vs. Ag/AgCl for (b) Mo_2B_5 and (e) W_2B_5 respectively. HER polarization curves before and after performing the long-term stability test for (c) Mo_2B_5 and (f) W_2B_5 . Electrochemical impedance spectroscopy (EIS) measurements were conducted to understand the interfacial properties and kinetics for the enhanced HER performance observed after the BP treatment. We measured the EIS of bulk and BP-treated Mo_2B_5 and W_2B_5 at 3 V for 1800s (Figure 10.10). Nyquist plots revealed that both BP-treated Mo_2B_5 and W_2B_5 exhibit highly improved electron transfer compared to their bulk materials as seen from their lower charge transfer resistance (R_{ct}) values. To illustrate, BP-treated

Mo_2B_5 and W_2B_5 produce lower R_{ct} values of 524.7 Ω and 453.9 Ω respectively relative to their bulk counterparts of Mo_2B_5 (21242.0 Ω) and W_2B_5 (2629.7 Ω). Since HER process involves electron transfer between the electrode material and the electrolyte interface, low R_{ct} value promotes the catalytic activity of the materials thus improving their HER efficiency. This finding provide a possible justification for the higher electrocatalytic activity of BP-treated Mo_2B_5 and W_2B_5 compared to their bulk counterparts (Figure 10.7 a).

Figure 10.10 Electrochemical impedance spectroscopy (EIS) measurements of (a) bulk W_2B_5 and BP-treated W_2B_5 at 3 V for 1800s as well as (b) bulk Mo_2B_5 and BP-treated Mo_2B_5 at 3 V for 1800s. Bar charts (c) and (d) compares the R_{ct} values of the untreated and BP-treated W_2B_5 and Mo_2B_5 materials tested. R_{ct} represents charge transfer resistance, R_b is short for bulk resistance while CPE stands for the constant phase element. The Nyquist plots were measured at frequencies between 10 000 kHz and 0.1 Hz and at an overpotential of 600 mV for all materials.

Previous density functional theory (DFT) calculations revealed that the B atom of binary molybdenum boride plays an important role in catalyzing HER. For example, that several

surfaces of MoB_2 were found to be active for HER with an optimal HER process occurring on B–B bridge sites of B-terminated MoB_2 (001) surface at a hydrogen coverage between 75% and 100%.³⁰ There have been reports that size of MoB_2 nanoparticles can affect its HER performance and that ultrathin molybdenum boride films can maximize the availability of surface active sites for improved HER activity.^{29,30} Through the BP treatment, Mo_2B_5 and W_2B_5 are downsized to micron/nano particles with decreased thickness. XPS reveals the presence of B^0 state of metal boride regardless of the oxidation of metal in the as-obtained particles. In this way, BP treatment not only exposes more surface active sites through downsizing of the particles, it also retains the active sites of B^0 state for HER catalysis. EIS measurements further prove that the BP-treated Mo_2B_5 and W_2B_5 give the lower R_{ct} values which favors the electron transfer between the electrocatalyst material and the electrolyte interface for a facile HER process. In consideration of these properties, BP-treated Mo_2B_5 and W_2B_5 show enhanced HER performance with lower overpotential and Tafel slope.

10.3 Conclusion

In summary, commercial Mo_2B_5 and W_2B_5 are treated by bipolar electrochemistry and their electrochemical properties towards HER are investigated. We show that bipolar electrochemical treatment performed at 3 V for 1800s effectively downsizes both Mo_2B_5 and W_2B_5 from tens of microns to several microns and even nanometer size. These downsized Mo_2B_5 and W_2B_5 particles are found to show lower charge transfer resistance and increased electrocatalytic activity towards HER compared with bulk counterparts. Various bipolar electrochemistry conditions (applied voltage and time) were studied to determine the optimum conditions of the treatment for electrocatalytic HER application. The use of high voltage (i.e. 10 V) in the BP treatment results in higher degree oxidation of the target materials and poorer HER performance. This simple bipolar electrochemistry

treatment offers an alternative strategy to develop electrocatalysts with enhanced HER performance and may in turn be extended to other transition metal based electrocatalysts.

10.4 Experimental Section

10.4.1 Materials

Sodium sulphate, concentrated sulfuric acid, and 20 wt % platinum on graphitized carbon (Pt/C) were purchased from Sigma-Aldrich. Mo₂B₅ and W₂B₅ were obtained from Mateck, Germany. Pt counter electrode, Ag/AgCl reference electrode, and glassy carbon (GC) working electrodes were purchased from CH instruments, Texas, USA. Ultrapure Milli-Q water was used in the preparation of solutions.

10.4.2 Apparatus

Scanning electron microscopy (SEM) and scanning transmission electron microscopy (STEM) were conducted with a JEOL 7600F field emission SEM (JEOL, Japan). SEM and STEM images were obtained at an acceleration voltage of 2 KV and 30 kV, respectively.

Transmission electron microscopy (TEM), selected area electron diffraction (SAED) and high resolution transmission electron microscopy (HR-TEM) were performed using EFTEM Jeol 2200 FS microscope (Jeol, Japan), a 200 keV acceleration voltage was used for measurement. Sample preparation was attained by drop casting the suspension (1 mg mL⁻¹ in water) on a TEM grid (Cu; 200 mesh; Formvar/carbon) and dried at 60 °C for 12 h. Elemental maps and energy dispersive spectrometer (EDS) spectra were acquired with SDD detector X-MaxN 80 T S from Oxford Instruments (England).

X-ray powder diffraction (XRD) data were collected at room temperature with an Bruker D8 Discoverer powder diffractometer with parafocusing Bragg-Brentano geometry using Cu K α radiation (λ = 0.15418 nm, U = 40 kV, I = 40 mA). Data were scanned with an

ultrafast detector Lynxeye XE over the angular range 10–80° (2 θ) with a step size of 0.02° (2 θ). Data evaluation was performed in the software package Eva.

X-ray photoelectron spectroscopy (XPS) was performed using an X-ray photoelectron Phoibos 100 spectrometer (SPECS, Germany), equipped with a monochromatic Mg K α X-ray radiation source at 1253 eV. Graphite was added to XPS measurement in order to obtain C 1s peak for calibration to 284.5 eV.

10.4.3 Bipolar Electrochemistry Treatment

Bipolar electrochemical treatment of Mo₂B₅ and W₂B₅ was conducted following the same protocol established by our group.³⁸ Aqueous dispersions of Mo₂B₅ and W₂B₅ with the concentration of 5 mg mL⁻¹ were prepared in deionized water by sonication for 3 hours. These suspensions were then diluted to 0.5 mg mL⁻¹ by adding deionized water and 0.5 M Na₂SO₄ to a total volume of 4 mL. This bipolar electrochemical treatment of Mo₂B₅ and W₂B₅ was carried out in an electrochemical cell at room temperature. Two platinum driving electrodes with a separation distance of 1.5 cm was immersed into the solution and a constant DC potential (3V, 5 V, 8 V, and 10 V) was supplied for a period of time under constant stirring conditions. Then, the suspension was left to settle for a minimum of 48 h, followed by centrifugation at a speed of 14000 rpm for 15 min to remove Na₂SO₄ and retrieve the products for characterization.

10.4.4 Electrochemical Measurement

0.5 mg mL⁻¹ concentration of Mo₂B₅ and W₂B₅ were prepared in ultrapure water and ultrasonicated for 3h in order to obtain homogeneous suspension. Bipolar electrochemistry treated Mo₂B₅ and W₂B₅ suspensions with the concentration of 0.5 mg mL⁻¹ were obtained following the protocol above. All electrochemical hydrogen evolution reaction (HER) measurements were performed by using Linear Sweep Voltammetry (LSV) with a μ Autolab type III electrochemical analyzer (Eco Chemie,

Netherlands) using NOVA 1.10 software. A three-electrode configuration where glassy carbon (GC), platinum electrode and Ag/AgCl electrode were used as working, counter and reference electrode respectively was adopted to measure the HER performance. Prior to immobilization of materials, GC electrode surface was renewed by polishing with 0.05 μm alumina particle slurry on a polishing pad and then washed with ultrapure water and dried. 4 μL aliquot of material suspension was dropcasted on the GC surface. These electrodes were then dried at room temperature to obtain a good distribution of test materials onto the GC surface. All HER measurements were conducted at room temperature with 0.5 M H_2SO_4 as the supporting electrolyte at a scan rate of 2 mV s^{-1} . The electrochemical stability test of BP-treated Mo_2B_5 and W_2B_5 was conducted in 0.5 M H_2SO_4 by using the 100 cyclic voltammetric scans at 100 mV s^{-1} . The potential windows of cyclic voltammetry corresponds to the HER current density of at least 0.1 mA cm^{-2} . Therefore, the potential window is between 0 to -0.55 V vs Ag/AgCl for Mo_2B_5 and 0 to -0.41 V vs Ag/AgCl for W_2B_5 . The HER long-term stability was also tested by applying a fixed potential of -0.55 V vs Ag/AgCl for Mo_2B_5 and -0.41 V vs Ag/AgCl W_2B_5 for 2 hours, respectively. 4 μl material suspensions was dropcasted on GC surface and dried under atmospheric conditions. For electrochemical stability measurements, 4 μl of 0.9 % Nafion solution was subsequently used to modify the electrode surface. The Nyquist plots were measured at frequencies between 10 000 kHz and 0.1 Hz and at an overpotential of 600 mV for bulk and treated Mo_2B_5 and W_2B_5 with 0.5 M H_2SO_4 as supporting electrolyte. The impedance data were fitted to a simplified Randles circuit (where constant phase element (CPE) replace the double layer capacitance) to obtain the charge transfer resistances.

10.5 Supporting Information

Figure 10.S1. STEM images of BP-treated Mo₂B₅ by applying a potential of 3 V for 1800s.

Figure 10.S2 STEM images of BP-treated W₂B₅ by applying a potential of 3 V for 1800s.

Figure 10.S3 Survey scan and high resolution XPS spectra of Mo_2B_5 and W_2B_5 after bipolar electrochemistry treatment at 10 V for 1800s: (a) survey scan of Mo_2B_5 , (b-c) high resolution XPS spectra of Mo 3d and B 1s region of Mo_2B_5 , (d) survey scan of W_2B_5 , (e-f) high resolution XPS spectra of W 4f and B 1s regions of W_2B_5 .

Figure 10.S4 STEM images of bipolar electrochemistry treated Mo_2B_5 by applying a potential of 10 V for 1800s.

Figure 10.S5 STEM images of bipolar electrochemistry treated W_2B_5 by applying a potential of 10 V for 1800s.

Table 10.S1 Comparison of non-noble metal based HER electrocatalytic activity in acidic medium with other literature.

Electrocatalyst	Electrolyte	Overpotential (mV) at 10 mA cm^{-2}	Tafel slope (mV dec^{-1})	Reference
BP-treated Mo_2B_5	0.5 M H_2SO_4	540	101	This work
BP-treated W_2B_5	0.5 M H_2SO_4	210	62.2	This work
MoB	1 M H_2SO_4	210	55	S1
α -MoB ₂	0.5 M H_2SO_4	149	74.2	S2
Mo_2B_4	0.5 M H_2SO_4	310	80	S3
MoB ₂	0.5 M H_2SO_4	300	75	S4
Mo_3B (film)	0.5 M H_2SO_4	249 at 20 mA cm^{-2}	52	S5
MoB ₂ nanoparticle	0.5 M H_2SO_4	154	49	S6
MoB/g- C_3N_4	1 M KOH	133	46	S7
MoP	0.5 M H_2SO_4	180 at 30 mA cm^{-2}	54	S8
Mo_2C	0.5 M H_2SO_4	208	56	S1

MoN	0.5 M H ₂ SO ₄	300 at 38 mA cm ⁻²	90	S9
Mo ₂ N	0.5 M H ₂ SO ₄	381	100	S10
WP ₂	0.5 M H ₂ SO ₄	161	57	S11
W ₂ C	1 M H ₂ SO ₄	300 at 23 mA cm ⁻²	118	S12

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Chapter 11

Conclusion and Epilogue

11.1 Conclusion

11.1.1 Part I: Electrochemistry of Layered Post-transition Metal Chalcogenides

11.1.2 Part II: Factors Affecting the Electrocatalytic Efficiency of Layered Transition Metal Dichalcogenides

11.1.3 Part III: Novel Fabrication Strategies for Electrochemical Applications

11.2 Epilogue

11.1 Conclusion

The global warming issue and global energy crisis make it critical to find the low cost and efficient technologies for production of renewable and clean fuels. Hydrogen is such a promising fuel with high energy density and clean byproduct. However, hydrogen production, especially electrochemical HER is limited by the slow reaction kinetic and high cost of the noble metal electrocatalysts. Therefore, we studied the electrochemistry of various layered materials in order to find the electrocatalysts for HER. In this thesis, **part I** focused on the fundamental electrochemistry of layered post-transition metal chalcogenides including gallium and indium chalcogenides which has been overlooked. Following part (**Part II**) studied and compared the electrochemical and electrocatalytic performances of several TMDs toward HER. **Part II** investigated the effects of exfoliated TMDs, amorphous TMDs as well as the TMDs incorporated with conductive substrate on HER. The last part (**Part III**) adopted the novel bipolar electrochemical method for feasible exfoliation and downsizing of layered materials for further electrochemical applications.

11.1.1 Part I: Electrochemistry of Layered Post-transition Metal Chalcogenides

Although numerous studies have revealed the electrochemical properties of TMDs for various applications. However, few studies have delved to the electrochemical properties of layered semiconducting post-transition metal chalcogenides. In **Part I**, the fundamental electrochemical properties of post-transition metal chalcogenides were comprehensively studied. The electrochemistry studies of gallium chalcogenides are presented in **Chapter 4** while indium chalcogenides in **Chapter 5**. Unlike the typical crystal structure of TMDs, gallium and indium chalcogenides have two metal atoms (M) and two chalcogen atoms (X) in each layer in X-M-M-X sequence. As for the inherent electrochemistry of gallium chalcogenides, it was found that all gallium chalcogenides

showed a small peak at -0.6 V, which may due to the reduction of Ga_2O_3 . In addition, GaTe was revealed to have the unique oxidation peaks at approximately +0.3 V, which resulted from the oxidation of Te. In the case of indium chalcogenides, the reduction peak of InSe at -1.6 V was observed, relating to the reduction of In_2O_3 . InTe also exhibited the oxidation peaks at around +0.3 V corresponding to Te, which is in agreement with the electrochemical behaviors of GaTe. Furthermore, the electrocatalytic activity of gallium and indium chalcogenides was also studied. All the gallium and indium chalcogenides were not good electrocatalysts with high onset potentials and Tafel slopes due to lower conductivity and less activity at bulk state. These studies provide fundamental electrochemical properties of post-transition metal chalcogenides, which has implications in their various applications.

11.1.2 Part II: Factors Affecting the Electrocatalytic Efficiency of Layered Transition Metal Dichalcogenides

Novel methods have been put forward to improve the electrocatalytic efficiency of TMDs toward HER. In **part II**, exfoliation of TMDs into nanosheets, preparation of amorphous TMDs and TMD hybrids with conductive substrate were studied to improve the electrocatalytic activity. The electrochemistry of bulk and exfoliated Group 5 TMDs was investigated in **Chapter 6**. Metallic vanadium dichalcogenides (VS_2 , VSe_2 and VTe_2) were exfoliated by chemical lithium intercalation. The degree of exfoliation followed the $\text{VS}_2 > \text{VSe}_2 > \text{VTe}_2$ order. However, the resulted vanadium dichalcogenides nanosheets were nonstoichiometric vanadium oxide and lithium vanadates characterized by XRD and XPS and the decreased chalcogen-to-metal ratio was observed after exfoliation, which highly deteriorated their electrocatalytic activity toward HER. Besides, both bulk and exfoliated vanadium dichalcogenides exhibited inherent oxidation and reduction behaviors, which can limit their applications.

Following, the electrochemistry of crystalline and amorphous TMDs were studied in **Chapter 7**. We synthesized crystalline and amorphous PtS₂ and comparatively investigated their electrochemical properties as electrocatalysts toward HER and OER. First of all, amorphous and crystalline PtS₂ displayed a similar reduction peak at -1.3 V ascribing to the reduction of Pt (IV) and a broad oxidation peak relating to the oxidation of S atom. Besides, amorphous PtS₂ was measured to have higher heterogeneous electron transfer rate than crystalline PtS₂, indicating amorphous materials is more suitable for sensing applications. Secondly, amorphous PtS₂ exhibited superior HER and OER performance than crystalline PtS₂ as amorphous materials have higher active sites due to the porous and nanostructured morphology proved by the electrochemically active surface area studies. Interestingly, the electrocatalytic activities of both amorphous and crystalline PtS₂ was modulated by electrochemical reduction pretreatment, in which the pretreatment removed the oxidized sulfate and increased the concentration of Pt (0). Lastly, the nanocomposites of Group 5 TMDs with graphene was investigated as the electrocatalysts toward HER, which was discussed in **Chapter 8**. Group 5 TMDs (VS₂, NbS₂ and TaS₂) incorporated with graphene were prepared by thermal exfoliation of graphene oxide with respective TMD precursors. Characterization by XRD and XPS revealed that the resulted composites mainly contained metal oxide and a small amount of metal sulfide. HER studies revealed that TMD hybrids with graphene showed higher performance than graphene at -2 mA cm⁻².

11.1.3 Part III: Novel Fabrication Strategies for Electrochemical Applications

Electrochemical methods such as electrodeposition, bipolar electrochemistry have been regarded as the easy and feasible approaches to fabricate the active electrocatalysts. In this part (**Part III**), bipolar electrochemistry was employed to exfoliate and downsize the layered materials for electrochemical applications. Nonconductive hexagonal boron

nitride was exfoliated by bipolar electrochemical treatment, as presented in **Chapter 9**. This research provides a scalable electrochemical method for exfoliation of layered materials. Then, bipolar electrochemical was applied to downsize the Mo_2B_5 and W_2B_5 and found downsized nanoparticles are more active toward HER as shown in **Chapter 10**. The nanostructured Mo_2B_5 and W_2B_5 particles showed lower charge transfer resistance and excellent catalytic activity than untreated Mo_2B_5 and W_2B_5 toward HER. This study offers an easy approach to tune the electrocatalytic activity toward HER and can be developed to other layered materials.

11.2 Epilogue

The demand for the renewable energy has promoted the development of the electrocatalysts for electrochemical water splitting. Low-cost, efficient and earth-abundant layered TMDs, especially Group 6 TMDs with superior electrocatalytic performance toward HER has been extensively studied. Besides, many strategies has been applied to improve the catalytic activity. However, several challenges need to be addressed for the application of the electrochemical energy conversion and storage system. Firstly, the large-scale, cost-effective strategies for the preparation of electrocatalysts with high quality and superior catalytic performance is of importance for the widespread practical applications. Furthermore, the stability of the electrocatalysts is affected by corrosion during the water electrolysis. Therefore, robust electrocatalysts or durable support need to be developed for the practical applications. In addition, safe operation and storage of produced hydrogen gas should also be taken into account. Efforts should be devoted to study the mass storage of hydrogen gas. Measures and engineering practices should be taken to safely operate the hydrogen gas.