Exploring layered metal chalcogenides : electrochemistry and application

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**EXPLORING LAYERED METAL CHALCOGENIDES –
ELECTROCHEMISTRY AND APPLICATION**

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SCHOOL OF PHYSICAL & MATHEMATICAL SCIENCES

NANYANG TECHNOLOGICAL UNIVERSITY

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A thesis submitted to the Nanyang Technological University
in partial fulfillment of the requirement for the degree of
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Summary

Layered metal chalcogenides have garnered considerable attention in recent years due to their vast array of applications. This class of materials was catapulted to fame by MoS₂, a prominent transition metal dichalcogenide (TMD), upon the discovery of its unique electrochemical and catalytic properties that marked a significant milestone in the pursuit of naturally abundant electrocatalysts for hydrogen evolution reaction (HER) that may, in the future, displace expensive platinum-based electrodes. High cost of platinum catalysts is one of the key hurdles towards transitioning into an affordable hydrogen economy. This thesis aims to examine the feasibility of layered metal chalcogenides as alternatives to platinum by exploring their inherent electrochemistry and catalytic HER performance across the different families. The wide spectrum of layered metal chalcogenides, formed by diverse metal and chalcogen constituents, confers versatility to their properties that are governed by elemental composition, structure and anisotropy. Across the periodic table, their trends in electrochemistry and HER electrocatalysis are established. In a bid to exploit layered metal chalcogenides in HER catalysis, in particular the TMDs of outstanding catalytic attributes, various methods are also investigated to optimise and control the electrocatalytic efficiency of TMDs with an emphasis on Group 6 TMDs such as MoS₂, WS₂, MoSe₂ and WSe₂. Strategies explored in this thesis include transition metal doping of TMDs, electrosynthesis of porous TMD structures and hybrids as well as electrochemical tuning. The successful electrodeposition of active TMD and hybrid electrocatalysts highlights the simplicity and versatility of the technique in fabricating different TMD structures and composites. Knowledge of the fundamental electrochemical aspects, trends and techniques will be advantageous when maximising

the properties of layered metal chalcogenides in prospective energy-related developments that embrace hydrogen economy.

List of Publications

First author articles

1. **Xinyi Chia**, Martin Pumera. *Layered Transition Metal Dichalcogenide Electrochemistry: Journey Across the Periodic Table*. **Chem. Soc. Rev.** **2018**, 47, 5602–5613.
2. **Xinyi Chia**, Nur Ayu Afira Sutrisnoh, Martin Pumera. *Tunable Pt-MoS_x Hybrid Catalysts for Hydrogen Evolution*. **ACS Appl. Mater. Interfaces** **2018**, 10, 8702–8711.
3. **Xinyi Chia**, Nur Ayu Afira Sutrisnoh, Zdeněk Sofer, Jan Luxa, Martin Pumera. *Morphological Effects and Stabilization of the Metallic 1T Phase in Layered V-, Nb-, and Ta-Doped WSe₂ for Electrocatalysis*. **Chem.-Eur. J.** **2018**, 24, 3199–3208.
4. **Xinyi Chia**, Martin Pumera. *Inverse Opal-Like Porous MoSe_x Films for Hydrogen Evolution Catalysis: Overpotential-Pore Size Dependence*. **ACS Appl. Mater. Interfaces** **2018**, 10, 4937–4945.
5. **Xinyi Chia**, Zdeněk Sofer, Jan Luxa, Martin Pumera. *Layered Noble Metal Dichalcogenides: Tailoring the Electrochemical and Catalytic Properties*. **ACS Appl. Mater. Interfaces** **2017**, 9, 25587–25599.
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13. Tijana Maric, Bahareh Khezri, Carmen C. Mayorga-Matinez, Muhammad Zafir bin Mohamed Nasir, **Xinyi Chia**, Martin Pumera. *Nanorobots Constructed from Nanoclay: Using Nature to Create Self-Propelled Autonomous Nanomachines*. **Adv. Funct. Mater.** **2018**, *28*, 1802762.
14. Yong Wang, Carmen C. Mayorga-Martinez, **Xinyi Chia**, Zdeněk Sofer, Martin Pumera. *Nonconductive Layered Hexagonal Boron Nitride Exfoliation by Bipolar Electrochemistry*. **Nanoscale** **2018**, *10*, 7298-7303.
15. Michaela Fojtů, **Xinyi Chia**, Zdeněk Sofer, Michal Masařík, Martin Pumera. *Black Phosphorus Nanoparticles Potentiate the Anticancer Effect of Oxaliplatin in Ovarian Cancer Cell Line*. **Adv. Funct. Mater.** **2017**, *27*, 1701955.
16. Shi Xuan Leong, Carmen C Mayorga-Martinez, **Xinyi Chia**, Jan Luxa, Zdeněk Sofer, Martin Pumera. *2H→1T Phase Change in Direct Synthesis of WS₂ Nanosheets via Solution-Based Electrochemical Exfoliation and Their Catalytic Properties*. **ACS Appl. Mater. Interfaces** **2017**, *9*, 26350-26356.
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18. Yong Wang, Zdeněk Sofer, Jan Luxa, **Xinyi Chia**, Martin Pumera. *Graphene/Group 5 Transition Metal Dichalcogenide Composites for Electrochemical Applications*. **Chem.-Eur. J.** **2017**, *23*, 10430-10437.

Thesis Organisation

This thesis consists of **twelve chapters (12)**. Beginning with **Chapter 1**, the reader is presented with the objectives and motivations of the thesis. **Chapter 2** sets the background for the research motivations originating from the energy predicament, recognizes the challenges towards attaining clean and sustainable energy production and includes a general introduction to the materials of interest – layered metal chalcogenides. **Chapter 3** highlights important considerations of electrochemical energy production by hydrogen evolution reaction (HER) and reviews published works on the electrochemical properties of layered metal chalcogenides and their success, in particular for the transition metal group, in HER applications.

Chapters 4 – 11 present a series of research directed by the objectives established in **Chapter 1**. **Chapters 4** and **5** will analyze the fundamental electrochemistry and trends of transition metal dichalcogenides as HER catalysts. Venturing beyond the transition metal group, **Chapters 6** and **7** investigate the electrochemistry and catalytic properties of other metal chalcogenides. **Chapters 8 – 11** explore strategies to tune the catalytic behavior of transition metal dichalcogenides to achieve desired aims for HER.

This work will be concluded in **Chapter 12** with a summary and a perspective of the field of layered metal chalcogenides as catalysts in the pursuit of the sustainable energy generation.

Chapter 1

Objectives of the Thesis

Sustainability is about fulfilling the needs of today while safeguarding assets to meet the needs of tomorrow. As stewards of the resources entrusted to us, this statement resonates with the global conviction to tide over our energy crisis. The dilemma, which we found ourselves in, arises from the antagonistic forces of an escalating consumption of energy with no end and a brisk attenuation of finite natural resources. Notably, our primary source of energy is derived from non-renewable fossil fuels that generate an enormous carbon footprint. The slew of efforts worldwide channeled into developing technologies and implementing measures for clean and sustainable energy drums up the importance of integrating sustainability goals with the core needs of governments, businesses and the community-at-large in the pursuit of economic growth.

On a technological front, a proposed solution to our energy predicament is via electrochemical water-splitting to produce hydrogen gas as a clean energy carrier. Hydrogen gas is utilised in fuel cells to supply electricity, and produces water as by-product with no carbon emissions. However, the water-splitting process requires an electrocatalyst to reduce the large thermodynamic barrier. Working towards a suitable catalyst, this thesis titled *“Exploring Layered Metal Chalcogenides – Electrochemistry and Application”* presents the possibility of a class of materials, known as the layered metal chalcogenides, by examining their fundamental electrochemistry, and consequently explores their use as electrocatalysts. The importance of layered metal chalcogenides as catalysts for hydrogen evolution reaction (HER) and its challenges are highlighted in **Chapter 2**. Illustrated in **Figure 1.1**, this thesis comprises two objectives and is arranged into two parts. **Part I** investigates the electrochemistry of various layered metal chalcogenides whereas **Part II** discusses the strategies formulated to tailor and maximize the efficiency of

transition metal dichalcogenides in the hydrogen production. Key factors influencing the catalytic behavior of layered metal chalcogenides crucial to catalyst design for hydrogen evolution are introduced in **Chapter 3**.

Part I: Electrochemistry of layered metal chalcogenides and trends

At the point of investigation, almost four years ago, layered metal chalcogenides research was in the nascent stage. In particular, the electrochemistry of layered metal chalcogenides was circumscribed to primarily MoS_2 and WS_2 , which are members of the Group 6 transition metal dichalcogenides (TMDs), while the bulk of metal chalcogenides remained uncharted. Moreover, the remarkable electrocatalytic properties of MoS_2 towards HER raised hopes of a class of naturally abundant materials able to rival that of the state-of-the-art platinum electrocatalysts. Currently, the high cost of platinum is a major drawback that limits the large-scale hydrogen gas production. Hence, the motivation in **Part I** of the thesis bridges the gap in literature, that is, the dearth of studies on electrochemical trends in the extensive library of layered metal chalcogenides. Furthermore, **Part I** elucidates factors due to the metal or chalcogen constituent and evaluates the catalytic prospects of metal chalcogenides towards HER. The trends in Group 5 TMDs are established in **Chapter 4**. The ditelluride family, specifically CoTe_2 and NiTe_2 , are investigated in **Chapter 5**. Beyond TMDs, thallium sulfide and tin chalcogenides are analysed in **Chapter 6** and **Chapter 7** respectively. The fascinating feature of Tl_2S is the structure – an inverse of MoS_2 ; that triggers questions on the electrochemical and catalytic behavior in relation to its structure. The study on tin chalcogenides compares between SnS and SnS_2 and delves into the effect of oxidation state of the metal center on its resultant properties.

Part II: Strategies tailoring electrocatalytic efficiency of transition metal dichalcogenides for hydrogen evolution

The intrinsic catalytic performance of Group 6 TMDs, including MoS₂, WS₂, MoSe₂ and WSe₂, has been established to be a far cry from the platinum-based electrocatalysts for HER. Hence, the rationale in **Part II** of the thesis is to explore methods capable of tailoring and enhancing the electrocatalytic efficiency of TMDs towards HER.

Incorporating trace amounts of transition metal, which is also known as doping, was among the initial methods discovered for elevating the catalytic efficiency of MoS₂. The effect of doping other Group 6 TMDs, besides MoS₂, was seldom studied. Experimenting with transition metal doped WSe₂, the results are discussed in **Chapter 8**.

Traditional syntheses of TMDs and composites usually require harsh experimental conditions and long duration. In contrast to the conventional methods, electrosynthesis provides a simple, efficient and versatile technique of fabricating TMDs and composites from electroactive precursors under ambient conditions. Electrodeposition of porous MoSe_x structures is a proof-of-concept on the versatility of the method to create various structured surfaces. Correlation between the pore size and the efficiency of MoSe_x electrocatalysts is investigated in **Chapter 9**. Using low and varying amounts of Pt precursors, electrodeposited Pt-MoS_x hybrids with tunable HER electrocatalytic properties are reported in **Chapter 10**.

In **Chapter 11**, electrochemical treatment of TMDs is demonstrated as an innovative and facile strategy that offers a point-of-control over the HER catalytic competencies of Group 6 TMDs through the application of an oxidative or reductive potential.

Figure 1.1 Overview of the challenges, broad aims and approaches undertaken in this thesis.

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Chapter 2

Introduction

2.1 *The Energy Conundrum*

2.2 *Living the Hydrogen Dream and the Challenge*

2.3 *Towards a Suitable Catalyst: Layered Metal Chalcogenides*

A short excerpt in chapter was published in the following review:

1. **Xinyi Chia**, Martin Pumera*. Layered Transition Metal Dichalcogenide Electrochemistry: Journey Across the Periodic Table. *Chem. Soc. Rev.* **2018**, 47, 5602-5613.

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The thesis author is the first author of the above paper.

2.1 The Energy Conundrum

Our demand for energy has grown over the years. The U.S. Energy Information Administration forecasted that the total energy consumption worldwide in year 2040 will surge to 736 quadrillion British thermal units (Btu) from 575 quadrillion Btu in 2015; equivalent to a 28% increment.¹ This is likely fuelled by the desire to advance living standards and to improve the quality of lives. At present, non-renewable fossil fuels such as coal, petroleum and natural gas continue to form an outsized share of the energy portfolio. These non-renewable energy sources run the risk of becoming depleted at breakneck pace to achieve economic growth and development, especially with the burgeoning economies of developing countries. This sends alarm bells ringing on the sustainability of businesses contingent on fossil fuel-based energy.

Moreover, the combustion of fossil fuels leaves behind a large carbon footprint. Burning fossil fuels releases copious amounts of greenhouse gases into the atmosphere including carbon dioxide and methane that exacerbate global warming. There is a metonym for global warming: climate change, which is synonymous with the melting of glaciers, rising sea levels and an adverse domino effect on the environment. Coal combustion contributed to 67% of the anthropogenic carbon dioxide emissions from the electricity sector in 2016.² The corollaries of the long-term extensive use of fossil fuels are apparent: energy insecurity and environmental damage. The stakes are high in the midst of mounting demand for energy. In light of the energy conundrum, there is an international conviction to adopt greener, low-carbon business practices and cut down on greenhouse gas emissions. As exemplified in the Paris Agreement to mitigate effects of climate change, a significant number of countries ratified to maintain a temperature rise “well below 2°C above pre-industrial levels”.

Despite the formidable challenge to meet demands for energy and to slash greenhouse gases, there is a silver lining – the quest for clean energy options that fulfil the criteria of being low- or zero-carbon, efficient and sustainable is in full swing. As a result, various renewable energy sources such as wind, geothermal and solar energy have emerged. However, they are largely subject to weather and climate conditions.³⁻⁵ Other practical concerns including efficient and cost-effective storage and implementation have yet to be addressed.^{6,7} Due to the intermittent nature and the absence of storage solutions, these renewable energy options are rendered less reliable than fossil fuel-derived energy. Therefore, for renewable energy options to become feasible on a large-scale, it is imperative to develop effective energy storage means.

2.2 Living the Hydrogen Dream and the Challenge

Electrochemical water splitting technology is a potential remedy to the problem of energy storage. This concept dates back to as early as 1874, to quote French author Jules Verne, “I believe that water will one day be employed as fuel, that hydrogen and oxygen which constitute it will furnish an inexhaustible source of heat and light. Water will be the coal of the future.”⁸ His futuristic vision has come to fruition in the form of fuel cells where energy can be stored for future use as hydrogen or oxygen that is derived from electrochemical water splitting (Figure 2.1).⁹⁻¹¹

Figure 2.1 Schematic illustration of the water splitting process, highlighting water as both the starting material and byproduct.

In the 1970s, the term “Hydrogen economy” was conceived to describe the prospect of creating an alternative energy system that is driven by hydrogen. The allure of hydrogen to become a part of the energy system lies in its ability to cleanly and efficiently convert between chemical and electrical energy and also offers the flexibility of integration into the energy system.

Hydrogen possesses a high energy density that deems it suitable as an energy carrier in fuel cells.¹² The fuel cell oxidizes hydrogen and reduces oxygen to produce water, in the process, releasing heat and converts the chemical energy into electricity that is available for downstream applications. This has been exemplified in the hydrogen fuel cell technology that has been thrust into the recent limelight for powering the world’s first passenger train that runs entirely on hydrogen - Coradia iLint by Alstom, a French rail company (Figure 2.2).¹³ The Coradia iLint regional train is an epitome of clean and sustainable rail transportation, producing only steam and water with no carbon emissions. The generation of electrical energy with hydrogen gives water as a clean byproduct,

granting it the advantage of being a clean energy vector above the fossil fuels.

Figure 2.2 The world's first hydrogen train, Coradia iLint by Alstom. Reproduced from Reference [13].

The production of hydrogen by the electrolysis of water, known as the electrochemical hydrogen evolution reaction (HER), relies on an external source of energy and remains a bottleneck to electrochemical water splitting. Due to the high activation barrier, HER is thermodynamically unfavourable and requires an electrocatalyst to speed up the process. Platinum (Pt) is currently recognized as the most efficient electrocatalyst for HER to date.¹⁴⁻
¹⁶ The drawback of Pt boils down to its high cost that is consequence of the low natural abundance and the widespread uses of Pt. Subsequently, the high cost of Pt hinders the massive commercialisation of HER application. In a bid to lower costs to achieve scalability, research efforts are set on a trajectory to explore efficient, earth-abundant and inexpensive alternative HER electrocatalysts to Pt. Among these reported electrocatalysts, the layered metal chalcogenides is a promising class of materials that has been identified for the production of renewable hydrogen energy.

2.3 Towards a Suitable Catalyst: Layered Metal Chalcogenides

The story of how layered metal chalcogenides gained traction in current research today begins from the intriguing properties of molybdenum disulfide (MoS_2) that ignited a slew of electrochemical applications encompassing batteries, supercapacitors, catalysts and even sensors.¹⁷⁻²⁰ Riding on the success of MoS_2 , which belongs to a subset of the layered metal chalcogenides called the transition metal dichalcogenides (TMDs), earth-abundant TMDs take the helm of research into electrocatalysis for energy generation and conversion.^{21, 22}

The layered nature of TMDs enables catalytic sites for HER to be readily accessible when thinned down into individual sheets. Each TMD layer consists of a transition metal atom (M) belonging to Group 4-10 sandwiched between two chalcogen atoms (X: S, Se, Te) and denoted as MX_2 in a single unit. Within each layer, the M-X bond is covalent. When multiple TMD layers are stacked, it becomes a bulk TMD material. The adjacent layers are held by weak van der Waals forces. These weak interactions between layers are overcome by exfoliation methods to attain thin sheets.²³⁻²⁵ Due to the unique structure of layered TMDs, anisotropic properties emerge from two sites on the TMD – the edge and basal plane. The electrochemistry of TMDs is tied to the type of surface orientation. The basal plane of MoS_2 has low surface energy in stark contrast to the edge.²⁶ Other observations, both theoretical and experimental, show that the edges of MoS_2 are catalytically active for HER while the basal plane is inert.²⁷⁻²⁹

Figure 2.3 a) Transition metal and chalcogen elements that form layered structures are highlighted in the periodic table. Reproduced from Reference [21]. b) Metal coordination and stacking sequences for 1T, 2H and 3R structures. Reproduced from Reference [30].

Different combinations of transition metal and chalcogen type in TMDs spawn an assortment of properties. The filling of d orbitals in the transition metal dictates the electronic structure of the TMDs.²¹ Across Group 4 to Group 10 TMDs, the electron count in the d orbital of the transition metal varies. Apart from the d electron count in the transition metal, the structural coordination of the transition metal and the chalcogen within the TMD also determines their electronic property.³¹ TMDs undertake 2H, 1T and

3R polymorphs in the respective forms of hexagonal, trigonal and rhombohedral stacking sequences as illustrated in Figure 2.3. Frequently encountered TMDs crystallize in the 2H or 1T phases where the bonding arrangement of the transition metal and chalcogen atom is trigonal prismatic or octahedral. In 2H-phase TMDs, the non-bonding d orbitals of the transition metal split into 3 degenerate states d_{z^2} (a_1), $d_{x^2-y^2,xy}$ (e) and $d_{xz,yz}$ (e'). Conversely, 1T-phase TMDs form degenerate d_{z^2,x^2-y^2} (e_g) and $d_{xz,yz,xy}$ (t_{2g}) orbitals. Completely filled orbitals result in semiconducting conductivity whereas partially occupied orbitals are metallic. Conditional on the transition metal, the more thermodynamically stable polymorph exists as the prevalent structure in natural bulk TMD. For example, Group 4 TMDs are usually found in octahedral 1T-phases while Group 6 TMDs are in trigonal prismatic 2H-phases. Certainly, the properties of TMDs are diverse and contingent on their constituent elements.

In view of the burgeoning interest in exploiting layered metal chalcogenides for electrochemical uses, investigating fundamental electrochemistry manifested by these versatile layered materials and establishing catalytic trends across different families of layered metal chalcogenides in the periodic table are prudent. The electrochemical information will provide a glimpse of their inherent properties and an assessment of their effective implementation as electrocatalysts.

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Chapter 3

Background and Literature Review

3.1 *Application of Layered Metal Chalcogenides*

3.2 *Electrochemistry of Layered Metal Chalcogenides*

**3.3 *Factors Influencing Electrochemical Hydrogen Evolution Reaction of Layered
Metal Chalcogenides***

**3.4 *Strategies to Enhance Hydrogen Evolution Performance of Layered Metal
Chalcogenides***

This chapter consists of excerpts from the following published reviews:

1. **Xinyi Chia**, Martin Pumera*. Layered Transition Metal Dichalcogenide Electrochemistry: Journey Across the Periodic Table. *Chem. Soc. Rev.* **2018**, *47*, 5602-5613.

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2. **Xinyi Chia**, Alex Yong Sheng Eng, Adriano Ambrosi, Shu Min Tan, Martin Pumera*. Electrochemistry of Nanostructured Layered Transition-Metal Dichalcogenides. *Chem. Rev.* **2015**, *115*, 11941-11966.

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The thesis author is the first author of the above papers.

3.1 Application of Layered Metal Chalcogenides: Hydrogen Evolution Reaction

One area of paramount importance in the field of sustainable energy generation¹ is using layered metal chalcogenides, especially the transition metal dichalcogenides (TMDs), as efficient and low-cost electrocatalysts for hydrogen evolution reaction (HER).²⁻⁹

To drive HER, a large energy input is necessary and thus, TMD electrocatalysts that are able to minimise HER overpotential are favoured. Besides HER overpotential, Tafel slope (b) is another yardstick to elucidate the efficiency of HER.¹⁰ Tafel slopes represent the increase in overpotential required to bring forth an increment in current density by one order of magnitude. By this definition, smaller Tafel slopes are preferred in a prospective HER electrocatalyst.

Under acidic conditions, the HER process occurring on the catalyst surface involves two main steps: adsorption of the proton and the release of the hydrogen molecule, and may be limited by any of the following steps:¹¹

Adsorption step (Volmer reaction): $\text{H}_3\text{O}^+ + \text{e}^- \rightarrow \text{H}_{\text{ads}} + \text{H}_2\text{O}$, $b \approx 120 \text{ mV dec}^{-1}$

Desorption step (Heyrovsky reaction): $\text{H}_{\text{ads}} + \text{H}_3\text{O}^+ + \text{e}^- \rightarrow \text{H}_2 + \text{H}_2\text{O}$, $b \approx 40 \text{ mV dec}^{-1}$

Desorption step (Tafel reaction): $\text{H}_{\text{ads}} + \text{H}_{\text{ads}} \rightarrow \text{H}_2$, $b \approx 30 \text{ mV dec}^{-1}$

Using density functional theory (DFT) calculations, several reports have demonstrated that the exchange current density of material for hydrogen evolution is correlated to the Gibbs free energy of the adsorbed H (ΔG_{H}) such that ΔG_{H} is an indicator of the electrocatalytic activity of the material.¹²⁻¹⁵ This is expressed in a ‘volcano’ relationship in that quantitatively depicts the Sabatier principle where the interaction between the catalyst and the intermediates are “just right”. At the optimum or thermoneutral value ($\Delta G_{\text{H}} \approx 0$), the hydrogen adsorption to the surface is neither extremely weak nor strong. Strong adsorption of hydrogen on the surface impedes desorption of molecular hydrogen

from the surface while the weak adsorption of hydrogen stalls the proton transfer process during adsorption. The state-of-the-art Pt catalyst, which requires negligible overpotentials to achieve a high rate of HER,¹⁶ exists near the top of the 'volcano' plot with ΔG_H approaching zero. It follows a general rule that materials showing ΔG_H closer to the thermoneutral value manifest higher HER activity.

HER electrocatalysis is a surface-dependent process.¹⁷ Thus, understanding the underlying electrochemistry of layered metal chalcogenides is key towards unravelling their properties. Recognising crucial factors and existing strategies that enhance the catalytic properties of the layered metal chalcogenides are fundamental towards rational development of layered metal chalcogenides as HER electrocatalysts.

3.2 Electrochemistry of Layered Metal Chalcogenides

Despite the proliferation of layered metal chalcogenide research in a multitude of electrochemical applications for sensing, energy storage and conversion, the irony is that current understanding of their inherent electrochemistry is inadequate. Knowledge on the inherent electrochemistry of these layered materials is indispensable because the materials may experience chemical or structural alterations during operational use. Inadvertently, their efficiency in electrochemical devices may be affected. In electrochemical sensing and electrocatalysis, inherent electrochemistry describes the innate redox behaviour of the electrode material when an electrochemical potential is applied.¹⁸

The inherent electrochemistry of TMDs is governed by the binary elemental constituents; the transition metal and the chalcogen, and the formation of inevitable surface oxides. Chorkendorff *et al.* first reported the inherent electrochemical behaviour

of MoS₂ performed in conditions employed for HER catalysis. Inherent oxidation of MoS₂ was recorded a maximum at 0.98 V vs. NHE (Figure 3.1).¹⁹ Subsequent scan showed a diminished anodic peak and a decline in HER activity which points to an irreversible oxidation. The broad anodic peak was correlated to the oxidation of the MoS₂ edge and the basal planes at 0.7 and 0.98 V vs. NHE due to a separate observation that edges were more susceptible towards corrosion than basal planes of bulk MoS₂.²⁰ XPS studies disclose alterations to the surface composition upon oxidation wherein MoS₂ oxidized to yield MoO₃, SO₄²⁻ and S₂²⁻ species. In the same study, similar observations were also noted for WS₂.¹⁹ Electro-reduction of MoS₂ was also found to be irreversible with a peak at -0.71 V vs. Ag/AgCl in aqueous-based electrolyte whereas re-oxidation was possible *ca.* 1.87 V in an organic electrolyte of acetonitrile and tetrabutylammonium tetrafluoroborate.²¹

Figure 3.1 Cyclic voltammograms of a) MoS₂ and b) WS₂ nanoparticles recorded relative to the NHE in experimental conditions of 0.5 M H₂SO₄ saturated with N₂ at scan rate of 2 mV s⁻¹. Reproduced from Reference [19].

Chemical exfoliation of Group 6 TMDs *via* organolithium reagents increases the current intensity of the inherent electrochemical signals resulting from a larger specific surface area when cleaved into layers. MoS₂ and MoSe₂ exfoliated with n-BuLi and PhLi

showcase redox signals of significantly higher current than the bulk.^{18, 22, 23} Similarly, n-BuLi- and sodium naphthalenide- exfoliated MoTe₂ and WTe₂ present amplified peak currents than before.²⁴ On the contrary, peak intensities of n-BuLi-exfoliated WS₂ and WSe₂ are relatively unchanged from the bulk.^{22, 23} The disparity in current intensity between TMDs is rationalised by passivated surfaces. Passivation inactivates the electrochemistry of the TMD where the tungsten dichalcogenides are more prone to oxidation than the molybdenum dichalcogenides.^{20, 25} Severe passivation of the bulk MoTe₂ and WTe₂ could have varied the trend. Among chalcogenides, ditellurides undergo oxidation fastest. The low inherent oxidation potential observed ~ 0.5 V substantiates this.²⁴

Figure 3.2 Inherent electrochemistry of Group 6 TMDs at neutral pH conditions. Cyclic voltammograms for a) bulk and exfoliated TMDs using b) sodium anthracenide and c) n-butyllithium. Reproduced from References [22-24].

Considering the thermodynamic stability of the TMDs from the potential-pH or Pourbiax diagrams,²⁶ preliminary insights into the participation of various elemental

species can be acquired. Under acidic conditions ($\text{pH} \approx 0.5$), TMDs such as MoS_2 and WS_2 are thermodynamically stable within a small potential window just above potentials before the onset of hydrogen evolution. However, the operating window usually fluctuates in practice. It is often assumed that the species predicted at highly oxidative or reductive potentials represent the most probable identities of the actual products. It remains difficult to pinpoint the species produced as a result of the varying levels of inherent redox reactions. Nevertheless, the intrinsic electrochemistry of TMDs restricts the operating potential window and poses a challenge to applications. As exemplified in MoS_2 , the working window is confined to a range between -0.6 and 0.7 V vs. Ag/AgCl .²⁷ The narrow operational region of MoS_2 is significantly smaller than carbon-based materials and inhibits the detection of nitroaromatic compounds, pesticides and mycotoxins.²⁷ Hence, awareness of the inherent electrochemical responses of TMDs may circumvent its limitations in proposed uses.

Being anisotropic, TMDs exhibit discernible electron transfer properties that arise from the edge and basal planes. Gerischer *et al.* investigated the mechanism of electron transfer at these two orthogonal planes of MoS_2 using $[\text{Fe}(\text{CN})_6]^{3-/4-}$, $\text{Fe}^{3+/2+}$ and $\text{Cu}^{2+/+}$ redox probes and established a correlation to the electronic structure of MoS_2 .²⁸ The HET rate of MoS_2 edge plane surpasses that of the basal surface. This phenomenon is attributed to the substantial overlap of the d_{xy} and $d_{x^2-y^2}$ orbitals of the Mo conduction band and the orbitals of the redox probes. Concurring with this study by Gerischer *et al.*, Pumera and co-workers ascertained that the edge plane of macroscopic MoS_2 crystals demonstrates fast HET rate where computed $k_{\text{obs}}^0 = 4.96 \times 10^{-5} \text{ cm s}^{-1}$ for $[\text{Fe}(\text{CN})_6]^{3-/4-}$ and $1.1 \times 10^{-3} \text{ cm s}^{-1}$ for $[\text{Ru}(\text{NH}_3)_6]^{3+/2+}$ redox probes.²⁹ In contrast, the pristine basal plane

showed sluggish HET rates approximating zero for both redox probes. Although the HET property of graphene is independent of the number of layers, exfoliation of the bulk TMD may either augment or worsen the HET rates towards $[\text{Fe}(\text{CN})_6]^{3-/4-}$. Compared to the respective bulk counterparts, faster HET rates were observed for exfoliated MoSe_2 and WS_2 across conventional organolithium reagents and aromatic intercalants (phenyllithium, sodium naphthalenide and sodium anthracenide); yet exfoliated MoS_2 and WSe_2 showed mixed responses –faster in some cases and slower in others- depending on the type of intercalant.^{22, 23}

Electrochemical treatment, elicits structural and electronic modifications to the material, and is a means to tailor the HET rates of TMDs. Zhang and co-workers prepared exfoliated MoS_2 nanosheets from the bulk natural MoS_2 by electrochemical Li intercalation and noted that an electro-reduction of the exfoliated MoS_2 nanosheets conferred improved conductivity to the material with faster HET rates for $[\text{Fe}(\text{CN})_6]^{3-/4-}$ and $[\text{Ru}(\text{NH}_3)_6]^{3+/2+}$ redox probes than before treatment.²¹ Furthermore, the same electrode platform was able to distinguish between oxidation signals of ascorbic acid, dopamine and uric acid compared to the bare glassy carbon electrode. Pumera and co-workers found that bulk and exfoliated MoS_2 also showed higher HET rates towards $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox couple upon a preliminary reductive treatment where the rate increment is more pronounced for the latter. A further step was taken to show that a preliminary oxidative treatment, however, deteriorated the HET rates of both bulk and exfoliated MoS_2 .³⁰ Density functional theory (DFT) calculations justify electron doping during electro-reduction to be the chief factor stabilizing the 1T-phase that improves the electron transfer and catalytic properties for hydrogen evolution.

Figure 3.3 Cyclic voltammograms of a) bulk MoS₂ and b) exfoliated MoS₂ towards 5 mM [Fe(CN)₆]^{4-/3-} redox probe before and after electrochemical treatments. Reproduced from Reference [30].

3.3 Factors Influencing Electrochemical Hydrogen Evolution Reaction of Layered Metal Chalcogenides

Surveying the literature on layered metal chalcogenides as electrocatalysts reveals a spate of studies exploring factors that govern their electrocatalytic behaviour. Chief among these factors that influence the HER performance of TMDs are the active sites, the intrinsic activity and the conductivity.

Earlier studies have suggested the HER active sites at TMDs occur at the edges. In 2005, Hinnemann *et al.* used the DFT calculations to show that the edges of MoS₂ are the active sites by using the nitrogenase model as an illustration.³¹ The sulfur edges of MoS₂ resembled that of the active sites of nitrogenase model, such that the sulfur edge is coordinated to the metal atoms. Similar to Pt and hydrogenase, the ΔG_H of these sulfur edges of MoS₂ approaches that of thermoneutral (Figure 3.4). In a separate study, Jaramillo and co-workers investigated the exchange current density dependence on the presence of edges and basal planes of MoS₂ for nanoparticles.³² A direct linear

dependence of exchange current density on the length of the active sites was observed while there was no correlation between the exchange current density and surface area of MoS₂ (Figure 3.4). Despite the experimental evidence of the HER active sites to be the edge planes of TMDs, the abovementioned studies measured the HER activities in the presence of both edge and basal planes and does not rule out the possibility that the basal plane does not participate in the HER catalysis. Therefore, further experimental evidence of the HER active site of TMDs is required and can be supplemented with more detailed investigations examining specific aspects that influence the HER catalytic activity of TMDs, as discussed below.

Figure 3.4 Comparisons of HER parameters between MoS₂ and various metallic and biological catalysts, as well as between the two plane orientations of MoS₂. a) Volcano curve of exchange current density plotted against DFT-calculated Gibbs free energy of adsorbed atomic hydrogen for nanoparticulate MoS₂ and the pure metals. Reproduced from Reference [32]. b) DFT-calculated free energy diagram for HER. Reproduced from

Reference [31]. Exchange current density plotted against c) MoS₂ area coverage and d) MoS₂ edge length. Reproduced from Reference [32].

Deeper insights into the HER performance of TMDs are gained by examining their intrinsic catalytic activity. The intrinsic activity of the TMDs towards HER is determined in terms of ΔG_H and the coverage of H (θ_H) at each metal or chalcogen edge, both of which are characteristic to the type of TMD. Since the first step of HER involves hydrogen binding to the catalyst surface, ΔG_H is a suitable descriptor for the rate of reaction. As mentioned above, optimal ΔG_H occurs at the thermoneutral value of 0 eV,^{33, 34} where the binding is neither weak nor strong. The other parameter θ_H is defined as the fraction of a monolayer that is HER active. Specific to the TMDs, θ_H is the fraction of chalcogen atoms on the edge or basal plane that enable hydrogen binding. Performing DFT calculations, Tsai *et al.* delved into the intrinsic catalytic activity of the TMDs.³⁵ Illustrated in Figure 3.5, the ΔG_H for the basal planes are *ca.* 2 eV across TMDs, which indicate that the basal plane is inert regardless the type of transition metal or chalcogen. All edges are noted to have ΔG_H close to zero except for the W-edge in WSe₂ and S-edge in MoS₂. The W-edge in WSe₂ binds weakly to hydrogen which limits the adsorption step (Volmer process) while the S-edge of MoS₂ binds too strongly to hydrogen which limits the desorption step (Heyrovsky or Tafel processes). The primary active site for MoS₂ is the Mo-edge; for WS₂ and MoSe₂, both the metal and chalcogen edges are active; for WSe₂, only the Se-edge is active. Among the four TMDs, MoSe₂ is predicted to be the most active catalyst, followed by WS₂ because they possess most thermoneutral energy at both edges and then MoS₂ and WSe₂. This is consistent with the experimental trends obtained from HER studies performed on chemical and liquid exfoliated TMDs.^{36, 37}

Figure 3.5 Structures and hydrogen adsorption free energies for MoS₂, WS₂, MoSe₂ and WSe₂. The most stable edge configurations are as shown. Reproduced from Reference [35].

The conductivity of the TMDs also plays a vital role in their HER efficiency. This arises from the chemical nature of the TMD when existing in various polymorphs,³⁸ with 2H- and 1T-phases as the most frequently encountered, and also from the electrical transport between the active site and the electrode.

Ion intercalation is a technique that alters the TMD structure from bulk, semiconducting 2H-phase to exfoliated, metallic 1T-phase which then produces promising catalysts with low overpotentials for HER. Lukowski *et al.* first made headlines by demonstrating the enhanced HER efficiency of MoS₂ and WS₂ due to the successful 2H→1T conversion by Li intercalation (Figure 3.6).^{39, 40} During intercalation, the electron transfer from organic anion to the TMD destabilises the 2H-phase, and converts into an octahedral 1T-structure. Both 1T-phase MoS₂ and WS₂ nanosheets exhibited stellar HER performance with overpotentials of -0.19 and -0.14 V and low Tafel slopes of 43 and 70 mV dec⁻¹ respectively.^{39, 40} Moreover, the charge-transfer resistance of the 1T-phase MoS₂ and WS₂ nanosheets are also significantly smaller compared to their respective 2H-phase

structure.^{39, 40} Being structurally different, 2H- and 1T- phases demonstrate dissimilar electrocatalytic activities. It has been verified in a comparative study that the 1T-phase MoS₂ consistently outperforms the 2H-phase samples regardless of the surface structures.⁴¹ The provenance of the electrocatalytic response of 1T-phase lies in the intrinsic conductivity and is unaffected by the number of edge sites antithesis of the edge-dependent 2H-phase.⁴²

Apart from the chemical nature of the TMD, the supporting platform for electrical transport is another important aspect of conductivity that influences HER of TMDs. Various TMD catalyst supports, the majority with MoS₂, such as Au,^{32, 43} activated carbon,³¹ carbon paper,¹⁹ graphite,⁴⁴ carbon nanotubes^{45, 46} and graphene-based materials⁴⁷⁻⁵³ have been experimented with. Amongst them, graphene-based materials have garnered much success in achieving remarkable HER catalysis, postulated to be associated with the large surface area, electrical and chemical coupling effect and conductivity of graphene. In one example, Li *et al.*⁵¹ synthesized MoS₂ on reduced graphene oxide (rGO) via a solvothermal reaction involving (NH₄)₂MoS₄ and N₂H₄ in GO to obtain a MoS₂/rGO hybrid endowed with outstanding catalytic activity (Figure 3.6). The resulting hybrid exhibited selective growth of MoS₂ nanoparticles that were well-dispersed on GO because GO prevented aggregation of MoS₂ nanoparticles. In doing so, the homogenous dispersion of MoS₂ on GO engendered numerous accessible sites for HER. Furthermore, electrical coupling to the graphene sheets also provided a conductive network to facilitate electron transfer from MoS₂ to the electrode. Hence, abundant catalytic sites and the conductive underlying graphene-based catalyst support system participate in conferring the MoS₂/rGO hybrid with excellent HER performance, having a low overpotential of 0.1 V and Tafel slope of 41

mV/dec. Likewise, a WS₂/rGO synthesized using hydrothermal reaction in a one-pot process by Shin and co-workers also showed laudable performance.⁵² Upon annealing, WS₂/rGO hybrid had a Tafel slope of 58 mV/dec and faster charge-transfer confirmed by electrochemical impedance studies. Interconnected rGO network provides efficient electrical contact between the WS₂ catalyst and the electrode that promote HER kinetics.

Figure 3.6 a) Left: Structure of 2H- and 1T- MoS₂. Centre: Polarization curves of 2H- and 1T- MoS₂, shown in the inset are their Tafel slopes. Right: Nyquist plots of 2H- and 1T- MoS₂. Reproduced from Reference [40]. b) Left: Solvothermal synthesis to obtain MoS₂/rGO hybrid. Right: Polarization curves of the MoS₂/rGO hybrid and control measurements (MoS₂ nanoparticles and rGO). Pt was included as a yardstick to assess performance of the catalyst. Reproduced from Reference [51].

3.4 Strategies to Enhance Hydrogen Evolution Performance of Layered Metal Chalcogenides

Current strategies to activate the TMDs for HER act upon the three factors considered above and attempt to: increase the number of active sites; enhance the intrinsic activity

of the TMD; and improve the conductivity between active sites and the catalyst substrate.

The first strategy towards improving the electrocatalytic activity of TMDs is to increase the amount of active sites. Increasing the number of active sites can be achieved through maximizing exposure of the edges or inducing defects in the TMDs.⁵⁴⁻⁶¹ Jaramillo and coworkers created a highly ordered double-gyroid MoS₂ bicontinuous network,⁵⁸ first by electrodepositing Mo onto a silica template and subsequently, sulfidizing with H₂S. This double-gyroid MoS₂ structure exhibited a high surface curvature preferentially exposing a significant portion edge sites (Figure 3.7). In doing so, this catalyst showed excellent catalytic behavior as manifested in low onset potentials of 0.15 V to 0.2 V (vs. RHE) and Tafel slope of 50 mV dec⁻¹. Cui *et al.* developed stable MoS₂ and MoSe₂ films with vertically aligned layers so that the edges were best exposed on the surface.⁵⁶ Despite their considerably large Tafel slopes ranging from 105–120 mV dec⁻¹, these edge-terminated films were found to have favorable exchange current densities in HER of 2.2×10^{-6} A cm⁻² and 2.0×10^{-6} A cm⁻² for MoS₂ and MoSe₂ respectively. In another example, the number of active sites can be increased by introducing defects to the basal plane, which is otherwise inert to HER. Xie *et al.* engineered a defect-rich MoS₂ structure by varying precursor concentration and thiourea amounts.⁵⁷ During the fabrication process of defect-rich MoS₂ nanosheets, thiourea was added in excess because adsorption of thiourea molecules on the surface led to partial inhibition of crystal growth, a defective structure ensued (Figure 3.7). The defect-rich MoS₂ nanosheets exposed additional active edge sites which were the defect-induced cracks on the basal plane, eventually engendering a high density of active sites at 1.8×10^{-3} mol g⁻¹. As anticipated, the exceptional HER performance of these defect-rich MoS₂ nanosheets was noted with low onset potential at

0.12 V and a Tafel slope of 50 mV dec⁻¹.

Figure 3.7 a) Synthesis procedure and structural model for mesoporous MoS₂ with a double-gyroid (DG) morphology. Reproduced from Reference [58]. b) Left: Synthesis of defect-free and defect-rich MoS₂ nanosheets. Right: SEM image of obtained defect-rich MoS₂ nanosheets. Reproduced from Reference [57].

Another activation strategy is to enhance the intrinsic catalytic activity of TMDs. This is exemplified by cobalt doping on the S-edge of MoS₂ and WS₂.¹⁹ As determined by computational studies, doping decreased the ΔG_H of the S-edge of both TMDs, from 0.18 to 0.1 eV in MoS₂ and 0.22 to 0.07 eV in WS₂. The lowered ΔG_H towards thermoneutral value correlates to enhanced intrinsic catalytic activity of the edges for HER. It has also been experimentally confirmed that both Co-doped TMDs exhibited better HER

performance than its undoped counterpart. DFT calculations revealed that 14 metal-doped MoS₂ structures have ΔG_H closer to thermoneutral than the S-edge as marked in the gray bands in Figure 3.8.⁶² Of these, six metal dopants namely Ru, Rh, Co, Fe, Mn and Ta exhibited notable improvements in ΔG_H toward the thermoneutral value, even prevailing over the HER active Mo-edge. At present, only a few of them such as Co, Fe and Ni had been experimentally tested to show improved HER performance, hence verifying the computed trend.^{19, 63-66} By a spontaneous interfacial redox technique to introduce low amounts of Pd atoms into MoS₂, the basal plane of MoS₂ becomes activated. The Pd-substituted MoS₂ demonstrated favourable ΔG_H of -0.02 eV at sulfur sites adjacent to the Pd that contribute to higher intrinsic activity towards HER.⁶⁷ Besides doping, the HER performance of TMDs have been enhanced by strain engineering.^{7, 68-70} The conversion from 2H- to 1T- WS₂ due to distortion and strain in the 1T-phase prompted a study on the effect of strain on WS₂ towards HER.⁶⁸ The DFT study established that an optimal strain value of 2.7% on 1T-WS₂ resulted in ΔG_H that was close to thermoneutral (Figure 3.8) whereas no effect of strain on the catalytic activity of 2H-WS₂ was observed. Applying strain on distorted 1T-phase Group 6 TMDs builds up the density of states near the Fermi level and stabilises the adsorbed H at the basal plane and this may have implications on the HER of the TMDs.⁶⁹ Straining MoS₂ nanosheets also tunes the intrinsic activity of the basal plane whereby surface straining with S-vacancies further enhances the catalytic performance.⁷⁰

Figure 3.8 a) The hydrogen adsorption energies (ΔG_H) of each transition metal doped MoS₂.

Reproduced from Reference [62]. b) Effect of varying tensile strain of 1T-Ws₂ on its free energy. The free energy of H⁺+e⁻ is by definition equal to that of ½ H₂ at standard conditions (1 bar of H₂ and pH = 0 at 300 K). The free energies for the intermediate adsorbed state H^{*} are calculated by DFT and corrected for zero point energies and entropy. Reproduced from Reference [68].

The third activation approach seeks to improve the conductivity of TMDs and has been materialized by a myriad of methods including doping, electrochemical treatment and a catalyst support. Semimetallic V-doped MoS₂ with intralayer V-doping attained by a solid-state reaction showed enhanced conductivity than prior to doping (Figure 3.9).⁷¹ The electronic properties, such as the conductivity and charge carrier density, of V-doped MoS₂ hinge on the level of V-doping. Tweaking the ratio of V and Mo in the samples potentially garners stellar HER performance as evident in a reported Tafel slope of 69 mV dec⁻¹. Electrochemical pre-treatment of both exfoliated and bulk MoS₂ films using various applied electro-potentials has been performed to achieve controlled tuning of their electron transfer kinetics and catalytic properties (Figure 3.9).³⁰ Electrochemical oxidative treatment was found to weaken the catalytic activity of MoS₂ films regardless exfoliated

or bulk. Conversely, a reductive pre-treatment resulted in enhanced HER activity. DFT calculations attributed this phenomenon to the structural destabilization of 2H-MoS₂ by electron doping into its conduction band when reduced. In contrast, reduction stabilizes the 1T-phase due to crystal field effects.

Numerous research groups have been actively exploring suitable catalyst supports for TMDs to enhance their conductivity and hence, HER performance. In a strategy that extends from the use of 2D rGO, 3D mesoporous graphene foam (MGF) has been proposed by Liu and co-workers as a catalyst support to boost the conductivity of TMDs.⁷² This group fabricated MoS₂ nanoparticles embedded on MGFs, resulting in MoS₂/MGF hybrid with highly dispersed MoS₂ nanoparticles on MGFs without aggregation (Figure 3.9), akin to reported observations in MoS₂/rGO hybrid.⁵¹ A high specific surface area and conductive graphene skeleton enabled rapid electron transfer in MoS₂/MGF, resulting in remarkable catalytic HER performance with a Tafel slope of 42 mV dec⁻¹.

Figure 3.9 a) Polarization curves recorded on GC electrode of V-doped MoS₂ nanosheets and undoped MoS₂. b) Nyquist plot of the V-doped MoS₂ nanosheets, inset shows pure MoS₂. Reproduced from Reference [71]. c) Effect of applied pre-treatment potentials of bulk and exfoliated MoS₂ on HER overpotential at -10 mA cm⁻². Reproduced from Reference [30]. d) Nyquist plot of electrodes modified with MoS₂/MGF, physical mixture containing MoS₂ and MGF and pure MoS₂ particles. Reproduced from Reference [72].

Finally, a multipronged approach combining two or more strategies has also emerged in the field to activate TMDs for HER. Cui and co-workers combined two TMD activation strategies: increase number of active sites; and enhance its intrinsic activity, on vertically aligned MoSe₂ and WSe₂ nanofilms.⁷³ Edge-terminated MoSe₂ and WSe₂ were perpendicularly aligned on rough and curved carbon fiber surfaces to maximize the exposure of active edge sites for HER. Both were demonstrated to be efficient HER

electrocatalysts having low overpotentials of -0.25 V and -0.3 V (vs. RHE) and Tafel slopes of 60 mV dec⁻¹ and 77 mV dec⁻¹ for MoSe₂ and WSe₂ respectively. Ni atoms were doped onto edge-terminated MoSe₂ nanofilms and found to enhance the HER activity (exchange current density increased to 2.8×10^{-3} mA cm⁻²) in a manner resembling Co-doping, whereby the intrinsic activity of the edge sites improved.¹⁹ It has also been reported that enhanced HER catalysis of S-doped MoSe₂ nanosheets of low overpotential at 0.16 V and Tafel slope at 58 mV dec⁻¹ stemmed from the increase in active sites and higher electrical conductivity.⁷⁴ Incorporating S into MoSe₂ causes stacking faults and plane defects and leads to edge plane curvature and non-uniform spacing between planes. Exposed edge sites and unsaturated S and Se lining the nanodomain walls served as active sites for hydrogen adsorption. Additionally, the enhanced charge-transfer kinetics for HER was inferred from the impedance measurement wherein Nyquist plots exhibited substantially lower charge-transfer resistance for S-doped MoSe₂ than undoped MoSe₂. Towards more active sites and higher conductivity, Chen and co-workers fabricated a MoSe₂/graphene hybrid featuring perpendicularly oriented MoSe₂ nanosheets on 3D graphene network.⁷⁵ The perpendicular orientation of MoSe₂ nanosheets engendered a higher density of active sites and accessible edges. The graphene network connects the graphite disc and MoSe₂ and improves the electrical contact at the electrode interface, thereby reducing resistance and facilitating HER. Collective effects of active sites and good conductivity elicited an impressive HER performance of a low onset potential at -0.05 V. In another work, a component-controllable WS_{2(1-x)}Se_{2x} nanotubes on carbon fibers was endowed with desirable electrocatalytic properties for HER.⁷⁶ Defects and exposed edges in WS_{2(1-x)}Se_{2x} nanotubes produced during synthesis process are deemed as the active sites. Nyquist plots

revealed fast charge-transfer resistance in $\text{WS}_{2(1-x)}\text{Se}_{2x}$ nanotubes. Therefore, the synergistic effect of increased active sites and good conductivity of $\text{WS}_{2(1-x)}\text{Se}_{2x}$ nanotubes led to better HER behavior than WS_2 and WSe_2 nanotubes. In a similar fashion, a ternary $\text{WS}_{2(1-x)}\text{Se}_{2x}$ particles grown on a 3D NiSe_2 foam exhibited an low overpotential of 0.09 V and a Tafel slope of 46.7 mV dec⁻¹.⁷⁷ The superior HER performance of $\text{WS}_{2(1-x)}\text{Se}_{2x}/\text{NiSe}_2$ foam was attributed to the large surface area, high conductivity and exposure of active sites or edges.

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Chapter 4

Electrochemistry of Group 5 Transition Metal Dichalcogenides

4.1 *Introduction*

4.2 *Results and Discussion*

4.2.1 *Characterisation*

4.2.2 *Inherent Electrochemistry*

4.2.3 *Heterogeneous Electron Transfer Properties*

4.2.4 *Electrocatalytic Property for Hydrogen Evolution*

4.2.5 *Density Functional Theory Calculations*

4.3 *Conclusion*

4.4 *Experimental Methods*

4.5 *Supporting Information*

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The thesis author was the primary investigator and first author of the above paper.

4.1 Introduction

Research into layered transition metal dichalcogenides (TMDs) is gradually gaining ground within the scientific community. Taking on a general formula of MX_2 , a TMD consists of a transition metal from groups 4-10 and a chalcogen (S, Se, Te), respectively denoted as M and X. MoS_2 , the archetypal TMD belonging to Group 6, has basked in the glory of its achievements to date, with a long list of promising uses in catalysis,¹⁻⁵ sensing,⁶ energy storage and conversion.^{7, 8} The success of MoS_2 revved up interest in other classes of TMDs beyond the semiconducting Group 6. Most notably, the Group 5 TMDs (where M= V, Nb, Ta and X= S, Se and Te) which are of metallic conductivity have stolen the limelight. This class of materials is prized for their low-dimensional crystal structure and exhibits interesting electronic properties such as superconductivity, charge density waves and Mott transition.^{9, 10} However, unlike MoS_2 , the electrochemical and electrocatalytic properties of the Group 5 TMDs have not been well-established at the moment.

At present, assiduous studies centering on the layered TMDs seek to provide an efficient electrocatalyst for hydrogen evolution reaction (HER). Hydrogen gas is raved as a “clean” energy candidate. Hydrogen production involves the electrolysis of water either by electrical or solar means and emits environmental-friendly oxygen as its by-product.¹¹ However, the process is thermodynamically unfavourable and requires an efficient electrocatalyst to facilitate the reaction. Currently, platinum (Pt) has been identified as the most efficient electrocatalyst. The drawback of Pt lies in its low natural abundance which inflates the cost of hydrogen production. Hence, the fervent pursuit to explore efficient and earth-abundant alternatives in a bid to lower production cost.

MoS_2 is one of the rising stars in the quest for alternatives due to its competent HER

performance^{3, 4} and its high natural abundance. The edges of MoS₂ are found to be the catalytic sites for HER.^{12, 13} Other layered TMDs, mainly members from Group 6, have also been studied for their HER efficiency.¹⁴⁻¹⁶ Based on the recent spate of density functional theory calculations^{17, 18} performed on Group 5 TMDs, they are postulated to be favorable electrocatalysts. Having close to thermoneutral Gibbs free energy of the adsorbed hydrogen (ΔG_H), the basal planes of the VS₂, NbS₂ and TaS₂ are considered supplementary HER active sites to their edges.¹⁸ The theoretical finding is verified insofar as the stellar HER efficiency of VS₂ synthesized by chemical vapour deposition that was recently reported by Yuan *et al.*¹⁹

There is strong dependence of the electronic structure of the TMDs on the coordination of the transition metal centre and its d-electron count which confers Group 6 to be semiconducting while Group 5 are true metals.²⁰ Lukowski *et al.* demonstrated that the HER efficiency of semiconducting Group 6 TMDs, specifically for MoS₂ and WS₂, improved dramatically after undergoing a transition from semiconducting 2H- to metallic 1T- phase *via* chemical exfoliation.²¹ The enhanced HER performance of metallic 1T-MoS₂ and 1T-WS₂, compared to their respective semiconducting 2H-phases, have been attributed to the faster electrode kinetics and proliferation of the catalytic sites which includes the basal planes in the metallic 1T polymorph. Given that Group 5 TMDs are also largely metallic by nature regardless 1T or 2H, they may rival or even surpass the HER performance exhibited by the semiconducting Group 6 TMDs.

Although the metallic nature and favourable ΔG_H of the Group 5 TMDs are touted to be advantageous for HER, this has not been experimentally substantiated yet. Herein, we experimentally demonstrate the HER efficiency for the complete set of Group 5 TMDs in

the bulk form and determine the best electrocatalyst among them. The HER electrocatalytic trends of the Group 5 TMDs are also discussed along with our theoretical studies. Besides their electrocatalytic properties, we also investigate the electrochemistry of the Group 5 TMDs and evaluate their electrochemical charge-transfer property. Systematic characterisation of the materials *via* scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS) are also performed. The nine Group 5 TMDs that are explored in this paper include VS_2 , VSe_2 , VTe_2 , NbS_2 , NbSe_2 , NbTe_2 , TaS_2 , TaSe_2 and TaTe_2 .

4.2 Results and Discussion

4.2.1 Characterisation

Prior to any electroanalysis of the Group 5 transition metal dichalcogenides (TMDs), we perform material characterization using scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS).

Figure 4.1 Scanning electron micrographs of the various Group 5 TMDs at a magnification of 10 000 $\times$. Scale bars represent 1 μm .

We examine the surface morphologies of the Group 5 TMDs by SEM. It is deduced that all samples demonstrate structural features typical of bulk materials. VS_2 appears as predominantly large pieces, a stark contrast to VSe_2 and VTe_2 with layered appearance. Between VSe_2 and VTe_2 , VSe_2 sheets are accordion-like and exhibit wider interlayer separation. Niobium materials; NbS_2 , NbSe_2 and NbTe_2 , manifest in irregular shapes. Large pieces with structures vaguely resembling thick layers and uneven ridges are apparent for NbS_2 and NbTe_2 , respectively while NbSe_2 exist in smaller pieces. All tantalum materials; TaS_2 , TaSe_2 and TaTe_2 , are found to be layers in close stacking with definite edges and basal planes. The calculated chalcogen-to-metal ratios on the basis of EDS for all Group 5 TMDs fall within the range of 1.5 and 2.1, approximating the projected stoichiometric ratio of 2.0 (as recorded in Table 4.S1 and the corresponding spectra and maps are presented in Figure

4.S1 and 4.S2).

Using XPS, we analyse the surface elemental composition and bonding information of the Group 5 TMDs up to a maximum depth of 10 nm. This will be useful towards understanding their electrochemistry which involves electron transfer processes on the surface of the material. The high-resolution spectra of V 2p, Nb 3d and Ta 4f peaks are illustrated in Figure 4.2 and their estimated distributions of the numerous oxidation states are presented in Tables 4.S3A - 4.S3C.

Figure 4.2 High resolution X-ray photoelectron spectra of V 2p, Nb 3d and Ta 4f regions of the Group 5 TMDs. The deconvoluted peaks correspond to the numerous oxidation states of V, Nb and Ta.

Based on XPS deconvolution of the Group 5 transition metal into various oxidation states, all Group 5 TMDs, except NbS₂, adopt +4 (denoted as the red line) as the principal state, concurring with the expected oxidation state in a dichalcogenide. Due to the proximity of the O 1s and V 2p signals, O 1s occurring at *ca.* 530 eV is also included to yield

a relatively level baseline and a better XPS fitting for V 2p.²² Evident in VS₂, VSe₂, and VTe₂, the fitted peaks for V 2p exhibit V⁴⁺ as the dominant species with significant contribution originating from the V 2p_{3/2} and V 2p_{1/2} signals at *ca.* 516.0 eV and 523.4 eV. These signals lie close to the reported literature values of 515.6 eV and 523.0 eV.²³ Similarly, the tantalum dichalcogenides; TaS₂, TaSe₂ and TaTe₂ also show the primary Ta 4f signal is attributed to the Ta⁴⁺ species as manifested in Ta 4f_{7/2} and Ta 4f_{5/2} binding energies of *ca.* 26.3 eV and 28.2 eV, in close agreement with an early study by McGuire *et al.*²⁴ While the main Nb 3d_{5/2} and Nb 3d_{3/2} binding energies in NbSe₂ and NbTe₂ at *ca.* 206.2 eV and 209.0 eV are characteristic of the Nb⁴⁺ species,^{24, 25} the bulk of Nb 3d signals in NbS₂ are attributed to the presence of Nb²⁺ and Nb⁵⁺. Prominent peaks of Nb 3d_{5/2} binding energies in NbS₂ at *ca.* 203.7 eV and 207.7 eV correspond to the respective Nb(II) and Nb(V) states.²⁵

Apart from the anticipated +4 oxidation state of the Group 5 transition metal, it is noteworthy that a substantial contribution from the +5 oxidation state is also detected in all Group 5 TMDs. Given the considerable oxygen content observed in the survey XPS scans for all materials (Table 4.S5), transition metal oxides occurring in the +5 oxidation state may be present. In vanadium dichalcogenides, the presence of V⁵⁺ species is indicated by the V 2p_{3/2} signal at *ca.* 517.8 eV which nears the V 2p_{3/2} binding energy of V₂O₅.^{26, 27} As the pentavalent state is found to be most stable oxidation state for niobium and tantalum,²⁸ its occurrence is no wonder. The peaks at *ca.* 207.7 eV and 210.4 eV, most noticeably in NbS₂ and NbSe₂, coincide with the Nb 3d_{5/2} and Nb 3d_{3/2} binding energies of Nb₂O₅.²⁹ The Ta 4f_{7/2} and 4f_{5/2} binding energies of Ta⁵⁺ species at *ca.* 27.6 eV and 29.5 eV in TaS₂, TaSe₂ and TaTe₂ lies in good agreement with the literature values reported for Ta₂O₅.^{24, 30}

In addition to the main XPS signal in tantalum dichalcogenides belonging to the Ta(IV) state, a distinctive shoulder signal at *ca.* 22.1 eV exists across TaS₂, TaSe₂ and TaTe₂. This signal is attributed to the Ta 4f_{7/2} binding energy of Ta(I) state³¹ which may be speculated to be in the form of Ta₂O due to the high oxygen content detected (Table 4.S5).

XPS deconvolution of the respective chalcogen of the Group 5 TMDs is shown in Figure 4.S4. In theory, the oxidation state of S, Se and Te chalcogen in all Group 5 TMDs is -2. Analysis of S 2p core level indicates the existence of S²⁻ species in VS₂, NbS₂ and TaS₂, and the peaks at *ca.* 160.8 eV and 162.0 eV are respectively indexed to S 2p_{3/2} and S 2p_{1/2}, appearing as a merged signal in VS₂ and as distinct signals in NbS₂ and TaS₂. A sulfate signal is also visible at a binding energy of 168.0 eV in VS₂, suggesting trace presence of SO₄²⁻ in VS₂.³² Deconvolution of Se 3d core level reveals that Se(0) and Se(-II) species exist in VSe₂, NbSe₂ and TaSe₂, wherein the observed peak at *ca.* 55.2 eV is attributed to Se(0) while Se²⁻ accounts for the other peak at *ca.* 53.5 eV.³³ Clearly, Group 5 sulfides and selenides possess a reasonable portion existing in the oxidation state of +2, concurring with the expected. Conversely, fitted peaks for Te 3d in Group 5 tellurides show that the majority is attributed to the Te(IV) species, most likely occurring as TeO₂, with significant contribution stemming from its characteristic doublets at *ca.* 575.3 eV and 585.6 eV corresponding to Te 3d_{5/2} and 3d_{3/2} binding energies.^{34, 35} Besides TeO₂, TeO₃ was also suggested to be present on the surface of the Group 5 TMDs as noted from the contribution of the Te 3d_{5/2} binding energy at *ca.* 576.3 eV. The anticipated Te²⁻ was detected, in visibly lower amounts relative to TeO₂, with its distinctive paired peaks of Te 3d_{5/2} and 3d_{3/2} signals at *ca.* 571.6 and 582 eV.^{35, 36} It can be rationalized that substantial amount of Te oxides formed, including TeO₂ and TeO₃, because the tellurides are more liable towards surface oxidation than sulfides or

selenides.³⁷

Interestingly, the calculated chalcogen-to-metal ratios of the Group 5 TMDs based on XPS analysis (Table 4.S3A - 4.S3C) reveal that the surface composition of tellurides are chalcogen-enriched whereas the selenides and sulfides are chalcogen-deficient. VTe_2 has a XPS chalcogen-to-metal ratio of 2.0, coinciding with the projected ratio. Other tellurides, NbTe_2 and TaTe_2 , exhibit chalcogen-enriched surfaces with ratios beyond 2.0; at 3.0 and 2.6 respectively. On the contrary to the tellurides, both sulfides and selenides demonstrate a ratio lower than the expected 2.0. Specifically, VS_2 , NbS_2 and TaS_2 show ratios at 1.1, 1.6 and 1.1 respectively. The selenides; VSe_2 , NbSe_2 and TaSe_2 , have ratios at *ca.* 1.0. With the exception of VTe_2 , we notice that the chalcogen-to-metal ratio for all the Group 5 TMDs provided by XPS analysis deviate considerably from 2.0. Conversely, the ratio derived from EDS analysis lies close to the ideal 2.0 (Table 4.S2). This disparity between the chalcogen-to-metal ratio provided by EDS and XPS analyses likely arises from the differences in surface composition and the bulk composition of the Group 5 TMDs, with possible passivation by surface oxides.

4.2.2 Inherent Electrochemistry

Presently, there has been inadequate research directed towards exploring the inherent electrochemistry of VS_2 , VSe_2 , VTe_2 , NbS_2 , NbSe_2 , NbTe_2 , TaS_2 , TaSe_2 and TaTe_2 . Inherent electrochemistry has been understood to be the characteristic redox reaction of the material when an electrochemical potential is applied.³⁸ Due to the different intrinsic components of the Group 5 TMDs, in terms of the transition metal or chalcogen type, the various Group 5 TMD materials are expectedly dissimilar in electrochemical behavior. Determining the inherent electrochemistry of Group 5 TMDs is crucial when designing

electrochemical applications; in particular in electrochemical sensing, because the innate signals may limit its operational potential window.³⁹ It is also of interest to note the effect of transition metal or chalcogen type on the inherent electrochemistry. With these ends in view, we studied the inherent electrochemistry of all Group 5 TMDs and their voltammograms are presented in Figure 4.3. Scan towards the positive and negative potentials were performed in three consecutive cycles to provide electrochemical information and establish the nature of the redox processes occurring on the surface of Group 5 TMDs.

Figure 4.3 Cyclic voltammograms recording the inherent electrochemistry of the various Group 5 TMDs; namely, Group 5 sulfides during the scans to the positive potentials (a-c) and to the negative potentials (d-f), Group 5 selenides during the scans to positive potentials (g-i) and to the negative potentials (j-l) and the Group 5 tellurides during the scans to positive potentials (m-o) and to the negative potentials (p-r). Conditions: background electrolyte, PBS (50 mM), pH 7.0; scan rate, 100 mV s^{-1} ; scans begin at 0.0 V vs. Ag/AgCl. The arrows denote initial scan direction.

Due to the extensive oxide contribution on the surface of most Group 5 TMDs, cyclic voltammetry of the more predominant Group 5 oxides has been conducted including V_2O_5 , Nb_2O_5 and Ta_2O_5 (recorded in Figure 4.S5). Comparing the redox signals of the Group 5 TMDs with that of the respective oxides, we notice several signals that are coincident. These signals may shed light on the electrochemical process occurring on the material. Among all vanadium dichalcogenides, the scan towards negative potentials for VSe_2 exhibits two reduction signals at *ca.* -0.8 V and -1.4 V vs. Ag/AgCl (Figure 4.3j) matching the characteristic cathodic peaks in V_2O_5 (Figure 4.S5b). Performing cyclic voltammetric scans on compounds of V(V) oxidation state; V_2O_5 , NaVO_3 and Na_3VO_4 , Ryan *et al.* proposed that the two reduction peaks observed at 1.4 V and 0.5 V vs. Al/ AlCl_3 in V_2O_5 originate from two different kinds of V(V) species whereby each undergoes a single electron reduction process into the V(IV) species.⁴⁰ Similarly, we may infer that the inherent electrochemistry of VSe_2 involves two distinct types of V(V) species reducing to V(IV) species. Both VS_2 and VTe_2 show a cathodic signal at *ca.* -1.5 V vs. Ag/AgCl (Figure 4.3d, 4.3p) that likely involves the reduction of a single type of V(V) species into V(IV) species. There are few similarities between the inherent electrochemistry of niobium dichalcogenides and Nb_2O_5 except for NbTe_2 . Consistent with the cathodic signal noted in Nb_2O_5 (Figure 4.S5c, 4.S5d), NbTe_2 observes a reduction peak at *ca.* -0.6 V vs. Ag/AgCl (Figure 4.3n, 4.3q) that aligns with a previous study which reported on the one-electron reduction of Nb(V) to Nb(IV) species occurring at -0.11 V vs. Ni/ Ni^{2+} .⁴¹ Across tantalum dichalcogenides, the inherent electrochemistry of Ta_2O_5 is apparent. TaS_2 exhibits a cathodic peak *ca.* -0.5 V vs. Ag/AgCl (Figure 4.3f), coinciding with the standard reduction

potential of Ta_2O_5 as formerly reported in literature to be -0.75 V vs. SHE .⁴² The cyclic voltammograms obtained for Ta_2O_5 depicts a cathodic peak *ca.* $-0.6 \text{ V vs. Ag/AgCl}$ which is also relatively close to the reported values. The scan towards the negative potentials for TaSe_2 and towards the positive potentials for TaTe_2 , each possess a reduction signal at *ca.* $-0.6 \text{ V vs. Ag/AgCl}$ corresponding to the reduction of Ta_2O_5 as experimentally shown. Ta oxide formation occurs at approximately 0.3 V vs. SCE . In particular, scans towards the positive potentials of TaS_2 and TaTe_2 showcases an oxidation peak at *ca.* $0.3 \text{ V vs. Ag/AgCl}$ could possibly be due to Ta oxide formation.⁴³

Scrutinizing further, we observe that that the inherent electrochemistry of niobium dichalcogenides forge close resemblance to that of the tantalum dichalcogenides. Beginning with their sulfides, the scans to the positive potentials of NbS_2 and TaS_2 reveal a moderate peak at *ca.* $0.4 \text{ V vs. Ag/AgCl}$. This signal may correspond to the oxidation of respective transition metal in oxidation state +4 into +5. Literature has also shown that the oxidation of Nb(VI) to Nb(V) occurs at $-0.4 \text{ V vs. Al/Al}^{3+}$,⁴⁴ existing close to our experimental signal when converted to *vs. Ag/AgCl*. While NbSe_2 has two distinct anodic signals at *ca.* 0.5 V and $1.2 \text{ V vs. Ag/AgCl}$, TaSe_2 shows only a single anodic signal. Both NbSe_2 and TaSe_2 share the conspicuous signal at *ca.* $1.2 \text{ V vs. Ag/AgCl}$ of similar current intensity *ca.* $90 \mu\text{A}$. For TaSe_2 , the passivation of the surface with Ta_2O_5 is plausible and found to occur at potentials between 1.2 V and $2.0 \text{ V vs. Ag/AgCl}$.⁴⁵ The scans to the positive potentials of NbTe_2 and TaTe_2 are almost identical. A well-defined oxidation peak emerges at *ca.* $0.3 \text{ V vs. Ag/AgCl}$ followed by an inconspicuous reduction signal at *ca.* $-0.7 \text{ V vs. Ag/AgCl}$. Intriguingly, with subsequent scans in NbTe_2 and TaTe_2 , the oxidation peak at *ca.* $0.3 \text{ V vs. Ag/AgCl}$ also declines by the same magnitude. Despite the similarities between the

scans to the positive potentials, their corresponding scans to the negative potentials showcase distinguishing features. Scans towards the negative potentials for NbS₂ and NbSe₂ display a shoulder signal at *ca.* -0.8 V vs. Ag/AgCl that alludes to the reduction of Nb(V) to Nb(III) species *via* a two-electron process.^{46, 47} In TaS₂ and TaSe₂, the Ta₂O₅ reduction signal is visible in scans towards the negative potentials.

The inherent electrochemistry of tellurium is clearly exemplified in VTe₂, NbTe₂ and TaTe₂, given their unusually similar voltammetric profiles. All tellurides (VTe₂, NbTe₂ and TaTe₂) demonstrate anodic signals at *ca.* 0.3 V vs. Ag/AgCl in both scan directions which coincide with the oxidative stripping of Te.⁴⁸ Moreover, VTe₂, NbTe₂ and TaTe₂, each has a reduction signal at *ca.* -1.0 V vs. Ag/AgCl during their scan to the negative potentials. This reduction signal can be ascribed to Te reduction to soluble Te²⁻ species.⁴⁹ In subsequent scans, it is noted that this particular signal disappears and another reduction signal materializes at *ca.* -0.7 V vs. Ag/AgCl. However, *ca.* -0.7 V vs. Ag/AgCl is also present in the scans to positive potentials. Hence, the oxidative feature at *ca.* 0.3 V vs. Ag/AgCl is a prerequisite to the subsequent signal at *ca.* -0.7 V vs. Ag/AgCl in the scans towards negative potentials. Akin to the reduction signal at *ca.* -1.0 V vs. Ag/AgCl, this subsequent signal stems from the cathodic stripping of Te,⁴⁸ except occurring at a lower potential.

The inherent electrochemistry of the vanadium dichalcogenides has inadvertently unveiled that the oxidation potential increases from VTe₂ < VSe₂ < VS₂ in the order of the respective chalcogen within the group. In brief, VTe₂ exhibits an anodic signal at *ca.* 0.3 V vs. Ag/AgCl; and VSe₂, at *ca.* 0.8 V vs. Ag/AgCl; while VS₂ has two signals, at *ca.* 1.0 V and 1.4 V vs. Ag/AgCl. These signals result from the electrochemistry of the corresponding chalcogens on the basis of Pourbaix diagrams. At *ca.* 0.4 V vs. Ag/AgCl, the Te chalcogen in

VTe₂ existing in oxidation state of -2 may oxidize to form species in states of +4 and +6, such as TeO₂, HTeO₃⁻ and HTeO₄⁻.⁵⁰ For VSe₂, the Se chalcogen undergoes an oxidation from -2 to +4 or +6 states at *ca.* 0.8 V vs. Ag/AgCl to yield HSeO₃⁻, SeO₃²⁻ or SeO₄²⁻.⁵¹ At highly anodic potentials beyond *ca.* 1.0 V vs. Ag/AgCl, the S chalcogen in VS₂ may oxidize into thermodynamically stable species like HSO₄⁻ and SO₄²⁻.⁵² Furthermore, the phenomenon of escalating oxidation potentials from VTe₂ < VSe₂ < VS₂ concurs with the susceptibility of the chalcogen type towards oxidation. The tendency for oxidation amplifies down the chalcogen group: S < Se < Te, in which the tellurides succumb to surface corrosion most readily.³⁷

Judging from subsequent scans, we determine, the nature of most electrochemical processes associated with the characteristic oxidation and reductions of the Group 5 TMDs, to be largely chemically irreversible. As observed in Figure 4.3, majority of the unique redox signals in the initial scans become diminished in current intensity or vanished completely in subsequent scans. Anomalous to the general trend, the tellurides maintained current intensities of their reduction signal at *ca.* -0.7 V vs. Ag/AgCl and oxidation peak at *ca.* 0.3 V vs. Ag/AgCl in the following cycles. Such features are attributed to the reversible nature of Te(-II) oxidation as determined by Lingane *et al.*⁵³

All the Group 5 TMDs studied exhibit electrochemistry that may be intrinsic to their surface oxides in addition to their respective metal or chalcogen components. In particular, the inherent electrochemistry of the tellurium chalcogen is most accentuated in the voltammograms of all Group 5 tellurides.

4.2.3 Heterogeneous Electron Transfer Properties

The heterogeneous electron transfer (HET) rate of an electrode material is a useful performance indicator towards evaluating the suitability of that material in electrochemical applications. An intrinsically fast HET rate lowers the overpotential required for an electrochemical reaction, and hence deemed a desirable attribute of a prospective electrode material. The classical Nicholson approach correlates the peak-to-peak separation (ΔE) with the observed HET rate constant (k_{obs}^0), whereby smaller ΔE corresponds to faster HET rates. The surface-sensitive nature⁵⁴ of $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox probe will be beneficial when examining the HET rates of the Group 5 TMDs. The voltammetric profiles of $[\text{Fe}(\text{CN})_6]^{3-/4-}$ on the Group 5 TMDs are depicted in Figure 4.4 (with all ΔE summarized in a histogram in Figure 4.S6) and their k_{obs}^0 are recorded in Table 4.S6. It is also important to note that the depicted voltammograms and computed k_{obs}^0 values were extracted from the subsequent cycles. Due to strong interference by the inherent electrochemical signals of several Group 5 TMDs in the initial scan cycles within the potential window of -0.4 and 0.7 V vs. Ag/AgCl, the observations of $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox signals may be unreliable in the initial cycles and hence, data from subsequent scans were used instead.

Figure 4.4 Cyclic voltammograms of 5 mM [Fe(CN)₆]^{3-/4-} on a) Group 5 sulfides, c) Group 5 selenides and e) Group 5 tellurides. Peak separations for [Fe(CN)₆]^{3-/4-} redox probe on the surfaces of b) Group 5 sulfides, d) Group 5 selenides and f) Group 5 tellurides. Conditions: background electrolyte, KCl (0.1 M); scan rate, 100 mV s⁻¹; all measurements are performed relative to the Ag/AgCl reference electrode.

Among all Group 5 TMDs, TaS₂ demonstrates fastest HET with a calculated k_{obs}^0 of $3.4 \times 10^{-3} \text{ cm s}^{-1}$ that is markedly higher than the bare GC electrode. Besides this, the current intensity of the [Fe(CN)₆]^{3-/4-} redox peaks generated by TaS₂ is at least 10 μA higher than the rest of the Group 5 TMDs, despite also modified with the same amount of material on the electrode. Evidently, both rapid electron transfer and higher redox current signals endow TaS₂ with properties favored in a prospective electrode material for

electrochemical sensing. Corroborating with this, Zhang *et al.* has experimented with TaS₂ nanosheets as potential sensing platforms capable of selective and sensitive detection of DNA.⁵⁵

In contrast to TaS₂ as the best-performing Group 5 TMD in terms of HET, the Group 5 tellurides typically exhibit the slowest electron transfer rates compared to the selenides or sulfides. On average, VTe₂, NbTe₂ and TaTe₂ possess k_{obs}^0 in the region of $\sim 10^{-4} \text{ cm s}^{-1}$ which is an order of magnitude lower than TaS₂. Moreover, the HET rates of tellurides are found to be even slower than the unmodified GC electrode. One possible explanation for the slow HET rates of tellurides is ascribed to tellurium chalcogen being most liable to surface oxidation among the chalcogenides. Significant amounts of tellurium oxides have been detected in the XPS analysis of VTe₂, NbTe₂ and TaTe₂ (Figure 4.S4), noticeably arising from TeO₂ and TeO₃. The presence of surface oxides on the tellurides may experience electrostatic repulsion from the negatively charged [Fe(CN)₆]^{3-/4-} redox probes which hindered the electron transfer.

The Group 5 selenides have HET rates that are comparable to that of the GC electrode. The k_{obs}^0 values of VSe₂, NbSe₂ and TaSe₂ are $1.4 \times 10^{-3} \text{ cm s}^{-1}$, $2.7 \times 10^{-3} \text{ cm s}^{-1}$ and $1.50 \times 10^{-3} \text{ cm s}^{-1}$, respectively, nearing that of the GC electrode.

The HET trends specific to a metal type or chalcogen type are associated with TaS₂. Considering affixing the transition metal component – tantalum, the electron transfer rate declines down the chalcogen group such that TaS₂ > TaSe₂ > TaTe₂. Keeping a constant chalcogen type – sulfur, improves the HET rate down the transition metal group wherein VS₂ < NbS₂ < TaS₂. However, these trends are not observed for an unchanged niobium and vanadium metal type or a fixed selenium and tellurium chalcogen type.

4.2.4 Electrocatalytic Property for Hydrogen Evolution Reaction (HER)

The electrocatalytic ability of the TMDs towards hydrogen evolution reaction (HER) has been a prime focus in the majority of electrochemical applications involving TMDs. In recent years, the promising HER performance of MoS₂ triggered a massive search within the scientific community for other layered TMDs as sustainable electrocatalysts for HER. Theoretically, metallic TMDs may outperform semiconducting TMDs as HER electrocatalysts given that computational studies affirmed the active basal planes of Group 5 TMDs, which are by nature metallic, for HER against the inert basal planes of Group 6 TMDs, which are semiconductors, including MoS₂ and WS₂.^{17, 18} Fuelled by this, we investigate the HER electrocatalytic properties of Group 5 TMDs in bulk form to sieve out the best HER electrocatalyst. We also determine any metal or chalcogen dependence on their HER electrocatalytic property.

Linear sweep HER measurements have been performed for all Group 5 TMDs. Linear voltammograms are categorized according to the metal type in Figure 4.5 and by chalcogen type in Figure 4.S7 for a clear illustration of any transition metal- or chalcogen-dependence. As Pt/C has been recognized as the best HER electrocatalyst to date, we have included Pt/C in our experiments as a yardstick to assess the HER efficiency of the Group 5 TMDs. The polarization curve for the bare GC electrode is also shown for reference.

Figure 4.5 Linear sweep profiles of hydrogen evolution reaction (HER) on GC electrodes modified with a) VS₂, VSe₂ and VTe₂, c) NbS₂, NbSe₂ and NbTe₂ and e) TaS₂, TaSe₂ and TaTe₂. Tafel plots for HER corresponding to b) VS₂, VSe₂ and VTe₂, d) NbS₂, NbSe₂ and NbTe₂ and f) TaS₂, TaSe₂ and TaTe₂. Histograms summarize the averages of g) HER overpotential at current density of -10 mA cm^{-2} and h) Tafel slopes for all the materials. Conditions: background electrolyte, H₂SO₄ (0.5 M); scan rate, 2 mV s^{-1} .

A reasonable gauge of the electrocatalytic performance for HER of the Group 5 TMDs is by comparing their overpotentials at a current density of -10 mA cm^{-2} ,⁴ usually

corresponding to a tangible level of hydrogen production. Across all Group 5 TMDs, we observe that VTe_2 exhibits the lowest overpotential of approximately 0.5 V vs. RHE against most other Group 5 TMDs of overpotentials hovering in the range of 0.9 to 1.1 V vs. RHE. Further inspection of their overpotentials unveils a trend for the vanadium dichalcogenides such that the HER overpotentials decreases down chalcogen group, as exemplified by VS_2 at highest overpotential of 1.0 V, closely followed by VSe_2 at marginally below 1.0 V, and the lowest, VTe_2 at 0.5 V vs. RHE. However, such chalcogen-dependence of the HER overpotential of the Group 5 TMDs was not witnessed in niobium and tantalum dichalcogenides. All niobium dichalcogenides show comparable overpotentials whereby NbS_2 , NbSe_2 and NbTe_2 differed by less than 0.1 V from each other. Analogous to the niobium dichalcogenides, the overpotentials of tantalum dichalcogenides appear to be similar as noted in little deviation of TaS_2 , TaSe_2 and TaTe_2 from each other. In Figure 4.S7, the HER overpotentials of Group 5 tellurides manifest strong transition metal-dependence with increasing overpotential in the order of $\text{VTe}_2 < \text{NbTe}_2 < \text{TaTe}_2$. No transition metal-dependence was observed for the Group 5 sulfides or selenides. Group 5 sulfides exhibit largely overlapping curves which coincide at 1.0 V vs. RHE at -10 mA cm^{-2} . Likewise, HER overpotentials of Group 5 selenides exist between 0.9 to 1.0 V vs. RHE at -10 mA cm^{-2} .

Apart from the HER overpotential at -10 mA cm^{-2} , the Tafel slope is another parameter that evaluates the electrocatalytic ability for HER and in fact, more frequently employed to elucidate the electrochemical mechanism on the TMD material. Tafel slope is understood to be the increase in overpotential required to elicit an increment in current density by one order of magnitude. By this definition, smaller Tafel slopes are preferred in a prospective HER electrocatalyst. Tafel slopes determine the rate-determining step in

the HER process, providing insights into the reaction pathway undertaken by the TMD material. The main steps in the hydrogen evolution mechanism on TMD surfaces are adsorption and desorption,^{3, 56} as summarized below :

As predicted, the Tafel slope of the most electrocatalytic Pt/C is the lowest of all with a value of 36 mV/dec and is limited by the desorption step, in accordance with reported Tafel slope values for Pt/C in the region of 30 and 40 mV/dec.⁵⁷ Out of all Group 5 TMDs, VTe₂ shows the lowest Tafel slope of 55 mV/dec. Other vanadium dichalcogenides; VS₂ and VSe₂, are respectively found to have Tafel slopes of 159 mV/dec and 112 mV/dec. Both Tafel slopes of VS₂ and VSe₂ correspond to adsorption as the slow step. Closer scrutiny of the vanadium dichalcogenides discloses that the Tafel slope lowers down the chalcogen group such that VS₂ > VSe₂ > VTe₂. Down the transition metal group, the Tafel slopes of Group 5 tellurides (Figure 4.S7) also increase sequentially from VTe₂ (55 mV/dec) to NbTe₂ (163 mV/dec) and to TaTe₂ with the largest Tafel value of 213 mV/dec. The niobium dichalcogenides are likely limited by the Volmer adsorption mechanism as demonstrated by Tafel slopes nearing 120 mV/dec wherein Tafel slopes of NbSe₂ and NbTe₂ are 133 mV/dec and 163 mV/dec correspondingly. There is a general observation that tantalum dichalcogenides show unusually high Tafel slope values of beyond 170 mV/dec.

We observe HER pre-waves in a few Group 5 TMDs such as VSe₂, NbS₂, NbSe₂ and NbTe₂. We draw similarities with their presence to the inherent electrochemistry discussed in the earlier section. The pre-wave occurring at *ca.* -0.7 V vs. RHE in VSe₂ when converted to vs. Ag/AgCl approximates the reduction of VSe₂ noted in Figure 4.3j stemming from the surface oxides like V₂O₅. For all niobium dichalcogenides, the HER pre-wave distinctly emerges at *ca.* -0.6 V vs. RHE. The pre-wave resembles the shoulder signal at *ca.* -0.8 V vs. Ag/AgCl in the scans towards negative directions for NbS₂ and NbSe₂ due to the reduction of Nb(V) to Nb(III) species.^{46, 47}

Subsequent LSV scans of VSe₂, NbS₂, NbSe₂ and NbTe₂ are recorded in Figure 4.S8 to investigate the presence of the HER pre-waves on their HER behaviour. In successive scans, these HER pre-waves disappeared or undermined in intensity. This observation parallels their inherent electrochemical profiles in Figure 4.3 whereby the intrinsic reduction peaks are absent or waned in subsequent scans. The absence of HER pre-waves of VSe₂ and NbS₂ in the second scan confirms the removal of surface passivation. Unlike VSe₂ and NbS₂, HER pre-waves remain noticeable in the second scans of NbSe₂ and NbTe₂ but at a lower intensity. Apart from the role of intrinsic electrochemical reduction of NbSe₂ and NbTe₂ in engendering the HER pre-waves, another reason may boil down to the different catalytic sites coexisting on the NbSe₂ and NbTe₂. Different types of active sites on the surface contribute to varying HER activities.

Most significantly, HER pre-waves have negligible effects on the electrocatalytic efficiencies of VSe₂, NbS₂, NbSe₂ and NbTe₂ as their HER behaviour in the subsequent scans approximates the initial HER measurement (Figure 4.S8). Using second scans of VSe₂,

NbS₂, NbSe₂ and NbTe₂ for comparisons (Figure 4.S9 and 4.S10) led to identical HER trends as the initial scans. Even with the elimination of the inherent reduction peak in VSe₂, the HER efficiencies of vanadium dichalcogenides continue to show chalcogen-dependence. Furthermore, the transition metal-dependence of Group 5 tellurides towards their HER properties appear unaffected by the diminished HER pre-wave of NbTe₂ in the subsequent scan.

The presence of pre-waves may pose a challenge towards determining the onset potential for HER process for the TMDs which is usually taken at low current densities of $\sim 0.1 \text{ mA cm}^{-2}$. Pre-waves mask the onset of HER due to the dominance of the inherent electrochemical reduction in that potential window. The onset potential is unsuitable to use as a parameter to assess the HER performance under such circumstances. Therefore, to prevent a misconstrued assessment of the HER efficiency of the Group 5 TMDs arising from their inherent electrochemistry, it is essential to investigate their HER efficiency at a higher current density, as we have demonstrated here.

In view of both performance indicators by HER overpotential at -10 mA cm^{-2} and Tafel slope analyses, the highest HER electrocatalytic efficiencies within Group 5 TMDs are unanimously observed in VTe₂, evident in its lowest overpotential and Tafel slope values of 0.5 V vs. RHE and 55 mV/dec.

The catalytic stability of the Group 5 TMDs was also studied in acidic conditions. All materials were subject to 100 cyclic voltammetry (CV) cycles in acid at their respective HER onset potential window whereby the current density is at least -0.1 mA cm^{-1} . The HER polarisation curves before and after the 100 CVs are recorded in Figure 4.S11. It is broadly

noted that all Group 5 TMDs are relatively catalytic stable in acid with no more than 0.1 V deviation between their HER overpotentials at -10 mA cm^{-2} before and after 100 CVs. While a mildly deteriorated HER performance was noted for Group 5 sulfides and tellurides, the Group 5 selenides show slightly improved HER behaviour requiring lower overpotentials. During the CV cycles in acidic medium, adsorbed species are likely removed or the active sites may become chemically changed. These factors contribute to the minor differences in HER behaviour after performing CV cycles in acid. To a large extent, the Group 5 TMDs demonstrate robust catalytic stability in acid with negligible shifts in their HER overpotentials at -10 mA cm^{-2} .

4.2.5 Density Functional Theory Calculations

We calculate the differential adsorption enthalpies of hydrogen to tantalum and niobium dichalcogenides. According to calculated results, the basal planes could become active at higher overpotential, because their adsorption enthalpies approach that of thermoneutral. The basal plane of TaS_2 and TaSe_2 has ΔG of 0.24 eV and 0.61 eV, respectively. This is in striking contrast to MoS_2 , in which the hydrogen adsorption onto basal plane is highly endothermic and the active sites for HER were experimentally determined to be at the edges rather than at the basal planes.¹² Nevertheless, the edge sites provide more favourable adsorption enthalpies than their basal planes for both TaS_2 and TaSe_2 . TaS_2 has ΔG of -0.09 eV at 50 % hydrogen coverage, while TaSe_2 has ΔG of 0.01 eV at 25 % hydrogen coverage. Our ΔG values and optimal coverage agree well to recent DFT study by Tsai *et al.*¹⁸ Both ΔG values lie close to zero, which is an ideal value according to the Sabatier's principle. Niobium dichalcogenides show character of adsorption very similar to their tantalum counterparts. Figure 4.6 reveals that the hydrogen atom adheres

more strongly to the edge of Ta and Nb disulfide than diselenide over the whole coverage range, while the chemical nature of the metal atom seems to be of minor influence. The trend of the increasing adsorption enthalpy as one descends through the group of dichalcogenides has been recently observed for platinum dichalcogenides.⁵⁸ The explanation of the trend lies mainly in the size of chalcogenide atom. As the size of chalcogenide atom increases, the bonding orbitals become larger and more diffused and, consequently, the bond between the atom and the hydrogen weakens. Figure 6 also shows that ΔG strongly increases at high hydrogen coverage, because adsorbed hydrogens repel each other.

Figure 4.6 The differential adsorption enthalpy ΔG of hydrogen to the edge of 2H-TaS₂, TaSe₂, NbS₂ and NbSe₂ calculated as a function of the edge coverage (upper panel). Lower panel shows ΔG of TaS₂ calculated on two edge models (nanostripe four and six units long). Crosses show ΔG for the hydrogen adsorption directly onto the Ta atom at the edge.

Therefore, both previous computational screening¹⁸ and our calculations suggest based on favourable ΔG that both TaS₂ and TaSe₂ shall be good HER catalysts, whereas our experimental results show only modest performance of them. This discord indicates there are other critical factors toward HER performance than ΔG only. Indeed, recent study by Huang *et al.*⁵⁹ of reaction mechanism of HER on MoS₂ found that ΔG did not play a direct role in determining the reaction barrier. Huang *et al.* revealed that the Volmer-Tafel reaction took place between hydrogens on adjacent Mo and S atoms. The hydrogen was adsorbed on the sulphur first as suggested by favourable ΔG , but then migrated to the molybdenum atom and finally reacted with a proton to form H₂. The hydrogen adsorbed at the Mo atom was therefore an important intermediate in the process. In this spirit, we calculate ΔG for hydrogen adsorption on the Ta atom at edge. The Ta-H intermediate seems however to be unlikely, because respective ΔG values are highly positive (Figure 4.6). The lowest ΔG of 0.68 eV is obtained for the 100 % coverage, but even at that coverage the adsorption onto sulphur atom is more favourable. Therefore, too high energy of the Ta-H intermediate may force hydrogen evolution to proceed via less effective mechanism and limit overall HER performance of tantalum dichalcogenides.

Nevertheless, there are further factors that may influence the HER efficiency of TMDs, such as the conductivity of the TMD, and number of active sites. In order to inspect the latter factor, we calculate ΔG using a larger edge model, which comprises six Ta atoms along the edge and offers a broader range of hydrogen coverage (Figure 4.6, lower panel). Although ΔG values are essentially close to those calculated for four atoms long edge, it becomes clear that the ΔG is close to thermoneutral for a narrow range around 50 % coverage only. A narrow range of effective hydrogen coverage may kinetically hamper

HER performance of the TaS₂. Furthermore, experimental results allude that the method of synthesis and number of the layers of the TMDs could have elicited electrocatalytic behaviour different than that expected from theory. Our as-synthesized bulk VS₂ exhibits large Tafel slope of 159 mV/dec and overpotential at 0.9 V vs. RHE which is strikingly dissimilar to the chemically vapor deposited VS₂.¹⁹ Yuan *et al.* reported that VS₂ nanosheets synthesized by chemical vapor deposition displayed impressive HER performance as manifested in its Tafel slope of 34 mV/dec rivalling that of Pt and a low HER overpotential of 68 mV vs. RHE at a current density of -10 mA cm⁻².¹⁹

Despite theoretical indications that the metallic Group 5 TMDs could outshine the semiconducting Group 6 TMDs as efficient electrocatalysts for HER, it has been experimentally shown to be otherwise. Among measured Group 5 dichalcogenides, only VTe₂ appears to be promising as the HER electrocatalyst. However, it is crucial to highlight that theoretical calculations consider firstly an idealized edge model – the ideal clean straight edge of single layered TMDs, and secondly only thermodynamics, the hydrogen adsorption enthalpy, while it is reaction barrier that determines the rate. Our experimental results thus provide a challenge for the future, more detailed, theoretical studies.

4.3 Conclusion

In closing, we have elucidated the inherent electrochemistry, and explored the electrochemical property of heterogeneous electron transfer (HET) and the electrocatalytic performance for hydrogen evolution reaction (HER) of the nine Group 5 TMDs in the bulk form; namely, VS₂, VSe₂, VTe₂, NbS₂, NbSe₂, NbTe₂, TaS₂, TaSe₂ and TaTe₂.

Their surface morphology, elemental and surface composition also have been systematically examined by SEM-EDX and XPS. The inherent electrochemistry of Group 5 TMDs has been ascribed to the electrochemical processes intrinsic to their constituent metal or chalcogen and the presence of surface oxides when potentials are applied. Moreover, among all Group 5 TMDs, we have shown that TaS₂ possesses fastest heterogeneous electron transfer (HET) rate at $3.4 \times 10^{-3} \text{ cm s}^{-1}$ which renders TaS₂ a suitable electrode material for electrochemical sensing applications. Compared to sulfides and selenides, slower HET rates have been consistently observed in the tellurides with magnitude of $\sim 10^{-4} \text{ cm s}^{-1}$. In the aspect of HER performance, VTe₂ has been identified as the best electrocatalyst for HER in terms of HER overpotential and Tafel slope, at 0.5 V vs. RHE and 55 mV/dec, respectively. While VTe₂ demonstrates impressive HER performance, other Group 5 TMDs generally show average HER performance, falling short of initial expectations. Within the vanadium dichalcogenides, the HER performance is correlated to the chalcogen type; whereby the electrocatalytic property increases down the chalcogen group such that VS₂ < VSe₂ < VTe₂. Additionally, the Group 5 tellurides exhibit transition-metal dependence whereby the HER performance adheres to the trend of VTe₂ > NbTe₂ > TaTe₂. Density functional theory (DFT) calculations for niobium and tantalum dichalcogenides have been executed. With the aid of our theoretical studies, we have also addressed the HER performance of Group 5 TMDs on the premises of thermodynamics and kinetics. Hence, this fundamental study on Group 5 TMDs has shed light on their electrochemical and electrocatalytic attributes. It is worthwhile to highlight that TaS₂ has distinctly fast HET rates that may be potentially exploited in sensing devices while the remarkable HER performance of VTe₂ deems it a competitive earth-abundant

electrocatalyst for hydrogen evolution.

4.4 Experimental Methods

4.4.1 Materials

Potassium ferrocyanide, hexaammineruthenium (III) chloride, potassium chloride, potassium phosphate dibasic, sodium phosphate monobasic, sodium chloride, sulfuric acid and platinum on carbon were purchased from Sigma Aldrich. Pt, Ag/AgCl and glassy carbon (GC) electrodes were purchased from CH Instruments, Texas, USA. The bulk Group 5 transition metal dichalcogenides: VS₂, VSe₂, VTe₂, NbS₂, NbSe₂, NbTe₂, TaS₂, TaSe₂ and TaTe₂ were obtained from Aldrich.

4.4.2 Apparatus

X-ray photoelectron spectroscopy (XPS) was performed with a Phoibos 100 spectrometer with a monochromatic Mg K α radiation as the X-ray source (SPECS, Germany). Survey scans were generated for all the nine samples. High-resolution spectra were also obtained for the Group 5 metals: V 2p, Nb 3d and Ta 4f; and their corresponding chalcogens: S 2p, Se 3d and Te 3d. The signals were calibrated using adventitious carbon at 284.5 eV. We considered relative sensitivity factors during the calculation of chalcogen-to-metal ratios and the deconvolution of V 2p, Nb 3d and Ta 4f. The deconvolution of V 2p, Nb 3d and Ta 4f was based on various oxidation states, using the oxides as a basis. Best curve fits for the high-resolution XPS spectra of V 2p, Nb 3d and Ta 4f were performed using the ratio of V 2p_{3/2} and V 2p_{1/2} doublet signals as 2:1; Nb 3d_{5/2} and Nb 3d_{3/2} as 3:2; and Ta 4f_{7/2} and Ta 4f_{5/2} as 4:3.

Scanning electron microscopy (SEM) was conducted on a JEOL 7600F field-emission scanning electron microscope (JEOL, Japan) either at gentle-beam mode at 2.0 kV or SEM

mode at 50 kV. Energy dispersive X-ray spectroscopy (EDS) data was obtained using an accelerating voltage of 20.0 kV.

Voltammetric measurements were recorded on a μ Autolab III electrochemical analyser (Eco Chemie B.V., Utrecht, The Netherlands) with the software NOVA version 1.8 (Eco Chemie). Electrochemical measurements of the transition metal dichalcogenide (TMD) materials were performed in a 3 mL voltammetric cell at room temperature (25 °C) in a default three electrode configuration. A platinum electrode and an Ag/AgCl electrode functioned as auxiliary and reference electrodes, respectively and a glassy carbon (GC, 3 mm diameter) electrode was adopted as the working electrode.

4.4.3 Procedures

Fundamental electrochemical studies were performed in 50 mM phosphate buffered saline (PBS) as the background electrolyte at pH 7. All cyclic voltammetry experiments were conducted at a scan rate of 100 mV s⁻¹. The voltammetric scan began at 0 V vs. Ag/AgCl; the potential at which redox processes were not expected to occur,⁶⁰ and scanned towards 1.8 V followed by a reverse sweep to -1.8 V for the scan to positive potentials, and first towards -1.8 V followed by a reverse sweep to 1.8 V before returning to 0 V for the scan to negative potentials. The nine TMD materials: VS₂, VSe₂, VTe₂, NbS₂, NbSe₂, NbTe₂, TaS₂, TaSe₂ and TaTe₂ samples were prepared in concentrations of 1 mg mL⁻¹ in deionised water and subject to first-time ultrasonication for 1.5 h to attain well-dispersed suspensions. Prior to each electrochemical measurement, the samples were ultrasonicated for a period of 10 minutes to maintain the homogeneous dispersion of the desired material. 4.0 μ L aliquot of the suspension was then drop casted on a GC electrode and dried to yield an electrode surface modified with 4.0 μ g film of the desired material.

Studies on heterogeneous electron transfer (HET) at TMD surfaces were executed in potassium chloride (0.1 M) as the supporting electrolyte for potassium ferrocyanide (5 mM) redox probe. Cyclic voltammetry scans were performed at a rate of 100 mV s⁻¹. To eliminate interference due to inherent electrochemistry, the first scan has been excluded. Instead, data from subsequent scans are used. The k_{obs}^0 values were calculated using the method devised by Nicholson that relates ΔE_p to a dimensionless parameter Ψ and consequently into k_{obs}^0 .⁶¹ The roughness of the electrode was not considered in the calculation of k_{obs}^0 . The diffusion coefficient $D = 7.26 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ was used to compute k_{obs}^0 values for $[\text{Fe}(\text{CN})_6]^{4-/3-}$.⁶²

Hydrogen evolution reaction (HER) measurements of these TMD materials were carried out using linear sweep voltammetry at a scan rate of 2 mV s⁻¹ in 0.5 M H₂SO₄ electrolyte. Linear sweep voltammograms are presented *versus* the reversible hydrogen electrode (RHE) using and the measured potentials are calculated using this equation⁶³ $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \times \text{pH} + E_{\text{Ag/AgCl}}^0$ where $E_{\text{Ag/AgCl}}$ is the measured potential, pH of 0.5 M H₂SO₄ electrolyte is zero and $E_{\text{Ag/AgCl}}^0$ refers to the standard potential of Ag/AgCl (1 M KCl) at 25 °C which is 0.235 V. Current density (mA cm⁻²) was calculated using the geometric area of the GC electrode (0.07 cm²). The exchange current density (j) provided in Table S7 in SI was determined from the respective Tafel regions of the TMD materials where the overpotential is 0 V vs. RHE.

The HER catalytic stability of the all TMDs were performed in 0.5 M H₂SO₄ electrolyte before and after 100 cyclic voltammetric scans at 100 mV s⁻¹. The cyclic voltammetric scan range of each of the Group 5 TMD corresponds to their HER onset region where the current density is at least -0.1 mA cm⁻². For VS₂, VSe₂, VTe₂, NbS₂ and NbSe₂ materials, the

cyclic voltammetric scan range is conducted from -0.235 V to -0.635 V vs. Ag/AgCl. The scan window is from -0.435 to -0.835 V and -0.535 to -0.935 V vs. Ag/AgCl for respectively TaS₂ and NbTe₂. TaSe₂ and TaTe₂ are scanned from -0.335 to -0.735 V vs. Ag/AgCl.

4.4.4 Theoretical Methods

DFT calculations were performed using the projector-augmented wave method implemented in the Vienna Ab initio Simulation Package (VASP).^{64, 65} The energy cutoff for the plane-wave expansion was set to 350 eV. We used optimized van der Waals functional optB86b-vdW functional,⁶⁶ which described very well the structural properties of various TaS₂ phases according to recent study.⁶⁷ We calculated the catalytic properties of TaS₂, TaSe₂, and NbSe₂, because they possess the same 2H crystal structure, which enables to separate the influence of the structure and chemical composition. For comparison, we included also the 2H-NbS₂. The free energy of the adsorption of atomic hydrogen (ΔG) is a quantity which can be used to describe the HER activity of the catalyst.¹² The ΔG of an ideal catalyst for HER should be as close to 0 as possible. We considered the adsorption of hydrogen onto the surface and edge sites of single layered dichalcogenides. The surface (basal plane) was modeled by a 4x4 supercell (16 Ta or Nb atoms) in connection with 3x3x1 k-point sampling. The layers were separated by 18 Å of vacuum. The edge was modeled by a 4x4 nanostripe, i.e. it contained four atoms along the edge and the nanostripe was four atoms wide. The nanostripe model of the as-cleaved edge of the 2H structure exposed both chalcogen terminated edge and metal terminated edge. Their specific structure (the coverage of chalcogen atoms on the edge) depends mainly on the chemical potential of sulphur containing compounds under the operating conditions. We focused on the metal terminated edge. We found that the most stable coverage for TaS₂ is at 50 % chalcogen

coverage, which is in accordance with earlier detailed study for MoS₂.⁶⁸ We therefore used 50 % coverage of the edge for all four dichalcogenides. The Brillouin zone of the nanostripe was sampled by 1x3x1 k-points where three k-points belonged to the only direction in which the cell was periodically repeated. As the edge contained four adsorption sites on sulphur and selenium atoms, possible hydrogen coverages of the edge were 25%, 50%, 75%, and 100%. The edge was gradually (one-by-one) covered with hydrogen atoms and the differential energy of adsorption ΔE was calculated as

$$\Delta E = E_{TOT}(nH^*) - E_{TOT}[(n-1)H^*] - 1/2 E_{TOT}(H_2)$$

The Gibbs free-energy of the adsorption atomic hydrogen (ΔG) was obtained as

$$\Delta G = \Delta E + \Delta E_{ZPE} - T\Delta S_H$$

Where, ΔE_{ZPE} and ΔS_H was the difference in zero point energy, and entropy between the adsorbed hydrogen and hydrogen in the gas phase. These thermal corrections were found to be independent of particular adsorption site, and thus ΔG at standard condition was determined by ΔE plus a thermal correction constant of 0.29 eV.¹²

4.5 Supporting Information

Figure 4.S1 EDS spectrum of VS_2 , VSe_2 , VTe_2 , NbS_2 , NbSe_2 , NbTe_2 , TaS_2 , TaSe_2 and TaTe_2 .

Table 4.S1 Elemental composition of Group 5 TMDs based on energy-dispersive X-ray spectroscopy.

TMD	V at. %	Nb at. %	Ta at. %	S at. %	Se at. %	Te at. %	C at. %	O at. %	Al at. %	Cl at. %	Si at. %
VS_2	19.55	-	-	33.02	-	-	22.50	24.79	0.15	-	-
VSe_2	14.10	-	-	-	22.65	-	36.94	25.93	-	-	0.39
VTe_2	29.07	-	-	-	-	44.67	25.20	-*	0.96	-	-
NbS_2	-	10.77	-	19.53	-	-	60.26	7.74	-	0.19	1.51
NbSe_2	-	9.97	-	-	17.08	-	63.30	9.35	-	-	-
NbTe_2	-	17.68	-	-	-	32.06	37.90	11.45	0.91	-	-
TaS_2	-	-	13.42	23.53	-	-	53.86	9.19	-	-	-
TaSe_2	-	-	9.73	-	17.84	-	61.08	11.35	-	-	-
TaTe_2	-	-	12.72	-	-	26.71	35.72	23.89	0.96	-	-

Table 4.S2 Chalcogen-to-metal ratios of Group 5 TMDs based on energy-dispersive X-ray spectroscopy.

Sample	Chalcogen/Metal Ratio
VS₂	1.7
VSe₂	1.6
VT_e₂	1.5
NbS₂	1.8
NbSe₂	1.7
NbT_e₂	1.8
TaS₂	1.8
TaSe₂	1.8
TaT_e₂	2.1

Figure 4.S2 Scanning electron micrographs and corresponding energy-dispersive X-ray maps of the various Group 5 TMDs.

Figure 4.S3 Wide scan XPS spectra of VS_2 , VSe_2 , VTe_2 , NbS_2 , NbSe_2 , NbTe_2 , TaS_2 , TaSe_2 and TaTe_2 .

Figure 4.S4 High resolution X-ray photoelectron spectra of S 2p, Se 3d and Te 3d regions of the Group 5 TMDs. The deconvoluted peaks correspond to the numerous oxidation states of S, Se and Te.

Table 4.S3A Tabulated chalcogen-to-metal ratios of VS₂, VSe₂ and VTe₂ based on high resolution X-ray photoelectron spectroscopy, with estimated distributions of the various oxidation states of vanadium after deconvolution of the V 2p peaks.

Sample	V(0)	V(II)	V(III)	V(IV)	V(V)	Chalcogen/Metal Ratio
VS ₂	10.0	17.4	10.9	46.6	15.1	1.1
VSe ₂	3.4	19.7	16.6	28.1	32.2	1.1
VTe ₂	8.2	16.9	18.4	24.4	32.1	2.0

Table 4.S3B Tabulated chalcogen-to-metal ratios of NbS₂, NbSe₂ and NbTe₂ based on high resolution X-ray photoelectron spectroscopy, with estimated distributions of the various oxidation states of niobium after deconvolution of the high resolution Nb 3d peaks.

Sample	Nb(0)	Nb(I)	Nb(II)	Nb(IV)	Nb(V)	Chalcogen/Metal Ratio
NbS ₂	1.5	16.5	40.0	18.8	23.2	1.6
NbSe ₂	4.7	0.1	3.7	32.3	59.2	0.9
NbTe ₂	4.5	2.8	7.5	44.9	40.3	3.0

Table 4.S3C Tabulated chalcogen-to-metal ratios of TaS₂, TaSe₂ and TaTe₂ based on high resolution X-ray photoelectron spectroscopy, with estimated distributions of the various oxidation states of tantalum after deconvolution of the high resolution Ta 4f peaks.

Sample	Ta(0)	Ta(I)	Ta(II)	Ta(IV)	Ta(V)	Chalcogen/Metal Ratio
TaS ₂	1.0	16.1	14.7	40.2	28.0	1.1
TaSe ₂	2.1	12.0	9.8	63.8	12.3	1.0
TaTe ₂	1.5	9.5	1.8	64.0	23.2	2.6

Table 4.S4 Estimated distributions of the various oxidation states of vanadium after deconvolution of the high resolution V 2p peaks and O 1s peaks based on XPS.

Sample	V(0)	V(II)	V(III)	V(IV)	V(V)	O 1s
VS ₂	4.2	7.4	4.6	19.9	6.5	57.4
VSe ₂	1.4	7.8	6.6	11.2	12.9	60.1
VTe ₂	2.8	5.8	6.3	8.3	10.9	65.9

Table 4.S5 Elemental compositions Group 5 TMDs based on wide-scan X-ray photoelectron spectroscopy.

Sample	V 2p	Nb 3d	Ta 4f	S 2p	Se 3d	Te 3d	C 1s	O 1s
VS ₂	6.2	-	-	29.9	-	-	27.6	36.3
VSe ₂	3.3	-	-	-	30.4	-	35.8	30.5
VTe ₂	1.1	-	-	-	-	14.2	30.4	54.3
NbS ₂	-	24.3	-	37.2	-	-	15.5	23.0
NbSe ₂	-	19.1	-	-	19.0	-	24.8	37.1
NbTe ₂	-	10.3	-	-	-	10.3	56.4	23.0
TaS ₂	-	-	20.8	18.0	-	-	29.4	31.8
TaSe ₂	-	-	18.5	-	18.5	-	27.7	35.3
TaTe ₂	-	-	13.6	-	-	10.7	27.0	48.7

Figure 4.S5 Cyclic voltammograms of a) V₂O₅ during scan to positive potentials and b) scan to the negative potentials, c) Nb₂O₅ during scan to positive potentials and d) scan to the negative potentials, e) Ta₂O₅ during scan to positive potentials and f) scan to the negative potentials. Conditions: background electrolyte PBS (50 mM) pH 7.0; scan rate, 100 mV s⁻¹; scans begin at 0.0 V vs. Ag/AgCl. The arrows denote initial scan direction.

Figure 4.S6 Summary of peak-to-peak separations of all Group 5 TMDs with their corresponding error bars. Conditions: background electrolyte, KCl (0.1 M); scan rate, 100 mV s⁻¹; all measurements are performed relative to Ag/AgCl reference electrode.

Table 4.S6 Table of heterogeneous electron transfer (HET) rate constant, k^0_{obs} , for all the Group 5 TMDs. The k^0_{obs} of the bare glassy carbon electrode is also computed as a basis for comparison.

Material	k^0_{obs} (cm s ⁻¹)
VS ₂	8.41×10^{-4}
VSe ₂	1.43×10^{-3}
VTe ₂	9.61×10^{-4}
NbS ₂	1.06×10^{-3}
NbSe ₂	2.75×10^{-3}
NbTe ₂	4.95×10^{-4}
TaS ₂	3.39×10^{-3}
TaSe ₂	1.50×10^{-3}
TaTe ₂	5.65×10^{-4}
GC	1.29×10^{-3}

Figure 4.S7 Linear sweep profiles of hydrogen evolution reaction (HER) on GC electrodes modified with a) VS₂, NbS₂ and TaS₂, c) VSe₂, NbSe₂ and TaSe₂ and e) VTe₂, NbTe₂ and TaTe₂. Tafel plots for HER corresponding to b) VS₂, NbS₂ and TaS₂, d) VSe₂, NbSe₂ and TaSe₂ and f) VTe₂, NbTe₂ and TaTe₂. Histograms summarize the averages of g) HER overpotential at current density of -10 mA cm⁻² and h) Tafel slopes for all the materials. Conditions: background electrolyte, H₂SO₄ (0.5 M); scan rate, 2 mV s⁻¹.

Table 4.S7 Table of exchange current density, j , for all the Group 5 TMDs. The j of the Pt/C is also computed as a basis for comparison.

Material	j (mA cm ⁻²)
VS ₂	3.80×10^{-5}
VSe ₂	1.89×10^{-5}
VTe ₂	1.83×10^{-7}
NbS ₂	1.20×10^{-3}
NbSe ₂	9.03×10^{-5}
NbTe ₂	7.90×10^{-4}
TaS ₂	1.71×10^{-4}
TaSe ₂	1.78×10^{-5}
TaTe ₂	1.47×10^{-4}
Pt/C	6.20×10^{-2}

Figure 4.S8 Polarisation curves demonstrating the effect of subsequent scans on the HER pre-waves of a) VSe₂, b) NbS₂, c) NbSe₂ and d) NbTe₂. Conditions: background electrolyte, H₂SO₄ (0.5 M); scan rate, 2 mV s⁻¹.

Figure 4.59 Polarisation curves demonstrating the effect of subsequent scans with the absent or diminished HER pre-wave on the HER trends of Group 5 TMDs. Linear sweep profiles of hydrogen evolution reaction (HER) on GC electrodes modified with a) VS_2 , VSe_2 and VTe_2 and b) NbS_2 , NbSe_2 and NbTe_2 . All Group 5 TMDs shown are first scans with the exception of VSe_2 , NbS_2 , NbSe_2 and NbTe_2 whereby their 2nd scans are used. Conditions: background electrolyte, H_2SO_4 (0.5 M); scan rate, 2 mV s^{-1} .

Figure 4.S10 Polarisation curves demonstrating the effect of subsequent scans with the absent or diminished HER pre-wave on the HER trends of Group 5 TMDs. Linear sweep profiles of hydrogen evolution reaction (HER) on GC electrodes modified with a) VS_2 , NbS_2 and TaS_2 , b) VSe_2 , NbSe_2 and TaSe_2 and c) VTe_2 , NbTe_2 and TaTe_2 . All Group 5 TMDs shown are first scans with the exception of VSe_2 , NbS_2 , NbSe_2 and NbTe_2 whereby their 2nd scans are used. Conditions: background electrolyte, H_2SO_4 (0.5 M); scan rate, 2 mV s^{-1} .

Figure 4.S11 HER polarisation curves of all Group 5 TMDs before and after 100 cyclic voltammetry cycles in sulfuric acid. Conditions: background electrolyte, H_2SO_4 (0.5 M); scan rate, 2 mV s^{-1} .

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Chapter 5

Electrochemistry of Transition Metal Ditellurides:

CoTe₂ and NiTe₂

5.1 *Introduction*

5.2 *Results and Discussion*

5.2.1 *Characterisation*

5.2.2 *Inherent Electrochemistry*

5.2.3 *Electrocatalysts for Hydrogen Evolution*

5.3 *Conclusion*

5.4 *Experimental Section*

5.5 *Supporting Information*

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The thesis author was the primary investigator and first author of the above paper.

5.1 Introduction

Two-dimensional (2-D) nanomaterials such as graphene and transition metal dichalcogenides (TMDs) are imperative for eventual developments as exemplified by their layered architectures.¹⁻³ Layered structures are prized possessions of 2-D materials due to the easy adaptation for copious electrochemical uses in accordance to the unique layer-dependent properties.⁴ At present, research into TMDs is taking off at full throttle. Represented by a general formula of MX₂, a TMD consists of a transition metal belonging to groups 4-10 and a chalcogen (S, Se or Te), respectively denoted as M and X. Each TMD layer contains repeating units of MX₂ that are covalently linked whereas van der Waals' interactions exist between loosely stacked layers of MX₂. Crowned as the prototype of TMDs, MoS₂ exudes anisotropy; in electronic, mechanical and electrochemical aspects,⁵⁻⁹ that catapulted the realm of TMDs to spotlight in the scientific community. Resonating with the versatile properties of MoS₂, TMDs have gained traction across a myriad of applications including batteries, supercapacitors, photovoltaics and sensors.^{6, 10-12}

Closer inspection of the TMD research to date reveals tremendous emphasis on transition metal disulfides and diselenides while the ditelluride family remains in their shadows. Despite the weak lustre of ditelluride research, electronic and bonding properties of the transition metal ditellurides come across as more intriguing than the disulfides or diselenides. As exemplified in 1T-MoS₂ and -WSe₂, a TMD usually adopts a CdI₂ layered phase whereby the transition metal centre is coordinated to 6 other chalcogen atoms in an octahedral geometry.^{6, 12} Contrarily, the classic description of TMDs as a CdI₂-type structure is unable to adequately reflect the bonding of the ditellurides from late transition metals. Progressing towards the right side of the period, the electronic

d band level successively lowers and high oxidation states of the transition metal cations destabilize to engender pyrite or marcasite structures instead of layered structures.¹³ Proceeding down the group from sulfur to tellurium decreases the electronegativity of the chalcogen and raises the energy level of the anionic *sp* valence band.¹³ Taken together, the lowered *d* band levels of the transition metal and the increased *sp* band energy of the chalcogen facilitate cationic-anionic redox interactions within the structure.¹⁴ In doing so, these interactions induce phase transitions and structural changes.¹⁴ Due to the highest *sp* band level in the tellurium chalcogen,¹⁵ such effects are most pronounced in transition metal ditellurides compared to the disulfides or diselenides.

Among the late transition metal ditellurides, CoTe₂ and NiTe₂ epitomize TMDs capable of exhibiting polymorphism. CoTe₂ assumes two distinct phases: orthorhombic marcasite and CdI₂ related type.¹⁵⁻¹⁷ Likewise, NiTe₂ has been documented in literature to undertake two structures: pyrite-like and CdI₂-type.^{13, 15, 18} Of interest to us, both CoTe₂ and NiTe₂ crystallize into layered phases, however the layered phase in Co-Te system is stabilized only for non-stoichiometric tellurium deficient composition. This structure is related to the structure of LiTiS₂ and contains Co-Co bonding which are responsible for interlayer interactions.¹⁵ Thus, the layered phase of CoTe₂ embrace characteristics of a three-dimensional material and are different from the traditional CdI₂-type shared by most layered TMDs. A recurring theme in the applications of layered TMDs is their ability to electrocatalyze the hydrogen evolution reaction (HER) in order to ride on hydrogen gas as a clean and renewable fuel.^{5, 6, 9, 12, 19-22} At the moment, platinum is the best HER electrocatalyst but its high cost and scarcity render it unsustainable in the long term. The edges of layered TMDs have been identified to be the active sites for HER whereas the

basal planes are inert.^{6, 12} Although several studies showed that marcasite-type CoTe₂ behaves as a promising electrocatalyst,^{23, 24} it is surprising that scientists have paid scant attention to layered CoTe₂ and NiTe₂. The unconventional layered structure of CoTe₂ and NiTe₂ sets them apart from the rest of the layered TMDs, and hence, piques curiosity about the implication on their electrocatalytic properties.

Herein, we investigate and compare the electrochemical properties of layered transition metal ditellurides, in particular, CoTe₂ and NiTe₂ by elucidating their inherent electroactivity. Moreover, we explored the potential of layered CoTe₂ and NiTe₂ as electrocatalysts for hydrogen evolution. Both transition metal ditellurides are systematically characterised with scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). The structure of CoTe₂ and NiTe₂ phases are shown on Scheme 1. Both phases have a similar space group (P-3m1). However, only NiTe₂ adopts the structure of CdI₂. In the case of the tellurium deficient cobalt telluride, the structure is derived from the CdI₂ structure comprising of metal-metal bonding and interlayer covalent interactions, not usually observed in traditional layered structures.

Scheme 4.1 The structure of a) CoTe_2 and b) NiTe_2 . Tellurium (red); metal (blue).

5.2 Results and Discussion

5.2.1 Characterisation

Prior to the electrochemical study, CoTe_2 and NiTe_2 were subject to a series of characterisation techniques to examine their morphology and composition. The characterisation methods employed include scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS).

Figure 5.1 Scanning electron micrographs of a) CoTe_2 and b) NiTe_2 . Scale bars represent 1 μm .

Both CoTe_2 and NiTe_2 exhibit layered structures that are hallmarks of 2-D transition metal dichalcogenides (TMDs) as captured by SEM in Figure 5.1. The close stacking of the CoTe_2 and NiTe_2 sheets indicate their existence in the bulk, non-exfoliated form. Between layers, van der Waals' interactions exist. Numerous well-defined edges are also a common morphological trait evident in both transition metal ditellurides. Elemental maps of CoTe_2 and NiTe_2 obtained using EDS are presented in Figure 5.S2 while their corresponding EDS spectra along with their elemental composition are respectively recorded in Figure 5.S1 and Table 5.S1. The chalcogen-to-metal ratio is computed to be 1.9 for both CoTe_2 and NiTe_2 which approximates the projected chalcogen-to-metal ratio of 2.0. Hence, the identities of CoTe_2 and NiTe_2 are verified.

The phase purity was proofed by X-ray diffraction. Both phases were single phase without any additional phases or unreacted tellurium. Both materials exhibit slight preferential orientation along (00l) direction due to the layered nature of synthesized materials. X-ray diffractograms are shown on Figure 5.2. Both phases exhibit P-3m1 symmetry, however NiTe_2 is CdI_2 structural type, the layered structure in CoTe_2 is stabilized only for tellurium deficient composition (below the metal to chalcogen ratio 1:1.8) and is

derived from the structure of LiTiS_2 (which is based on CdI_2 structural symmetry) and contain cobalt-cobalt bonds (see Scheme 1).

Figure 5.2 X-ray diffractograms of $\text{CoTe}_{1.8}$ and NiTe_2 .

The surface elemental composition and valence states of the transition metal ditellurides are analysed by XPS. XPS is a surface-sensitive technique with resolution to a maximum depth of 10 nm. As the electrochemistry of CoTe_2 and NiTe_2 involves electron transfer processes on the material surface, the information gathered from XPS will pave the way towards their understanding. In Figure 5.S3, the wide-scan XPS spectra for CoTe_2 and NiTe_2 confirm the presence of Co, Ni and Te. C 1s and O 1s signals are inevitable due to the environment. The samples were affixed on carbon tape for analysis and the telluride materials undergo oxidation readily. Figure 3 illustrates the high resolution core level spectra of Co 2p, Ni 2p and Te 3d regions for the transition metal ditellurides.

Figure 5.3 High resolution X-ray photoelectron spectra of CoTe_2 for the regions: a) Co 2p and b) Te 3d. High resolution X-ray photoelectron spectra of NiTe_2 for the regions c) Ni 2p and d) Te 3d.

The Co 2p core level XPS spectrum of CoTe_2 manifests 4 distinct peaks. The peaks located at 277.3 eV and 279.8 eV correspond to the Co $2p_{3/2}$ binding energy, whereas 292.2 eV and 295.5 eV correspond to the Co $2p_{1/2}$ binding energy. The deconvolution of Co 2p signals (Figure 5.3a) reveals that the surface of CoTe_2 comprises Co(0) and CoO species in addition to the CoTe_2 phase. The presence of elemental Co on the surface is confirmed by the Co $2p_{3/2}$ and $2p_{1/2}$ binding energies at 277.3 eV and 292.2 eV respectively.²⁵ The Co $2p_{3/2}$ signal at 279.8 eV is deconvoluted into CoTe_2 at 279.6 eV and CoO at 280.7 eV. Parallel to this, the Co $2p_{1/2}$ signal at 295.5 eV also has contribution from the CoTe_2 and CoO species. Formation of surface oxides like CoO is a result of the susceptibility of CoTe_2 towards corrosion.²⁶ Using Co $2p_{3/2}$ binding energies as reference, the signals of our CoTe_2 sample align with the literature values for CoTe and CoTe_2 which has been reported to be

within a range of 778.5 and 781.2 eV encompassing nanostructures, films or hybrids.²⁶⁻³⁰

The proximity in signals may be attributed to the valence state of Co. Akin to CoTe with an oxidation state of Co²⁺,^{28, 29} a divalent oxidation state of Co has been suggested for CoTe₂ in a separate study on CoTe₂/carbon nanotube hybrid.²³ The X-ray absorption near edge structure (XANES) analysis on CoTe₂/carbon nanotube hybrid revealed the oxidation state of Co to be +2 due to the Te₂²⁻ dimer.²³ The Co K-edge jump of CoTe₂ was also situated between the absorption edge of Co foil and Co oxide.²³ Moreover, Co 2p satellite peaks²⁶ at *ca.* 786.5 eV and 801.9 eV (Figure 3a) are typical of a Co²⁺ state in CoTe₂.

The Ni 2p core level region of NiTe₂ is presented in Figure 5.3c. The pair of prominent signals at 854.6 eV and 872.5 eV is indexed to Ni 2p_{3/2} and 2p_{1/2} binding energies respectively. Scrutinizing further, we observe a set of shoulder signals at the respective Ni 2p_{3/2} and 2p_{1/2} binding energies of 852.5 eV and 869.8 eV. While the shoulder signals point to traces of elemental Ni, deconvolution of the principal Ni 2p signals indicate presence of NiO and NiTe₂. Our experimental Ni 2p_{3/2} binding energy of NiTe₂ is higher than *ca.* 853 eV as quoted in previous XPS studies on NiTe₂.^{13, 31} Literature values of the Ni 2p_{3/2} binding energy of elemental Ni portray a variance of 0.3-0.5 eV from that of NiTe₂.^{32, 33} The higher empirical binding energy of NiTe₂ likely stems from the partially overlapping signal contributed by NiO occurring at 855.8 eV. Drawing comparisons to other nickel dichalcogenides, the Ni 2p_{3/2} signals are located at 853.6 eV for NiS₂ and 853.2 eV for NiSe₂.³⁴ It is important to highlight that both NiS₂ and NiSe₂ exist in Ni²⁺ oxidation state and crystallize in a pyrite-type structure with X₂²⁻ anions. Unlike NiS₂ and NiSe₂, NiTe₂ adopts a layered structure as piled sheets of NiTe₂ are witnessed in Figure 5.1. Despite the dissimilar crystal structures, a Ni 2p broad satellite peak at *ca.* 861.0 eV (Figure 5.3c) noted

for NiTe₂ has also been sighted in XPS studies performed on other nickel chalcogenides whereby Ni undertakes an oxidation state of +2.^{35, 36} Satellite peaks originate from a shake-up process that is affiliated to paramagnetism.³⁷ As inferred, NiTe₂ is a paramagnet. This deduction achieves a consensus with earlier works documenting the weak paramagnetic nature of NiTe₂.^{38, 39} Of paramount significance, this satellite feature in NiTe₂ lends credence to the proposition by Bensch *et al.* that Ni exists in the d⁸ state and hence, affirms that the Ni in NiTe₂ has a valency of 2.^{13, 31}

XPS deconvolution of Te 3d spectra for CoTe₂ and NiTe₂ (Figure 5.3b, 5.3c) bears salient resemblance to each other. Both reveal a pair of doublets that is characteristic of MTe₂ (M = Co, Ni) and TeO₂ species. In particular, the distinct pair of doublets (Te 3d_{5/2} and 3d_{3/2}) at binding energies of *ca.* 572.2 eV and 582.6 eV, and *ca.* 575.7 eV and 586.1 eV, are respectively assigned to MTe₂ and TeO₂. The Te 3d_{5/2} binding energies for CoTe₂ and NiTe₂ concur reasonably with reported values of 573.0 eV and 572.8 eV.^{23, 29, 31} IrTe₂, another ditelluride species, also has a Te 3d_{5/2} signal at 573.0 eV which nears that of CoTe₂ and NiTe₂.¹⁵ Detecting TeO₂ on CoTe₂ and NiTe₂ surfaces is prevalent in literature, often attributed to the rapid oxidation of telluride compounds with atmospheric oxygen.^{26, 31, 40} Given that the oxidation state of the transition metal Co and Ni is +2, the Te species in CoTe₂ and NiTe₂ is formulated to be Te₂²⁻. Bensch *et al.* had also arrived at a similar conclusion.¹³ Specific to NiTe₂, electronic band structure calculations determined that the oxidation state of Te lies between -1 and -1.5 due to the short Te-Te interlayer and through-slab distances.¹³ The oxidation state of Te was further refined to -1.2 by virtue of correlating Te-Te distances with the oxidation states of anion in Te₂²⁻ and Te²⁻.¹³

On the basis of wide-scan XPS data, the chalcogen-to-metal ratio (Table 5.S2) is

derived to be 3.2 for CoTe₂ and 3.4 for NiTe₂. It is apparent that chalcogen-enrichment occurs on the surface of both tellurides wherein the chalcogen-to-metal ratio deviates considerably from the theoretical ratio of 2.0. One reason behind the tellurium-enriched surfaces is the substantial passivation of CoTe₂ and NiTe₂. Apparent in Figure 5.3b and 5.3c, the Te 3d peaks originating from the TeO₂ component are more intense compared to MTe₂ phase; TeO₂ prevails over the MTe₂ phase. The calculated chalcogen-to-metal ratios of other transition metal ditellurides such as NbTe₂ and TaTe₂ were also found to approximate 3.0 which are beyond the ideal of 2.0.²¹ Apart from the role of surface oxides, tellurium-rich tellurides possess anionic networks consisting of homonuclear Te-Te bonds.²⁷ Another point of interest is the disparity in chalcogen-to-metal ratios provided by EDS and XPS analyses. EDS analysis discloses the bulk composition of CoTe₂ and NiTe₂ whereas XPS analysis reveals their surface composition. Surface composition of CoTe₂ and NiTe₂ is largely influenced by the propensity of tellurium towards oxidation compared to other chalcogen types, specifically, sulfur or selenium.^{21, 41}

5.2.2 Inherent Electrochemistry

Hitherto the inherent electrochemistry of the layered transition metal ditellurides, CoTe₂ and NiTe₂, remains a mystery. By definition, inherent electrochemistry has been understood to be the characteristic redox reaction of the material in the presence of an applied electrochemical potential.¹² Knowledge of their intrinsic electrochemical behavior is pivotal for the development of their electrochemical applications. For instance, in electrochemical sensing, the characteristic redox signals of the materials may interfere with the measurements and hence, limit their potential window for operation.⁴² We charted the innate electroactivities of CoTe₂ and NiTe₂ and their voltammograms are as

depicted in Figure 5.4 wherein reported potentials are relative to the Ag/AgCl electrode. Scans towards positive and negative potentials were performed in three consecutive cycles to elicit electrochemical information on the surface of transition metal ditellurides.

Figure 5.4 Cyclic voltammograms of CoTe₂ during a) scan to positive potentials and b) scan to negative potentials, and NiTe₂ during c) scan to positive potentials and d) scan to negative potentials. Conditions: background electrolyte, phosphate buffered saline (50 mM); pH 7.0; scan rate, 100 mV s⁻¹; all measurements performed relative to the Ag/AgCl reference electrode.

Two distinct oxidation features are observed for CoTe₂ while NiTe₂ manifests a lone oxidation signal. Both transition metal ditellurides share an oxidation signal at *ca.* 0.2 V originating from their identical telluride chalcogen. Yet the distinguishing voltammetric trait between the transition metal ditellurides can in fact be ascribed to the conspicuous anodic peak at *ca.* 1.4 V in CoTe₂ which is not noted for NiTe₂. This signal resembles the “2-component” oxidative signal of Co oxide supported on CoTe₂ phase due to surface

modification.⁴³ McKendry *et al.* has assigned its occurrence to the surface oxidation of Co and Te, in particular, the XPS data suggested the attenuation of surface CoO and TeO with the concomitant growth of Co(III) oxides and formation of soluble tellurate.⁴³ Based on our context, however, the anodic peak at *ca.* 1.4 V has an apparent singular component which we attribute to the Co(II) oxidation to Co(III). At highly oxidizing potentials of *ca.* 1.4 V, there is passivation of CoTe₂ to yield insoluble Co oxides. The absence of an anodic peak arising from the Ni component in NiTe₂ may be engendered by the instability of Ni valency > 2. Co provides Co(III) valence state such that a large field of Co₃O₄ exists in oxidizing, neutral to basic pH conditions.⁴⁴ In contrast, Ni₃O₄ has not been reported in the water stability field by Brookins.^{44, 45} Since Ni nanoparticles have been found to be electrochemically-inert in works associated to Li-ion batteries,^{46, 47} the absent intrinsic electroactivity of the Ni component in NiTe₂ is not entirely unexpected.

Markedly alike voltammetric profiles of both CoTe₂ and NiTe₂ embody the dominance of tellurium electrochemistry. For both scan directions of CoTe₂ and NiTe₂, the anodic signal at *ca.* 0.2 V exemplifies the oxidative stripping of Te. Anodic stripping of Te has been reported to occur over potentials of *ca.* 0.1 V to 0.4 V in literature.⁴⁸⁻⁵⁰ Analogous to CoTe₂ and NiTe₂, Group 4 and 5 transition metal ditellurides also demonstrate this oxidative feature due to the Te chalcogen at *ca.* 0.25 V and 0.3 V respectively.^{21, 22} More strikingly, all cathodic peaks of CoTe₂ and NiTe₂ arise from the tellurium chalcogen. The modest signal at *ca.* -0.8 V is indicative of Te(IV) species reducing to the elemental state.⁵¹ Given that the initial scans to the negative potentials in CoTe₂ and NiTe₂ lack this signal, we infer that the anodic Te stripping at *ca.* 0.2 V is a prerequisite to the Te(IV) reduction at *ca.* -0.8 V. In other words, these 2 signals involve a correlated process. The well-defined cathodic peak

at *ca.* -1.3 V is diagnostic of the reductive stripping of Te(0) to soluble Te²⁻.⁵¹ This highly cathodic potential required to occasion the reduction of tellurium species to the oxidation state of -2 suggests that $\text{Te} + 2\text{e}^- \rightarrow \text{Te}^{2-}$ is the thermodynamic bottleneck to the electro-reduction of tellurium chalcogen in CoTe₂ and NiTe₂.⁵¹ Other transition metal ditellurides, such as those VTe₂, NbTe₂ and TaTe₂,²¹ showcase the potential-determining step for Te reduction at *ca.* -1.0 V, that is lower in potential than observed for CoTe₂ and NiTe₂.

To a large extent, the inherent redox processes of CoTe₂ and NiTe₂ are classified as chemically reversible in nature. Prominently, the current intensities of the signals at *ca.* 0.2 V and *ca.* -0.8 V are maintained in subsequent scans to the positive potentials. CoTe₂ shows an anodic peak at *ca.* 1.4 V with increased current intensity in the following scans in both directions.

5.2.3 Electrocatalyst for Hydrogen Evolution

The electrocatalytic allure of layered TMDs in water-splitting reactions beckons the prospect of layered CoTe₂ and NiTe₂ as electrocatalysts for hydrogen evolution reaction (HER). The HER performance of these transition metal ditellurides is delineated in Figure 5 in terms of their linear sweep voltammograms and their Tafel slopes in 0.5 M H₂SO₄ electrolyte. Pt/C, which is the best-performing HER electrocatalyst at present, has been included to aid in the assessment of CoTe₂ and NiTe₂ as prospective electrocatalysts under the same experimental condition.

Figure 5.5 a) Linear sweep voltammograms for hydrogen evolution reaction (HER) on CoTe₂ and NiTe₂ and their b) Tafel plots. Histograms summarise the averages of c) HER overpotential at -10 mA cm⁻² and d) Tafel slopes. Conditions: background electrolyte, H₂SO₄ (0.5 M); scan rate, 2 mV s⁻¹; all measurements are performed relative to the Ag/AgCl reference electrode and corrected to reversible hydrogen electrode (RHE) potential.

On the account of practical design parameters for water splitting systems, a current

density at a magnitude of 10 mA cm⁻² translates to at least a 10 % solar-to-hydrogen efficiency and thus, deemed a conventional figure of merit for evaluating HER electrocatalysts.^{20, 52} Judging by the overpotentials at this current density benchmark, the HER performance of CoTe₂ and NiTe₂ are comparable; respectively requiring 0.58 V and 0.56 V vs. RHE to achieve -10 mA cm⁻². While both transition metal ditellurides barely eclipse the electrocatalytic expertise of Pt/C premised on the higher HER overpotential *ca.* 0.6 V in CoTe₂ and NiTe₂ against 0.05 V in Pt/C, the catalytic activities of transition metal ditellurides show unequivocal competency over the bare glassy carbon (GC) electrode.

Furthermore, one other frequently used performance metric is the Tafel slope. The Tafel slope describes the increase in overpotential that attains a rise in current by an order of magnitude. A small value for Tafel slope is preferred in an electrocatalyst because the desired current density could be reached with less overpotential. Besides its function as a kinetic parameter, Tafel slope analysis unveils the reaction pathway assumed by different material surfaces for hydrogen evolution where the Tafel slope determines the rate-limiting step. The HER mechanism involves adsorption and desorption processes shown below accompanied by the Tafel slope (*b*).^{19, 53, 54}

1. Adsorption *via* the Volmer process:

2. Desorption *via* the Heyrovský process:

or Desorption *via* the Tafel process:

Among all materials, Pt/C exhibits the lowest Tafel slope at 38 mV dec⁻¹ and is limited by the desorption step, in good adherence to reported Tafel slope values for Pt/C in the region of 30 and 40 mV dec⁻¹.⁵⁴ Conversely, the highest Tafel slope of 116 mV dec⁻¹ is obtained for the bare GC and thus, indicates that the adsorption Volmer process as the rate-determining. Despite the tie game between CoTe₂ and NiTe₂ in their almost-equivalent HER overpotential, NiTe₂ outperforms CoTe₂ in the aspect of their Tafel slopes. NiTe₂ demonstrates a Tafel slope of 44 mV dec⁻¹, noticeably lower than that CoTe₂ at 51 mV dec⁻¹. Due to the proximity of their Tafel slope values to 40 mV dec⁻¹, desorption *via* the Heyrovský process is likely the limiting step in HER. As the Tafel slope data bears out, CoTe₂ and NiTe₂ offer nearly platinum-like Tafel slopes and hence, manifest similar kinetics of HER as platinum. NiTe₂, in particular, is able to rival that of Pt given the marginal difference in their Tafel slope values by 6 mV dec⁻¹.

The stark resemblance between the electrocatalytic behaviour of CoTe₂ and NiTe₂ for HER led us to infer that the HER process on CoTe₂ and NiTe₂ may be dominated by the electrochemical desorption on the tellurium atom. Former Tafel analyses performed on tellurium electrode in acidic conditions recorded Tafel slope values, 40 mV dec⁻¹, 48 mV dec⁻¹ and 50 mV dec⁻¹, corresponding to a desorption-limited process.^{55, 56} Additionally, an electrochemical study involving an array of Ni compounds remarked that the general shape of the Tafel line of NiTe₂ mirrors that of Te.⁵⁶

CoTe₂ and NiTe₂ demonstrate robust stability in acid as illustrated in Figure 5.S4 with no deterioration of their catalytic activity for HER. There is a marginal drop in the HER overpotentials of both ditellurides after 100 cycles in acid over a potential range corresponding to the onset of HER occurring at a current density of at least -0.1 mA cm⁻²

(Figure 5.S5). Tafel slopes for both CoTe₂ and NiTe₂ remain unwavering in the region of 40-50 mV dec⁻¹.

5.3 Conclusion

In summary, we have explored the inherent electrochemistry of layered CoTe₂ and NiTe₂. The characteristic electrochemical feature of CoTe₂ is the ostensible anodic peak at *ca.* 1.4 V vs. Ag/AgCl due to the oxidation of Co component. There is no electrochemical feature stemming from the Ni component observed in NiTe₂. Interestingly, the Te chalcogen electrochemistry is accentuated in the electrochemical profiles of CoTe₂ and NiTe₂ with several common redox signals. Most significantly, we show that layered CoTe₂ and NiTe₂ are prospective electrocatalysts for hydrogen evolution wherein they exhibit desirable traits of requiring low overpotentials at *ca.* 0.6 V vs. RHE along with low Tafel slope values. Between the layered transition metal ditellurides, NiTe₂ emerges as a stronger contender for electrocatalytic hydrogen evolution as supported by the lower Tafel slope of 44 mV dec⁻¹. The corollary to this is the fast kinetics in NiTe₂ electrocatalyst for hydrogen evolution which parallels that of platinum. Consequently, this discussion contributes to the knowledge on layered transition metal ditellurides and can be tapped on for their future development in electrochemical applications.

5.4 Experimental Section

5.4.1 Materials

Cobalt (<100 mesh; 99.9%), Nickel (<100 mesh; 99.9%) and tellurium (99.999%) were obtained from Mateck, Germany. *N,N*-dimethylformamide potassium chloride, potassium phosphate dibasic, sodium phosphate monobasic, sodium chloride, sulfuric acid, potassium hydroxide and platinum on carbon were purchased from Sigma Aldrich. Pt,

Ag/AgCl and glassy carbon (GC) electrodes were purchased from CH Instruments, Texas, USA.

5.4.2 Synthesis

The stoichiometric amount of Ni and Te corresponding to 10 g of NiTe₂ and the stoichiometric amount of Co and Te corresponding to 10 g of CoTe_{1.8} were placed in quartz glass ampoule and evacuated on the base pressure of 1×10^{-3} Pa by diffusion pump. The ampoule was melt sealed by oxygen-hydrogen welding torch under vacuum. The synthesis of CoTe_{1.8} was performed by heating the reaction mixture in ampoule on 1000 °C for 2 hours using a heating rate 5 °C/min. Subsequently was cooled on 700 °C using a cooling rate 2 °C/min and after 24 hours was cooled on room temperature using cooling rate 0.5 °C/min. NiTe₂ was synthesized by heating the ampoule with reaction mixture on 1000 °C with heating rate 5 °C/min. After 24 hours was the reaction mixture cooled on room temperature using cooling rate 1 °C/min.

5.4.3 Apparatus

X-ray photoelectron spectroscopy (XPS) was performed with a Phoibos 100 spectrometer with a monochromatic Mg K_α radiation as the X-ray source (SPECS, Germany). Survey scans were generated for all samples. High-resolution spectra were also obtained for the Co 2p, Ni 2p and Te 3d. Relative sensitivity factors during the deconvolution of Co 2p, Ni 2p and Te 3d were accounted for to achieve best fit curves, using ratios of Co 2p_{3/2} and Co 2p_{1/2} as 2:1, Ni 2p_{3/2} and Ni 2p_{1/2} as 2:1 and Te 3d_{5/2} and Te 3d_{3/2} as 3:2.

Scanning electron microscopy (SEM) was performed with a JEOL 7600F field-emission scanning electron microscope (JEOL, Japan) at 5.0 kV. Energy dispersive X-ray spectroscopy (EDS) data were obtained at an accelerating voltage of 15.0 kV.

Voltammetric measurements were recorded on a μ Autolab III electrochemical analyser (Eco Chemie B.V., Utrecht, The Netherlands) with the software NOVA version 1.8 (Eco Chemie). Electrochemical measurements of the transition metal dichalcogenide (TMD) materials were performed in a 3 mL voltammetric cell at room temperature (25 °C) in a default three electrode configuration. A platinum electrode and an Ag/AgCl electrode functioned as auxiliary and reference electrodes, respectively and a glassy carbon (GC, 3 mm diameter) electrode was adopted as the working electrode.

5.4.4 Procedures

Electrochemical measurements were performed in 50 mM phosphate buffered saline (PBS) as the background electrolyte at pH 7. All cyclic voltammetry experiments were conducted at a scan rate of 100 mV s⁻¹. The voltammetric scan began at 0 V; the potential at which redox processes were not expected to occur,⁵⁷ and scanned towards 1.8 V followed by a reverse sweep to -1.8 V for the scan to positive potentials, and first towards -1.8 V followed by a reverse sweep to 1.8 V for the scan to negative potentials before returning to 0 V. CoTe₂ and NiTe₂ samples were prepared in concentrations of 2 mg mL⁻¹ in *N,N*-dimethylformamide and subject to first-time ultrasonication for 1.5 h to attain well-dispersed suspensions. Prior to each electrochemical measurement, the samples were ultrasonicated for a period of 10 minutes to maintain the homogeneous dispersion of the desired material. 1.0 μ L aliquot of the suspension was then drop casted on a GC electrode and dried to yield an electrode surface modified with 2.0 μ g film of the desired material. Hydrogen evolution reaction (HER) measurements of CoTe₂ and NiTe₂ were carried out using linear sweep voltammetry at a scan rate of 2 mV s⁻¹ in 0.5 M H₂SO₄ electrolyte. Linear sweep voltammograms are presented *versus* the reversible hydrogen electrode (RHE)

using and the measured potentials are calculated using this equation $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \times \text{pH} + E^0_{\text{Ag/AgCl}}$ where $E_{\text{Ag/AgCl}}$ is the measured potential, pH of 0.5 M H₂SO₄ electrolyte is zero and $E^0_{\text{Ag/AgCl}}$ refers to the standard potential of Ag/AgCl (1 M KCl) at 25 °C which is 0.235 V.

The catalytic stability of the ditellurides in acid was performed in 0.5 M H₂SO₄ before and after 100 cyclic voltammetry cycles at a scan rate of 100 mV s⁻¹ over a potential range of -0.205 to -0.605 V vs. Ag/AgCl. This potential range corresponds to the onset region of HER.

5.5 Supporting Information

Table 5.S1 Elemental compositions of CoTe₂ and NiTe₂ based on energy-dispersive X-ray spectroscopy. Their chalcogen-to-metal ratios are also included.

Material	Co at. %	Ni at. %	Te at. %	C at. %	O at. %	Chalcogen/Metal Ratio
CoTe ₂	23.1	-	43.8	31.1	2.0	1.9
NiTe ₂	-	22.8	42.6	30.8	3.8	1.9

Figure 5.S1 Energy-dispersive X-ray spectra of a) CoTe_2 and b) NiTe_2 . **Figure 5.S2** Scanning electron micrographs and the corresponding energy-dispersive X-ray maps of CoTe_2 and NiTe_2 .

Table 5.S2 Elemental compositions of CoTe_2 and NiTe_2 based on wide-scan X-ray photoelectron spectroscopy. Their chalcogen-to-metal ratios are also included.

Material	Co at. %	Ni at. %	Te at. %	C at. %	O at. %	Chalcogen/Metal Ratio
CoTe_2	6.60	-	20.81	41.67	30.92	3.2
NiTe_2	-	3.32	11.33	50.56	34.79	3.4

Figure 5.S3 Wide-scan X-ray photoelectron spectra of a) CoTe_2 and b) NiTe_2 . The survey spectra were calibrated to the adventitious C 1s peak at 284.8 eV.

Figure 5.S4 HER polarisation curves of a) CoTe₂ and b) NiTe₂ before and after 100 cyclic voltammetry cycles in sulfuric acid. The corresponding Tafel plots for c) CoTe₂ and d) NiTe₂ before and after 100 cyclic voltammetry cycles. Conditions: background electrolyte, H₂SO₄ (0.5 M); scan rate, 2 mV s⁻¹.

Figure 5.S5 Cyclic voltammograms of a) CoTe₂ and b) NiTe₂ to examine catalytic stability in acid. Conditions: background electrolyte, H₂SO₄ (0.5 M); scan rate, 100 mV s⁻¹.

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Chapter 6

Electrochemistry of an Anti-MoS₂ Structure Metal Chalcogenide: Tl₂S

6.1 *Introduction*

6.2 *Results and Discussion*

6.2.1 *Electronic Structure*

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6.2.5 *Electrocatalytic Performance in Hydrogen Evolution Reaction*

6.3 *Conclusion*

6.4 *Experimental Section*

6.5 *Supporting Information*

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The thesis author was the primary investigator and first author of the above paper.

6.1 Introduction

At present, tremendous interest is brewing in low-dimensional materials that demonstrate high anisotropy. Of prominence, scientific progress in transition metal dichalcogenides has been overwhelming in the fields of electronics, energy generation and storage and sensing applications.¹⁻³ Other metal chalcogenides, beyond the transition metal group, received occasional attention and are often shadowed by the successes of transition metal dichalcogenides. However, in the recent years, there has been rekindled interest in Group 13 chalcogenides.⁴ Exhibiting intrinsic vacancy structures, Group 13 chalcogenides are generally semiconducting in nature.⁵ The Group 13 elements are able to combine with chalcogens forming binary⁴ and ternary compounds with a chain or layered structure.⁶⁻¹⁰ In particular, thallium chalcogenides manifest in numerous composites as determined by thallium dominant oxidation states of Tl(I) and Tl(III). As exemplified in thallium-sulfur structures, polymorphs including Tl₂S, TlS, Tl₄S₃ and Tl₂S₅ have been reported.¹¹⁻¹⁴ Both TlS and Tl₄S₃ are considered to possess mixed valency because thallium coexists as Tl(I) and Tl(III) within the same compound. TlS is more precisely represented as $Tl^{1+}[Tl^{3+}(S^{2-})_2]$ whereas Tl₄S₃; as $[Tl^{1+}]_3[Tl^{3+}(S^{2-})_3]$. Unlike TlS and Tl₄S₃, thallium(I) sulfide Tl₂S consists of a single oxidation state, namely the monovalent Tl(I) state exhibiting the inert pair 6s² configuration. Moreover, among all sulfide polymorphs, Tl₂S was found in nature as a rare mineral carlinite described to be soft and in dark grey or black color.¹⁵ Crystallographic studies revealed that the atomic arrangement of Tl₂S resembles the anti-CdCl₂ structure but with strong distortions.^{16, 17} One sheet of Tl₂S contains a sulfur atom layer sandwiched between two layers of Tl atoms. Viewing along the z-axis, the structure adopts an octahedral geometry whereby the central sulfur atom coordinates to 6 other thallium atoms. In each STl₆ octahedron, the Tl-S distance

varies between 2.82 and 3.09 Å.¹⁷ The Tl-Tl contacts are relatively short between the adjacent Tl₂S sheets at approximately 3.62 Å.¹⁷ Tl₂S has a unique structure which is the inverse of transition metal dichalcogenides such as 1T-MoS₂ where the metal atom is the central atom instead of the chalcogen (Figure 6.1a).¹⁸ Since electrochemical research in transition metal dichalcogenides has garnered much interest,¹⁹⁻²² this prompted us to wonder how a metal chalcogenide like Tl₂S having an inverted structure would perform, in particular, in electrochemical applications for sensing and energy purposes.

There has been limited research in the aspect of Tl₂S electrochemistry and its electrochemical applications. Despite one study on Tl₂S using abrasive stripping coulometry and voltammetry,²³ electrochemical studies in the past generally investigated the effect of thallium ions on various reactions.^{24, 25} Hence, very little is known about the inherent electrochemistry exhibited by Tl₂S. Electrochemical water-splitting processes are sustainable methods to generate energy. One example of such electrochemical process is the hydrogen evolution reaction (HER) whereby hydrogen is a clean energy carrier. A major drawback is the slow kinetics of HER which hampers the reaction rate rendering HER infeasible for industrial applications.²⁶ Even though platinum has been identified to be the best electrocatalyst for HER, it is expensive for large-scale uses due to its scarcity.^{27, 28} To overcome this, scientists have been in fervent pursuit of viable electrocatalysts as alternatives to Pt. To date, transition metal dichalcogenides proved to be promising for this purpose.^{19, 29-32}

Herein, we embark on a fundamental study to investigate the inherent electrochemistry of Tl₂S and to examine the electrochemical and electrocatalytic abilities of Tl₂S. In turn, we evaluate the suitability of Tl₂S as a prospective material in sensing as

well as a HER electrocatalyst. Moreover, we investigate how the anti-MoS₂ structure of Tl₂S influences its electronic properties and we show that Tl₂S has unusually low band dispersion.

6.2 Results and Discussion

6.2.1 Electronic Structure

The crystal structure of Tl₂S (see Figure 6.1a, mineral carlinite) adopts a slightly distorted anti-CdCl₂ structure type (C19, R3m). The origin of this distortion is clearly seen from the calculated electron density (Figure 6.1b, left panel) and is associated with the stereoactivity effect of Tl-6s² inert pair, which is oriented to different directions on the neighboring thallium atoms. This gives rise to a tripled unit cell along *a* and *b* directions (in hexagonal setting, see the right panel in Figure 6.1b). Surprisingly, the admixture of Tl-6p states into the Tl-6s band amounts only 3%, so the main contribution invoking the stereoactivity effect comes from the interstitial plane wave basis.

Figure 6.1 a) The schematic drawing of Tl₂S structure (S-yellow, TI – red) and the thallium octahedral with sulfur in the centers and inserted elemental cell. b) Valence electron density of Tl₂S viewed perpendicular to 001 direction (left panel) revealing a slight 6s² inert pair stereoactivity effect of surface thallium atoms. The corresponding structure drawing (right panel) is given for comparison.

The band structure around the Fermi level (Figure 6.2) is constituted by a valence band with a predominant S-3p character separated from the conduction band by an indirect band gap, $\Delta E_g = 0.80$ eV. The TI-6s states mainly participate in the band located ~ 0.6 eV below the valence band minimum which is relatively broad (3.5 eV) and thus substantially

involved in chemical bonding. This contradicts the anticipated non-bonding character of the Tl-6s states. In fact, only a narrow feature with a peaked density of states located at -6 eV can be attributed to highly localized charge carriers. Not shown in Figure 6.2 is the narrow Tl-5d band (-10.7 eV), which is split into $5d_{3/2}$ (-11.8 eV) and $5d_{5/2}$ (-9.6 eV) due to spin-orbit coupling. In general, the electronic structure in the vicinity of Fermi level is characterized by exceptionally flat bands, which makes the doped charge carriers very susceptible to possible localization. The electron transport necessary for an effective electrocatalytic activity would be thus impeded considering this rigid band model. Nonetheless, the real electronic structure can be considerably altered by introduction of various crystal defects including the surface states.

Figure 6.2 Band structure (per unit cell, 9 formula units) and the density of states (DOS, per one formula unit) of Tl₂S.

The electric transport measurements performed on crystals prepared from powder Tl₂S at room temperature revealed an apparent hole-like doping and a very low

concentration of charge carriers, $7 \times 10^{13} \text{ cm}^{-3}$. Combining the Hall coefficient $R_H = 5200 \text{ cm}^3 \text{ C}^{-1}$ with the resistivity $\rho = 44 \text{ } \Omega\text{m}$ yields the mobility $\mu = 21 \text{ cm}^2 \text{ V}^{-1} \text{ cm}^{-1}$ which is not that low in regard of the anticipated high tendency to localization. However, lowering the temperature by $15 \text{ }^\circ\text{C}$ (283 K) results in a change from hole to electron conductivity, an increase of charge carrier concentration to $1 \times 10^{15} \text{ cm}^{-3}$ and a simultaneous suppression of their mobility to $1.2 \text{ cm}^2 \text{ V}^{-1} \text{ cm}^{-1}$. Further cooling then leads to an abrupt increase of resistivity beyond the measurable range. This suggests that the transport data at room temperature can be interpreted in terms of a compensation effect of two kinds of doped charge carriers; hole-like and electron-like, coexisting in the concentrations $\sim 1 \times 10^{15} \text{ cm}^{-3}$ and a low mobility $\sim 1 \text{ cm}^2 \text{ V}^{-1} \text{ cm}^{-1}$, which quickly turns down on decreasing temperature for both channels, the hole channel being closed a few Kelvins above the electron channel.

Based on the DFT total energies of Tl₂S and the constituting elements (metallic Tl, P6₃/mmc, and orthorhombic S₈, Fddd) the enthalpy of formation of Tl₂S, $\Delta_f H(0 \text{ K}) = -124 \text{ kJ mol}^{-1}$ was assessed. This is a much more exothermic value than the reported enthalpy of formation $\Delta_f H(0 \text{ K}) = -92 \text{ kJ mol}^{-1}$,³³ which is, however, based on an estimation approach. Nonetheless, it is closer to the estimated value than the DFT result without including spin-orbit interaction $\Delta_f H(0 \text{ K}) = -142 \text{ kJ mol}^{-1}$.

6.2.2 Characterisation

The surface properties of synthesized Tl₂S were examined; in particular, the morphology and elemental surface composition of the synthesized Tl₂S. This was achieved by systematic characterization of the synthesized Tl₂S using scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS). The phase purity was probed by X-ray diffraction (XRD).

Figure 6.3 Scanning electron micrographs of synthesized Tl₂S sample at various magnifications. SEM images were obtained at a) 5000 × and b) 40 000 ×. Scale bars represent 1 μm in a) and 100 nm in b).

Figure 6.3 illustrates the morphology of Tl₂S captured on SEM at various magnifications of 5000 × and 40 000 ×. Both basal planes and edges of the Tl₂S are depicted in Figure 6.3a. It is apparent that the synthesized Tl₂S exists in bulk state with a rough appearance and exhibits thickness approximately between 0.5 to 1 μm. Each bulk mass is built up of numerous rod-like structures stacked in all directions as magnified in Figure 6.3b. Within each bulk mass, majority of them are packed such that each rod-like structure is assembled on top of another one in a parallel or horizontal manner.

Figure 6.4 Scanning electron micrograph of Tl₂S for EDS and the corresponding X-ray dispersive maps shown for elemental sulfur, thallium, carbon and oxygen.

By EDS, elemental mapping of the material verifies the presence of Tl and S in the

material as evident in Figure 6.4. Due to the overlapping characteristic X-ray signals of Tl and S at about 2.3 keV, an accurate EDS quantification cannot be provided. Therefore, we subsequently perform XPS to deduce the surface elemental composition of Tl₂S.

Figure 6.5 High resolution X-ray photoelectron spectra of a) Tl 4f region and b) S 2p region of Tl₂S. Deconvoluted peaks correspond to Tl(0 or III) or Tl(I) oxidation states. c) Wide scan X-ray photoelectron spectrum of Tl₂S. All spectra are calibrated to the adventitious C 1s peak at 284.5 eV.

Table 6.1 Chalcogen-to-metal ratio of Tl₂S derived from high resolution X-ray spectroscopy, with estimated distributions Tl(0 or III) and Tl(I) after deconvolution of the high resolution Tl 4f peak.

Material	Tl(0 or III) at. %	Tl(I) at. %	Chalcogen/Metal
Tl ₂ S	28.2	71.8	0.43

Table 6.2 Elemental composition of Tl₂S based on wide-scan resolution X-ray spectroscopy.

Material	Tl 4f at. %	S 2p at. %	C 1s at. %	O 1s at. %
Tl ₂ S	39.1	12.1	25.8	23.0

As presented in Figure 6.5c, the wide-scan XPS of Tl₂S identified distinct signals of Tl 4f paired at *ca.* 118 eV and 123 eV, S 2p at *ca.* 161 eV, C 1s at *ca.* 284 eV and O 1s at *ca.* 531 eV, confirming the presence of Tl and S in the earlier EDS data. The elemental distribution of the respective atomic percentages in Tl₂S is compiled in Table 2 with slightly less than 50 at. % attributed to C 1s and O 1s. The oxygen content originates dominantly from the surface adsorbed oxygen and its compounds like CO₂. The small peak at *ca.* 169 eV on the S 2p high resolution spectra in Figure 6.5b indicate trace oxidation of sulfur to S(VI) state.³⁴ However, no Tl₂SO₄ was detected by Raman spectroscopy. Furthermore, passivation of the surface is likely to have introduced oxide species such as Tl₂O and Tl₂O₃,^{35, 36} partially accounting for the contribution of Tl(I) and Tl(III) observed.

The high resolution core level of Tl 4f peak with deconvolution analysis of Tl bonding modes in Tl₂S is depicted in Figure 6.5a. Tl₂S manifests a pair of Tl 4f characteristic signals (4f_{7/2} and 4f_{5/2}) at *ca.* 118 eV and *ca.* 123 eV, primarily arising from the Tl(I) oxidation state. The observed splitting between 4f_{7/2} and 4f_{5/2} states is in very good agreement with DFT calculation results yielding -102 eV and -106 eV (referred to Fermi level). The paired Tl 4f_{7/2} and 4f_{5/2} signals are deconvoluted into several oxidation states, namely, Tl(0) at *ca.* 117.5 eV and 122.0 eV, T (I) at *ca.* 118.6 eV and 123.1 eV and Tl(III) at *ca.* 117.5 eV and 122.0 eV.³⁷⁻³⁹ It is of interest to note that the signals of Tl(III) occur at lower binding energies than Tl(I) deviating from other Group 13 elements. Thallium has an electronic configuration denoted as [Xe] 4f¹⁴ 5d¹⁰ 6s² 6p¹ in ground state and possesses 6s² and 6p¹ as valence

electrons. Due to the inert pair effect,^{40, 41} Tl exhibits a preference for the oxidation state +1 by an electron configuration 6s² 6p⁰. As observed by photoelectron spectroscopy measurements and reported in literature, Tl(III) showed lower binding energy compared to Tl(I).^{35, 37, 42} Tl-6s² pair can affect the energy of 4f states, which are at the border between the semi-core and core orbitals, by shielding them from the effect of crystal field. Hence its function must be opposite to the canonical shielding effect of core electrons which effectively screen the nuclear charge and bring about an increase of orbital energies.

Moreover, the proportion of Tl(I) species present in the Tl₂S is considerably significant due to the stability of Tl(I) oxidation state. The amount of Tl(I) species has been quantified to be 71.8 at. % (recorded in Table 6.1) with the remaining 28.2 % of thallium ascribed to either Tl(0) or Tl(III) states. The close proximity of binding energies between Tl(0) and Tl(III) state renders them indistinguishable. However, due to the reactivity of the elemental thallium it is more likely to suppose a partial surface oxidation of Tl(I) to Tl(III) rather than the presence of Tl(0). Based on the high resolution XPS data, the chalcogen-to-metal ratio for Tl₂S has been computed to be 0.43 which approximates the expected at 0.5.

The high purity of Tl₂S was further proved by X-ray fluorescence spectroscopy (XRF). The method is capable of detecting the elements from fluorine to heavier elements with the detection limit below 10 ppm. No impurities with the exception of calcium with a concentration of 270 ppm (±50 ppm) were detected. Due to high stability of calcium sulfide and the bonding characteristics of Ca²⁺ the calcium dissolution within Tl₂S structure is very unlikely. Hence, its presence in the samples can be interpreted as a result of surface contamination from laboratory environment.

The X-ray diffraction provided the presence of rhombohedral (space group R3)

thallium sulfide without any detectable impurity phases. The X-ray diffraction pattern is shown in Figure 6. The most intensive reflections were indexed.

Figure 6.6 The X-ray diffraction pattern of Tl₂S with indexed reflections.

The Raman spectroscopy was performed to investigate the structural properties of Tl₂S and the presence of possible impurities. In order to interpret the observed Raman spectroscopy data, phonon calculations were performed for an undistorted structure (space group R3m) requiring the ab-initio calculations of Hellmann-Feynman forces acting on the individual atoms in superstructures with six independent atomic displacements. Unfortunately, due to dynamic instability of the undistorted structure the acoustic and three lower lying optical modes exhibit negative frequencies in some regions within the Brillouin zone. Nevertheless, the two main broad features observed in the Raman spectrum can be attributed to a doubly degenerate E_u mode at lower wavenumber and a single A_{2u} mode at higher wavenumber corresponding predominantly to S-atoms displacements along 110 and 111 directions (100 and 001 in hexagonal notation) at the Γ -point. Although these modes are Raman inactive for the undistorted structure (D_{3d} local symmetry around

sulfur atom), they become both Raman and IR active and split into several modes due to structure distortion and local symmetry lowering (C_3 or C_1 for sulfur sites). The experimental results of Raman spectroscopy are shown on Figure 6.7. In the Raman spectra can be seen to main phonon modes at 280.4 cm^{-1} and 160 cm^{-1} denoted as A_{2u} and E_u respectively. Since the E_u phonon mode is degenerate, the addition modes can be observed at 143 cm^{-1} , 171 cm^{-1} and 192 cm^{-1} . The phonon mode at 171 cm^{-1} can be associated with the double degeneration of E_u phonon mode, while the other two can be probably attributed to defects within the Tl₂S structure. The measurement was performed at 12 K, since the Tl₂S exhibit extremely low radiation threshold. In addition, we performed the measurement of Tl₂SO₄ to identify the possible impurities formed by oxidation of Tl₂S. The characteristic band of S-O stretching of sulfate ion is present at 961 cm^{-1} and the additional modes at 426 cm^{-1} and 1097 cm^{-1} can be observed (Figure 6.S1). None of these phonon modes were observed on Tl₂S samples at 12 K. The room temperature measurement show only broad bands associated with the A_{2u} and E_u phonon modes of undistorted structure. The increase of laser power from 0.5 mW on 2.5 mW led to local damage of Tl₂S and its oxidation on Tl₂SO₄ by local heating. The results of room temperature Raman spectroscopy are shown on Figure 6.S2.

Figure 6.7 The Raman spectrum of Tl₂S. The measurement was performed using 532 nm laser (5 mW) at 12 K.

Further characterization of electronic structure was performed by photoluminescence spectroscopy. Since the Tl₂S is the semiconductor with indirect band-gap and the material can be damaged by higher laser power, the measurement was performed at 12 K. The relatively low intensity and the broadening of photoluminescence spectra originate from its electronic structure with extremely flat bands forming an indirect band-gap. The observed maxima at 1020 nm correspond to the band-gap of 1.22 eV, which is in good agreement with band-gap structure calculation since the DFT based theoretical values typically underestimate the real band-gap width. The results are shown in Figure 6.S3.

After examining the morphology and surface composition of Tl₂S, we investigated its electrochemistry to acquire knowledge about the inherent electrochemical properties. We also studied the electrochemical and electrocatalytic performances of Tl₂S in terms of its heterogeneous electron transfer (HET) rate and its efficiency for hydrogen evolution reaction (HER).

6.2.3 Inherent Electrochemical Property

We explore the inherent electrochemistry of TI₂S by performing cyclic voltammetry in two scan directions: towards positive and negative potentials. The voltammograms of the scans at pH 7.0 are displayed in Figure 6.8 with distinct redox peaks. Such features suggest the participation of various species and we will attempt to identify them here. Three consecutive scans were also recorded to establish the nature of electrochemical processes in TI₂S.

Figure 6.8 Cyclic voltammograms of TI₂S during a) scan to positive potentials and b) scan to negative potentials. Blank SPCE during c) scan to positive potentials and d) scan to negative potentials. Conditions: supporting electrolyte, PBS (50 mM), pH 7.0; scan rate, 100 mV s⁻¹; all measurements are performed relative to the Ag/AgCl reference electrode. Arrows indicate the direction of initial scan.

The voltammetric scans were first conducted on unmodified screen-printed electrodes (SPCE) as depicted in Figure 6.8c and Figure 6.8d. For both directions, no peaks were noted on the unmodified SPCE; indicative of the absence of electroactive moieties

on the SPCE. Hence, we have ascertained that the redox signals shown in Figure 6.8a and 6.8b of Tl₂S modified on SPCE mainly stem from the Tl₂S material and ruled out the possibility of redox signals due to SPCE.

In Figure 6.8a and Figure 6.8b, we identify four characteristic redox signals of Tl₂S at *ca.* 0.4 V, -0.5 V, -1.0 V and -1.5 V vs. Ag/AgCl during both scan directions suggesting that Tl₂S has innate electroactivity. Besides these four characteristic signals, there was also a modest oxidation signal at *ca.* 1.5 V vs. Ag/AgCl noted for the scan towards positive potentials. Among the four characteristic signals, the most striking features are the anodic peak at *ca.* -0.5 V vs. Ag/AgCl and the two cathodic peaks at *ca.* -1.0 V and -1.5 V vs. Ag/AgCl. The anodic peak at *ca.* -0.5 V vs. Ag/AgCl arises from the oxidation of thallium metal: $\text{Ti} \rightarrow \text{Ti}^+ + \text{e}^-$. Concurring with literature, Zhang *et al.* also observed an oxidation peak of thallium at -0.5 V vs. Ag/AgCl using abrasive stripping coulometry.²³ The cathodic peak at -1.0 V vs. Ag/AgCl, originating from *ca.* -0.75 V, is the reverse process to the anodic peak at -0.5 V vs. Ag/AgCl. This cathodic peak at -1.0 V vs. Ag/AgCl corresponds to the reduction of Tl(I) oxidation state to Tl(0): $\text{Ti}^+ + \text{e}^- \rightarrow \text{Ti}$. Similar findings by Scharifker *et al.* reported the stripping of thallium to Tl(I) ions at -0.61 V vs. SCE and electrodeposition of thallium at -1.1 V vs. SCE from Tl⁺ solution.²⁵ In another study by Cheng *et al.*, anodic and cathodic peaks of thallium were also noted at *ca.* -0.7 V and -0.9 V vs. SCE respectively in good agreement with our data.²⁴ As quoted from literature,²³ the other cathodic peak at -1.5 V vs. Ag/AgCl is likely attributed to the reduction of thallium sulfide to thallium metal: $\text{Tl}_2\text{S} + 2\text{e}^- \rightarrow 2\text{Ti} + \text{S}^{2-}$,⁴³ generating S²⁻ ions in the process. Under strongly reducing potentials, Tl₂S exhibits poor stability and its reduction to thallium and sulfide ions is probable.⁴³ Upon closer scrutiny, we notice there is another cathodic peak at *ca.* 0.4 V vs.

Ag/AgCl. This inconspicuous cathodic peak is easily overlooked, and we assign its emergence to TI(III) reduction to TI(I) ions in a two-electron process: $\text{TI}^{3+} + 2\text{e}^- \rightarrow \text{TI}^+$. Scharifker *et al.* also highlighted this TI(III) to TI(I) reduction process occurring at 0.54 V vs. SCE²⁵ which lies in good agreement with our experimental data. Based on the Eh-pH diagram, TI^{3+} species occupies a negligible domain whereas the TI^+ state dominates a significant portion of the domain, strongly suggesting that the TI^{3+} species has a lower stability than TI^+ .^{43, 44} As affirmed by the XPS deconvolution analysis, TI^{3+} species is present in paltry amounts compared to TI^+ and this justifies the weak current intensity of reduction peak at *ca.* 0.4 V vs. Ag/AgCl (of 40 μA ; first scan to negative potentials) relative to that at *ca.* -1.0 V vs. Ag/AgCl (of 560 μA ; first scan to negative potentials) triggered by TI(I) species. During the first scan towards positive potentials, we also observe a feeble reduction signal at *ca.* 0.4 V vs. Ag/AgCl of 30 μA due to TI^{3+} reduction and a more prominent cathodic signal at *ca.* -1.0 V vs. Ag/AgCl of 310 μA as a result of TI^+ reduction. The intensity of the redox peaks is proportional to the amount of electroactive moieties present. By virtue of the current intensities, it is apparent that the TI(I) species is indeed present in substantial amounts compared to TI(III). Furthermore, the modest oxidation signal evident in the initial scan at *ca.* 1.5 vs. Ag/AgCl could likely allude to the oxidation of TI(I) to TI(III). Hence, this provides the source of TI^{3+} for the reduction process at *ca.* -0.4 V vs. Ag/AgCl.

We notice that in subsequent scans, the current intensities of the distinct redox peaks are diminished. Consider the scan to positive potentials, the oxidation peak at *ca.* -0.5 V vs. Ag/AgCl with a current intensity of 250 μA during the first scan falls to 200 μA and 140 μA in the second and third scans respectively. The cathodic peaks at *ca.* -1.0 V vs. Ag/AgCl also exhibits a drop in current intensity from 310 μA in the initial scan to 120 μA and 92

μA in the following scans. Similarly, the cathodic peak at *ca.* -1.5 V vs. Ag/AgCl with a high current intensity of 620 μA during the first scan becomes depleted to comparatively negligible intensities in subsequent scans. Clearly, the electrochemical processes at these potentials are highly reversible and do not proceed to completion in a single scan. While the distinct signals show dwindling current intensities in successive scans, the modest reduction signal at *ca.* 0.4 V vs. Ag/AgCl retains a current intensity of 30 μA even in subsequent scans. Presence of metallic thallium formed at reduction electrochemical potentials destabilizes Tl(III) species and engenders the reaction: $\text{Tl}^{3+} \rightarrow 2 \text{Tl} + 3 \text{Tl}^+$ resembling the reduction to Tl(I).⁴⁵ Constant supply of metallic thallium in the system sustains this reaction, thereby maintaining the current intensity of the reduction process of Tl(III) to Tl(I). These observations in the current intensities of the respective redox signals are also replicated in the scan towards negative potentials. However, it is interesting to note that current intensities of the scan towards negative potentials at all the redox potentials are visibly larger than that in the scan towards positive potentials wherein the oxidation peak at *ca.* -0.5 V vs. Ag/AgCl has a current intensity of 700 μA, cathodic peaks at *ca.* 0.4 V, -1.0 V and -1.5 V vs. Ag/AgCl are at respective intensities of 40, 560 and 760 μA. The disparity in current intensities between the scans to positive and to negative potentials suggests that preceding reductions at *ca.* -1.0 V and -1.5 V vs. Ag/AgCl during the scan to negative potentials introduce additional oxidizable moieties; for instance, metallic thallium is available for oxidation to Tl(I) species at *ca.* -0.5 V vs. Ag/AgCl. In turn, a dramatically higher current intensity at 700 μA is generated in the scan towards negative potentials relative to that in the scan towards positive potentials.

Since redox signals are more prominent during the scan to negative potentials than

scan to positive potentials, we adopted the negative scan direction for a pH study. A single scan to the negative potentials was performed on Ti₂S modified SPCE for various pH from 2 to 12. All voltammetric profiles are shown in Figure 9a and the shifts in electrochemical potentials for anodic peak at *ca.* -0.5 V vs. Ag/AgCl and cathodic peaks at *ca.* 0.4V, -1.0 V and -1.5 V vs. Ag/AgCl are summarized in Figure 9b. Across various pH, the electrochemical potentials of the distinct peaks at *ca.* -0.5 V, -1.0 V and -1.5 V vs. Ag/AgCl remain fairly constant with a deviation of not more than 0.2 V. The electrochemical processes occurring at these potentials are unaffected by pH and are deemed to be pH-independent. On the contrary to the distinct peaks at *ca.* -0.5 V, -1.0 V and -1.5 V vs. Ag/AgCl, the modest cathodic signal at *ca.* 0.4 V vs. Ag/AgCl has a strong dependence on pH. This signal is absent in the acidic region when pH falls below 6 whereas in the alkaline pH region, we observe a negative linear correlation between the electrochemical peak potential with pH. The signal appears to progressively shift towards lower electrochemical potentials from *ca.* 0.4 V vs. Ag/AgCl at pH 7 to *ca.* 0.03 V vs. Ag/AgCl at pH 12 when pH of the electrolyte becomes increasingly alkaline. We assigned this cathodic signal to the reduction of Ti³⁺ to Ti⁺: $\text{Ti}^{3+} + 2\text{e}^- \rightarrow \text{Ti}^+$. Known to be a strong oxidant, Ti³⁺ is susceptible to hydrolysis unlike Ti⁺ and hence the electrochemical potential of the reaction will be influenced by pH.^{25, 45, 46} Ti³⁺ is stable only in acidic media and thus, readily undergoes reduction to Ti⁺ in alkaline conditions which explains the observed phenomenon. The H⁺: e⁻ ratio for this cathodic peak is calculated to be 1:1 under alkaline conditions. We may postulate this due to the formation of Ti(III) complexes like [Ti(OH)₄]⁻⁴⁷ or salts such as insoluble Ti(OH)₃ species⁴⁸ at the electrode surface under alkaline conditions. The reduction process of Ti³⁺ to Ti⁺ is possibly dominated by the Ti(OH)₃ processes in increasingly alkaline electrolyte.⁴⁷ In basic

conditions, Tl(OH)₃ is reduced to Tl(OH) *via* the process: $\text{Tl(OH)}_3 + 2\text{e}^- \rightarrow \text{Tl(OH)} + 2\text{OH}^-$ ⁴⁵

which also translates to having a H⁺: e⁻ ratio of 1:1 when written as $2\text{H}^+ + \text{Tl(OH)}_3 + 2\text{e}^- \rightarrow \text{Tl(OH)} + 2\text{H}_2\text{O}$.

Figure 6.9 a) Cyclic voltammograms of Tl₂S across a pH range from 2 to 12. b) Summarized data of the shift in electrochemical potential of redox signals across pH. Conditions: supporting electrolyte, PBS (50 mM), pH 2-12; scan rate, 100 mV s⁻¹; all measurements are performed relative to the Ag/AgCl reference electrode.

6.2.4 Heterogeneous Electron Transfer

Next, we examine the electrochemical performance of Tl₂S material using heterogeneous electron transfer (HET) rate as a parameter. Generally, a fast HET rate is ideal for sensing applications. Two redox probes, [Fe(CN)₆]^{3-/4-} and [Ru(NH₃)₆]^{3+/2+}, are employed to evaluate its electron transfer property. [Fe(CN)₆]^{3-/4-} is surface-sensitive⁴⁹ and its electron transfer occurs *via* an inner-sphere mechanism. Conversely, [Ru(NH₃)₆]^{3+/2+} is an outer-sphere redox probe and is insensitive to surface structures⁵⁰, hence serving as an experimental control to confirm the results in [Fe(CN)₆]^{3-/4-}.

Figure 6.10 Cyclic voltammograms of 5 mM a) [Fe(CN)₆]^{3-/4-} and b) [Ru(NH₃)₆]^{3+/2+} on Tl₂S and bare glassy carbon electrode. Conditions: 5 mM [Fe(CN)₆]^{3-/4-} or [Ru(NH₃)₆]^{3+/2+} in 0.1 M KCl; scan rate, 100 mV s⁻¹; all measurements are performed relative to the Ag/AgCl reference electrode. Nyquist plots of c) both Tl₂S and MoS₂. A histogram illustrating the impedimetric signal of Tl₂S and MoS₂ represented as d) R_{ct}. All measurements were performed in 10 mM K₄[Fe(CN)₆]/K₃[Fe(CN)₆] in PBS buffer at pH 7.0.

According to Figure 6.10a, the peak-to-peak separation (ΔE) of Tl₂S material in the presence of [Fe(CN)₆]^{3-/4-} redox couple is 0.41 V while bare glassy carbon (GC) electrode has a narrower ΔE of 0.19 V. Using the classical Nicholson method,⁵¹ the HET rates (k_{obs}^0) were determined to be $6.3 \times 10^{-5} \text{ cm s}^{-1}$ for Tl₂S material and $1.4 \times 10^{-3} \text{ cm s}^{-1}$ for the bare GC electrode (HET rates are further summarized in Table 6.S1). Tl₂S has a k_{obs}^0 that is two-orders of magnitude smaller than the bare GC. The slow k_{obs}^0 of Tl₂S suggests that Tl₂S has intrinsically poor conductivity and hence, are not favored in the area of electrochemical sensing. We set to investigate what is the influence of potential impurities in the form of thallium oxide.⁴⁹ This is elucidated in experimental measurements with Tl₂O₃ as presented

in Figure S4. Compared to Tl₂S, Tl₂O₃ depicts a wider ΔE of 0.52 V and a slower HET rate derived to be $1.5 \times 10^{-5} \text{ cm s}^{-1}$. Clearly, the presence of oxides impedes electron transfer. As the ΔE of Tl₂S is disparate from Tl₂O₃, we would consider that there is minimal surface passivation on Tl₂S. There is no difference of ΔE between Tl₂S and bare GC electrode in presence of [Ru(NH₃)₆]^{3+/2+} redox probe as presented in Figure 10b. Thus, we have ascertained that the measured data in [Fe(CN)₆]^{3-/4-} redox probe for Tl₂S and GC surface are caused by surface changes when GC electrode is modified with Tl₂S.

Using electrochemical impedance spectroscopy, we compared between the resistance of Tl₂S and MoS₂ towards heterogeneous electron transfer in the presence of Fe(CN)₆^{3-/4-} redox probe, with the measurements illustrated in Figure 6.10c and 6.10d. The charge transfer resistance is, inversely correlated to k_{obs}^0 and, quantified by the diameter of the semicircle in the Nyquist plot.

According to Figure 6.10c, it has become apparent that the overlaying Nyquist plots of Tl₂S and MoS₂ depict a wider semicircle diameter for Tl₂S compared to MoS₂, corresponding to a higher electron transfer resistance exhibited by Tl₂S than MoS₂. The charge transfer resistance (R_{ct}) of Tl₂S at 7500 Ω is distinctly higher than MoS₂ at 500 Ω . Based on this electrochemical impedance study, we infer that Tl₂S demonstrates a considerably slower rate of heterogeneous electron transfer than MoS₂.

6.2.5 Electrocatalytic Performance in Hydrogen Evolution Reaction

We proceed to determine the electrocatalytic capability of Tl₂S and evaluate its prospective use as an electrocatalyst for hydrogen evolution reaction (HER) is shown on Figure 6.11. Tafel slope and onset potential are employed as HER performance indicators. We define the HER onset potential as the potential at -1 mA cm⁻² which equals 10 % of the

maximum current density reached. Pt/C has been widely regarded as the ideal HER electrocatalyst and has been included in the HER measurements as a basis for comparison with Ti₂S. As Ti₂S is of anti-CdCl₂ type structure whereas 1T-MoS₂ has a CdCl₂ type structure, we adapted the HER performance of MoS₂ from our previous study²⁰ to illustrate how strikingly dissimilar structures can affect HER. Analysis of the Tafel slopes also enables the rate-determining steps in HER for each material to be deduced. The following are the possible rate-determining steps:^{26, 30, 52}

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

Figure 6.11 a) Polarization curves for hydrogen evolution and b) corresponding Tafel plots using Ti₂S, MoS₂, GC and Pt/C based electrodes. Presented in bar charts are the averages of c) Tafel slopes and d) Onset potential at current density of -1 mA cm⁻² and their corresponding error bars for all materials. Conditions: background electrolyte, H₂SO₄ (0.5

M); scan rate, 2 mV s⁻¹, all measurements are performed relative to the Ag/AgCl reference electrode and corrected to reversible hydrogen electrode (RHE) potentials. Data of MoS₂ was reprinted from our previous work using the same experimental conditions.²⁰

From Tafel slope analysis, Tl₂S yielded a Tafel slope of 140 mV/dec. This value lies closest to the value of 120 mV/dec corresponding to the Volmer process. As such, the limiting step of Tl₂S is inferred to be the adsorption step (Volmer). The onset HER potential of Tl₂S occurred at -0.65 V vs. RHE. While the HER onset of Pt/C takes place at -0.03 V vs. RHE, which is a markedly lower potential than Tl₂S, the bare GC exhibits a later onset potential at -0.91 V vs. RHE. Therefore, Tl₂S demonstrates higher HER catalytic efficiency than the bare GC and may be considered for use as a prospective HER electrocatalyst. However, compared to MoS₂ which exhibits a significantly earlier onset potential at -0.42 vs. RHE, Tl₂S fares worse as a HER electrocatalyst. The charge-transfer resistance of Tl₂S 7500 Ω is consequentially higher than MoS₂ at 500 Ω . The slower electron transport deems Tl₂S unfavorable for HER relative to MoS₂. To investigate whether traces of thallium oxides or sulfates in Tl₂S may potentially govern the HER performance of Tl₂S, we experiment with two oxygen-containing thallium materials; namely, Tl₂O₃ and Tl₂SO₄. The linear sweep voltammograms of Tl₂O₃ and Tl₂SO₄ are recorded in Figure 6.S5. The HER onset potential of Tl₂O₃ and Tl₂SO₄ are at -0.78 V and -0.83 V respectively, suggesting that both Tl₂O₃ and Tl₂SO₄ display diminished HER electrocatalytic behaviour than Tl₂S. Juxtaposed with Tl₂O₃ and Tl₂SO₄ (Figure 6.S5), the distinctly earlier HER onset of Tl₂S is indicative that the HER performance of Tl₂S stems from its innate electrocatalytic performance and is not a contribution from either Tl₂O₃ or Tl₂SO₄.

In view of the structure topology and the respective hydrogen affinity towards sulfur

and thallium, the hydrogen attachment likely takes place on the crystallites edges with naked sulfur atoms. A screening ab-initio calculation carried out on an idealized undistorted structure (a supercell corresponding to stoichiometry Tl₃₀S₁₅H₂ with slabs perpendicular to layers and 15 Å thick vacuum between the slabs) yielded a highly exothermic value of absorption energy -1 eV with respect to H₂/H⁺ suggesting a facile saturation of these sites by hydrogen and a difficult desorption. However, considering the inequivalency of sulfur atoms on the crystal edge and a decreased tendency to electron doping with increasing H-content one can expect that the adsorption of additional hydrogen will be less energetically favorable, which was confirmed by the experimental measurement on HER in sulfuric acid.

6.3 Conclusion

We performed the electronic structure calculations on Tl₂S and obtained a band-gap of $E_g = 0.8$ eV. Synthesized Tl₂S was characterized in detail using SEM-EDS, XPS, XRD and Raman spectroscopy. We investigated its electrochemistry in detail and evaluated the prospective use of Tl₂S in electrochemical sensing and electrocatalysis. Tl₂S is determined to be inherently electroactive as manifested in the four crucial redox signals at *ca.* 0.4 V, -0.5 V, -1.0 V and -1.5 V vs. Ag/AgCl. The process at each of these electrochemical potentials has also been elucidated. Tl₂S exhibits intrinsically slow HET rates. In HER electrocatalysis, Tl₂S appears promising as a prospective material compared to GC but pales in comparison to MoS₂ because Tl₂S has low conductivity and hence, slow electrode kinetics. Hence, awareness of Tl₂S electrochemistry could transform them into beneficial applications. Furthermore, the DFT calculations showed that Tl₂S exhibits unusually flat band-gap dispersions. It is clear that anti-MoS₂ structure brings about interesting features to the

field of TMDs.

6.4 Experimental Methods

6.4.1 Materials

Thallium(I) nitrate (99.9%) was obtained from Sigma-Aldrich, Czech Republic. Nitric acid (>68%) was obtained from Penta, Czech Republic. Hydrogen sulphide (99.9%) was obtained from Linde Gas, Czech Republic. Potassium chloride, potassium phosphate dibasic, sodium phosphate monobasic, sodium chloride, potassium hydroxide, phosphoric acid, *N,N*-dimethylformamide (DMF), potassium ferrocyanide, potassium ferricyanide, hexammineruthenium (III) chloride, platinum on carbon and molybdenum sulfide were purchased from Sigma Aldrich. Pt, Ag/AgCl, screen-printed carbon electrodes (SPCEs) and glassy carbon (GC) electrodes were purchased from CH Instruments, Texas, USA.

6.4.2 Synthesis

Tl₂S was synthesized by reaction of thallium nitrate with hydrogen sulphide. 100 mL of 5 wt.% solution of thallium nitrate was acidified by nitric acid on pH = 4.0. The solution was bubbled with hydrogen sulphide (100 mL/min) for four hours. Formed Tl₂S was separated from solution by suction filtration and the product was washed with deionized water till neutral pH. Tl₂S was dried in vacuum oven for 48 hours at 50°C.

10 g of Tl₂S prepared by reaction of thallium nitrate with hydrogen sulphide was placed in a quartz glass ampoule (15×140 mm) which was pumped down using oil diffusion pump. The ampoule was sealed at 1×10^{-3} Pa using oxygen-hydrogen torch. Tl₂S was heated up to 610 °C using 5 °C/min heating rate and after 1 hour at 610 °C the ampoule was cooled to room temperature by applying a cooling rate 1 °C/min. The crystalline mass was mechanically separated into plates with dimensions suitable for transport measurement with

size about 3×4 mm and thickness below 1 mm.

6.4.3 Apparatus

Scanning electron microscopy (SEM) was conducted using a JEOL 7600F field-emission scanning electron microscope (JEOL, Japan) at 2 kV. Energy dispersive X-ray spectroscopy data were measured at an accelerating voltage of 15 kV.

X-ray photoelectron spectroscopy (XPS) was performed on Phoibos 100 spectrometer with a Mg K_α X-ray source (SPECS, Germany) at 1245 eV. Survey and high-resolution spectra were obtained for TI 4f and S 2p. The relative sensitivity factors were also adopted for the calculation of chalcogen-to-metal ratios and for deconvolution of the oxidation states in TI. The chalcogen metal ratio was calculated using the respective areas of the high resolution scans of TI 4f and S 2p.

X-ray powder diffraction data were collected at room temperature with an Bruker D8 Discoverer powder diffractometer with parafocusing Bragg-Brentano geometry using CuK_α radiation ($\lambda = 0.15418$ nm, U = 40 kV, I = 30 mA). Data were scanned with an ultrafast detector X'Celerator over the angular range 5-80° (2 θ) with a step size of 0.0167° (2 θ) and a counting time of 20.32 s step⁻¹. Data evaluation was performed in the software package HighScore Plus 3.0.

An Axios sequential WD-XRF spectrometer (PANalytical, The Netherlands) was used to perform XRF analysis. It is equipped with Rh anode end-window X-ray tube fitted with 50 μ m Be window. Measured data were collected by software SuperQ in vacuum. The obtained data were evaluated by standardless software Omnian. The analyzed powders were pressed onto H₃BO₃ pellets with total thickness about 5mm and diameter of 40 mm without any binding agent and covered with 4 μ m supporting polypropylene (PP) film.

The electric transport measurements were performed in PPMS-9 T apparatus (Quantum Design) using a four-point method in longitudinal arrangement (Resistivity option). The Hall coefficient was evaluated from the slope of Hall voltage vs. magnetic field dependence recorded in the range from – 4 to + 4 T.

An inVia Raman microscope (Renishaw, England) was used for Raman spectroscopy measurements. The spectrometer operates in backscattering geometry with a CCD detector. Nd-YAG laser (532 nm, 50 mW) was used with 50× magnification objective. The instrument calibration was achieved with a silicon reference which yields a peak position at 520 cm⁻¹. To avoid sample damage no more than 5% of the total 50 mW laser power was used. The Raman and photoluminescence measurement at low temperature was performed in Janis closed cycle vibration isolated cryostat for microscopy. The measurement was performed at 12 K using 20× magnification long working distance objective.

Voltammetric measurements were recorded on a μAutolab III electrochemical analyser (Eco Chemie B.V., Utrecht, The Netherlands) using the software NOVA version 1.8 (Eco Chemie). Electrochemical measurements were performed in a 3 mL voltammetric cell at room temperature (25 °C) in a three electrode configuration. A platinum electrode and an Ag/AgCl electrode functioned as auxiliary and reference electrodes, respectively. Two types of electrodes were employed as working electrodes. During inherent electrochemical studies, a screen-printed carbon electrode (SPCE, 8 mm diameter) served as the working electrode. A glassy carbon (GC, 3 mm diameter) functioned as the working electrode during measurements of heterogeneous electron transfer (HET) and hydrogen evolution reaction (HER).

Electrochemical measurements of the materials were performed in a 5 mL voltammetric cell at room temperature (25 °C) in a three electrode configuration. A platinum electrode and an Ag/AgCl electrode functioned as auxiliary and reference electrodes, respectively and a glassy carbon (GC, 3 mm diameter) electrode was adopted as the working electrode.

6.4.4 Electronic structure calculations

The band structure and total energy of Tl₂S was calculated within density functional theory (DFT) using APW+lo basis set and generalized gradient approximation (GGA, PBE96 parametrization scheme⁵³) for exchange correlation potential as implemented in the Wien2k software package.⁵⁴ The plane wave cut-off energy of 240 eV and the tetrahedron method with the *k*-mesh 8x8x8 were used. The calculation was performed as non-spin polarized. Due to non-negligible relativistic effects on heavy Tl atom the spin-orbit (S-O) coupling was included by applying the second variational procedure on the scalar-relativistic eigenstates. The basis was extended by a relativistic 5p_{1/2} local orbital centered at Tl atom in the case of S-O calculation. The structure data for the bulk Tl₂S were adopted from Giester *et al.*, however, the unit cell volume optimization was applied.¹⁷

6.4.5 Procedures

Cyclic voltammetry experiments were performed at a scan rate of 100 mV s⁻¹ in 50 mM phosphate buffered saline (PBS) as the background electrolyte across pH 2.0 to 12.0. The voltammetric scans began at 0 V. At this electrochemical potential, no redox processes were expected to occur.⁵⁵ For the scan to positive potentials, it was first scanned toward +1.8 V followed by a reverse sweep towards -1.8 V. Conversely, it was scanned towards -1.8 V initially and then reversed to +1.8 V during the scan to negative potentials. Both scans were eventually returned to 0 V. The Tl₂S sample was suspended in ultrapure water

at concentrations of 1 mg mL⁻¹ and ultrasonicated for 2 h when newly prepared to attain general homogeneity. Subsequently, the Tl₂S sample was ultrasonicated for a period of 10 min prior to each electrochemical measurement to maintain the uniform suspension. 16.0 µL aliquot of the suspension was then drop-casted on a SPCE. The solvent was left to evaporate at room temperature under the lamp to yield an electrode surface randomly modified with a 16.0 µg film of the desired material.

Prior to performing measurements on a GC electrode, the GC electrode was polished with 0.05 µm alumina particle slurry on a polishing pad and rinsed with ultrapure water to restore the electrode surface to a mirror finish. Tl₂S and Tl₂O₃ were prepared in a concentration of 2 mg/mL in DMF. After ultrasonication for 10 min, 2 µL of aliquot of dispersion was drop casted on the GC electrode surface. The DMF solvent was left to evaporate under the lamp which modified the electrode surface with a randomly coated film of 4.0 µg of desired material. Cyclic voltammetry experiments were performed at a scan rate of 100 mV s⁻¹ on Tl₂S-modified GC electrodes for redox probes: potassium ferrocyanide (5 mM) and hexaamineruthenium (III) chloride in KCl (0.1 M) background electrolyte. The k_{obs}^0 value were derived from the Nicholson method.⁵¹ The roughness of the electrode was not factored into the calculation of k_{obs}^0 . The diffusion coefficient $D = 7.26 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ was used to compute the k_{obs}^0 value for [Fe(CN)₆]^{4-/3-}.⁵⁶

Tl₂S and MoS₂ were prepared in a concentration of 2 mg/mL in DMF. After ultrasonication for 10 min, 2 µL of aliquot of dispersion was drop casted on the GC electrode surface. The DMF solvent was left to evaporate under the lamp which modified the electrode surface with a randomly coated film of 4.0 µg of desired material. Impedance measurements were recorded between 0.1 MHz and 0.1 Hz at a sinusoidal voltage perturbation of 10 mV

amplitude. The measurements were performed with 10 mM K₄[Fe(CN)₆]/K₃[Fe(CN)₆] redox probe in 50 mM PBS pH 7.0. Randles equivalent circuit was used to fit the acquired impedance spectra, represented as Nyquist plots in the complex plane. R_{ct} was derived from the difference in impedance between the material and the bare GC.

The hydrogen evolution reaction (HER) performance of TI₂S was also performed on GC electrode using the dispersion prepared in a concentration of 2 mg/mL in DMF. Pt/C dispersion was also prepared to the same concentration of 2 mg/mL in DMF. Similarly, TI₂O₃ and TI₂SO₄ were also prepared in a concentration of 2 mg/mL in DMF for comparison. The dispersions were ultrasonicated for 10 min before 2 µL of aliquot of the material was drop casted on the GC electrode surface and left to dry. HER measurements were carried out *via* linear sweep voltammetry at a scan rate of 2 mV s⁻¹ in 0.5 M H₂SO₄ electrolyte. Linear sweep voltammograms are presented *versus* the reversible hydrogen electrode (RHE). Measured potentials (vs. Ag/AgCl) are corrected to RHE using this equation⁵⁷ $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \times \text{pH} + E^0_{\text{Ag/AgCl}}$. $E_{\text{Ag/AgCl}}$ is the measured potential, pH of 0.5 M H₂SO₄ electrolyte is zero and $E^0_{\text{Ag/AgCl}}$ refers to the standard potential of Ag/AgCl (1 M KCl) at 25°C which is 0.235 V.

6.5 Supporting Information

Figure 6.S1 The Raman spectra of Tl₂SO₄.

Figure 6.S2 The Raman spectra of Tl₂S measured at room temperature using different laser power.

Figure 6.S3 The photoluminescence spectrum of Tl₂S measured at 12 K using 532 nm laser (5 mW).

Figure 6.S4 Cyclic voltammograms of 5mM a) [Fe(CN)₆]^{3-/4-} and b) [Ru(NH₃)₆]^{3+/4+} on Tl₂S, Tl₂O₃ and bare glassy carbon electrode. Presented in bar charts are the average peak-to-peak separations (ΔE) of Tl₂S, Tl₂O₃ and bare glassy carbon electrode in the presence of c) [Fe(CN)₆]^{3-/4-} and d) [Ru(NH₃)₆]^{3+/4+}. Conditions: 5 mM [Fe(CN)₆]^{3-/4-} or [Ru(NH₃)₆]^{3+/4+} in 0.1 M KCl; scan rate, 100 mV s⁻¹; all measurements are performed relative to the Ag/AgCl reference electrode.

Table 6.S1 Table of heterogeneous electron transfer (HET) rate constant, k_{obs}^0 for all the materials in the presence of 5 mM [Fe(CN)₆]^{3-/4-}.

Material	k_{obs}^0 (cm s ⁻¹)
GC	1.43×10^{-3}
TI ₂ S	6.27×10^{-5}
TI ₂ O ₃	1.49×10^{-5}

Figure 6.S5 a) Linear sweep voltammograms for hydrogen evolution for comparisons between TI₂S, TI₂O₃ and TI₂SO₄ and b) corresponding onset potential at a current density of -1 mA cm⁻². GC is also included for comparison. Conditions: background electrolyte, H₂SO₄ (0.5 M); scan rate, 2 mV s⁻¹, all measurements are performed relative to the Ag/AgCl reference electrode and corrected to reversible hydrogen electrode (RHE) potentials.

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Chapter 7

Electrochemistry of Tin Chalcogenides:

SnS *versus* SnS₂

7.1 *Introduction*

7.2 *Results and Discussion*

7.2.1 Characterisation

7.2.2 Inherent Electrochemistry

7.2.3 Heterogeneous Electron Transfer

7.2.4 Electrocatalytic Property

7.3 *Conclusion*

7.4 *Experimental Section*

7.5 *Supporting Information*

The results and discussion in this chapter were published in the following manuscript:

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The thesis author was the primary investigator and first author of the above paper.

7.1 Introduction

The vast technological promise of two-dimensional (2-D) layered nanomaterials sets scientists in a race to uncover more. Presently, 2-D layered transition metal dichalcogenides (TMDs) is taking a prominent lead; running a gamut of applications from Li-ion batteries,¹ supercapacitors^{2,3} to solar cells.⁴ While TMDs have garnered enthusiasm in diverse fields, other metal chalcogenides, beyond the transition metal group, are often overlooked.⁵ Nevertheless, a recent spate of studies has ramped up interest for Group 14 metal chalcogenides, in particular, the tin (Sn) chalcogenides.⁶⁻⁹ In this regard, Sn chalcogenides embrace several composites, as dictated by the versatile oxidation characteristics of Sn and the chalcogen. As epitomized in tin-sulfur structures, the reported binary compounds include SnS, Sn₂S₃, Sn₃S₄, Sn₄S₅ and SnS₂.¹⁰⁻¹⁶ Amongst them, SnS and SnS₂ are derived from a single oxidation state whereas the rest comprise mixed phases. SnS and SnS₂ are distinguishable from their appearance wherein SnS is grey and SnS₂ is golden yellow.¹⁷ SnS₂, which occurs naturally in berndtite mineral,¹⁷ crystallizes into a hexagonal unit cell. Analogous to the TMDs, specifically 1T-MoS₂, SnS₂ adopt a CdI₂ structure consisting of the central Sn(IV) atom covalently bonded to six other S chalcogen atoms in the octahedral sites.^{9, 16} Also known as herzenbergite,¹⁷ SnS displays an orthorhombic structure congruent with GeS wherein each Sn(II) atom is coordinated to six S chalcogen atoms such that a highly distorted octahedral geometry ensues at room temperature.^{9, 16} The distortion generates Sn-S bonds of unequal lengths with three short Sn-S bond lengths of *ca.* 2.7 Å and another three longer Sn-S bonds at *ca.* 3.4 Å. SnS and SnS₂ are layered chalcogenides structurally akin to TMDs such that strong covalent bonding exists within the plane and weak van der Waals' interactions occur between layers.^{9, 16, 18, 19} The 2-D layered nature of Sn chalcogenides efficiently accommodates large

volume changes during cycling.^{20, 21} Likewise, the interlayer spacing of Sn chalcogenides provides sites for intercalation of Li or Na ions.^{20, 22} Equipped with these crystallographic features, Sn chalcogenides are extensively exploited in electrode materials for lithium and sodium ion batteries.^{7, 23-26}

Apart from battery uses, studies on SnS and SnS₂ have long reached a crescendo in the realms of photocatalysis and photovoltaics, thanks to their electronic and optical properties.²⁷⁻³⁰ As bulk crystals, SnS and SnS₂ respectively exhibit p-type and n-type semiconductor character.^{9, 31} SnS₂ has a band gap of ~2.2 eV and absorbs visible light.³² Conversely, SnS has a narrow band gap of ~1.2 eV and demonstrates optical activity in the near-infrared region.^{27, 33} Lately, Sn chalcogenides have been also introduced to be potentially useful as supercapacitors.^{34, 35} Reasons behind the runaway success of Sn chalcogenides in a myriad of applications boil down to their earth abundance, low toxicity and versatile attributes.³⁶

These traits of Sn chalcogenides, particularly the high natural abundance, bode well for prospective uses as electrocatalysts in energy-related technologies. In the face of dwindling supplies of fossil fuels and escalating carbon emissions, oxygen and hydrogen energy carriers, which are environmentally-benign, have been touted as the panacea to the energy crisis. Currently, platinum (Pt) is established as the best-performing electrocatalyst for hydrogen evolution reaction (HER).³⁷ Yet, the low natural abundance of Pt drives up the cost, thereby deterring the proliferation of its industrial use. Beginning with MoS₂ which spearheaded the tide of research into layered TMDs as HER electrocatalysts,^{38, 39} the scientific community has been on the hunt for earth-abundant layered materials that potentially rival the performance of Pt. Therefore, layered metal

chalcogenides such as SnS and SnS₂ are worth exploring.

Even though the emphasis of Sn chalcogenides research has centered on potential applications, current studies neither discussed the electrochemistry of SnS and SnS₂, nor drew comparisons between the valencies of Sn or their distinct crystal structures on their electrochemical or electrocatalytic properties. Hence, a work reconciling their valence and structural differences with the electrochemical or electrocatalytic characteristics is warranted to address these gaps in literature.

Herein, we examine the electrochemical properties of layered SnS and SnS₂. In particular, we explore their inherent electroactivities and heterogeneous electron transfer rates. Additionally, we evaluate the implications of orthorhombic SnS and hexagonal SnS₂ on their electrocatalytic abilities for energy storage applications such as hydrogen evolution reaction (HER). Considering their crystal structures, we undertake density functional theory (DFT) calculation to construe their electrocatalytic showing, in particular for the divergent HER properties of Sn chalcogenides. A thorough characterization of Sn chalcogenides is conducted using scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), X-ray diffraction and X-ray photoelectron spectroscopy (XPS). Understanding the electrochemistry of SnS and SnS₂ will offer new perspectives into their development in electrochemical applications.

7.2 Results and Discussion

7.2.1 Material Characterization

The as-synthesized SnS and SnS₂ were characterized using multiple techniques including scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), X-ray diffraction and X-ray photoelectron spectroscopy (XPS).

Figure 7.1 Scanning electron micrographs of a) SnS at magnifications of 1000 × and b) 5000 × and c) SnS₂ at magnifications of 8000 × and d) 40 000 ×. Scale bars corresponding to the micrographs are also shown.

SEM was employed to compare and contrast the surface morphologies of SnS and SnS₂. Their respective scanning electron micrographs are presented in Figure 7.1 in various magnifications. A striking similarity between SnS and SnS₂ is their layered nature. As illustrated in Figure 7.1, layered structures in SnS and SnS₂ are discernible. There are distinct separations between layers; this is most evident in SnS. The layers in SnS and SnS₂ are also assembled in close stacking which is a feature of bulk materials.

Using EDS, we perform elemental analysis of SnS and SnS₂. Elemental distribution analysis *via* elemental mapping indicates a defined compositional profile of Sn and S elements for both SnS and SnS₂ (Figure 7.S1). Recorded in Table 7.S1, the computed chalcogen-to-metal ratio for SnS is 0.9 and 1.8 for SnS₂. In both cases, the computed ratios approach the expected ratios of 1.0 and 2.0, for SnS and SnS₂ respectively. Chalcogen-to-

metal ratios acquired from our XPS analysis also affirmed the EDS data. By XPS, we obtained chalcogen-to-metal ratios of 1.1 for SnS and 1.8 for SnS₂ (Table 7.S2). Hence, bulk layered SnS and SnS₂ materials have been successfully synthesized with precise stoichiometry.

The X-ray diffraction showed single phase purity of both SnS and SnS₂. SnS crystallizes in the space group Pbnm and has an analogical structure to black phosphorus, which is isoelectronic with SnS. The SnS₂ has a space group P-3m1 which is typical for several layered transition metal dichalcogenides (structure type CdI₂). The results of X-ray diffraction as well as the corresponding structures are shown on Figure 7.2. The measured lattice parameters are $a=4.3283$, $b=11.2015$, and $c=3.9925$ Å for orthorhombic SnS, and $a=b=3.6459$, $c=5.8968$ Å for SnS₂.

Figure 7.2 The X-ray diffractogram of SnS and SnS₂ and corresponding structures. The diffraction lines correspond to PDF# card no. 01-083-1705 (SnS₂) and PDF# card no. 01-075-1803 (SnS).

We examined the surface chemical compositions of SnS and SnS₂ using XPS analysis. It is essential to be aware of their surface composition in a bid to elucidate the

electrochemistry of Sn chalcogenides. Species present on the material surface play an active role in electrochemical reactions. Figure 7.3 displays the high resolution XPS core level spectra of Sn 3d and S 2p regions for SnS and SnS₂. Atomic percentages of the deconvoluted states of Sn are recorded in Table 7.S3.

On the basis of XPS analysis of Sn 3d regions for Sn chalcogenides (Figure 7.3a), the principal valencies of SnS and SnS₂ surfaces are ratified to be +2 and +4 respectively. SnS manifests a pair of doublet signals that corresponds to Sn(0) and Sn(II) states at respective Sn 3d_{5/2} and Sn 3d_{3/2} binding energies of 484.8 and 493.3 eV in the Sn(0) state; and of 486.1 and 494.5 eV in the Sn(II) state. Between the two states of Sn, we observe sharper peaks or peaks of higher intensity for Sn(II) than Sn(0). Moreover, literature data for SnS reported Sn 3d_{3/2} binding energy to be 494.1 eV,^{40, 41} close to our observed Sn(II) state. This suggests that Sn(II) is the dominant state in SnS which agrees with theoretical expectation. Likewise, SnS₂ also demonstrates a pair of strong peaks at 486.0 and 494.5 eV that is indexed to Sn 3d_{5/2} and Sn 3d_{3/2} binding energies of the Sn(II) state. Sn(II) signals in SnS₂ has also been noted by Yu *et al.* whereby SnS₂ nanosheets were found to exhibit a pair of distinct Sn 3d peaks at 486.2 and 494.6 eV.²⁸ Scrutinizing further, there is a pair of broad shoulder peaks at Sn 3d_{5/2} and Sn 3d_{3/2} binding energies of 487.0 eV and 495.4 eV that is characteristic of Sn(IV) species.^{6, 42} The prominent Sn(II) signals in SnS₂ may lead us into presuming +2 as the main oxidation state. However, computed relative atomic percentages of various states (Table 7.S3) of SnS₂ reveal Sn(IV) as the major species, contributing to slightly more than 50 %. Therefore, SnS₂ is deduced to be largely +4 even though the Sn(II) state is also significant.

Clearly, the surfaces of Sn chalcogenides are not of uniform Sn valence state. SnS has

substantial Sn(0) and Sn(II) surface contribution. While Sn(II) state is anticipated in SnS, the presence of Sn(0) may result from extensive Sn-Sn bonding in SnS. Since SnS₂ occupies a larger domain relative to SnS in the Pourbaix diagram,⁴³ the modest presence of Sn(IV) in SnS may arise from traces of SnS₂ due to surface imperfections of SnS. Similarly, we may speculate the significant Sn(II) contribution in SnS₂ arising from mixed valences of SnS and SnS₂ existing on the surface. Inevitably, surface oxidation of both Sn chalcogenides is plausible given that their oxygen content have been detected to be at least 10 % by wide scan XPS analysis (Table 7.S2). Due to the multivalence of Sn as Sn(II) or Sn(IV) states, thermodynamically stable Sn oxides tend to manifest as SnO or SnO₂ on the surface of SnS and SnS₂.⁴⁴

The high resolution S 2p core level analysis shows prevalent S²⁻ species in SnS and SnS₂. In SnS, the presence of S²⁻ signals at S 2p_{3/2} binding energy of 160.9 eV coincides with electrodeposited SnS thin films at 161.1 eV.⁴⁰ Similarly, the S 2p_{3/2} peak in SnS₂ located at 161.5 eV is nearly consistent with SnS₂ superstructures³⁰ and nanocrystals⁴⁵ reported to be at 161.7 eV. There is a perceptible shift in S 2p_{3/2} and 2p_{1/2} doublets towards higher binding energies from 160.9 and 162.0 eV in SnS to 161.5 and 162.7 eV in SnS₂. This may correlate to the increase in oxidation state of Sn from +2 in SnS to +4 in SnS₂.

Figure 7.3 High resolution X-ray photoelectron spectroscopy spectra of a) Sn 3d region and b) S 2p region for SnS (top) and SnS₂ (bottom). Each pair of fitted peaks with matching color corresponds to the respective spin-orbit coupled peaks. Calibration was performed using the adventitious C 1s peak referenced at 284.5 eV.

Taken together, the characterization data has revealed SnS and SnS₂ as layered bulk materials and confirmed their stoichiometric ratios to be approximately 1.0 for SnS; and 2.0 for SnS₂. Moreover, surfaces of SnS and SnS₂ contain Sn species in other valencies though Sn(II) and Sn(IV) were deemed the major species in SnS and SnS₂ respectively. Trace amounts of Sn oxides in the form of SnO or SnO₂ may also coexist on the surfaces of Sn chalcogenides.

7.2.2 Inherent Electrochemistry

Despite the plethora of electrochemical studies on SnS and SnS₂ as supercapacitors^{34,}

⁴⁶ and batteries,^{7, 24, 47} it is surprising that little is known about their inherent

electrochemistry to date. We define inherent electrochemistry as the characteristic redox reaction of the material that itself undergoes when an electrochemical potential is applied.¹⁸ Layered TMDs including the extensively studied MoS₂ and WS₂,^{18, 48, 49} among others,^{5, 50} have been found to exhibit innate electroactivities that potentially limit their operating potential windows. Such inherent electrochemical activities alter the efficacy of TMDs as electrode materials, especially in electrochemical sensing.⁵¹ Indeed, it is imperative to determine the intrinsic electrochemical behavior of SnS and SnS₂ at the pinnacle of their emergent applications. The difference in Sn valencies in SnS and SnS₂ is expected to elicit dissimilar electrochemical behavior. Of interest, we note the effect of Sn oxidation state on the inherent electrochemistry. Working towards these aims, we surveyed the intrinsic electroactivities of SnS and SnS₂ and their voltammograms are presented in Figure 7.4. Scans towards both positive and negative potentials were performed, along with three consecutive cycles, to provide electrochemical information on the innate redox reactions occurring on surfaces of Sn chalcogenides. The measurements were performed relative to the Ag/AgCl reference electrode.

Figure 7.4 Cyclic voltammograms of a) SnS during the scan to positive potentials and b) the scan to negative potentials, and c) SnS₂ during the scan to positive potentials and d) the scan to negative potentials. Conditions: background electrolyte, phosphate buffered saline (50 mM), pH 7.0; scan rate, 100 mV s⁻¹; all measurements are performed relative to the Ag/AgCl reference electrode. Arrows indicate the initial scan direction.

Sn chalcogenides are readily distinguished from their voltammetric profiles since the intrinsic redox signals of SnS₂ are more ostensible than SnS. Voltammetric scan to positive potentials appears unexciting for SnS with the absence of redox signals while we notice a meek reduction signal in SnS₂. This moderate reduction wave at -1.0 V in SnS₂ originated from the reduction of SnS₂ to SnS. Early work also described that constant electrolysis of SnS₂ at -1.0 V vs. Ag/AgCl initiated the reduction to SnS.¹⁷ Examining the scans towards negative potentials of Sn chalcogenides, we identified a single reduction wave in SnS at -1.5 V and three distinct reduction peaks in SnS₂ at -1.0 V, -1.2 V and -1.5 V. We observe a stark contrast between the current intensities of the reduction signal at -1.0 V in both scan directions of SnS₂. A weak current intensity of 25 μA was recorded for the scan towards

positive potentials whereas a strong signal of 140 μA was measured in the scan towards negative potentials. The disparity highlights that a preliminary scan to the positive potentials may have depleted the number of electroreducible moieties on SnS₂ available for reduction to SnS. The single broad reduction wave which materialized at -1.5 V in SnS parallels that in SnS₂. At this potential, reduction to metallic tin occurs.¹⁷ Apart from this cathodic signal at -1.5 V, SnS is deemed to be generally electrochemically inactive.

Among the reduction signals of SnS₂ during the scans to the negative potentials, the electrochemical process corresponding to the modest cathodic peak at -1.2 V in pH 7.0 demonstrates robust pH-dependence. Figure 7.S4 exemplifies a negative linear correlation between the electrochemical peak potential with pH of electrolyte. The signal peaks at -1.1 V in acidic pH 3.0, gradually shifting towards increasingly negative electrochemical potentials in alkaline pH, for instance, -1.3 V at pH 12.0. We derive the $\text{H}^+:\text{e}^-$ ratio to be 1:2 and ascribe this process to the reduction of Sn oxides, more precisely, $\text{SnO}_2 + \text{H}^+ + 2\text{e}^- \rightarrow \text{HSnO}_2^-$. The current intensity for this electrochemical process is the lowest at 50 μA out of the three cathodic processes in SnS₂ because the reduction of SnO₂ is limited by the low stability of HSnO_2^- and the wide cathodic protection window of SnO₂.^{43, 52}

Interestingly, all reduction peaks of SnS and SnS₂ do not exhibit any anodic counterpart at pH 7.0. Concurring with this observation, oxidation of Sn(II) to Sn(IV) was reported to be unfeasible within the electrochemical window of an ionic liquid from -2.0 V to 1.3 V vs. Ag/AgCl.⁵³ It had also been suggested that the tetravalent species was unstable when complexing ions were absent, thereby inhibiting the oxidation of the divalent state.^{53, 54} Zhang *et al.* noted that anodic dissolution of Sn occurred at -0.395 V vs. Ag/AgCl in 1 M HCl electrolyte.¹⁷ However, this was not reflected in our voltammograms which were

performed in PBS pH 7.0. The rate of corrosion hinges on pH whereby the rate increases in highly acidic or alkaline electrolyte, yet proceeds negligibly under neutral conditions.^{43,}

⁵² Moreover, mixtures of Sn oxides, comprising SnO and SnO₂, that coat the surfaces of Sn chalcogenides constitute protective films that resist further oxidation of SnS and SnS₂.⁵²

Primarily, inherent electrochemical reductions of SnS and SnS₂ are chemically irreversible. As shown in their scans towards negative potentials in Figure 7.4b and 7.4d, the reduction peaks of SnS and SnS₂ detected in the initial scan virtually vanished in subsequent scans. The visible broad inherent peak during the first cycle of the scan to positive potentials of SnS₂ also disappeared in repeated cycles. Besides, their voltammograms were devoid of oxidative waves. Therefore, intrinsic reduction processes of Sn chalcogenides proceed to completion in the first scan. Likewise, Heyrovsky *et al.* and Pool *et al.* arrived at the same conclusion that reducing Sn(IV) to Sn(II) was irreversible.^{54,}
⁵⁵ In particular, excess amounts of strong ligands were required for the reversible 2e⁻ reduction of SnCl₃⁻ to SnCl₂ from Sn(IV) to Sn(II).⁵⁴ Going further, the irreversible Sn(II) reduction might be associated with the irreversibility of the 2e⁻ couple involving SnCl₂ to Sn(Hg) as described by Pool *et al.* ⁵⁴ However, another study using SnO₂ colloid determined the process to be fast and reversible⁵⁵ which disputes the irreversibility of Sn(II) reducing to Sn(0). Therefore, future studies in this area are necessary to validate the nature of Sn(II) reduction.

Sn chalcogenides are characterized by different oxidation states and can be identified by their inherent electrochemistry. This is based on their distinctive reduction profiles in the cathodic region where a single and several signals were respectively detected in SnS and SnS₂. In turn, a wider operating potential window exists for SnS than SnS₂.

7.2.3 Heterogeneous Electron Transfer

Heterogeneous electron transfer (HET) rate is customarily measured to evaluate the suitability of electrode materials for electrochemical applications. A key attribute of an ideal electrode material for electrochemical sensing is a fast HET rate because just a small overpotential is required for the electrochemical process to ensue. The Nicholson method correlates the peak-to-peak separation (ΔE) to the HET rate constant, k_{obs}^0 , such that a wide separation between the redox peaks translates into sluggish HET rate and small k_{obs}^0 .⁵⁶ It is essential to point out that the k_{obs}^0 is discussed as an experimentally observed rate constant and does not represent the true value. We examine the HET rates of Sn chalcogenides in the presence of $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox probe. The surface sensitivity of $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox probe towards various electrode materials offers an advantage in studying the differences between SnS and SnS₂.⁵⁷ The voltammetric profiles of $[\text{Fe}(\text{CN})_6]^{3-/4-}$ on SnS and SnS₂-modified electrodes and their corresponding ΔE are depicted in Figure 7.5 and their k_{obs}^0 are recorded in Table 7.S4. The electrochemical performance of $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox probe was measured over a range from -0.3 V to +0.7 V. As this region lies beyond the onset of the inherent reduction peaks manifested by SnS and SnS₂ as mentioned in the earlier **Section 7.2.2 Inherent Electrochemistry**, any interference arising from their inherent electrochemistry is eliminated.

SnS₂ yields markedly narrower ΔE compared to SnS. The calculated k_{obs}^0 of SnS₂ is $1.1 \times 10^{-3} \text{ cm s}^{-1}$ ($\Delta E = 197 \text{ mV}$) whereas SnS is an order of magnitude lower at $1.9 \times 10^{-4} \text{ cm s}^{-1}$ ($\Delta E = 329 \text{ mV}$). Evidently, SnS₂ displays intrinsically faster HET kinetics than SnS. Therefore, SnS₂ is the preferred electrode material over SnS in electrochemical sensing. The array of literature further documents the extensive use of SnS₂ in electrochemical sensing. Frequent studies employed SnS₂ nanocomposites in electrode materials due to

their high electrical conductivity and surface-to-volume ratio. SnS₂ nanocomposites including gold nanoparticles and single-walled carbon nanotubes had been fabricated as electrochemical sensors capable of detecting biomolecules such as glucose, dopamine and uric acid.^{58, 59} Additionally, novel biosensors developed by immobilizing proteins like glucose oxidase on SnS₂ also garnered success in glucose sensing.^{60, 61} The large surface area of the prepared SnS₂ facilitated electron transfer between the protein and electrode surface. Despite the involvement of SnS₂ in numerous sensing research, SnS experiences a dearth of studies possibly a consequence of its inherently slower HET kinetics relative to SnS₂ as confirmed from the k_{obs}^0 .

The oxygen content in Sn chalcogenides may also influence their HET rates, to a small extent. As reflected in the wide-scan XPS analysis (Table 7.S2), SnS contains marginally higher oxygen content than SnS₂ by 10.0 %. The oxygen content is suggested to be in the form of oxides such as SnO or SnO₂ adsorbed on surfaces of Sn chalcogenides. Such surface oxides may face electrostatic repulsion from the negatively-charged [Fe(CN)₆]^{3-/4-} redox probes which hampers the electron transfer. Even though [Fe(CN)₆]^{3-/4-} redox probe is surface sensitive, it demonstrates insensitivity towards oxygen groups and thus, the role of oxides on the electron transfer properties of Sn chalcogenides is trivial.⁵⁷

Both Sn chalcogenides do not fare better than the bare glassy carbon (GC) electrode in terms of HET. SnS₂ has a calculated k_{obs}^0 on par with the GC while SnS is significantly slower. The current intensities of both SnS and SnS₂ are also approximately equivalent yet their anodic currents are substantially lower than that of the GC by 20 μA .

Figure 7.5 a) Cyclic voltammograms of [Fe(CN)₆]^{3-/4-} (5 mM) on SnS, SnS₂ and glassy carbon (GC). b) Summary of peak-to-peak separations of Sn chalcogenides with their corresponding error bars. Conditions: background electrolyte, KCl (0.1 M); scan rate, 100 mV s⁻¹; all measurements are performed relative to the Ag/AgCl reference electrode.

7.2.4 Electrocatalytic Property

We subsequently turn our attention to investigate the electrocatalytic properties of SnS and SnS₂ for hydrogen evolution reaction (HER).

Figure 7.6 a) Linear sweep voltammograms for hydrogen evolution reaction on SnS, SnS₂, Pt/C and GC. b) Tafel plots for all materials. Conditions: background electrolyte, H₂SO₄ (0.5 M); scan rate, 2 mV s⁻¹; all measurements are performed relative to the Ag/AgCl reference electrode and corrected to reversible hydrogen electrode (RHE) potentials.

Sn chalcogenides demonstrate electrocatalytic behavior towards HER as illustrated in Figure 7.6. HER kinetics encompasses a facile two-electron transfer while oxygen reduction

and oxygen evolution reactions demand multiple proton-coupled electron transfers that are kinetically slow.⁶² We included Pt/C as a reference to assess the extent of HER electrocatalysis by SnS and SnS₂. For a rational evaluation of catalytic performance, the overpotential at a current density of -10 mA cm^{-2} has been employed to emulate a competitive level of efficiency in electrochemical water-splitting applications.⁶³ At a current density of -10 mA cm^{-2} , the Sn chalcogenides flaunt higher HER efficiency than the bare GC electrode. The HER overpotentials of SnS and SnS₂ are 0.88 V and 0.73 V respectively. Therefore, SnS₂ requires a lower overpotential and is more electrocatalytic for HER than SnS. Since SnS₂ has a chalcogen-to-metal ratio of 1.8 whereas SnS has a lower ratio of 1.1 (Table 7.S2), we may possibly infer that a higher chalcogen-to-metal ratio or S chalcogen-enriched Sn chalcogenides yields stronger electrocatalytic activity.

HER performances of TMDs are governed by a medley of factors which may also be extended to metal chalcogenides, including SnS and SnS₂. Key aspects include the active sites, intrinsic activity and the conductivity.¹⁸ Active sites for HER are established to be the edges of TMDs while their basal planes are inert.^{38, 39} Enhanced HER electrocatalytic activity of SnS₂ relative to SnS suggests a larger number of HER active sites reside in SnS₂. The immense size of the SnS crystals, as we witnessed in Figure 7.1 spanning beyond 50 μm in diameter, renders the edge-to-basal site ratio of SnS to become considerably lower than SnS₂ which exists as small fragments. Additionally, the edges of SnS, unlike SnS₂, have been determined to be largely inert for HER (Figure 7.7) according to density functional theory (DFT) calculation, as will be subsequently discussed in detail. Apart from the role of active sites of Sn chalcogenides for HER, the underlying reason for their corresponding electrocatalytic activities stems from the intrinsic catalytic activities of SnS and SnS₂.

Intrinsic activity for HER is often quantified by the Gibbs free energy of adsorbed H (ΔG_H) such that a material with thermoneutral ΔG_H (i.e. $\Delta G_H \approx 0$ eV) is supposed to be the most effective for HER. Pt/C is, by far, the best electrocatalyst and its ΔG_H approximates 0 eV.⁶⁴ The competent HER performance of SnS₂ indicates that the interaction of hydrogen with the SnS₂ surface is closer to thermoneutral than in the case of SnS. We performed DFT calculation of ΔG_H to elucidate this issue.

Figure 7.7 The Gibbs free energy of hydrogen adsorption (ΔG_H) on the edge of 1T-SnS₂ as a function of hydrogen coverage (upper panel). The geometry and ΔG_H for the adsorption on the armchair cliff-type edge, zig-zag cliff edge, and basal plane of SnS (lower panel). The sulfur atoms are depicted yellow, tin in blue, and hydrogen in gray.

Figure 7.7 displays calculated ΔG_H for the edge of SnS₂ and SnS. SnS₂ is certainly the better catalyst of these two. Its ΔG_H values are endothermic and lie within an interval of 0.18 – 0.50 eV. The lowest values of ΔG_H are found for 50% and 75% hydrogen coverage. This shows a different character of hydrogen adsorption than that in isostructural platinum dichalcogenides,⁶⁵ which showed monotonic increase of ΔG_H as a function of hydrogen coverage. The hydrogen atoms bind to the sulfur atom at the edge of SnS₂, but the bond

is weaker than the H-S bond in most dichalcogenides (c.f. MoS₂, WS₂, TaS₂, NbS₂, PtS₂ have negative ΔG_H for the adsorption at 25 % coverage⁶⁶). The weak H-S bonding in the S-edge of SnS₂ promotes the H-H bond formation on two adjacently adsorbed hydrogen atoms.

The edges of SnS are generally unreactive towards hydrogen, since the values of ΔG_H are highly endothermic (Figure 7.7, lower panel). It should be noted that there are several possible edge terminations for puckered structure of the SnS layer (Figure 7.2). We found that the armchair and zig-zag edge terminations, present in the isostructural black phosphorus structure,^{67, 68} are energetically unfavorable in SnS with respect to the cliff-type edge termination (Figure 7.7, lower panel). The armchair edges cut SnS along a line parallel to the x-axis, so that its projection resembles a graphene armchair edge, whereas zig-zag edge is produced by a cut along the z-axis. The single-layer SnS includes two atomic layers and two kinds of Sn-S bonds, resulting in two kinds of a possible edge termination for both armchair and zig-zag edge. The cliff termination of the zig-zag edge has the surface energy of 0.29 eV/Å, whereas the zig-zag edge has the surface energy of 0.67 eV/Å. The cliff termination of the armchair edge has the surface energy of 0.35 eV/Å, sufficiently close to the energy of cliff zig-zag edge that both types of edge can be expected in SnS samples. On the armchair-cliff edge, hydrogen adsorbs preferentially to the edge sulfur atom, and this process has ΔG_H of 0.95 eV. On the zig-zag cliff edge, hydrogen prefers the bridge site between two Sn atoms at the edge ($\Delta G_H = 1.17$ eV). The adsorption onto the basal plane is even less likely, since it has ΔG_H of 1.59 eV. Overall, the values of ΔG_H are too high for SnS to work as the HER catalyst, which explains its modest HER performance observed in experiment (Figure 7.6).

Tafel analysis was executed next to elucidate the HER electrochemical mechanisms of

Sn chalcogenides. The reaction pathways of HER on TMD surfaces are summarized into the following rate-determining steps:^{69, 70}

1. Adsorption:

2. Desorption:

Among all materials, Pt/C exhibits the smallest Tafel slope (*b*) of 38 mV/dec which falls within the range of reported Tafel slopes in literature for Pt from 30 to 40 mV/dec.³⁷ According to this experimental value, the Heyrovsky desorption of H₂ on Pt/C surface is rate-limiting. Tafel slope of SnS is determined to be 96 mV/dec which is lower than for SnS₂ at 150 mV/dec. The limiting step of HER for SnS and SnS₂ is Volmer adsorption because their slopes are broadly closest to the theoretical value of 120 mV/dec.

It is also noteworthy that the electrocatalytic ability of SnS had been previously studied to improve dramatically when mounted on a suitable conductive support. Shinde *et al.* successfully synthesized a SnS/N-doped reduced graphene (SnS/N-rGr) hybrid affords a small onset potential of -125 mV vs. RHE for HER and Tafel slope of 38 mV/dec rendering it to be highly electrocatalytic for HER.⁸ Prior to using N-rGr as a support material, the SnS nanoparticles exhibited weak HER activity with Tafel slope of 226 mV/dec.

Upon closer scrutiny, pre-waves are observed in SnS₂ at -0.4 V and -0.6 V vs. RHE. Matching these signals with the inherent reduction peaks of SnS₂ (Figure 7.4), the signal at -0.6 V vs. RHE, in other words, equivalent to -0.9 V vs. Ag/AgCl, lies in close proximity to the observed peak at -1.0 V. Hence, -0.6 V vs. RHE was assigned to the reduction into SnS.¹⁷

The pre-wave at -0.4 V vs. RHE did not tally with any of the inherent electrochemical signals. We deduce its presence to result from the huge variance in catalytic activities among the HER sites in SnS₂.⁴⁹

7.3 Conclusion

Summing up, we have presented a comprehensive investigation into the electrochemical and catalytic properties of layered Sn chalcogenides. SnS and SnS₂ showcase inherent electrochemistry in the cathodic region. Between them, SnS₂ exhibits more accentuated electroactivity. This is substantiated by three conspicuous inherent signals in SnS₂ at -1.0 V, -1.2 V and -1.5 V vs. Ag/AgCl placed in juxtaposition to a single peak at -1.5 V vs. Ag/AgCl in SnS. Therefore, SnS₂ has a narrower operating potential window than SnS and deliberation is essential when applied for electrochemical sensing. We have determined that the HET rate of SnS₂ is an order of magnitude faster than SnS. The markedly faster electron transfer in SnS₂ is advantageous for sensing applications. We have also explored the prospects of these materials as alternative electrocatalysts in HER. Sn chalcogenides manifest remarkable electrocatalytic behavior towards HER with both low HER overpotentials that outperform the bare GC electrode. Furthermore, SnS₂ demonstrated higher HER efficiency than SnS. On the basis of the crystal structures of Sn chalcogenides, DFT calculation demonstrated their intrinsic HER activities. Sulfur edges in SnS₂ are active sites for H adsorption as documented by favorable ΔG_H . In contrast, ΔG_H for SnS are deemed to incompatible for HER electrocatalysts. Moreover, the surface chalcogen-to-metal ratio may represent a potential point of control in the HER electrocatalytic performance of the Sn chalcogenides. Our findings offer insights that are fundamental to layered Sn chalcogenides and provide an assessment of their

electrochemical properties for energy-related applications. The knowledge will be vital towards paving the way for Sn chalcogenides, especially SnS₂, as feasible earth-abundant HER electrocatalysts.

7.4 Experimental Section

7.4.1 Materials

Ammonium chloride and isopropanol were obtained from Penta, Czech Republic. Tin (99.999%), tin(II) chloride and sulphur (99.999%) was obtained from Strem, Germany. Potassium ferrocyanide, hexaammineruthenium (III) chloride, *N,N*-dimethylformamide potassium chloride, potassium phosphate dibasic, sodium phosphate monobasic, sodium chloride, sulfuric acid, potassium hydroxide and platinum on carbon were purchased from Sigma Aldrich. Pt, Ag/AgCl and glassy carbon (GC) electrodes were purchased from CH Instruments, Texas, USA.

7.4.2 Synthesis

The synthesis of SnS was performed from elements. Stoichiometric amount of S and Sn for 10 g of SnS was placed in quartz glass ampoule (inner dimensions 20 x 120 mm). The ampoule was evacuated on pressure below 2×10^{-3} Pa and melt sealed using oxygen-hydrogen torch. The ampoule was heated on 900 °C for 1 hour. The heating rate was 5 °C/min and the cooling rate was 1 °C/min.

The synthesis of SnS₂ was performed by reaction of tin(II)chloride with sulphur and ammonium chloride. 9.0 g of SnCl₂, 3.9 g of S and 4.3 g of NH₄Cl was mixed in agate mortar (molar ratio 1:3:2) and placed in quartz tube. The loosely capped tube with reaction mixture was heated on 350 °C for 200 minutes. The reaction mixture was leached with water and formed SnS₂ was separated by suction filtration and washed with water and

isopropanol. Formed product was dried in vacuum oven for 24 hours at 50°C. SnS₂ was mixed with 1 g of S in agate mortar and heated for 5 hours on 300 °C in quart tube under argon atmosphere. The unreacted sulfur was extracted by carbon disulfide, finally the SnS₂ was ultrasonicated with isopropanol and separated by suction filtration. SnS₂ was dried in vacuum oven for 48 hours at 50°C before further use.

7.4.3 Apparatus

X-ray photoelectron spectroscopy (XPS) was performed with a Phoibos 100 spectrometer with a monochromatic Mg K_α radiation as the X-ray source (SPECS, Germany). Survey scans were generated for all samples. High-resolution spectra were also obtained for the Sn 3d and S 2p. We considered relative sensitivity factors during the calculation of chalcogen-to-metal ratios and the deconvolution of Sn 3d. Best curve fits for the high-resolution XPS spectra of Sn 3d were performed using the ratio of Sn 3d_{5/2} and Sn 3d_{3/2} as 3: 2.

Scanning electron microscopy was performed with a JEOL 7600F field-emission scanning electron microscope (JEOL, Japan) at 5kV. Energy dispersive X-ray spectroscopy data were obtained at an accelerating voltage of 15kV.

X-ray diffraction was performed with a Bruker D8 Discoverer diffractometer in Bragg–Brentano parafocusing geometry using CuK_α radiation. Diffraction patterns were collected for 2 θ values from 10° to 80°. The data obtained were evaluated using HighScore Plus 3.0e software.

Voltammetric measurements were recorded on a μ Autolab III electrochemical analyser (Eco Chemie B.V., Utrecht, The Netherlands) with the software NOVA version 1.8 (Eco Chemie). Electrochemical measurements of the transition metal dichalcogenide (TMD) materials were performed in a 3 mL voltammetric cell at room temperature (25 °C) in a

default three electrode configuration. A platinum electrode and an Ag/AgCl electrode functioned as auxiliary and reference electrodes, respectively and a glassy carbon (GC, 3 mm diameter) electrode was adopted as the working electrode.

7.4.4 Procedures

Fundamental electrochemical studies were performed in 50 mM phosphate buffered saline (PBS) as the background electrolyte at pH 7. All cyclic voltammetry experiments were conducted at a scan rate of 100 mV s⁻¹. The voltammetric scan began at 0 V; the potential at which redox processes were not expected to occur,⁷¹ and scanned towards 1.8 V followed by a reverse sweep to -1.8 V for the scan to positive potentials, and first towards -1.8 V followed by a reverse sweep to 1.8 V before returning to 0 V for the scan to negative potentials. SnS and SnS₂ were prepared in concentrations of 2 mg mL⁻¹ in *N,N*-dimethylformamide and subject to first-time ultrasonication for 1.5 h to attain well-dispersed suspensions. Prior to each electrochemical measurement, the samples were ultrasonicated for a period of 10 minutes to maintain the homogeneous dispersion of the desired material. 2.0 µL aliquot of the suspension was then drop casted on a GC electrode and dried to yield an electrode surface modified with 4.0 µg film of the desired material. Studies on heterogeneous electron transfer (HET) at SnS and SnS₂ surfaces were executed in potassium chloride (0.1 M) as the supporting electrolyte for potassium ferrocyanide (5 mM) redox probe. Cyclic voltammetry scans were performed at a rate of 100 mV s⁻¹. To eliminate interference due to inherent electrochemistry, the first scan has been excluded. Instead, data from subsequent scans are used. The k_{obs}^0 values were calculated using the method devised by Nicholson⁵⁶ that relates ΔE_p to a dimensionless parameter Ψ and consequently into k_{obs}^0 . The roughness of the electrode was not considered in the

calculation of k_{obs}^0 . The diffusion coefficient $D = 7.26 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ was used to compute k_{obs}^0 values for $[\text{Fe}(\text{CN})_6]^{4-/3-}$.⁷²

Hydrogen evolution reaction (HER) measurements of Sn chalcogenide materials were carried out using linear sweep voltammetry at a scan rate of 2 mV s^{-1} in $0.5 \text{ M H}_2\text{SO}_4$ electrolyte. Linear sweep voltammograms are presented *versus* the reversible hydrogen electrode (RHE) using and the measured potentials are calculated using this equation⁷³ $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \times \text{pH} + E_{\text{Ag/AgCl}}^0$ where $E_{\text{Ag/AgCl}}$ is the measured potential, pH of $0.5 \text{ M H}_2\text{SO}_4$ electrolyte is zero and $E_{\text{Ag/AgCl}}^0$ refers to the standard potential of Ag/AgCl (1 M KCl) at 25°C which is 0.235 V .

7.4.5 Density Functional Theory Calculations

DFT calculations were performed using the projector-augmented wave method implemented in the Vienna Ab initio Simulation Package (VASP).^{74, 75} The energy cutoff for the plane-wave expansion was set to 350 eV . We used optimized van der Waals functional optB86b-vdW functional,⁷⁶ which described very well the adsorption energies⁷⁷ as well as the structural properties of various TaS₂ phases.⁷⁸ By optimization of the rhombohedral (Pbnm space group) crystal structure of SnS, we obtained the lattice parameters $a=4.308$, $b=11.211$, and $c=4.012 \text{ \AA}$, in excellent agreement with our X-ray diffraction data (Figure 7.2). For the 1T structure (space group P-3m1) of SnS₂, we obtained $a=b=3.67$, $c=5.95 \text{ \AA}$, again in agreement with X-ray experiment. The mutual agreement with experiment justifies our choice of functional.

The free energy of the adsorption of atomic hydrogen (ΔG) is a quantity which can be used to describe the HER activity of the catalyst.³⁹ The ΔG of an ideal catalyst for HER should be as close to 0 as possible. We considered the adsorption of hydrogen onto the surface and

edge sites of single layered SnS and SnS₂. The surface (basal plane) was modeled by a 4x4 supercell in connection with 3x3x1 k-point sampling. The individual layers were separated by 18 Å of vacuum. The edge was modeled by a 4x4 nanostripe, i.e. it contained four atoms along the edge and the nanostripe was four atoms wide. The Brillouin zone of the nanostripe was sampled by 3x1x1 k-points where three k-points belonged to the only direction in which the cell was periodically repeated. For the SnS cliff-type edge,⁶⁷ we considered hydrogen adsorption on both sulfur and tin atom. The edge of 1T-SnS₂ contained four adsorption sites on sulfur atoms, so we considered four possible hydrogen coverages of 25%, 50%, 75%, and 100%. The edge was gradually (one-by-one) covered with hydrogen atoms and the differential energy of adsorption ΔE was calculated as

$$\Delta E = E_{TOT}(nH^*) - E_{TOT}[(n-1)H^*] - 1/2 E_{TOT}(H_2)$$

The Gibbs free-energy of the adsorption atomic hydrogen (ΔG) was obtained as

$$\Delta G = \Delta E + \Delta E_{ZPE} - T\Delta S_H$$

Where, ΔE_{ZPE} and ΔS_H was the difference in zero point energy, and entropy between the adsorbed hydrogen and hydrogen in the gas phase. These thermal corrections were found to be independent of particular adsorption site, and thus ΔG at standard condition was determined by ΔE plus a thermal correction constant of 0.29 eV.³⁹

7.5 Supporting Information

Figure 7.S1 Energy dispersive X-ray maps of SnS and SnS₂. Scale bars represent 10 μm .

Figure 7.S2 Energy dispersive X-ray spectra of SnS and SnS₂.

Table 7.S1 Elemental composition of Sn chalcogenides based on energy-dispersive X-ray spectroscopy. Chalcogen-to-metal ratios are also computed for SnS and SnS₂.

TMD	Sn at. %	S at. %	C at. %	O at. %	Al at. %	Chalcogen/Metal Ratio (i.e. S/Sn)
SnS	32.4	30.7	28.7	6.6	1.6	0.9
SnS ₂	21.2	37.9	36.1	3.6	1.2	1.8

Figure 7.S3 Wide-scan X-ray photoelectron spectra of a) SnS and b) SnS₂. The survey spectra were calibrated to the adventitious C 1s peak at 284.5 eV.

Table 7.S2 Elemental compositions of Sn chalcogenides based on wide-scan X-ray photoelectron spectroscopy. Chalcogen-to-metal ratios are also computed for SnS and SnS₂.

TMD	Sn at. %	S at. %	C at. %	O at. %	Chalcogen/Metal Ratio (i.e. S/Sn)
SnS	18.9	20.6	37.4	23.1	1.1
SnS ₂	20.8	37.1	29.0	13.1	1.8

Table 7.S3 Table of atomic percentages of Sn(0), Sn(II) and Sn(IV) states of Sn chalcogenides acquired from high resolution X-ray photoelectron spectroscopy. The calculated percentages provide a general view of Sn chalcogenides and should not be considered in absolute terms.

TMD	Sn (0) at. %	Sn (II) at. %	Sn (IV) at. %
SnS	43.5	40.2	16.3
SnS ₂	5.6	43.8	50.6

Figure 7.S4 a) Cyclic voltammograms of SnS₂ across pH 2 to 12, in view are the potential window from -0.4 to -1.4 V. b) Summarized data of the shift in electrochemical potential of cathodic signals for SnS₂ across pH. Conditions: supporting electrolyte, PBS (50 mM); pH 2-12; scan rate, 100 mV s⁻¹. All measurements are performed relative to the Ag/AgCl reference electrode.

Figure 7.S5 a) Wide-scan X-ray photoelectron spectroscopy (XPS) spectra of SnS₂ after reduction at -1.3 V. High resolution resolution XPS spectra of b) Sn 3d region and c) S 2p region for reduced SnS₂. Each pair of fitted peaks with matching color corresponds to the respective spin-orbit coupled peaks. Calibration was performed using the adventitious C

1s peak referenced at 284.5 eV.

Table 7.S4 Elemental composition of reduced SnS₂ based on wide-scan X-ray photoelectron spectroscopy. Chalcogen-to-metal ratios are also computed. Note: The Cl detected originates from the bare screen-printed electrode.

TMD	Sn at. %	S at. %	C at. %	O at. %	Cl at. %	Chalcogen/Metal Ratio (i.e. S/Sn)
SnS ₂ -Red	12.5	18.1	44.2	22.5	2.8	1.5

Table 7.S5 Table of atomic percentages of Sn(0), Sn(II) and Sn(IV) states of reduced SnS₂ acquired from high resolution X-ray photoelectron spectroscopy. The calculated percentages provide a general view of reduced SnS₂ and should not be considered in absolute terms.

TMD	Sn (0) at. %	Sn (II) at. %	Sn (IV) at. %
SnS ₂ -Red	5.0	74.0	21.0

Table 7.S6 Table of heterogeneous electron transfer rate constant (k_{obs}^0) of Sn chalcogenides calculated from their peak-to-peak separations according to the Nicholson method.

Material	k_{obs}^0 (cm s ⁻¹)
SnS	$1.9 \cdot 10^{-4}$
SnS ₂	$1.1 \cdot 10^{-3}$
Glassy Carbon (GC)	$1.1 \cdot 10^{-3}$

Figure 7.S6 a) Overpotentials required for hydrogen evolution reaction on SnS, SnS₂ and Pt/C at a current density of -10 mA cm⁻². b) Tabulated values for the Tafel slopes of SnS, SnS₂, Pt/C and GC. Error bars are also shown.

Figure 7.57 Wide-scan X-ray photoelectron spectroscopy (XPS) spectra of a) SnS and b) SnS₂ after oxidation at -1.5 V vs. Ag/AgCl. Calibration was performed using the adventitious C 1s peak referenced at 284.5 eV.

Figure 7.58 High resolution resolution XPS spectra of a) Sn 3d region and b) S 2p region for the oxidized SnS and SnS₂. Each pair of fitted peaks with matching color corresponds to the respective spin-orbit coupled peaks. Calibration was performed using the adventitious C 1s peak referenced at 284.5 eV.

Table 7.S7 Elemental compositions of oxidized Sn chalcogenides based on wide-scan X-ray photoelectron spectroscopy. Chalcogen-to-metal ratios are also computed for oxidized SnS and SnS₂. Note: The Cl detected originates from the bare screen-printed electrode.

TMD	Sn at. %	S at. %	C at. %	O at. %	Cl at. %	Chalcogen/Metal Ratio (i.e. S/Sn)
SnS-Ox	2.0	0.0	58.3	30.0	9.7	N.A.
SnS ₂ -Ox	3.8	4.4	66.1	15.8	9.9	1.1

Table 7.S8 Table of atomic percentages of Sn(0), Sn(II) and Sn(IV) states of oxidized Sn chalcogenides acquired from high resolution X-ray photoelectron spectroscopy. The calculated percentages provide a general view of Sn chalcogenides and should not be considered in absolute terms.

TMD	Sn (0) at. %	Sn (II) at. %	Sn (IV) at. %
SnS-Ox	1.9	54.4	43.7
SnS ₂ -Ox	2.9	51.4	45.7

Figure 7.S9 Full Nyquist plots of SnS and SnS₂ measured at HER overpotential of 1.0 V (vs. RHE). Conditions: background electrolyte, H₂SO₄ (0.5 M); scan rate, 2 mV s⁻¹; all measurements are performed relative to the Ag/AgCl reference electrode and corrected to reversible hydrogen electrode (RHE) potentials.

Figure 7.S10 Randles-equivalent circuits utilized to model impedance spectra for a) heterogeneous electron transfer in [Fe(CN)₆]^{3-/4-} (5 mM) and b) hydrogen evolution reaction in H₂SO₄ (0.5 M).

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Chapter 8

Group 5 Transition Metal Doped WSe₂ for Electrocatalysis

8.1 *Introduction*

8.2 *Results and Discussion*

8.2.1 *Characterisation*

8.2.2 *Inherent Electrochemistry*

8.2.3 *Electrocatalysis: Hydrogen Evolution*

8.3 *Conclusion*

8.4 *Experimental Section*

8.5 *Supporting Information*

The results and discussion in this chapter were published in the following manuscript:

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Morphological Effects and Stabilization of the Metallic 1T Phase in Layered V-, Nb-, and Ta-Doped WSe₂ for Electrocatalysis. *Chem. -Eur. J.* **2018**, *24*, 3199-3208.

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8.1 Introduction

Transition metal dichalcogenides (TMDs) have gained recent eminence in the scientific community sparked by their intriguing properties and exciting prospects for a myriad of applications. Presently, numerous studies tapped on the versatile attributes of TMDs and demonstrated their prospective use in batteries,^{1, 2} supercapacitors,^{3, 4} photovoltaics,^{5, 6} field-effect transistors,⁷ sensing⁸ and catalysis.^{3, 9-15} TMDs adopt a general formula of MX₂ where M is a transition metal and X is a chalcogen (S, Se, Te). A typical layered TMD comprises transition metal atoms sandwiched between two chalcogen atoms where X-M-X bonds are held by strong covalent bonding within each layer. Between layers, presence of van der Waals' interactions permits loose stacking of TMD sheets. The layered nature of TMDs confers them with anisotropic qualities such that starkly different properties arise when TMDs are thinned down to a single layer.^{16, 17}

Amongst layered TMDs, Group 6 TMDs have been placed on a pedestal in the aspect of clean energy electrocatalysis, gleaned from the extensive research and perpetual success of MoS₂ as an electrocatalyst for hydrogen evolution reaction (HER).^{3, 4, 10, 11, 18, 19} Due to the exponential surge in demand for energy, renewable sources of fuel such as hydrogen and alcohols are rhapsodized over as the remedy to imminent environmental crises of global warming and depletion of natural resources like fossil fuels. The mass production of hydrogen gases *via* electrochemical water splitting requires an electrocatalyst, usually platinum-based, to reduce the thermodynamic activation barrier in a bid to accelerate the reaction. Yet the low natural abundance of platinum raises costs and led to the proposition of naturally abundant TMDs as an alternative to platinum for their promising electrocatalytic activities.

Envisioning TMDs as future electrocatalysts to combat ecological woes inspires

assorted strategies to enhance their electrocatalytic properties. These strategies are founded on the main factors governing the electrocatalytic efficiency, namely the active sites, the intrinsic activity and the conductivity between active sites and catalyst substrate of the TMDs.^{3, 10} In particular, the doping strategy effectively combines one or more factors to activate the catalytic property. A case-in-point on the active sites is that Re-doped MoS₂ fullerenes exhibit enhanced HER activity due to the higher density of edges.²⁰ Edges are the active sites for HER whereas the basal planes are inert.^{19, 21} Chorkendorff and co-workers reported that the intrinsic catalytic activity of Co-doped S-edge of MoS₂ and WS₂ improves because Gibbs free energy of hydrogen adsorption (ΔG_H) of the S-edge lies closer to thermoneutral ($\Delta G_H \approx 0$ eV) after doping.¹⁸ This was also experimentally confirmed whereby both Co-doped TMDs performed better for HER than before.¹⁸ Furthermore, V-doped MoS₂ was deemed a semimetal and showed a 40-fold increase in conductivity that accounts for its enhanced electrocatalytic activity towards HER.²² When a TMD is doped, the electronic band structures become modified.^{23, 24} As such, this affects the above factors contingent on the eventual catalytic behavior.

Upon scrutiny of doped TMDs reported in literature, MoS₂ has indeed been fervently explored juxtaposed with fewer works on WSe₂, despite also a member of the Group 6 TMDs. To date, attempts to tune the physical properties of WSe₂ by doping include using Re dopants to induce the transition of WSe₂ from natural p-type to n-type and the addition of p-type dopants such as Nb and Ta into the WSe₂ lattice to control electrical conductivity.^{25, 26} Nevertheless, little is known about the impact of doping on the electrochemical and electrocatalytic properties of WSe₂ in spite of the vast array of research into doped MoS₂ as an electrocatalyst. A computational study on Group 5

transition metal (V, Nb or Ta)-doped WSe₂ reveals that the doped WSe₂ systems exhibit metallic character, unlike the pristine semiconducting WSe₂, as holes are introduced into the valence band and hence, increases the charge carrier concentration similar to p-type doping.²⁷ Therefore, Group 5 transition metal-doped WSe₂ demonstrate faster electronic transport.²⁷

The favorable electronic transport of Group 5 transition metal-doped WSe₂ bodes well for electrochemical and electrocatalytic applications of WSe₂. It is also crucial to highlight that there are essentially two ways in which dopants are incorporated into a TMD: the direct substitution of dopant atoms into the TMD lattice and the interstitial sites or the intercalation of dopant atoms between sheets of layered TMDs.^{23, 24} On the grounds of thermodynamics, it has been computed that V, Nb and Ta dopants prefer to substitute W atoms as a consequence of their similar atomic sizes.²⁷ Herein, we perform a broad study on the electrochemical behavior of V-, Nb- and Ta- doped WSe₂ and the implications of WSe₂ doping towards HER electrocatalysis. Moreover, we present a thorough characterization of WSe₂ materials, before and after doping with Group 5 transition metals, by X-ray powder diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS) to elucidate any changes in morphology and composition.

8.2 Results & Discussion

8.2.1 Characterization

All WSe₂ materials, before and after doping with Group 5 transition metals, are characterized using a series of techniques comprising X-ray powder diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS).

Figure 8.1 X-ray diffraction patterns of a) undoped WSe₂, b) V-doped WSe₂, c) Nb-doped WSe₂ and d) Ta-doped WSe₂.

As gathered from Figure 8.1, the X-ray diffractograms depict that all Group 5 transition metal-doped WSe₂ exist in a single phase without any additional phases. Significant broadening of diffraction pattern was observed for WSe₂ after doping with Group 5 transition metals. This broadening originates from reduction of crystallite size in a-b plane. All samples exhibit preferential orientation in (00l) direction due to their layered structure.

This finding is in agreement also with microscopy investigation showing a reduction of individual particle sizes, where well developed hexagonal plates can be observed.

Figure 8.2 Scanning electron micrographs of undoped WSe₂, V-doped WSe₂, Nb-doped WSe₂ and Ta-doped WSe₂. Scale bars represent 1 μm.

Figure 8.2 displays the scanning electron micrographs of Group 5 transition metal-doped WSe₂. Magnified areas of all SEM micrographs are shown in Figure 8.S2. WSe₂ exists as huge pieces of closely stacked sheets to yield an average thickness approximating 0.5 μm. Thus, this confirms that WSe₂ is not exfoliated. Upon doping with Group 5 transition metals, there is a paradigm shift in the morphology of WSe₂ from huge pieces to smaller fragments. Thickness of the pieces in WSe₂ is also reduced when doped with Group 5 transition metals. Flake-like structures are a common observation in V-, Nb- and Ta- doped WSe₂. One interesting feature about the flake-like structures is that they assemble in layers with close stacking. These layers are most defined in Nb- and Ta-doped WSe₂ (Figure 8.S2)

due to the visible interlayer gap. Given the small interlayer separation, all Group 5 transition-metal WSe₂, like the parent WSe₂, are bulk layered materials.

Energy dispersive X-ray maps and the derived elemental composition are presented in Figure 8.S1 and Table 8.S1 respectively. Trace amounts of dopants, V, Nb and Ta, are detected across the respective Group 5 transition metal-doped WSe₂ at a dopant level corresponding to at least 2% of the elemental composition of the transition metal-doped WSe₂ (Table 8.S2). The computed chalcogen-to-metal ratios of all Group 5 transition metal-doped WSe₂ lie within a range of 1.9 to 1.8, therefore coinciding to the undoped WSe₂ at 1.9 (Table 8.S2) which is close to the ideal chalcogen-to-metal ratio of 2.0.

The similar trend was observed also for the TEM images, where the undoped WSe₂ shows slightly higher particle size. The doped WSe₂ samples are hexagonal and have diameters up to few hundred of nanometers. All samples exhibit well developed crystal structure with hexagonal symmetry. TEM and HR-TEM images are shown on Figure 8.3. The HR-TEM images manifest an undoped WSe₂ predominated by the presence of the 2H-phase, while upon doping shows dominantly 1T arrangements of structure. The elemental distribution maps obtained by TEM are shown on Figure 8.S3. All doped samples demonstrate homogeneously distributed dopant elements over the individual crystals without any visible phase separation.

Figure 8.3 TEM images of undoped WSe₂, V-doped WSe₂, Nb-doped WSe₂ and Ta-doped WSe₂ and corresponding SAED image showing hexagonal symmetry of crystals. Scale bars represent 200 nm. HR-TEM image of undoped WSe₂, V-doped WSe₂, Nb-doped WSe₂ and Ta-doped WSe₂. Scale bars represent 5 nm.

XPS provides information on the surface elemental composition of the WSe₂ materials before and after doping. As electrochemistry is a surface-dependent study, such information is exceptionally useful for analyzing the electrochemical performance of the Group 5 transition metal-doped WSe₂. XPS survey scans of all the WSe₂ materials are captured in Figure 8.S4 and the surface elemental compositions are recorded in Table 8.S3. High resolution XPS scans of the dopant regions, as presented in Figure 8.4, confirms presence of V, Nb and Ta on the surface of the Group 5 transition metal-doped WSe₂. The XPS deconvolution of the dopant regions into various oxidation states enables us to determine the valence states of V, Nb and Ta in the doped WSe₂. In the deconvolution of V 2p region, the baseline also takes into account the O 1s signal at *ca.* 530 eV due to the proximity of the O 1s and V 2p signals, so that a level baseline can be obtained for the XPS fitting (Figure 8.S5).²⁸ The high resolution XPS of the W 4f core level and Se 3d core level regions before and after doping are shown in Figure 8.5 and Figure 8.S6 respectively.

Figure 8.4 High-resolution X-ray photoelectron spectra of dopants: a) V 2p core level region in V-doped WSe₂, b) Nb 3d core level region in Nb-doped WSe₂ and c) Ta 4f core level region in Ta-doped WSe₂.

Based on the deconvolution of the core level dopant regions (Figure 8.4), all Group 5

transition metal-doped WSe₂ undertake +5 as the primary oxidation state. Evident in V-doped WSe₂, the fitted peaks for V 2p exhibit V⁵⁺ as the dominant species with significant contribution originating from the V 2p_{3/2} and V 2p_{1/2} signals at *ca.* 516.9 eV and 524.1 eV which nears the reported V 2p signals of V₂O₅.^{29, 30} Likewise, the main Nb 3d_{5/2} and Nb 3d_{3/2} binding energies in Nb-doped WSe₂ at *ca.* 207.8 eV and 210.6 eV are characteristic of the Nb⁵⁺ species.³¹ The Ta-doped WSe₂ shows a primary Ta 4f signal at Ta 4f_{7/2} and Ta 4f_{5/2} binding energies of *ca.* 27.2 eV and 29.1 eV that originate from the Ta(V) state.³²

It is also noteworthy to mention that aside from the principal pentavalent species detected in the Group 5 transition metal dopants, a considerable portion of the deconvoluted states suggest co-existence of the other valence states. Most prominently, the shoulder signal manifested by the Ta-doped WSe₂ corresponds to the Ta(II) state with Ta 4f_{7/2} and Ta 4f_{5/2} binding energies at *ca.* 24.1 eV and 26.1 eV.³² Ta(II) and Ta(V) states in Ta-doped WSe₂ are equally dominant. Similar to the Ta-doped WSe₂, the shoulder peak in Nb-doped WSe₂ at *ca.* 203.7 eV is attributed to the Nb(II) state.³³ While the divalent state is detected in notable amounts alongside the primary pentavalent dopant form for both Nb- and Ta- doped WSe₂, V-doped WSe₂ show V(IV) as the secondary state. The deconvoluted V 2p signal of V⁴⁺ occurs at V 2p_{3/2} and V 2p_{1/2} binding energies of 516.0 eV and 523.4 eV. These values coincide with binding energies of vanadium dichalcogenides: VS₂, VSe₂ and VTe₂.⁹

Figure 8.5 High-resolution X-ray photoelectron spectra of W 4f core level region for a) WSe₂, b) V-doped WSe₂, c) Nb-doped WSe₂ and d) Ta-doped WSe₂.

Prior to doping, WSe₂ demonstrates a semiconducting 2H-phase as evident in the doublets identified at 32.7 eV and 34.9 eV that is respectively indexed to the W 4f_{7/2} and W 4f_{5/2} binding energies (Figure 8.5). The 2H-phase is also the thermodynamically stable structure for Group 6 TMDs and thus, most ubiquitous in MoS₂, WS₂, MoSe₂ and WSe₂. A noticeably broad signal occurring at the higher binding energy to this 2H-phase arises from the W⁶⁺ species, whereby the W(IV) state of WSe₂ oxidizes into W(VI) state, existing in the form of oxides like WO₃.^{34, 35} W 4f_{7/2} and W 4f_{5/2} signals originating from the W(VI) state are observed at 35.9 eV and 38.1 eV.

After doping with Group 5 transition metals, the W 4f core level regions of V-, Nb- and

Ta- doped WSe₂ exhibit unanimous increase in the metallic 1T-phase; a marked contrast to the trace presence of metallic 1T-phase in the undoped WSe₂. As noted in all Group 5 transition metal-doped WSe₂, the distinct pair of W 4f_{7/2} and 4f_{5/2} signals at lower binding energies of *ca.* 32.1 eV and 34.3 eV confirms the dominance of the metallic 1T-phase while the semiconducting 2H-phase takes a backseat. As density functional theory calculation has previously determined that V-, Nb- and Ta- doped WSe₂ display metallic character unlike the pristine semiconducting WSe₂,²⁷ we have experimentally verified this with the significant contribution of metallic phase in doped WSe₂. By this observation, it is inferred that doping V, Nb or Ta to WSe₂ elicits a phase stabilization of the 1T-phase³⁶ and an overall phase transition from the initially semiconducting 2H-trigonal prismatic WSe₂ to a metallic 1T-octahedral WSe₂. Consistent with a previous study involving Nb- and Ta- doped WS₂, Nb- and Ta- dopants led to a substantial increase in the 1T-phase of the doped-WS₂ relative to the undoped counterpart.³⁷ This is not entirely unanticipated because TMDs are known to adopt several polymorphs.¹⁰ A classic illustration is the lithium intercalation of MoS₂ with alkali metals to induce a phase transformation from 2H- to 1T- phase.^{38, 39} The reverse 1T- to 2H- transformation has also been documented during the Li- intercalation of TaS₂.⁴⁰ Another feature characteristic of the Group 5 transition metal-doped WSe₂ is the diminished levels of the oxidized W(VI) state compared to undoped WSe₂.

As recorded in Table 8.S4, the chalcogen-to-metal ratio computed by XPS for WSe₂ before and after doping points to a chalcogen-enriched surface. The computed ratios for all WSe₂ materials fall in the range between 2.5 and 2.9, and deviate from the theoretical ratio of 2.0. On the other hand, the chalcogen-to-metal ratio of all WSe₂ materials based on EDS analysis approximates the expected ratio of 2.0. The stark inconsistency of the

chalcogen-to-metal ratio derived from EDS and XPS analyses is reconciled by the different surface and bulk composition of the WSe₂ materials. In particular, the passivation of surface oxides on the WSe₂ materials likely influences the surface composition. Group 5 transition metals detected by XPS analysis show dopant levels between 7% and 20% of the elemental composition in the respectively doped WSe₂ in good agreement to the data provided by EDS analysis.

8.2.2 Inherent Electrochemistry

Inherent electrochemistry is understood as the redox processes that the material undergoes when an electrochemical potential is applied.³ Awareness of the inherent electrochemical properties of the material is important towards evaluating the suitability of the material in electrochemical sensing applications. These intrinsic redox signals may inadvertently interfere with measurements and hence, limits the electrochemical potential window of operation in sensing applications. Since doping has been postulated to modify properties of TMDs,²⁴ we explore the inherent electrochemistry of WSe₂ before and after doping with Group 5 transition metals. Cyclic voltammetry was performed over a wide potential window from -1.8 V to 1.8 V vs. Ag/AgCl in two scan directions. The acquired voltammetric profiles are shown in Figure 8.6.

Figure 8.6 Cyclic voltammograms of a) WSe₂ during the scan to positive potentials and b) the scan to negative potentials, c) V-doped WSe₂ during the scan to positive potentials and d) the scan to negative potentials, e) Nb-doped WSe₂ during the scan to positive potentials

and f) the scan to negative potentials and g) Ta-doped WSe₂ during the scan to positive potentials and h) the scan to negative potentials. Conditions: background electrolyte, PBS (50 mM), pH 7.0; scan rate, 100 mV s⁻¹; all measurements are performed relative to the Ag/AgCl reference electrode. Arrows indicate the scan direction.

At first glance, the voltammetric profiles across Group 5 transition metal-doped WSe₂ as well as the undoped WSe₂ show a similar anodic feature at *ca.* 0.8 V. The distinctive oxidative peak observed at *ca.* 0.8 V is assigned to two key reasons. First, this can be explained by the oxidation of the elemental constituents that make up WSe₂. For instance, two scenarios are likely: the oxidation of the transition metal, tungsten, from an oxidation state of +4 to +6 or the oxidation of the chalcogen, selenium, from -2 to higher oxidation states of +4 or even +6, as recounted in our recent findings.^{3, 34, 35, 37} Apart from the intrinsic dependence on constituent elements, an earlier work by Chorkendorff and co-workers found that the edges and basal planes of layered materials like TMDs show different susceptibility to electro-oxidation and hence, also partially responsible for the electrochemical profiles of the TMDs.¹⁸ Preceding this, Kautek and Gerischer discovered the preferential oxidation of bulk MoS₂ at the edges while no corrosion was noted at the basal planes.⁴¹ Correlating this to the two anodic peaks in the voltammogram of MoS₂, Chorkendorff and co-workers assigned the more intense signal occurring at a lower potential to the oxidation of the edge whereas the other signal, milder and at a higher potential, was assigned to the oxidation of the basal plane.¹⁸ Since the edges undergo oxidation readily unlike the basal planes, the oxidation of the edges in all WSe₂ materials may also be responsible for this distinct oxidation signal. Closer inspection of this anodic signal across all WSe₂ materials unveil that the current intensity of the peak is dramatically

higher in Group 5 transition metal doped-WSe₂ than the undoped WSe₂. Recalling the morphology of the Group 5 transition metal doped-WSe₂ in Figure 8.2 and Figure 8.3, the smaller and thinner fragments of the doped-WSe₂ unambiguously create a higher edge-to-basal plane ratio than the undoped WSe₂ which exist in bulky pieces. Thus, a larger extent of edge-oxidation would occur in the doped WSe₂ and in turn amplify the oxidation signal.

While no visible reduction peaks are observed in all scans towards positive potentials, the scans towards negative potentials present unique cathodic features of all WSe₂ materials. The absence of reduction peaks in all scans towards positive potentials indicates the lower electroactivity of the reducible groups of the WSe₂ materials when subjected to an initial oxidation. The undoped WSe₂ manifests a slight reduction signal at *ca.* -1.4 V due to the reduction of W(VI) to W(IV) state upon comparison with the inherent electrochemical signals of WO₃.^{34, 35} However, this signal is not detected in V-, Nb- and Ta-doped WSe₂ as a result of reduced WO₃ levels. High resolution XPS spectra of the W 4f core level region in Figure 8.5 disclose substantial amounts of WO₃ present in the undoped WSe₂ that becomes depleted upon doping with V, Nb and Ta. It is interesting to highlight that V-, Nb- and Ta- doped WSe₂ consistently undergo a mild reduction at *ca.* -0.9 V (as shown in the inset of Figure 8.6) that concurs with the intrinsic electrochemical feature of Group 5 metal transition metal diselenides (VSe₂, NbSe₂ and TaSe₂).⁹

Judging from the signals in the three consecutive scans, the innate oxidative and reductive processes of the WSe₂ materials are determined to be irreversible. All redox signals either completely vanish after the initial scan or diminish in intensity in the subsequent scans. Of interest, the anodic signal at *ca.* 0.8 V of undoped WSe₂ disappears

immediately after the initial scan as opposed to the V-, Nb- or Ta- doped WSe₂ where this anodic signal wanes in subsequent scans.

8.2.3 Electrocatalysis: Hydrogen Evolution

The advent of doped TMDs as activated electrocatalysts in clean-energy production, thanks to the enhanced intrinsic activity, conductivity and higher density of active sites of the TMDs upon doping,^{3, 10, 20, 24, 42} has cast the spotlight on the electrocatalytic performance of Group 5 transition metal doped-WSe₂. Replete with brilliant expectations, we investigate the electrocatalytic properties of WSe₂ before and after doping with V, Nb and Ta for hydrogen evolution reaction (HER) using linear sweep voltammetry.

Figure 8.7 illustrates the linear sweep voltammograms of the undoped and Group 5 transition metal-doped WSe₂ materials for HER in 0.5 M H₂SO₄ electrolyte. A striking similarity across the Group 5 transition metal doped-WSe₂ is a gentle pre-wave at *ca.* -0.5 V vs. RHE. The emergence of this pre-wave may be explained by the inherent reduction of the Group 5 transition metal doped-WSe₂ in the potential window under acidic conditions.

Common figures of merit employed during the assessment of the electrocatalytic performance of TMD materials towards HER include the overpotential and Tafel slope.⁴³ Overpotential at a current density of -10 mA cm⁻² is taken as the benchmark for comparison because this is the current density where tangible hydrogen production occurs and also the functional current density for efficient photochemical water splitting.⁴³ Tafel slope (*b*) defined as the increment in overpotential to achieve a unit rise in current density. Analysis of Tafel slopes provides an understanding of the HER mechanism on TMD surfaces whereby the rate-determining steps can be established. The possible rate-limiting steps and the corresponding Tafel slope values are summarized as such:^{44, 45}

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

Figure 8.7 a) Linear sweep voltammograms of the hydrogen evolution reaction on glassy carbon electrodes modified with undoped WSe₂, V-doped WSe₂, Nb-doped WSe₂ and Ta-doped WSe₂. b) Tafel plots for all the materials. Histograms summarize the averages of c) HER overpotential at a current density of -10 mA cm^{-2} and d) Tafel slopes for all the materials. Conditions: background electrolyte, H_2SO_4 (0.5 M); scan rate, 2 mV s^{-1} .

On the basis of HER overpotentials at -10 mA cm^{-2} , a trend is established in support of improved electrocatalytic activity for all Group 5 transition metal doped-WSe₂ showcasing comparable overpotentials of -0.75 V vs. RHE against the significantly higher overpotential of -0.85 V vs. RHE in the undoped WSe₂. The phenomenon of Group 5 transition metal

doped-WSe₂ behaving as better HER electrocatalysts than undoped WSe₂ is also replicated in the comparison of Tafel slopes. V-doped WSe₂, Nb-doped WSe₂ and Ta-doped WSe₂ exhibit Tafel slopes of 113 mV dec⁻¹, 124 mV dec⁻¹ and 136 mV dec⁻¹ respectively. Evidently, all Group 5 transition metal doped-WSe₂ possess considerably lower Tafel slopes than undoped WSe₂ of 176 mV dec⁻¹. Therefore, faster HER kinetics occurs on the surfaces of the doped-WSe₂ relative to the undoped counterpart.

Equipped with lower overpotentials and lower Tafel slopes than the undoped WSe₂, all Group 5 transition metal-doped WSe₂ indeed confirm doping as an effective strategy to activate the electrocatalytic property of WSe₂ towards hydrogen evolution. Chief amongst factors governing the HER performance of WSe₂ is the higher conductivity in terms of the chemical nature of the TMD upon doping with V, Nb or Ta.^{3, 10} As reflected in our XPS analysis (Figure 8.5), V-, Nb- and Ta-doped WSe₂ demonstrated prevailing levels of metallic 1T-phase compared to the undoped WSe₂ existing in the predominant semiconducting 2H-phase. The improved HER efficiency of MoS₂ and WS₂ due to phase transition from 2H to a more catalytic 1T polymorph has been reported in a spate of studies.^{46, 47} Between the 2H- and 1T-phase, the 1T-phase is more conductive as it possesses higher charge-transfer kinetics that promotes the HER process.^{3, 11} The TEM images further affirm the dominance of 1T upon doping (Figure 8.3). Apart from the higher conductivity due to the prevalent metallic 1T-phase, the concomitant effect of abundant active edge sites^{19, 21} after doping with V, Nb and Ta also increases the HER efficiency. The morphology of V-, Nb- or Ta-doped WSe₂ as fragmented flakes that we witnessed in Figure 8.2 and Figure 8.3 engenders a higher density of edge-to-basal ratio. This presents a larger number of active sites for HER compared to the bulky chunks of undoped WSe₂.

Despite the lower Tafel slopes of Group 5 transition metal doped-WSe₂ relative to the undoped WSe₂, there is no effect of doping on the rate-determining step of the HER process on WSe₂. The HER processes on doped-WSe₂ are limited by the Volmer adsorption step due to the proximity of the Tafel slope values to 120 mV dec⁻¹. The rate-determining step for the HER mechanism on undoped WSe₂ is also likely to be adsorption given that the Tafel slope value is beyond 120 mV dec⁻¹. Hence, the rate-limiting step for HER on WSe₂ remains unchanged regardless of doping with V, Nb or Ta.

In a bid to elucidate the interfacial charge transfer properties of the doped WSe₂ materials, we have performed electrochemical impedance spectroscopy (EIS) measurements in 0.5 M H₂SO₄ electrolyte to simulate HER conditions. The charge transfer resistance (R_{ct}) is determined by the diameter of the fitted semicircle obtained from the modified Randles circuit. Overlaying Nyquist plots of all doped WSe₂ materials manifest a wider semicircle diameter than the undoped WSe₂ as depicted in Figure 8.S7. The computed average R_{ct} for V-, Nb- and Ta- doped WSe₂ are 470, 410 and 630 Ω respectively whereas the undoped WSe₂ is determined to be markedly higher at 1120 Ω . Therefore, HER kinetics of WSe₂ becomes substantially faster after doping with Group 5 transition metals. In other words, surfaces of V-, Nb- and Ta- doped WSe₂ exhibit higher conductivity towards HER than the undoped WSe₂ that account for the improved HER efficiency of WSe₂ upon doping.

Following the study on EIS, we proceeded to determine the electrical conductivity of the doped WSe₂ materials using an interdigitated gold (Au) electrode system. The gradient of the I-V curve measured for each of the material is directly proportional to its conductivity. We are then able to perform a qualitative comparison on the conductivity of

WSe₂ before and after doping with the various Group 5 transition metals. The conductivities of the materials are as such: V-doped WSe₂ > Ta-doped WSe₂ > Nb-doped WSe₂ > undoped WSe₂ with undoped WSe₂ as reflected in Figure 8.S8 and the corresponding values are presented in Table 8.S5. Evidently, doping increases the conductivity of the WSe₂. The undoped WSe₂ is the least electrical-conducting as shown in its negligible slope of $7 \times 10^{-5} \text{ mA V}^{-1}$ and highest resistance of $\sim 10^7 \Omega$. Conversely, V-doped WSe₂ has the steepest gradient of 12.6 mA V^{-1} and lowest resistance of 79.3Ω .

On the basis of the findings in both EIS and conductivity measurements, we observe an overall enhanced conductivity of WSe₂ after doping with Group 5 transition metals.

Another important metric in the choice of electrode materials as durable HER electrocatalysts is their stability in acid. We examined the catalytic doped WSe₂ materials under acidic conditions by 2 methods: cycling and fixed potential. In the former method, all materials were subject to 100 cyclic voltammetry (CV) cycles in acid at their respective HER onset potential window. The onset of HER corresponds to the potential region where current density is at least -0.1 mA cm^{-2} . Figure 8.8 illustrates the HER polarisation curves before and after the 100 CVs. Across V-, Nb- and Ta- doped WSe₂, there is no significant deterioration in their HER catalytic performance evident in the overlapping of the polarisation curves. At a current density of -10 mA cm^{-2} , the HER overpotentials of all doped WSe₂ materials after 100 CVs are the same as before. However, in the case of undoped WSe₂, a noticeably weaker HER performance occurs after 100 CV cycles whereby the overpotential required for HER increased by over 0.1 V. Hence, the doped WSe₂ show generally robust catalytic stability while the undoped WSe₂ pales in comparison. Using the fixed potential method, we identified a potential at $-0.735 \text{ V vs. Ag/AgCl}$ that lies within

the onset region of HER. Both doped and undoped WSe₂ materials were subject to constant electrochemical reduction at this chosen potential for a period of 4000 s and their current density was recorded as reflected in Figure 8.S10. The respective measured current densities of all WSe₂ materials corroborated with their individual HER onset behaviour where V-doped WSe₂ shows highest onset current density of $\sim 0.7 \text{ mA cm}^{-2}$ for HER, followed closely by Nb- and Ta- doped WSe₂ with equivalent current densities at $\sim 0.5 \text{ mA cm}^{-2}$ while undoped WSe₂ exhibits lowest current density of $\sim 0.2 \text{ mA cm}^{-2}$. Over 4000 s, the HER onset current densities of all WSe₂ are remains fairly constant and are not undermined for at least 4000 s, indicating their acid stability. By virtue of both stability tests, the doped WSe₂ materials are deemed as generally stable catalysts in acid and do not compromise on their HER activity even after a long duration.

Figure 8.8 Linear sweep voltammograms of the hydrogen evolution reaction before and after 100 cyclic voltammetry cycles for a) undoped WSe₂, b) V-doped WSe₂, c) Nb-doped

WSe₂ and d) Ta-doped WSe₂. Conditions: background electrolyte, H₂SO₄ (0.5 M); scan rate, 2 mV s⁻¹.

8.3 Conclusion

In summary, we have performed a comprehensive study into the effect of doping Group 5 transition metals on WSe₂ and investigated their inherent electrochemical properties along with their electrocatalytic properties for hydrogen evolution. Aspects of morphology and elemental composition in bulk and surface layers before and after doping have also been systematically analyzed. Upon doping, a mild reduction signal manifests in V-, Nb- or Ta- doped WSe₂. Besides this modest cathodic signal, all Group 5 transition metal-doped WSe₂ exhibit essentially the same electroactive signals as the WSe₂ parent compound with a characteristic anodic peak resulting from the electrochemistry of the constituent elements in WSe₂. These intrinsic electroactivities may limit their use as electrode materials in electrochemical applications. Doping is found to elevate the electrocatalytic efficiency of WSe₂ towards hydrogen evolution. Armed with lower HER overpotentials and Tafel slopes, V-, Nb- and Ta- doped WSe₂ outperformed the WSe₂ parent compound. Improvement in the HER efficiency after doping has been linked to the increase number of active sites and the dominance of metallic 1T-phase in all Group 5 transition metal-doped WSe₂. After doping, we note a morphological change from bulky sheets to fragmented flakes and thicker to thinner sheets, increasing the edge-to-basal plane ratio and hence introducing more active edge sites for HER. While the undoped WSe₂ adopts mainly semiconducting 2H-phase, doping with V, Nb or Ta likely led to the stabilization of the catalytic 1T-phase which induced the 2H to 1T phase transition in WSe₂. This is also accompanied by an improved HER performance of WSe₂ upon doping. These

findings are vital to the TMD research community and offer insights into the effectiveness of doping in electrocatalytic applications.

8.4 Experimental Section

8.4.1 Materials

Tungsten (99.9%), vanadium (99.5%), niobium (99.5%) and tantalum (99.5%) in powder form were obtained from Alfa Aesar, Germany. Selenium (99.999%) was obtained from Mateck, Germany. *N,N*-dimethylformamide (DMF), ammonium tetrathiomolybdate ((NH₄)₂MoS₄), sulfuric acid, potassium chloride, potassium phosphate dibasic, sodium chloride and sodium phosphate dibasic were purchased from Sigma-Aldrich, Singapore. Glassy carbon (GC) electrode with diameter of 3 mm, Pt electrode and silver-silver chloride (Ag/AgCl) electrode were obtained from CH Instruments, Texas, USA. Ultrapure water was used for the preparation of electrolytes.

8.4.2 Synthesis

The undoped and doped tungsten selenides were synthesized from elements in evacuated quartz ampoules. The metals in powder form and selenium granules were weighted in stoichiometric amount corresponding to the 6 g of W_{0.95}DOP_{0.05}Se₂ where DOP denotes the dopant (V, Nb or Ta).

The ampoule was evacuated on the base pressure of 1×10^{-3} Pa and melt sealed by oxygen-hydrogen torch. The starting elements were mechanically mixed in ampoule for ten minutes before heat treatment. The two-step heat treatment was performed. In the first step the ampoule was heated on 600 °C for 48 hours. Before the second heating step, the ampoule was mechanically homogenized for 15 minutes. In the second step was the ampoule heated on 800 °C for 48 hours and finally on 850 °C for 24 hours. The heating and

cooling rate was in all cases 5 °C/min.

8.4.3 Apparatus

Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) were performed at an accelerating voltage of 5 kV and 15 kV respectively using JEOL 7600F field-emission scanning electron microscope (JEOL, Japan). X-ray photoelectron spectroscopy (XPS) was done using Phoibos 100 spectrometer with monochromatic Mg K α X-ray source (SPECS, Germany).

X-ray powder diffraction data were collected at room temperature on Bruker D8 Discoverer powder diffractometer with parafocusing Bragg–Brentano geometry using CuK α radiation (λ = 0.15418 nm, U = 40 kV, I = 40 mA). Data were scanned over the angular range 5–90° (2 θ) with a step size of 0.019° (2 θ). Data evaluation was performed in the software package EVA.

Transmission electron microscopy images were obtained using EFTEM Jeol 2200 FS microscope. Sample was prepared by drop casting of sample suspension (1 mg/mL) on 200 mesh TEM grid. Elemental maps and EDS spectra were enquired with SDD detector X-MaxN 80 T S from Oxford Instruments (England).

Electrochemical measurements using cyclic voltammetry (CV), linear sweep voltammetry (LSV) and chronoamperometry (CA) were carried out in a 6-ml electrochemical glass cell at room temperature (25 °C). Three-electrode configuration was utilized with modified GC, Pt and Ag/AgCl electrodes as working, counter and reference electrodes respectively. The voltammetric measurements were obtained using μ Autolab Type III electrochemical analyzer (Eco Chemie, Utrecht, The Netherlands) with NOVA software version 1.8 (Eco Chemie).

8.4.4 Procedures

Bulk layered TMD materials (V-doped WSe₂, Nb-doped WSe₂, Ta-doped WSe₂ and WSe₂) were prepared as suspensions with concentrations of 2 mg ml⁻¹ in DMF and subject to a first-time ultrasonication for 1.5 hour to attain well-dispersed samples. Before any electrochemical measurements, the GC electrode was renewed by first polishing on a polishing pad using 5 µm alumina particles followed by 0.05 µm alumina particles. The GC electrode was washed with ultrapure water after each polish. Each suspension was also ultrasonicated for 10 minutes prior to any electrochemical measurements to maintain the homogeneity. After which, 2.0 µl of the sample was drop casted onto the GC electrode and left to dry. The procedure was then repeated for another time to obtain a modified GC electrode with 4.0 µg film of material.

For inherent electrochemistry studies of TMD layered materials, CV was performed at a scan rate of 100 mV s⁻¹ with 50 mM phosphate buffer saline (PBS), pH 7.0 as the supporting electrolyte. The PBS electrolyte was purged with nitrogen gas (N₂) for 10 minutes before any voltammetric measurements. A scan towards positive potentials was conducted by starting the scan at 0 V towards the positive potential (e.g. 1.8 V) before the scan was reversed to -1.8 V and ended back at 0 V. A scan towards negative potentials was also performed similarly with the scan being directed towards the negative potential first (e.g. -1.8 V) followed by a reverse scan to 1.8 V before returning to 0 V.

For HER measurements, 0.5 M sulfuric acid was utilized as a background electrolyte and LSV was performed at a scan rate of 2 mV s⁻¹.

Electrochemical impedance spectroscopy (EIS) experiments were conducted within a frequency range of 0.1 MHz to 0.1 Hz at a sinusoidal voltage perturbation of 10 mV amplitude. The measurements were performed in H₂SO₄ (0.5 M) electrolyte at

superimposed DC potential of -0.925 V (vs. Ag/AgCl) for EIS under HER conditions.

For conductivity measurements, current-voltage measurements (I-V curves) were acquired by an interdigitated gold electrode platform (Au-IDE) by drop-casting $2\text{ }\mu\text{L}$ of each material suspension onto the electrode surface with $10\text{ }\mu\text{m}$ spacing. The electrode was dried under a lamp to produce a random distribution of material film on the interdigitated area that connects the two Au electrode ends. Linear sweep voltammetry was performed at a scan rate of 20 mV s^{-1} when recording the I-V curves.

The HER catalytic stability of the all WSe₂ materials were performed in $0.5\text{ M H}_2\text{SO}_4$ electrolyte before and after 100 cyclic voltammetric scans at 100 mV s^{-1} . The cyclic voltammetric scan range of each material corresponds to their HER onset region where the current density is at least -0.1 mA cm^{-2} . For V-, Nb- and Ta- doped WSe₂ materials, the cyclic voltammetric scan range is conducted from -0.385 V to -0.785 V vs. Ag/AgCl. The scan window is from -0.435 to -0.835 V vs. Ag/AgCl for undoped WSe₂.

In another method using chronoamperometry, the HER catalytic stability of all WSe₂ materials are subject to a fixed electro-reduction treatment of -0.735 V vs. Ag/AgCl; a potential that exists within their HER onset potential window to provide a current density of at least -0.1 mA cm^{-2} . The constant electro-reduction takes place in $0.5\text{ M H}_2\text{SO}_4$ electrolyte over a 4000-second duration.

Triplicate measurements were performed for material for all electrochemical studies and the potentials are relative to Ag/AgCl unless stated otherwise.

8.5 Supporting Information

Table 8.S1 Table of elemental composition of transition metal-doped WSe₂ materials based on energy-dispersive X-ray spectroscopy.

Sample	W 4f at. %	Se 3d at. %	Dopant at. %	C at. %	O at. %
WSe ₂	14.00	26.06	-	48.20	11.75
V-doped WSe ₂	15.37	29.75	1.60 (V)	37.58	15.70
Nb-doped WSe ₂	13.32	23.66	0.61 (Nb)	49.82	12.66
Ta-doped WSe ₂	9.30	16.56	1.79 (Ta)	60.23	12.13

Table 8.S2 Table chalcogen-to-metal ratio and the composition of transition metal-doped WSe₂ materials based on energy-dispersive X-ray spectroscopy.

Sample	Composition	Chalcogen-to-Metal Ratio
WSe ₂	WSe _{1.9}	1.9
V-doped WSe ₂	V _{0.1} WSe _{1.9}	1.9
Nb-doped WSe ₂	Nb _{0.04} WSe _{1.8}	1.8
Ta-doped WSe ₂	Ta _{0.2} WSe _{1.8}	1.8

Figure 8.S1 Energy dispersive X-ray maps of undoped WSe₂ and all Group 5 transition metal-doped WSe₂.

Figure 8.S2 Scanning electron micrographs showing magnified areas for WSe₂, V-doped WSe₂, Nb-doped WSe₂ and Ta-doped WSe₂. Scale bars represent 1 μm.

Figure 8.S3 The TEM images and corresponding elemental distribution maps of tungsten, selenium and dopant. All scale bars corresponds to 250 nm.

Table 8.S3 Table of surface elemental composition of transition metal-doped WSe₂ materials based on the survey scans of X-ray photoelectron spectroscopy (XPS). The C 1s signal was calibrated to 284.8 eV.

Sample	W 4f at. %	Se 3d at. %	Dopant at. %	C at. %	O at. %
WSe ₂	16.12	42.23	-	27.70	13.95
V-doped WSe ₂	15.78	38.68	1.11 (V 2p)	27.78	16.65
Nb-doped WSe ₂	15.23	40.94	1.54 (Nb 3d)	26.81	15.48
Ta-doped WSe ₂	14.29	41.66	2.16 (Ta 4f)	23.89	18.00

Table 8.S4 Table of chalcogen-to-metal ratio and the composition of transition metal-doped WSe₂ materials based on of X-ray photoelectron spectroscopy (XPS).

Sample	Composition	Chalcogen-to-Metal Ratio
WSe ₂	WSe _{2.6}	2.6
V-doped WSe ₂	V _{0.07} WSe _{2.5}	2.5
Nb-doped WSe ₂	Nb _{0.1} WSe _{2.7}	2.7
Ta-doped WSe ₂	Ta _{0.2} WSe _{2.9}	2.9

Figure 8.S4 Wide-scan X-ray photoelectron spectra of a) WSe₂, b) V-doped WSe₂, c) Nb-doped WSe₂ and d) Ta-doped WSe₂.

Figure 8.S5 High resolution X-ray photoelectron spectrum of O 1s and V 2p regions of the V-doped WSe₂.

Figure 8.S6 High-resolution X-ray photoelectron spectra of Se 3d core level region for a) WSe₂, b) V-doped WSe₂, c) Nb-doped WSe₂ and d) Ta-doped WSe₂.

Figure 8.S7 a) Nyquists of WSe₂, V-doped WSe₂, Nb-doped WSe₂ and Ta-doped WSe₂. b) Histogram illustrating the impedimetric signal of WSe₂, V-doped WSe₂, Nb-doped WSe₂ and Ta-doped WSe₂ represented as R_{ct} . Conditions: background electrolyte, H₂SO₄ (0.5 M).

Table 8.S5 Table of values for current-voltage (I-V) curve gradient and resistance computed based on conductivity measurements performed on interdigitated gold electrode for Group 5 transition metal-doped WSe₂ materials.

Sample	Gradient (mA V ⁻¹)	Resistance (Ω)
WSe ₂	7.010^{-5}	$1.4 \cdot 10^7$
V-doped WSe ₂	12.6	79.3
Nb-doped WSe ₂	4.6	228.2
Ta-doped WSe ₂	8.9	112.3

Figure 8.S8 Current-Voltage (I-V) curves of a) WSe₂, V-doped WSe₂, Nb-doped WSe₂ and Ta-doped WSe₂ recorded on interdigitated gold electrode and b) magnified current region for WSe₂.

Figure 8.S9 Cyclic voltammograms of all WSe₂ materials to examine catalytic stability in acid. Conditions: background electrolyte, H₂SO₄ (0.5 M); scan rate, 100 mV s⁻¹.

Figure 8.S10 a) HER polarisation curves of all WSe₂ materials magnified to a current density of 1 mA cm⁻² to observe the onset region of HER. b) Chronoamperogram showing the negligible degradation of onset HER current density at an applied potential of -0.735 V vs. Ag/AgCl. Conditions: background electrolyte, H₂SO₄ (0.5 M).

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Chapter 9

Porous MoSe_x Structures for Electrocatalysis

9.1 *Introduction*

9.2 *Results and Discussion*

9.2.1 *Electrosynthesis of MoSe_x Films*

9.2.2 *Electrocatalysis at MoSe_x Films*

9.2.3 *Electrocatalysis at Porous MoSe_x Surfaces*

9.3 *Conclusion*

9.4 *Experimental Section*

9.5 *Supporting Information*

The results and discussion in this chapter were published in the following manuscript:

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The thesis author was the primary investigator and first author of the above paper.

9.1 Introduction

The energy conundrum that persists as a prime focus on the agenda of many countries is an aftermath of the heavy reliance on non-renewable resources, like coal and fossil fuels, to meet escalating energy demands since time immemorial. In the last decade, governmental efforts worldwide have taken enormous strides to cut that Gordian knot. These are exemplified in the generous funds to develop clean energy technologies and the implementation of policies that promote the mainstream use of renewable resources in the energy sector. In particular, hype over hydrogen-powered cars and trains accentuates hydrogen as a viable energy carrier thanks to its high energy density, non-polluting by-product and sustainable production from water-splitting.^{1, 2} Hitherto platinum (Pt) is the best electrocatalyst for hydrogen evolution reaction (HER) but its low natural abundance renders it expensive for mass usage in industries. Therefore, earth-abundant transition metal dichalcogenides (TMDs) have been sought after as alternative catalysts. Amidst them, the Group 6 TMDs especially MoS₂, MoSe₂ and WS₂ are feted by scientists, with considerable works documenting their remarkable HER performance.³⁻¹⁰ The active sites for HER in TMDs are the edges as opposed to the inert basal planes.^{11, 12} For MoS₂, the S-edge is most catalytic whereas both the metal- and chalcogen- edge sites in MoSe₂ and WS₂ are active for HER.¹¹⁻¹³

Syntheses of the TMDs are broadly classified into top-down and bottom-up approaches. In the top-down technique, the bulk TMDs are subject to chemical exfoliation using lithium intercalants or liquid exfoliation in suitable solvents to thin them down into few layers or even single layers.^{6, 14, 15} The bottom-up approach encompasses a myriad of methods such as solvothermal or hydrothermal synthesis and chemical vapour deposition.^{6, 15-17} However, these synthetic methods occur under energy-demanding

conditions; requiring high temperatures, a lengthy duration and often involve toxic reagents. Conversely, electrochemical synthesis of TMDs is a solution-based method compatible with ambient conditions that offers intrinsic advantages tied to low cost and scalability.¹⁸ Additionally, the electrodeposition method conveniently manipulates a spectrum of synthetic variables from pH, solvent type to deposition potential or current to tailor morphology and control growth of TMD material.^{9, 19-23} Thus, the versatility of electrodeposition facilitates the modification of the composition or morphology of TMDs to exploit their desired properties for HER.

Porous structures on material surfaces play indispensable roles in surface confined processes, especially to enhance the activity in catalysis.²⁴⁻²⁶ Recently, a few published works reported that porous MoSe₂ nanostructures exhibit improved HER catalytic activity compared to the non-porous counterpart.²⁷⁻²⁹ The enhancement was associated to the larger electrochemical active surface area and hence, increased number of active sites for HER. However, these porous MoSe₂ nanostructures were fabricated using traditional methods of exfoliation or wet chemical techniques. One greener approach to create porous MoSe₂ structures is using a polystyrene bead template-assisted electrosynthesis method which has been proved effective for MoS₂.¹⁹ Polystyrene beads are commercially available in different sizes and the removal step after electrodeposition is facile. The varied sizes of polystyrene beads engender porous MoSe₂ of differing sizes, in turn providing an opportunity to elucidate the pore size-dependence of MoSe₂ on their catalytic properties, which has not been disclosed despite the vast literature on porous structured TMD materials.^{19, 24, 27-29}

Herein, we explore electrochemical cathodisation as a means to electrosynthesize

porous MoSe_x films from molybdenum and selenium precursors; molybdic acid (H₂MoO₄) and selenium dioxide (SeO₂), and polystyrene beads as the hard template. An illustration of this electrosynthesis is outlined in Scheme 9.1. Using polystyrene beads of uniform sizes ranging from 0.1 μm to 1.0 μm, porous MoSe_x films of various pore sizes in the inverse opal configuration are fabricated and investigated for their electrocatalytic performance for hydrogen evolution. The correlation between pore size and catalytic activity is also established for electrodeposited porous MoSe_x films.

Scheme 9.1 Illustration of the electrochemical fabrication of the inverse opal porous MoSe₂ films.

9.2 Results and Discussion

9.2.1 Electrochemical synthesis of MoSe_x films

The electrochemical synthesis of MoSe_x films takes advantage of the notion of “induced co-electrodeposition” whereby the initial deposition of either the metal or the chalcogen component at a certain cathodic potential triggers the other to deposit. The

eventual co-electrodeposition of molybdenum and selenium simultaneously yields MoSe_x films. Such phenomenon has been recorded in literature using an electrolytic bath comprising a selenium precursor, usually H₂SeO₃ or SeO₂, and a molybdate species present in molybdenum precursors including H₂MoO₄ or Na₂MoO₄.^{20, 21, 30, 31} A key consideration in the preparation of the electrolyte mixture is that a high concentration of molybdenum precursor and a relatively lower concentration of selenium precursor are required to proximate the electrode potentials of deposition.^{20, 21}

In this study, the electrosynthesis of MoSe_x films occurs in an electrolytic bath consisting of 50 mM H₂MoO₄ and 20 mM SeO₂ in aqueous 0.2 M NH₄OH. The inherent electrochemistry of H₂MoO₄ and SeO₂ precursor solutions are individually examined in aqueous NH₄OH to gain awareness of the probable electrochemical processes. Cyclic voltammograms of the precursor solutions are presented in Figure 9.S1. A distinct reductive wave emerges at -0.8 V and peaks at -1.2 V along with an anodic signal at -0.6 V is observed for the H₂MoO₄ precursor. At first sight, the cyclic voltammogram of SeO₂ precursor seemingly displays electrochemical inertness. Inspecting further, a mild reduction signal is noted at -0.6 V, accompanied by a minor oxidation peak appears at 0.4 V. The inherent cathodic peaks of the precursors are of interest to us when determining a suitable potential for electrodeposition because these signals correspond to the reduction of SeO₂ and most prominently, the hexavalent MoO₄²⁻ reduction to Mo(IV) or Mo(0).^{20, 21} Armed with this knowledge, we perform preliminary screening of the potential range between -0.6 V and -1.2 V in the presence of both precursors to identify an optimal potential that permits the simultaneous electro-reduction of MoO₄²⁻ and SeO₂ to generate MoSe_x films.

Using chronoamperometry, the electrochemical potentials screened are -0.6 V, -0.8 V, -0.9 V, -1.0 V and -1.2 V vs. Ag/AgCl. At each screened potential, electrochemical cathodisation takes place for 10 minutes to attain visible films of deposits on the glassy carbon (GC) electrode substrate. The electrodeposited films at the various potentials are characterised using X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) to determine their elemental composition and morphology.

Figure 9.1 High resolution X-ray photoelectron spectra of MoSe_x films for a) Mo 3d and b) Se 3d regions when electrodeposited at -0.8 V, -0.9 V and -1.0 V vs. Ag/AgCl.

High resolution X-ray photoelectron spectra of electrodeposited MoSe_x films for the core level Mo 3d and Se 3d regions for the array of screened electrochemical potentials are shown in Figure 9.1 and 9.S2.

At lower cathodic potentials of -0.6 V and -0.8 V, the detected Mo 3d and Se 3d signals, which unequivocally mark the valences of unreacted metal and chalcogen precursors, point to the incomplete electrosynthesis of MoSe_x. The pair of Mo 3d_{5/2} and 3d_{3/2} binding energies at 232.9 eV and 236.1 eV is diagnostic of the Mo(VI) oxidation state in the MoO₄²⁻ metal precursor and its passivation to form MoO₃, an insoluble oxide.^{22, 32} This is

supplemented by the prevalent Se 3d signal at 59.9 eV contributed by the 3d_{5/2} and 3d_{3/2} binding energies (at 59.4 eV and 60.3 eV) of the Se(IV) oxidation state of the SeO₂ chalcogen precursor^{33, 34} witnessed in the deposits formed at -0.6 V and -0.8 V potentials. Apart from the unreacted SeO₂ peak, another Se 3d signal of an equivalent intensity occurs at a lower binding energy of 55.8 eV for the electrodeposited film at -0.8 V. This signal suggests presence of elemental selenium that might have resulted from the partial reduction of SeO₂,³⁴ otherwise not observed for the deposit formed at -0.6 V.

Proceeding to higher electrochemical potentials of -0.9 V and -1.0 V, a paradigm shift in the profile of the Mo 3d and Se 3d signals towards lower binding energies heralds the effective electro-reduction of the metal and chalcogen precursors to form MoSe_x films. The Mo 3d spectra at both potentials depict two pairs of doublets; one pair of higher binding energies belongs to the Mo⁶⁺ oxidation state whereas the other pair is characteristic to tetravalent Mo. Furthermore, the Mo 3d_{5/2} and 3d_{3/2} binding energies at 229.7 eV and 232.9 eV confirms the successful reduction of MoO₄²⁻ metal precursor to MoSe_x wherein the oxidation state of Mo decreases from +6 to +4.^{9, 35} Dissimilar to the lower cathodic potentials at -0.6 V or -0.8 V, the signal attributed to the Mo⁶⁺ may originate from the re-oxidation of Mo⁴⁺ or even oxidation of MoSe₃ upon exposure to air as reported in previous works.^{8, 27} For both potentials, deconvolution of the Se 3d peak manifests two pairs of doublets with the Se 3d_{5/2} binding energies positioned at 54.6 eV and 55.5 eV, indexed to Se²⁻ and Se(0) respectively.^{31, 34} Therefore, the emergence of the Se²⁻ at -0.9 V and -1.0 V is crucial evidence to SeO₂ precursor reducing to selenides. Due to the presence of Se²⁻, together with the Mo⁴⁺ and Mo⁶⁺ species, it is likely that the electrodeposited MoSe_x films take on both MoSe₂ and MoSe₃ forms. EDS analysis (Table 9.S1) further

confirms this with the stoichiometric chalcogen-to-metal ratio of MoSe_x films electrodeposited at -0.9 V and -1.0 V to be 2.7 and 2.0 respectively. Therefore, the MoSe_x films are amorphous in nature where $2 \leq x \leq 3$. Moreover, the MoSe_x films deposited at these potentials are brown in color and adhere to the electrode substrate, unanimous with numerous reports involving MoSe₂ synthesis.^{20-22, 27, 31}

Between electrochemical potentials of -0.9 V and -1.0 V, the electrosynthesis of MoSe_x films *via* electro-reduction is found to be more extensive at the former potential (i.e. -0.9 V). Despite the co-existence of both tetravalent and hexavalent Mo states, the principal valency of Mo in MoSe_x films is four when electrodeposited at -0.9 V, given that the signal intensity of the Mo(IV) oxidation state prevails over that for the Mo(VI) state. On the contrary, we note almost equal dominance in signal intensity between the Mo⁴⁺ and Mo⁶⁺ states. Likewise, the Se²⁻ signal dominates the elemental selenium contribution at -0.9 V while the opposite happens at -1.0 V wherein the elemental selenium forms the majority of the electrodeposit.

Going beyond the potential of -1.0 V, for instance at -1.2 V (Figure 9.S2), leads to electrodeposits with primarily Mo⁶⁺ species and a mix of Se²⁻ and Se(0) species. As inferred from the trace amounts of Mo⁴⁺ and unreacted SeO₂ in the electrodeposit, electro-reduction of the metal precursor is limited at -1.2 V while chalcogen precursor continues to undergo reduction. Hence, this potential of -1.2 V may be the threshold potential that deters “induced co-electrodeposition”. Instead of both the metal and chalcogen precursors becoming electrochemically reduced concurrently and then deposited as films, the electro-reduction of the latter is preferred, as reasoned by thermodynamics or kinetics factors.

MoSe_x films electrodeposited between -0.8 V and -1.0 V are analysed by SEM for insights into their morphology. As depicted in Figure 9.S3, nucleation sites begin to appear at -0.8 V. Yet these sites, in nanometer dimensions, are scarce and the bulk of the screen-printed carbon electrode (SPCE) substrate remains visible in the background. At -0.9 V, the MoSe_x film acquires a generally smooth surface. Growth of MoSe_x film completely covers the SPCE substrate. Sites of nucleation on MoSe_x accumulate to form particles as massive as 1 μm. The MoSe_x thicken in layers at -1.0 V and some crevices are observed. New nucleation sites continue to appear on the uppermost layer, running a gamut of sizes ranging from 5 nm to 0.5 μm, engendering a bumpy morphology on an otherwise smooth MoSe_x surface beneath.

9.2.2 Electrocatalysis at MoSe_x films

MoSe₂, akin to other Group 6 transition metal dichalcogenides (TMDs), is widely touted as an electrocatalyst for hydrogen evolution reaction (HER). We investigate the HER performance of MoSe_x films at various cathodic potentials in a bid to determine the optimum cathodic potential for electrodepositing MoSe_x with the best electrocatalytic ability for HER. Polarisation curves for HER of the electrodeposited MoSe_x films at the screened potentials are presented in Figure 9.2.

Key parameters used in the assessment of the electrocatalytic performance for HER include the overpotential to elicit a current density at -10 mA cm⁻² and the Tafel slope. At a current density of -10 mA cm⁻², production of H₂ is first tangible and therefore, confirms the effective electrocatalysis. By definition, Tafel slope is the increase in overpotential required to raise the current density by an order of magnitude. Based on this understanding, a smaller Tafel slope indicates a more efficient electrocatalyst than a larger

Tafel slope. More frequently seen, Tafel slope provides a clue to the HER mechanism undertaken on the material surface and the assignment of the most probable rate-determining step. Briefly, the two-step HER process can be summarised as follows:³⁶

Adsorption *via* the Volmer process

Desorption *via* the Heyrovsky process

Or desorption *via* the Tafel process

Figure 9.2 a) Linear sweep voltammograms upon hydrogen evolution of MoSe_x films electrodeposited at various potentials from -0.6 V to -1.2 V and b) their overpotentials at current density of -10 mA cm⁻² recorded in histograms. c) Tafel graphs of the MoSe_x films

electrodeposited at various potentials and d) their Tafel slope values recorded in histograms. Conditions: electrolyte, H₂SO₄ (0.5 M); scan rate, 5 mV s⁻¹.

The MoSe_x film electrosynthesized cathodically at -0.9 V outshines all other screened potentials as an electrocatalyst for HER, showcasing the lowest HER overpotential of 0.38 V and the smallest Tafel slope of 145 mV dec⁻¹ amongst others. The Tafel slope suggests that the HER process on the MoSe_x film deposited at -0.9 V is limited by the Volmer-adsorption step. Equipped with a marginally higher HER overpotential of 0.42 V and a Tafel slope of 192 mV dec⁻¹, the film electrodeposited at -1.0 V comes second to -0.9 V. The MoSe_x film deposited at -0.6 V is the least ideal for HER catalysis evident in the highest overpotential of 0.8 V required to attain a current density of -10 mA cm⁻² and a Tafel slope beyond 200 mV dec⁻¹. The competent HER performance of MoSe_x films electrodeposited at -0.9 V and -1.0 V stems from the mixed composition of MoSe₂ and MoSe₃, which are catalytic, as construed from our XPS analyses (Figure 9.1). Pre-waves are also observed for MoSe_x films deposited at -0.9 V and -1.0 V. The occurrence of pre-waves is due to the intrinsic electrochemistry of MoSe₂ surfaces, in particular the exfoliated MoSe₂, in consensus with prior reports.^{37, 38} Ambrosi *et al.* compared the electrocatalytic activity between bulk and exfoliated MoSe₂.³⁸ At -10 mA cm⁻², there was substantial lowering of the HER overpotential from beyond 0.6 V for the bulk MoSe₂ to 0.38 V upon exfoliation.³⁸ Similarly, the technique of cathodic electrodepositing MoSe_x films, specifically at -0.9 V, is able to outperform the electrocatalytic performance of the bulk MoSe₂ and rival that of exfoliated MoSe₂ in aspect of the overpotential.

Out of all the screened electrochemical potentials, -0.9 V is deduced to be the most favourable potential for electrodeposition of MoSe_x films to achieve the maximum HER

catalysis. Having settled on the cathodic deposition potential, we next investigate the effect of electrodeposition time on the HER performance of the MoSe_x films. The deposition times tested are for periods of 5, 10 and 20 minutes and the linear sweep voltammograms for HER are illustrated in Figure S4. Broadly, the HER performance of MoSe_x films electrodeposited at -0.9 V is independent of deposition time. At a current density of -30 mA cm⁻², where the level of H₂ production is increased, the HER overpotential required lies in the region of 0.68 V and 0.71 V across deposition times. Likewise, regardless of deposition time, there is little deviation in their Tafel slopes averaging at 130 mV dec⁻¹. Therefore, adsorption remains the rate-determining step in the HER mechanism for MoSe_x electrodeposited at -0.9 V despite different deposition times.

9.2.3 Electrochemical synthesis of porous MoSe_x surfaces

We undertake the technique of template-assisted electrodeposition to explore the feasibility of fabricating porous MoSe_x surfaces at the earlier optimized potential of -0.9 V. Polystyrene beads, of diameters 0.1 to 1.0 μm, are adopted as the hard template (Figure 9.S5). After electrodepositing MoSe_x, the template removal step was performed by dissolution of the polystyrene beads upon immersion in toluene for 12 hours. For ease of evaluation of the surface morphology under the SEM, indium-tin oxide (ITO)-coated slide, which has a smooth surface unlike the rough appearance of the blank SPCE, was employed as the substrate for electrodeposition of porous MoSe_x films. SEM was performed after dissolving the template in toluene. Deposition time was varied to determine the morphology of porous MoSe_x films at different stages of growth. Further details on the template-assisted electrodeposition procedure are described in **Section 9.4 Experimental Methods**.

After template removal of the polystyrene beads in toluene, porous MoSe_x films were captured at a few deposition durations: 5, 10, 20 and 30 minutes to monitor their growth. As a model of illustration, scanning electron micrographs for electrosynthesized porous MoSe_x films upon removal of 0.6 μm polystyrene beads across deposition times are portrayed in Figure 9.3. By the same token, Figure 9.S6, 9.S7 and 9.S8 chart the morphology of the porous MoSe_x films after removal of 0.1, 0.3 and 1.0 μm polystyrene beads respectively, where MoSe_x films with pore sizes of 0.1, 0.3 and 1.0 μm ensue. The growth mechanism is postulated to be identical across all sizes of polystyrene bead template whereby the film growth occurred over the substrate as well as on the surface of the polystyrene particle. This has been formerly witnessed by our group in the template-assisted electrodeposition of porous MoS₂ using polystyrene bead template sizes of 0.24 and 3.0 μm .¹⁹

Figure 9.3 Scanning electron micrographs of MoSe_x films obtained after 0.6 μm

polystyrene beads were dissolved in toluene. MoSe_x film was electrodeposited onto an ITO-coated slide after a) 5 min, b) 10 min, c) 20 min and d) 30 min.

Figure 9.3 vividly delineates the development of the inverse opal-like porous MoSe_x film containing 0.6 μm pores across deposition time. 5-10 minutes of MoSe_x deposition lead to no apparent porous structures. Increasing the deposition time to at least 20 minutes generates widespread porous structures in multiple layers. After 30 minutes of electrodeposition, porous structures stay discernible and the wall between each cavity thickens. However, some of the cavities have evolved into closed shell-type, forming hollow spheres at this deposition duration. The disparity between 5-10 minutes and 20-30 minutes of deposition time is a consequence of insufficient shell thickness at short deposition time to sustain the structural integrity of the pores upon the removal of the template whereas longer deposition time strengthens the wall; therefore, the porous MoSe_x structure is maintained even without the template. The stages of growth of 0.6 μm porous MoSe_x structures parallel that of 1.0 μm porous MoSe_x structures as captured in Figure 9.S8. Using polystyrene particles of 1.0 μm diameter as the template, porous structures resembling hemispheres are obtained after 20 minutes of deposition and a small number of entirely hollow spheres are formed after 30 minutes of deposition (Figure 9.S8c and 9.S8d). The thick cavity walls stabilise these structures and retains them even after template removal. Porous structures are absent between 5-10 minutes of deposition due to the collapse of the weak shell when the template is removed (Figure 9.S8a and 9.S8b).

The size of the polystyrene bead template used in the MoSe_x electrodeposition influences the deposition time required to fabricate porous structures. Porous MoSe_x

structures formed by smaller bead diameters (0.1 and 0.3 μm) require a shorter time and a longer time is necessary for those of larger diameters (0.6 and 1.0 μm). While at least 20 minutes is needed to achieve MoSe_x porous structures for 0.6 and 1.0 μm cavity sizes, overgrowth of the MoSe_x film that led to complete closure of the pores of 0.1 and 0.3 μm sizes manifest as patches of thick growth on several parts of the porous structures that lay beneath (Figure 9.S6c and 9.S7c). These porous structures vanish after increasing the deposition time to 30 minutes attributed to the thick and extensive growth of MoSe_x above these fine porous structures (Figure 9.S6d and 9.S7d). In stark contrast to the 0.6 or 1.0 μm -sized porous MoSe_x structures, which only began to strengthen and form after 20 minutes, 10 minutes was sufficient to create self-sustaining 0.3 μm -sized porous MoSe_x structures, and just 5 minutes for 0.1 μm -sized porous MoSe_x structures (Figure 9.S6a and 9.S7b).

Figure 9.4 Scanning electron micrographs of porous MoSe_x films with pore size of a) 0.1 μm ,

b) 0.3 μm , c) 0.6 μm and d) 1.0 μm after dissolution of the polystyrene beads in toluene.

To fabricate extensively porous MoSe_x films of various pore sizes as portrayed in Figure 9.4 with minimal overgrowth of the film, the optimum deposition time are defined as follows: 5 minutes for 0.1 μm , 10 minutes for 0.3 μm and 20 minutes for 0.6 and 1.0 μm . These deposition times are used to grow the respective porous MoSe_x structures on the GC electrode to ascertain their electrocatalytic properties.

9.2.4 Electrocatalysis at porous MoSe_x surfaces

The electrosynthesized porous MoSe_x surfaces of assorted pore sizes (0.1, 0.3, 0.6 and 1.0 μm) are examined for their electrocatalytic performance towards HER. In particular, we survey the dependence of pore size of porous MoSe_x films on their HER catalysis. Despite the differing deposition time used to construct these porous networks on MoSe_x, we rule out deposition time as a factor that significantly affects the electrocatalytic ability of surfaces given the relatively unchanged HER overpotentials at -30 mA cm^{-2} spanning across 5 to 20 minutes of MoSe_x deposition as studied in Figure 9.S4. Linear sweep voltammograms for HER on the porous MoSe_x films of varying pore sizes are demonstrated in Figure 9.5.

Figure 9.5 a) Linear sweep voltammograms upon hydrogen evolution of porous MoSe_x films of varied pore sizes from 0.1 μm to 1.0 μm and b) Tafel plots of the porous MoSe_x films. Histograms for c) hydrogen evolution overpotential at current density of -30 mA cm⁻² and d) Tafel slope values of the porous MoSe_x films. Conditions: electrolyte, H₂SO₄ (0.5 M); scan rate, 5 mV s⁻¹.

Considering the HER overpotential at -30 mA cm⁻², the electrocatalytic performance of the porous MoSe_x films is contingent on pore size such that smaller pores are favoured over the larger ones. Porous MoSe_x films of 0.1 and 0.3 μm -sized pores exhibit low HER overpotentials that are comparable to each other at 0.57 V and 0.61 V. When the pore size is increased to 0.6 μm, there is a dramatic inflation in the HER overpotential to 0.82 V. At largest pore diameter of 1.0 μm, the HER overpotential required becomes 0.76 V, significantly higher than smaller pore sizes of 0.1 and 0.3 μm. The anomalously high HER

overpotential in 0.6 μm -sized pores may arise from the multi-layered porous structures, as we recall the scanning electron micrographs in Figure 9.4c, deviating from the other sizes which manifest in a single porous layer. The stacked porosity increases the likelihood of trapping the hydrogen bubbles, thus hindering their effective desorption from the surface. Another concomitant symptom of the intermittent release of accumulated bubbles from the surface in the porous MoSe_x network materialize as the random spikes in the linear sweep profile of 0.6 μm -sized porous MoSe_x films unlike the smoother voltammograms of the other porous MoSe_x films. In an attempt to verify this, we electrosynthesize a monolayer of 0.6 μm -sized porous MoSe_x films using modified experimental parameters; specifically shorter deposition duration and a lower amount of sacrificial polystyrene bead template. The linear sweep profile (Figure 9.S9) of the monolayer porous MoSe_x film presented a smoother appearance because fewer bubbles adhered to the surface in contrast to that for the multilayered porous MoSe_x network. Moreover, the HER overpotential of the monolayer porous MoSe_x film is found to be marginally lower than that for the multilayer porous MoSe_x film of the same pore size. Faster detachment of bubbles from the monolayer film than from the multilayer film enables active sites to be readily available for HER that results in slight enhancement in HER efficiency.

The electrocatalytic activities of these porous MoSe_x films are also studied on the basis of their Tafel slopes. Porous MoSe_x films of 0.1 μm –sized pores demonstrate the lowest Tafel slope of 118 mV dec^{-1} , and numerically closest to 120 mV dec^{-1} , this corresponds to the adsorption step as rate-limiting in HER. The upshot of the Tafel slope analysis for the porous MoSe_x of various sizes is unambiguous and adheres to a trend as

such: $0.1 < 0.3 < 0.6 < 1.0 \text{ }\mu\text{m}$. Even though pore sizes are increased to $1.0 \text{ }\mu\text{m}$ where porous MoSe_x films showcase highest Tafel slope of 138 mV dec^{-1} , the Volmer-adsorption step remains as the slow step in the HER mechanism. Hence, HER pathways assumed by the porous MoSe_x films are independent of pore size in the tested range. Moreover, the Tafel slope exhibited by all porous MoSe_x films regardless of pore size concurs with that of vertically aligned MoSe₂ between 105 to 120 mV dec^{-1} .¹⁰

In light of the HER performance indicators discussed above, pore size is indeed an important feature to consider when designing an electrocatalyst. Lowest HER overpotential and Tafel slope render porous MoSe_x films with $0.1 \text{ }\mu\text{m}$ -sized pores as the most competent electrocatalyst for hydrogen evolution.

Figure 9.6 Contact angle measurements for electrodeposited porous MoSe_x surfaces of varying pore sizes: a) $0.1 \text{ }\mu\text{m}$, b) $0.3 \text{ }\mu\text{m}$, c) $0.6 \text{ }\mu\text{m}$ and d) $1.0 \text{ }\mu\text{m}$.

Using static contact angle measurements, the surface wettability of all electrosynthesized porous MoSe_x films is also surveyed for its role in influencing their electrocatalytic behaviour for HER. Figure 9.6 captures the behaviour of a sessile water

droplet across porous MoSe_x surfaces ranging from pore sizes of 0.1 to 1.0 μm . For surfaces with 0.1 μm -pore sizes, the contact angle is 87° and is also the smallest contact angle recorded. Larger pore-sizes of 0.3, 0.6 and 1.0 μm display higher contact angles of 99°, 113° and 129° respectively. It is unveiled that higher contact angles are measured for porous MoSe_x films containing larger pore sizes. In turn, porous MoSe_x surface with 0.1 μm -sized pores is considered the least hydrophobic whereas the surface with 1.0 μm -sized pores is most hydrophobic amongst all. More notably, the HER performance of porous MoSe_x of pore size 0.6 and 1.0 μm , of which their measured contact angles are relatively larger, pales in comparison to that for MoSe_x surfaces having pore sizes of 0.1 or 0.3 μm that display smaller contact angles. Correlating the surface wettability of surfaces to their electrocatalytic performance for hydrogen evolution reaction (HER), we deduce that surfaces demonstrating larger contact angles hinder the HER efficiency due to higher hydrophobic effects. Such observation abides to separate reports on Pt-TiO₂ nanotubes and MoS₂ nanoflowers that recently explored the relationship between HER efficiency and wettability.^{39, 40} It is also crucial to highlight that the adhesion force of a surface to a gas bubble, which is associated with its surface wettability,⁴¹ may partially affect the catalytic behaviour of the surface for HER. On a hydrophilic surface, the produced hydrogen gas bubbles in HER process adhere weakly to the surface. The low adhesion force of a hydrophilic surface accelerates the detachment of the hydrogen gas bubbles from the surface during HER. Therefore, the exposure of active sites to the electrolyte is maintained and the catalytic activity increases. Conversely, a hydrophobic surface experiences a high adhesion force that traps gas bubbles on the surface, posing as a detriment to its HER catalytic activity. On a broader context, the wettability properties of porous MoSe_x films

may also be tailored using pore size as a point of control to acquire desired properties for HER.

9.3 Conclusion

We have demonstrated the effective electrosynthesis of MoSe_x films from an aqueous electrolyte containing H₂MoO₄ and SeO₂ precursors *via* a potentiostatic procedure that taps on the simultaneous electro-reduction of the metal and chalcogen species. Characterisation of the electrosynthesized MoSe_x films, where ascertained to be 2 ≤ x ≤ 3, was performed by XPS, SEM and EDS for compositional and morphological information. Combining this electrodeposition technique in tandem with polystyrene beads as the hard template, porous MoSe_x films with four different pore sizes (0.1, 0.3, 0.6 and 1.0 μm) were successfully fabricated. All porous MoSe_x films display catalytic activity that largely auger well for hydrogen evolution. Of which, the 0.1 μm-sized porous MoSe_x films emerge as the strongest contender, attaining the lowest HER overpotential of 0.57 V at a current density of -30 mA cm⁻² where hydrogen production is at an increased level. Besides the low overpotential, the Tafel slope was found to be the lowest at 118 mV dec⁻¹ that correlates to Volmer-adsorption as the rate-determining step in the HER mechanism. The adsorption step was also concluded to limit the HER for 0.3, 0.6 and 1.0 μm-sized porous MoSe_x films wherein their Tafel slopes approximate 120 mV dec⁻¹. Despite the negligible effect of pore size on the rate-determining step in HER, we establish a correlation between the pore size of porous MoSe_x films and HER overpotential that ultimately determines the catalytic ability of the material. As the trend pans out, fine porous MoSe_x structures with pore sizes of 0.1 and 0.3 μm outperform those with larger pore sizes of 0.6 and 1.0 μm for hydrogen evolution in terms of HER overpotential. This observed HER behaviour may be attributed

to the surface wettability properties, which are tuneable, across a spectrum of pore sizes for porous MoSe_x films. Electrodeposition of TMDs provides a versatile yet green synthesis to create TMDs of varied morphology with active electrocatalytic properties. In the long run, this paves the way forward for sustainable research into clean energy production.

9.4 Experimental Methods

9.4.1 Materials

Molybdic acid, selenium dioxide, ammonium hydroxide, potassium chloride, sulfuric acid, ammonium chloride, polystyrene beads (sulfate-modified, 0.1 μm, aqueous suspension, 10% solids), polystyrene beads (sulfate-modified, 0.3 μm, aqueous suspension 10% solid), polystyrene beads (sulfate-modified, 0.6 μm, aqueous suspension 10% solid), polystyrene beads (sulfate-modified, 1.0 μm, aqueous suspension 10% solid) and indium tin oxide (ITO)-coated glass slides were purchased from Sigma–Aldrich. Toluene was purchased from J.T. Baker Chemicals. Pt, Ag/AgCl, glassy carbon (GC) and screen-printed carbon (SPCE) electrodes were purchased from CH Instruments, USA.

9.4.2 Apparatus

All voltammetric experiments were performed on an electrochemical analyzer (μAutolab III; Eco Chemie, The Netherlands) connected to a personal computer and controlled by NOVA software Version 1.8. Voltammetric measurements and electrochemical deposition were performed using a three-electrode configuration: the GC as the working electrode, the Pt and Ag/AgCl as the counter electrode and reference electrode, respectively.

Scanning electron microscopic (SEM) images were obtained by using a SEM system (model 7600F, JEOL, Tokyo, Japan) at an accelerating voltage of 5 kV. Energy dispersive X-ray spectroscopic (EDS) analysis was performed on an EDS analyser (Oxford Instruments) at

15 kV.

X-ray photoelectron spectroscopy (XPS) was performed on a Phoibos 100 spectrometer (SPECS, Germany) using a monochromatic Mg X-ray radiation source). During the deconvolution of high resolution spectra of Mo 3d and Se 3d regions, relative sensitivity factors were taken into account to attain best fit curves, using specific area ratios of 3d_{5/2} and 3d_{3/2} as 3:2.

Contact angle measurements were conducted on a Theta Lite tensiometer (Attension) equipped with a Firewire digital camera. Static contact angles were measured using a 2 µL ultrapure water droplet. The measurement was performed at least three times on different areas of each substrate.

9.4.3 Procedures

Electrodeposition of MoSe_x films were performed in an electrolytic bath of 50 mM H₂MoO₄ and 20 mM SeO₂ dissolved in 0.2 M aqueous NH₄OH. Prior to any electrodeposition, the GC electrode was polished to a mirror finish on a polishing pad using 5.0 µm alumina particles followed by 0.05 µm alumina particles and rinsed with ultrapure water. Chronoamperometry was performed at various potentials for 10 min under stirring at 500 rpm to attain a thin film of electrodeposited material. These potentials range from -1.2 V to -0.6 V to determine an optimum potential. After electrodeposition, the electrode was rinsed with ultrapure water and dried at room temperature before electrochemical measurements. For SEM, EDS and XPS characterization of the films, the same electrodeposition procedure was adopted but the GC electrode was replaced with a SPCE. Porous MoSe_x films were electrodeposited on ITO-coated slides under the optimized electrochemical deposition procedure. Commercially obtained ITO-coated slides were

sliced into dimensions of 2 cm in length and 0.5 cm in width. The ITO surface exposed in the electrolytic bath was defined using an insulating parafilm layer to reveal an active area of 0.5 cm × 0.5 cm. Before the formation of porous nanostructures, a preliminary layer of MoSe_x film was electrodeposited for a period of 5 min at -0.9 V in the electrolytic bath consisting of 50 mM H₂MoO₄ and 20 mM SeO₂ dissolved in 0.2 M aqueous NH₄OH. This preliminary electrodeposited MoSe_x film on the ITO-coated slide was then rinsed with water and dried under the lamp. A 4 μL aliquot of a 0.5% aqueous dispersion of 0.1 μm polystyrene beads was then cast on the surface of the preliminary electrodeposited MoSe_x film with uniform coverage and then left to dry for 30 min to obtain a film of polystyrene beads on the surface. The ITO-coated slide was then immersed into the electrolytic bath for electrodeposition for 5 to 20 min of film growth. The polystyrene bead template was removed by submerging the active electrode area of the ITO slide into toluene for 12 h in order to dissolve the polystyrene beads and deliver a surface containing porous MoSe_x films. The procedure was repeated for polystyrene beads of sizes: 0.3, 0.6 or 1.0 μm; to achieve a range of pore structures. In the electrochemical measurements of the porous MoSe_x films, this procedure was performed on a GC electrode instead of the ITO slide. Linear sweep voltammetry was performed at 5 mV s⁻¹ in the presence of H₂SO₄ electrolyte (0.5 M). The polarisation curves are plotted with respect to the reversible hydrogen electrode (RHE) after the calibration of measured Ag/AgCl potentials.

9.5 Supporting Information

Figure 9.S1 Cyclic voltammograms of a) 50 mM H_2MoO_4 and b) 20 mM SeO_2 . Conditions: background electrolyte, 0.2 M aqueous NH_4OH ; scan rate, 100 mV s^{-1} ; all scans begin from 0 V vs. Ag/AgCl towards the negative potentials.

Figure 9.S2 High resolution X-ray photoelectron spectra of a) Mo 3d and b) Se 3d regions of electrodeposited MoSe_x films at -0.6 V and of a) Mo 3d and b) Se 3d regions of electrodeposited MoSe_x films at -1.2 V.

Table 9.S1 Elemental compositions of electrodeposited MoSe_x on screen-printed carbon electrode (SPCE) at various potentials and its chalcogen-to-metal ratio based on energy-dispersive X-ray spectroscopy.

Material	C at. %	O at. %	Cl at. %	Se at. %	Mo at. %	Chalcogen-to-Metal Ratio
Blank SPCE	95.75	2.25	2.00	-	-	-
MoSe _x (-0.8 V)	95.06	3.75	1.10	0.02	0.09	0.2
MoSe _x (-0.9 V)	74.26	13.64	2.41	7.09	2.62	2.7
MoSe _x (-1.0 V)	55.55	23.57	1.62	12.87	6.39	2.0

Figure 9.S3 Scanning electron micrographs of a) bare SPCE, electrodeposited MoSe_x films on SPCE at b) -0.8 V, c) -0.9 V and d) -1.0 V.

Figure 9.S4 a) Polarisation curves for hydrogen evolution reaction (HER) of electrodeposited MoSe_x films across 5 to 20 min of deposition time and b) their corresponding Tafel plots. Histograms of c) HER overpotentials at current density of -30 mA cm⁻² and d) average Tafel slopes for the electrodeposited MoSe_x films at varied duration of deposition. Error bars are also included. Conditions: electrolyte, H₂SO₄ (0.5 M); scan rate, 5 mV s⁻¹.

Figure 9.S5 Scanning electron micrographs of a) 0.1 μm, b) 0.3 μm, c) 0.6 μm and d) 1.0 μm sized polystyrene beads cast on the ITO-coated slides prior to film growth.

Figure 9.S6 Scanning electron micrographs of MoSe_x films obtained after 0.1 μm polystyrene beads were dissolved in toluene. MoSe_x film was electrodeposited onto an ITO-coated slide after a) 5 min, b) 10 min, c) 20 min and d) 30 min.

Figure 9.S7 Scanning electron micrographs of MoSe_x films obtained after 0.3 μm polystyrene beads were dissolved in toluene. MoSe_x film was electrodeposited onto an ITO-coated slide after a) 5 min, b) 10 min, c) 20 min and d) 30 min.

Figure 9.S8 Scanning electron micrographs of MoSe_x obtained after 1.0 μm polystyrene beads were dissolved in toluene. MoSe_x film was electrodeposited onto an ITO-coated

slide after a) 5 min, b) 10 min, c) 20 min and d) 30 min.

Figure 9.S9 a) Linear sweep voltammograms of monolayer and multilayer porous MoSe_x containing 0.6 μm-sized pores. b) Scanning electron micrograph of monolayer porous MoSe_x films with 0.6 μm-sized pores.

Figure 9.S10 Static contact angle measurement for a non-porous electrodeposited MoSe_x film (~ 69°) using a sessile water droplet.

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Chapter 10

Pt-MoS_x Hybrid Electrocatalysts

10.1 *Introduction*

10.2 *Results and Discussion*

10.2.1 *Electrosynthesis of Pt-MoS_x Composites*

10.2.2 *Characterisation of Pt-MoS_x Composites*

10.2.3 *Electrocatalysis at Pt-MoS_x Surfaces*

10.3 *Conclusion*

10.4 *Experimental Section*

10.5 *Supporting Information*

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The thesis author was the primary investigator and first author of the above paper.

10.1 Introduction

As the world's energy sector lights the path to a clean and sustainable future, hydrogen has emerged as a strong contender for a renewable energy source.^{1, 2} Hydrogen is produced by the electrochemical splitting of water, which is an environmentally-benign process, and leaves zero carbon footprint when consumed. There is a requisite for the electrochemical hydrogen evolution reaction (HER): to overcome the high thermodynamic barrier using a suitable catalyst. Platinum (Pt) is amongst the first catalysts to make a foray into the hydrogen economy and continues to take the honour of the most efficient electrocatalyst to date. However, the low natural abundance of Pt renders exorbitant prices and impedes the widespread use. As an alternative to Pt, molybdenum disulfide (MoS₂), an archetypal transition metal dichalcogenide (TMD), which is earth-abundant and inexpensive, has been fervently pursued as a prospective electrocatalyst.³⁻⁹

Spearheaded by the promising catalytic properties of earth-abundant MoS₂ towards hydrogen evolution reaction (HER), current research is teeming with strategies that aim towards enhancing MoS₂ as an electrocatalyst. Common approaches include exposing the edge sites of MoS₂,^{7, 10} also known as the catalytic sites, and to incorporate dopant atoms or alloying; usually with transition metals such as Ni, Co or Fe, that can alter the intrinsic activity of MoS₂.^{6, 11-13} Using the latter approach, minimal amounts of noble metals like rhodium (Rh) or Pt have been combined with MoS₂ while retaining the activity for HER catalysis.^{14, 15} As postulated in a few of the works, the Pt-like activity of these composites is fundamentally shaped by the Sabatier's principle¹⁶ whereby the most efficient HER catalyst assumes a Gibbs free energy for adsorbed H (ΔG_H) that is thermoneutral (0 eV). In other words, the adsorption energy is neither too endothermic ($\Delta G_H > 0$ eV) nor too exothermic ($\Delta G_H < 0$ eV). When the adsorption energy is too endothermic, the proton

adsorption step will be slow whereas at too exothermic energies, the hydrogen desorption step will be hindered. Under both circumstances, the HER process will be hampered. Taking into account the Sabatier's principle, Cheng *et al.* designed a Rh-MoS₂ composite, such that two types of surfaces are created – one for adsorption and the other for desorption.¹⁷ This Rh-MoS₂ composite was endowed with a catalytic activity exceeding that of Pt and Tafel slopes lower than Pt. Beyond MoS₂ composites, noble metal/silicon nanowires hybrid by Zhu *et al.* also employed this rationale in the catalyst design.¹⁸ Hence, in a bid to fabricate composite MoS_x materials, Pt is a natural choice of element for integrating into our MoS_x system founded on the superior electrocatalytic ability of Pt towards HER and the supplementary surface of favourable ΔG_H that Pt provides.

Composite TMD materials are conventionally prepared by synthetic methods.^{19, 20} A typical example of a simple, top-down approach from the TMD is *via* in situ reduction of the noble metal nanocrystals on the TMD using a reducing agent.¹⁵ Various bottom-up procedures from precursors include hot-injection,²¹ hydrothermal synthesis,²²⁻²⁴ chemical vapour deposition²⁵⁻²⁷ and thermal annealing.^{28, 29} Majority of the bottom-up methods are advantageous for high quality composite materials but involve harsh conditions such as high temperature or pressure and multiple steps spanning over a long duration. For a case-in-point, Chen and co-workers had utilised bottom-up procedures to fabricate Pt nanoparticles on MoS_x on conducting substrates like graphene and Si nanowires that require numerous steps and reflux conditions for hours.^{30, 31} Unlike most of these traditional methods, electrodeposition is a one-pot bottom-up synthesis technique that occurs at ambient conditions.^{4, 11, 32-35} Moreover, electrodeposition embraces the versatile choice of substrate, readily available reagents, fast reaction process and the convenient

set-up.³⁶ Despite the numerous advantages of electrodeposition, this technique is rarely exploited to create TMD hybrid materials. One of the few electrodeposited TMD composites is the ternary cobalt- or nickel- WS_x that displayed robust and efficient HER electrocatalysis.³⁷ Therefore, we extend the electrodeposition technique to fabricate a noble metal-TMD composite that is a functional catalyst for hydrogen evolution.

Herein, we report the single-step electrosynthesis of Pt-MoS_x hybrids at a reductive potential. We investigate the electrocatalytic properties of the electrosynthesized Pt-MoS_x hybrids of various elemental compositions and in turn, explore the possibility of tailoring the catalytic activity by varying Pt precursor concentration.

10.2 Results and Discussion

10.2.1 Electrosynthesis of Pt-MoS_x composites

Chronoamperometry is employed in this work to fabricate Pt-MoS_x hybrid materials of varied elemental compositions by electrosynthesis. When designing parameters for electrosynthesis of Pt-MoS_x composites using chronoamperometry, the underlying idea is to identify an electrochemical potential that enables the co-electrodeposition of Pt and MoS₂ from the electrolyte. To begin, cyclic voltammetry was first performed to understand the inherent electroactivities of the precursors – tetrathiomolybdate as the source of MoS₂ and a platinum plating solution as the Pt source. Figure 10.S1a and Figure 10.S1b show the cyclic voltammograms of the ammonium tetrathiomolybdate and the platinum plating solution respectively, in 0.2 M KCl background electrolyte. These cyclic voltammetric scans start at 0 V and proceed towards increasingly cathodic potentials. Since early reports have demonstrated the electrosynthesis of MoS₂ from its [MoS₄]²⁻ precursor *via* a reduction process,³⁸⁻⁴⁰ it is of definite interest to us to determine a suitable reductive potential to

achieve the co-electrodeposition of Mo, S and Pt. The tetrathiomolybdate precursor exhibits a prominent reductive signal at -1.2 V that is responsible for the cathodic electrodeposition of MoS₂. The cathodic electrodeposition of MoS₂ from [MoS₄]²⁻ occurs such that the +6 oxidation state of molybdenum in [MoS₄]²⁻ is reduced to the +4 valency in MoS₂, concisely written as: [MoS₄]²⁻ + 2e⁻ + 4H⁺ → MoS₂ + 2H₂S.³⁸⁻⁴⁰ Unlike the cyclic voltammogram of the tetrathiomolybdate precursor with a single distinct cathodic signal, the Pt precursor presents an electrochemical drama with several inherent redox signals. Despite the numerous peaks, majority occur in the oxidative region, which are ruled out as potentials for cathodic reduction, whereas a sharp cathodic signal at -0.4 V, albeit dwarfed by the onset of hydrogen evolution reaction (HER), is crucial to the electrodeposition of Pt. Based on the identified cathodic signals, -1.2 V and -0.4 V, of the precursors, an electrochemical reduction at -1.3 V was performed over 10 min on polished glassy carbon (GC) electrode in an electrolyte bath comprising 10 mM [MoS₄]²⁻ and varied concentrations of Pt precursors between 2.6 and 6.4 mM to form co-electrodeposited Pt-MoS_x hybrid materials. At higher negative potentials beyond -1.3 V, proton reduction dominates over the intended cathodic co-electrodeposition of Pt and MoS₂. Due to the proton reduction process, the increased level of H₂ production at the working electrode renders the electrode surface less favourable for deposition and in turn deters the formation of co-electrodeposited Pt-MoS_x hybrid materials. Applying a constant potential of -1.3 V, the electrodeposition process is manifested as the increasing deposition current density with respect to time and eventually reaches a plateau upon completion. For illustration, the chronoamperometric profile of the electrodeposited MoS₂ is plotted in Figure 10.S2.

10.2.2 Characterisation of Pt-MoS_x composites

The electrodeposited Pt-MoS_x composites are subject to an array of characterisation techniques to examine their morphology and composition. For comparison, MoS₂ and Pt obtained by electrodeposition are also analysed. These include scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS). Electrodeposition was performed on screen-printed electrodes (SPCEs) for the above analysis while retaining the same electrochemical parameters.

Figure 10.1 Scanning electron micrographs of electrodeposited a) MoS₂, b) Pt, c) Pt(6.4)-MoS_x, d) Pt(4.3)-MoS_x, e) Pt(3.2)-MoS_x and f) Pt(2.6)-MoS_x. Concentration (in mM) of Pt precursor used is denoted in brackets. Scale bars denote 1 μm.

Surface morphologies of the electrodeposited materials are captured in Figure 10.1 with magnified micrographs provided in Figure 10.S3. All materials obtained by electrosynthesis manifest as nanoparticles that are largely spherical. Electrodeposited MoS₂ appears in sizes of approximately 30-40 nm. Electrodeposited Pt exists in petal-like structures, constituting clusters of nanoparticles. At higher concentrations of Pt precursor, Pt-MoS_x composites such as Pt(6.4)-MoS_x and Pt(4.3)-MoS_x occur as massive nanoparticles of 1 μm in diameter due to particle agglomeration. Conversely, lower amounts of Pt precursors led to electrodeposition of smaller nanoparticles. Figure 10.S5 depicts the EDS elemental maps of all electrodeposited materials and confirms the presence of Mo, S and Pt in all Pt-MoS_x composites. For all Pt-MoS_x composites, we observe homogenous distribution of Mo and S, therefore strongly pointing to MoS_x formation.

The surface elemental compositions of the electrodeposited materials are elucidated by XPS. XPS signals of Mo, S and Pt in Pt-MoS_x composites are visible in the survey XPS scans (Figure 10.S6), therefore further affirming the effective co-electrodeposition of Pt and MoS_x. According to the XPS survey scans, the stoichiometric surface composition of the Pt-MoS_x hybrids using different concentrations of Pt precursor are recorded in Table 10.S3 and 10.S4. The surface stoichiometric composition for the electrodeposited film from [MoS₄]²⁻ electrolyte yields MoS_{1.9}, verging on the expected composition of MoS₂. With 6.4 mM of Pt precursor in the [MoS₄]²⁻ electrolyte, a Pt_{1.8}MoS₂ composite was obtained with a significant portion of Pt constituting the hybrid. Paring down the Pt precursor concentration to 4.3 mM created a Pt_{0.1}MoS_{2.5} hybrid enriched with surface chalcogen. Using Pt precursors at concentrations as low as 3.2 and 2.6 mM yielded the respective Pt_{0.2}MoS_{0.6} and Pt_{0.3}MoS_{0.8} hybrids of dominant Mo constitution. The

stoichiometric bulk composition of the various composites is also determined by EDS and presented in Table 10.S1 and 10.S2. The dissonant stoichiometric compositions between EDS and XPS analyses is attributed to variances in the surface and bulk compositions of the Pt-MoS_x hybrids. As our study pertains to properties stemming from electrochemistry and electrocatalysis, both of which are surface-dependent processes, it is most apposite that the Pt-MoS_x hybrids will be referred to their surface stoichiometric composition derived from XPS.

High resolution core level spectra of Mo 3d, Pt 4f and S 2p regions for all electrodeposited Pt-MoS_x composites, along with MoS₂ and Pt, are separately shown in Figure 10.2, Figure 10.3 and Figure 10.S7.

Figure 10.2 High resolution X-ray photoelectron spectra of Mo 3d region for electrodeposited a) MoS₂ (0), b) Pt only (12.8) , c) Pt_{1.8}MoS₂ (6.4), d) Pt_{0.1}MoS_{2.5} (4.3), e) Pt_{0.2}MoS_{0.6} (3.2) and f) Pt_{0.3}MoS_{0.8} (2.6) where the concentration (in mM) of Pt precursor used is denoted in brackets.

Cathodic electrodeposition of MoS₂ film is reflected in the dominance of Mo⁴⁺ and S²⁻ in XPS profiles of Mo 3d and S 2p region of MoS₂ (Figure 10.2a and 10.S7a). In particular, the deconvoluted Mo 3d region depicts a 3d_{5/2} signal of electrodeposited MoS₂ film at a binding energy of 228.9 eV confirming the presence of Mo(IV) state that has originated from the reduction of [MoS₄]²⁻ precursor to MoS₂.^{34 32, 41} Another pair of prominent Mo 3d

signals centred at 3d_{5/2} and 3d_{3/2} binding energies of 232.5 eV and 235.7 eV correspond to the hexavalent Mo(VI) state. The existence of Mo⁶⁺ states suggests possible surface passivation of MoS₂ with MoO₃. The conspicuous oxygen peak in the survey XPS scan (Figure 10.S6) lends credence to the occurrence of Mo oxides. Deconvolution of the S 2p region of MoS₂ (Figure 10.S7a) resulted in S²⁻ and S₂²⁻ chemical states at 161.8 eV and 163.0 eV, and 163.2 eV and 164.4 eV corresponding to 2p_{3/2} and 2p_{1/2} binding energies.^{32, 34, 41} Of which, the bulk of the S 2p signal in MoS₂ is contributed by the S²⁻ species, akin to that of natural occurring MoS₂ and majority of the commercial MoS₂ particles.⁴² A small extent of the S 2p signal is derived from bridging S₂²⁻ ligands that stems from amorphous MoS_x structures such as MoS₃ as reported in a spate of MoS₂ electrodeposition studies.^{4, 11, 34, 43}

The concentration of Pt precursor dictates the proportion of Mo(IV) and Mo(VI) states in the electrodeposited composites as witnessed in the varying Mo 3d peak profiles of Pt_{1.8}MoS₂, Pt_{0.1}MoS_{2.5}, Pt_{0.2}MoS_{0.6} and Pt_{0.3}MoS_{0.8}. The shape profile of Mo 3d and S 2p regions of both Pt_{1.8}MoS₂ and Pt_{0.1}MoS_{2.5} composites electrodeposited from respective Pt precursor concentrations of 6.4 mM and 4.3 mM resembles each other (Figure 10.2c, 10.2d, 10.S7c and 10.S7d); a distinct Mo 3d doublet signal at 3d_{5/2} and 3d_{3/2} binding energies of 232.4 eV and 235.4 eV accompanied by a shoulder peak attributed to S 2s signal at 227.0 eV. This distinct Mo 3d doublet is ascribed to Mo⁶⁺ species that is also the primary Mo state in Pt_{1.8}MoS₂ and Pt_{0.1}MoS_{2.5} composites. The deconvoluted S 2p region of Pt_{1.8}MoS₂ and Pt_{0.1}MoS_{2.5} composites are also similar; both comprising a significant S²⁻ signal and a broad signal due to adsorbed SO₄²⁻. At relatively lower concentrations of Pt precursors of 3.2 mM and 2.6 mM, the Mo 3d spectra manifest as an unequivocal pair of

doublets indexed to Mo valences of four and six in Pt_{0.2}MoS_{0.6} and Pt_{0.3}MoS_{0.8} hybrids (Figure 10.2e and 10.2f). The S 2p spectra of Pt_{0.2}MoS_{0.6} and Pt_{0.3}MoS_{0.8} hybrids demonstrate a melange of SO₄²⁻, S²⁻ and S₂²⁻ moieties (Figure 10.S7e and 10.S7f). While the intensity of tetravalent Mo(VI) signals prevail over that of the hexavalent Mo(VI) signals in for Pt_{0.2}MoS_{0.6}, the contribution of Mo⁴⁺ is tantamount to that of Mo⁶⁺ in Pt_{0.3}MoS_{0.8}. The proportion of S²⁻ is considerably higher than that of the bridging S₂²⁻ ligands in both hybrids. Among the Pt-MoS_x hybrids, it is apparent that characteristic peaks of Mo⁴⁺ and S²⁻, which herald MoS₂ formation, are more accentuated when the concentration of Pt precursor used is lower. The Mo 3d and S 2p XPS spectra of all Pt-MoS_x hybrids point to the amorphous nature of MoS_x.

Figure 10.3 High resolution X-ray photoelectron spectra of Pt 4f region for electrodeposited a) MoS₂ (0), b) Pt only (12.8) , c) Pt_{1.8}MoS₂ (6.4), d) Pt_{0.1}MoS_{2.5} (4.3), e) Pt_{0.2}MoS_{0.6} (3.2) and f) Pt_{0.3}MoS_{0.8} (2.6) where the concentration (in mM) of Pt precursor used is denoted in brackets.

In the absence of [MoS₄]²⁻ precursor, electrochemically reducing the Pt precursor at -1.3 V yields a deposit that is mainly elemental Pt as indicated in the Pt 4f spectrum in Figure 10.3b. Core level Pt 4f region of the Pt precursor deposit depicts a pair of doublets at 4f_{7/2} and 4f_{5/2} binding energies of 70.1 eV and 73.5 eV assigned to zero-valent Pt.⁴⁴ We

observe other interesting features such as a tailing signal towards higher binding energy and a separate mild peak at higher binding energy. Deconvolution of these features engender Pt(II) and Pt(IV) states at 72.0 eV and 74.4 eV corresponding to 4f_{7/2} binding energies.⁴⁴⁻⁴⁶

Upon the formation of Pt-MoS_x hybrids, there is a unanimous shift in the principal Pt 4f doublets from elemental Pt deposit towards higher binding energies in Pt_{1.8}MoS₂, Pt_{0.1}MoS_{2.5}, Pt_{0.2}MoS_{0.6} and Pt_{0.3}MoS_{0.8} composites. Across all Pt-MoS_x composites (Figure 10.3c, 10.3d, 10.3e and 10.3f), the primary Pt 4f doublets occur at Pt 4f_{7/2} and Pt 4f_{5/2} binding energies of 72.5 eV and 75.8 eV corresponding to the Pt(II) state.^{45, 46} The dominant Pt(II) oxidation state in the Pt-based hybrids is a distinguishing feature that has also been documented in alloy formation such as with Fe, Ni or Co.^{44, 47, 48} Hence, the Pt-MoS_x composites are successfully obtained by electrochemical reduction. The provenance of the shifts in the Pt 4f signal lies in the interaction between Mo and Pt, similar to the charge transfer from transition metal atoms to the Pt atoms when the alloy forms.^{44, 47, 48} Apart from the predominant Pt(II) state of the Pt-MoS_x hybrids, a minor contribution due to Pt(IV) due to PtO₂ passivation on surfaces is detected. Trivial amounts of zero-valent Pt are also found in Pt_{0.2}MoS_{0.6} and Pt_{0.3}MoS_{0.8} composites, which are obtained in low concentrations of 3.2 mM and 2.6 mM of Pt precursors, as shown in the modest Pt 4f signal at 70.1 eV.

10.2.3 Electrocatalysis at Pt-MoS_x Composites

Linear sweep voltammograms due to hydrogen evolution in air-saturated H₂SO₄ of the electrodeposited MoS₂, Pt and Pt-MoS_x hybrid, which were obtained by electro-reduction at -1.3 V vs. Ag/AgCl, are illustrated in Figure 10.4.

Figure 10.4 a) Linear sweep voltammograms for hydrogen evolution reaction (HER) on electrodeposited MoS₂, Pt and their co-deposited Pt-MoS_x composites. b) Tafel plots for all electrodeposited materials. Histograms summarise the averages of c) HER overpotential at -10 mA cm⁻² and d) Tafel slopes. Conditions: background electrolyte, H₂SO₄ (0.5 M); scan rate, 2 mV s⁻¹; all measurements are performed relative to the Ag/AgCl reference electrode and corrected to reversible hydrogen electrode (RHE) potential.

Performance indicators employed to assess the HER performance of the electrodeposited Pt-MoS_x composites are the overpotential and the Tafel slope. The overpotential at a current density of -10 mA cm⁻² is a suitable benchmark because hydrogen production is tangible. Additionally, this is the current density estimated for a solar-to-hydrogen device with ~12% efficiency.⁵ The Tafel slope is understood as increase in overpotential required to generate a magnitude rise in the current density, therefore

shedding light on the electrochemical kinetics of the TMD material for HER. The Tafel slope also provides information on the HER mechanism pathway undertaken by the TMD material. HER occurs in two steps:⁴⁹ first, an electrochemical adsorption *via* the Volmer process ($b \approx 120 \text{ mV dec}^{-1}$); second, either an electrochemical desorption *via* the Heyrovsky process ($b \approx 40 \text{ mV dec}^{-1}$) or recombination step *via* the Tafel process ($b \approx 30 \text{ mV dec}^{-1}$). The rate-determining step for HER is then identified from the Tafel slope value (b).

Living up to expectations, all Pt-MoS_x hybrids exhibit improved HER performance compared to the electrodeposited MoS₂ in regard to lower HER overpotentials required to achieve a perceptible level of hydrogen production. At -10 mA cm^{-2} current density, electrodeposited MoS₂ has an overpotential of 0.22 V that fall within a range of reported values in literature for MoS₂ materials.^{4, 7, 10, 50} Anticipated to be the best electrocatalyst, electrodeposited Pt from a 12.8 mM Pt precursor bath shows the lowest HER overpotential of 0.08 V. Based on the HER overpotentials, the HER performance of the Pt-MoS_x hybrids are as follows: $\text{Pt}_{1.8}\text{MoS}_2 > \text{Pt}_{0.1}\text{MoS}_{2.5} > \text{Pt}_{0.2}\text{MoS}_{0.6} > \text{Pt}_{0.3}\text{MoS}_{0.8}$. The concentration of Pt precursor used in the electrosynthesis is a key factor influencing the HER performance of the Pt-MoS_x hybrids. Pt_{1.8}MoS₂ that was electrodeposited in the highest Pt precursor concentration of 6.4 mM demonstrates a HER catalytic performance that rivals that of electrodeposited Pt evident in the overlapping polarization curves. Requiring a HER overpotential of 0.1 V, chalcogen-enriched Pt_{0.1}MoS_{2.5} that is electrodeposited from a Pt precursor of 4.3 mM exhibits a vivid improvement in HER catalytic activity from Pt-free MoS₂ by more than 50 %. Molybdenum-dominant Pt_{0.2}MoS_{0.6} and Pt_{0.3}MoS_{0.8} electrodeposited from lower concentrations of Pt precursor of 3.2 mM and 2.6 mM show

HER overpotentials of 0.20 V and 0.16 V respectively. Relative to MoS₂, the catalytic behaviour of Pt_{0.2}MoS_{0.6} and Pt_{0.3}MoS_{0.8} are enhanced by nearly 10 % and 30 % respectively. Moreover, the electrodeposited Pt-MoS_x hybrids via this one-step, one-pot process at ambient conditions displayed HER performance surpassing that of Pt-MoS_x composites/graphene prepared by the hydrothermal method involving steps that were manifold.³⁰ Hence, electrochemical deposition is deemed to be both an effective and efficient method of TMD composite synthesis. The convenience of this technique does not compromise the electrocatalytic activity of the as-electrosynthesized Pt-MoS_x composite.

Tafel slope analysis also discloses a similar trend with the electrodeposited materials that have been observed with the HER overpotentials where all Pt-MoS_x composites outperform Pt-free MoS₂. The Tafel slopes of Pt_{1.8}MoS₂ and Pt_{0.1}MoS_{2.5} tied at 48 mV dec⁻¹ are significantly higher than Pt-free MoS₂ at 89 mV dec⁻¹. Similarly, Pt_{0.2}MoS_{0.6} and Pt_{0.3}MoS_{0.8} adopt equivalent Tafel slopes of 61 mV dec⁻¹ that are indicative of faster HER kinetics at the catalytic sites than MoS₂. The slow step of Pt-MoS_x hybrids is matched to the Heyrovsky process associated to the electrochemical desorption analogous to that of electrodeposited Pt which displays a Tafel slope of 46 mV dec⁻¹. In contrast, the HER mechanism occurring on MoS₂ is limited by the electrochemical adsorption step. Hence, the incorporating of Pt into MoS_x system elicits a paradigm change to the fundamental catalytic properties of the MoS₂ where the rate-limiting step in the HER pathway is transformed and HER kinetics is augmented. All Pt-MoS_x hybrids share identical rate-determining step with the electrodeposited Pt and diverge the Volmer process that limits HER in MoS₂. In particular, Pt_{1.8}MoS₂ and Pt_{0.1}MoS_{2.5} demonstrate Tafel slopes that are almost Pt-like, deviating by a marginal 2 mV dec⁻¹ from electrodeposited Pt.

A HER mechanism for the Pt-MoS_x composites can be premised on the Tafel slope analysis. The Pt-MoS_x hybrid possesses different sites of adsorption and desorption in the HER process. The Pt component, which has a strong H adsorption, is the active site of the Pt-MoS_x composites for the proton adsorption step. In the desorption process, the MoS_x constituent of the Pt-MoS_x hybrid functions as the main active site. Compared to Pt component, the MoS_x constituent has a relatively larger Gibbs free energy of adsorbed H that favors the desorption step.⁵¹ As inferred from several hybrid catalysts,^{17, 18} the HER mechanism of the electrodeposited Pt-MoS_x is also postulated to involve a hydrogen spill-over effect. A hydrogen spill-over effect is described as the migration of the adsorbed H to a different site of the hybrid. The proposed HER mechanism of the Pt-MoS_x hybrid follows the three steps: adsorption of H⁺ on Pt component of the Pt-MoS_x hybrid, migration of the adsorbed H on Pt component to the MoS_x component of the Pt-MoS_x hybrid (hydrogen spill-over effect), and desorption of H₂ from the MoS_x component of the Pt-MoS_x hybrid. Since the low values of the Tafel slope indicate that the Heyrovsky desorption process (H⁺ + M-H + e⁻ → H₂ + M) limits the HER on the Pt-MoS_x composites, the HER mechanism occurring on the hybrids may be represented as such:

- 1) Adsorption of H: Pt-MoS_x + H⁺ → H-Pt-MoS_x
- 2) Migration: H-Pt-MoS_x → Pt-MoS_x-H
- 3) Desorption of H₂ *via* Heyrovsky process: H⁺ + Pt-MoS_x-H + e⁻ → H₂ + Pt-MoS_x

It is also noteworthy to mention that while both Pt and MoS_x components of the hybrid adopt instrumental roles in the HER mechanism of the Pt-MoS_x hybrid, the Pt component takes a larger slice of the pie in facilitating that process. Given that the Tafel slopes of Pt-MoS_x point to desorption as the rate-determining process, wherein MoS_x constituent

provides the H₂ desorption site, it is within reason to infer that the Pt component demonstrates higher activity in driving the HER process by equipping Pt-MoS_x hybrids with a more efficient proton adsorption step.

The interfacial charge transfer properties of the Pt-MoS_x composites are examined by conducting electrochemical impedance spectroscopy (EIS) measurements in 0.5 M H₂SO₄ electrolyte to simulate HER conditions. The charge transfer resistance (R_{ct}) is defined by the diameter of the fitted semicircle obtained from the modified Randles circuit (Figure 10.58b). Figure 10.5 illustrates Nyquist plots of all Pt-MoS_x composites compared against that of MoS₂. All Pt-MoS_x composites exhibit smaller semicircle diameters than the electrodeposited MoS₂. The average R_{ct} for Pt_{1.8}MoS₂, Pt_{0.1}MoS_{2.5}, Pt_{0.2}MoS_{0.6} and Pt_{0.3}MoS_{0.8} are computed to be 57, 173, 379 and 425 Ω respectively whereas the MoS₂ is determined to be distinctly higher at 612 Ω . This observation corresponds to the trend such that Pt-MoS_x composites that were electrodeposited from higher concentrations of Pt precursor yielded decreasing charge transfer resistance for HER; which in turn coincides with the HER efficiency of Pt_{1.8}MoS₂ > Pt_{0.1}MoS_{2.5} > Pt_{0.2}MoS_{0.6} > Pt_{0.3}MoS_{0.8}. Moreover, Pt-MoS_x hybrids show significantly faster HER kinetics compared to MoS₂. Therefore, the higher conductivity of Pt-MoS_x hybrids relative to MoS₂ is also one of the factors that led to their enhanced HER efficiency.

Figure 10.5 a) Nyquist plots of electrodeposited MoS₂ and Pt-MoS_x composites. b) Histogram illustrating the impedimetric signal of MoS₂ and Pt-MoS_x composites represented as R_{ct} . Conditions: background electrolyte, H₂SO₄ (0.5 M).

Scrutinizing further at regions of low current density (Figure 10.S9), a HER pre-wave is observed for electrodeposited MoS₂ but absent for all Pt-MoS_x composites. The presence of a pre-wave has been linked to either the inherent electrochemistry manifested by the material or more notably, the active species responsible for the HER process. Merki *et al.* elucidated the origin of the pre-wave of MoS_x materials to result from the reduction of MoS₃ to MoS₂ wherein the XPS signals for S₂²⁻ were absent after the HER, thus, the active species was accredited to be MoS₂.³⁴ Due to the proximity of our HER pre-wave for electrodeposited MoS₂ to that reported by Merki *et al.*,³⁴ this feature likely corresponds to the reduction of S₂²⁻ to S²⁻ accelerating the onset of HER. The lack of pre-waves for all Pt-MoS_x materials simplifies the context. In the case of Pt-MoS_x hybrids, there are no inherent reduction processes that occur prior to or concurrently with HER to alter their composition. The as-electrosynthesized Pt-MoS_x hybrids present themselves as HER-active and do not convert into a more catalytic species during HER.

Another figure of merit when evaluating HER catalysts is stability. S-enriched and Mo-enriched Pt hybrids, respectively Pt_{0.1}MoS_{2.5} and Pt_{0.2}MoS_{0.6}, are selected to explore their susceptibility to acid corrosion. The HER polarization curves of Pt_{0.1}MoS_{2.5} and Pt_{0.2}MoS_{0.6} and their corresponding Tafel slopes before and after 1000 cyclic voltammetric scans (Figure 10.S10) are recorded in Figure 10.S11. On the basis of HER overpotential and Tafel slope parameters, the HER performance of both hybrids are enhanced. After 1000 cyclic voltammetric scans, Pt_{0.1}MoS_{2.5} has a marginal decline in overpotential by 0.01 V and an affiliated decrease in Tafel slope by 8 mV dec⁻¹. Likewise, Pt_{0.2}MoS_{0.6} shows a notably elevated catalytic activity with an overpotential that is 0.03 V lower and a Tafel slope that has decreased to 46 mV dec⁻¹. Upon potential cycling, the active sites of the hybrids may become chemically altered to result in higher catalytic activity. Generally, there is no deterioration in the catalytic performance of both hybrids after 1000 voltammetric scans, and thus, are considered to be stable electrocatalysts for HER. Moreover, minimal morphological changes were observed for both Pt_{0.1}MoS_{2.5} and Pt_{0.2}MoS_{0.6} hybrids after 1000 voltammetric scans as depicted in Figure 10.S12. The fabrication technique of Pt-MoS_x hybrids using electro-reduction proves to be operational for creating stable composites for electrochemical applications.

10.3 Conclusion

In summary, the electrochemical technique of fabricating Pt-MoS_x composites by electro-reduction from Pt precursor and ammonium tetrathiomolybdate at a fixed potential of -1.3 V vs. Ag/AgCl is a scalable and tailorable way to create Pt-MoS_x composites. Different concentrations of Pt precursors used in the electrolytic bath generate distinct elemental composition, namely Pt_{1.8}MoS₂, Pt_{0.1}MoS_{2.5}, Pt_{0.2}MoS_{0.6} and Pt_{0.3}MoS_{0.8}.

Regardless of the hybrid composition, the HER catalytic behaviour of the Pt-MoS_x composites surpasses MoS₂ in terms of overpotential and Tafel slope. The rate-determining step in the HER mechanism of all hybrids is largely ascertained to be the Heyrovsky desorption, which is equivalent to that of electrodeposited Pt, whereas the Volmer adsorption limits HER on electrodeposited MoS₂. Hence, trace amounts of Pt in millimolar concentrations is adequate to tweak the catalytic properties of MoS₂ system to achieve a HER performance that rivals Pt. The tunable nature of electrosynthesis from multiple precursors embraces the versatile and economical fabrication of hybrid materials as competent and robust electrocatalysts for hydrogen evolution.

10.4 Experimental Methods

10.4.1 Materials

Ammonium tetrathiomolybdate, sulfuric acid and potassium chloride were purchased from Sigma-Aldrich, Singapore. Platinum TP concentrate (50 g L⁻¹) was purchased from Technic Inc., Singapore. Glassy carbon (GC) electrode with diameter of 3mm, Pt counter electrode and Ag/AgCl reference electrode were obtained from CH Instruments, Texas, USA.

10.4.2 Apparatus

All voltammetric experiments were performed on Autolab PGSTAT101 electrochemical analyzer (Methrom Autolab B.V., The Netherlands) connected to a personal computer and controlled by NOVA software Version 1.8 (Methrom Autolab B.V.). Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) were obtained by using a Model 7600F field-emission SEM (JEOL, Tokyo, Japan) operating at an accelerating voltage of 5 kV and 15 kV respectively. X-ray photoelectron spectroscopy (XPS) was

performed with a Phoibos 100 spectrometer and a monochromatic Mg X-ray radiation source (SPECS, Germany). Calibration was performed using the adventitious C 1s peak referenced at 284.5 eV.

Electrochemical measurements were carried out with cyclic voltammetry (CV), linear sweep voltammetry (LSV) and chronoamperometry (CA) in a 6 mL electrochemical cell at room temperature (25 °C). A three-electrode configuration was adopted with GC, Pt and Ag/AgCl electrodes as working, counter and reference electrodes respectively.

10.4.3 Procedures

An electrodeposition bath consisting of 10 mM (NH₄)₂MoS₄ was prepared in 0.2 M KCl solution. 10 mM (NH₄)₂MoS₄ was dissolved in 0.2 M KCl of supporting electrolyte. In the electrodeposition of MoS₂, no platinum TP concentrate was added to the bath. To attain a range of Pt-MoS_x composites, various the Pt precursor concentrations (in mM) prepared in the electrodeposition bath are 6.4, 4.3, 3.2 and 2.6. For electrodeposition of Pt only, the electrodeposition bath only contains 12.8 mM of Pt precursor in 0.2 M KCl solution in the absence of (NH₄)₂MoS₄. Prior to any electrodeposition, the GC electrode was polished to a mirror finish on a polishing pad using 5.0 µm alumina particles followed by 0.05 µm alumina particles and rinsed with ultrapure water. Chronoamperometry was performed at -1.3 V for 10 min under stirring at 500 rpm to attain a thin film of electrodeposited material. After electrodeposition, the electrode was gently rinsed with ultrapure water and left to dry at room temperature before electrochemical measurements. For SEM, EDS and SEM characterization of the films, the same electrodeposition procedure was adopted but the GC electrode was replaced with a screen printed carbon electrode (SPCE).

Hydrogen evolution reaction (HER) measurements were performed *via* LSV at a scan rate

of 2 mV s⁻¹ in 0.5 M sulfuric acid was utilized as a background electrolyte. For HER stability test in acidic medium, HER measurements were performed before and after 1000 CV cycles at a scan rate of 100 mV s⁻¹ between -0.3 V and -0.2 V. The CV scan range is characterized by the HER onset region of the Pt-MoS_x composites, which is defined as the region where the current density is at least 0.1 mA cm⁻².⁵²

Electrochemical impedance spectroscopy (EIS) experiments were conducted within a frequency range of 0.1 MHz to 0.1 Hz at a sinusoidal voltage perturbation of 10 mV amplitude. The measurements were performed in H₂SO₄ (0.5 M) electrolyte at superimposed DC potential of -0.16 V (vs. Ag/AgCl) for EIS under HER conditions.

Triplicate measurements were performed for each Pt-MoS_x composite in all electrochemical studies and the potentials measured are relative to Ag/AgCl unless stated otherwise.

10.5 Supporting Information

Figure 10.S1 Cyclic voltammograms of a) 10 mM (NH₄)₂MoS₄ and b) 13 mM platinum concentrate. Conditions: background electrolyte, 0.2 M KCl; scan rate, 100 mV s⁻¹; all scans begin from 0 V vs. Ag/AgCl towards the negative potentials.

Figure 10.S2 Chronoamperogram of electrodeposited MoS₂ from 10 mM (NH₄)₂MoS₄ in 0.2 M KCl. Conditions: applied potential, -1.3 V; duration, 10 min.

Figure 10.S3 Scanning electron micrographs of electrodeposited a) MoS₂, b) Pt, c) Pt(6.4)-MoS_x, d) Pt(4.3)-MoS_x, e) Pt(3.2)-MoS_x and f) Pt(2.6)-MoS_x. Concentration (in mM) of Pt precursor used is denoted in brackets. Scale bars denote 1 μ m.

Figure 10.S4 Scanning electron micrograph of bare screen-printed electrode. Scale bar represents 1 μm .

Table 10.S1 Table of elemental composition of Pt-MoS_x materials based on the energy dispersive X-ray spectroscopy. Concentration (in mM) of Pt precursor used is denoted in brackets.

Sample	Mo at. %	S at. %	Pt at. %	C at. %	O at. %	Cl at. %
MoS ₂	3.53	5.54	-	75.45	13.45	-
Pt only	-	-	37.94	55.44	6.62	-
Pt(6.4)-MoS _x	3.23	9.95	16.11	45.64	22.35	2.71
Pt(4.3)-MoS _x	1.34	1.41	1.44	81.93	12.11	1.76
Pt(3.2)-MoS _x	0.95	0.47	0.20	85.18	11.73	1.46
Pt(2.6)-MoS _x	0.13	0.1	0.04	93.49	4.36	1.89

Table 10.S2 Table of stoichiometric formula of Pt-MoS_x materials determined from energy dispersive X-ray spectroscopy (EDS). Concentration (in mM) of Pt precursor used is denoted in brackets.

Sample	Stoichiometric Formula of Composite
MoS ₂	MoS _{1.5}
Pt only	-
Pt(6.4)-MoS _x	Pt _{4.9} MoS _{3.1}
Pt(4.3)-MoS _x	Pt _{1.1} MoS _{1.1}
Pt(3.2)-MoS _x	Pt _{0.2} MoS _{0.5}
Pt(2.6)-MoS _x	Pt _{0.3} MoS _{0.8}

Figure 10.S5 Energy X-ray dispersive spectroscopy mapping of the electrodeposited materials and their respective elements of interest.

Table 10.S3 Table of surface elemental composition of Pt-MoS_x materials based on the survey scans of X-ray photoelectron spectroscopy (XPS). The C 1s signal was calibrated to 284.5 eV. Concentration (in mM) of Pt precursor used is denoted in brackets.

Sample	Mo 3d at. %	S 2p at. %	Pt 4f at. %	C 1s at. %	O 1s at. %
MoS ₂	11.99	22.90	-	44.02	21.09
Pt only	8.86	10.96	16.22	38.20	25.75
Pt(6.4)-MoS _x	9.38	18.62	16.47	36.12	19.41
Pt(4.3)-MoS _x	8.57	3.41	0.98	43.45	43.59
Pt(3.2)-MoS _x	9.98	5.73	2.11	42.14	40.04
Pt(2.6)-MoS _x	0.13	0.10	0.04	93.49	4.36

Table 10.S4 Table of stoichiometric formula of Pt-MoS_x materials determined from the survey scans of X-ray photoelectron spectroscopy (XPS). The C 1s signal was calibrated to 284.5 eV. Concentration (in mM) of Pt precursor used is denoted in brackets.

Sample	Stoichiometric Formula of Composite
MoS ₂	MoS _{1.9}
Pt only	-
Pt(6.4)-MoS _x	Pt _{1.8} MoS ₂
Pt(4.3)-MoS _x	Pt _{0.1} MoS _{2.5}
Pt(3.2)-MoS _x	Pt _{0.2} MoS _{0.6}
Pt(2.6)-MoS _x	Pt _{0.3} MoS _{0.8}

Figure 10.S6 Wide-scan X-ray photoelectron spectra of the following electrodeposited materials: a) MoS₂ (0), b) Pt only (12.8), c) Pt_{1.8}MoS₂ (6.4), d) Pt_{0.1}MoS_{2.5} (4.3), e) Pt_{0.2}MoS_{0.6} (3.2) and f) Pt_{0.3}MoS_{0.8} (2.6) where the concentration (in mM) of Pt precursor used is denoted in brackets.

Figure 10.S7 High resolution X-ray photoelectron spectra of S 2p region for electrodeposited a) MoS₂ (0), b) Pt only (12.8), c) Pt_{1.8}MoS₂ (6.4), d) Pt_{0.1}MoS_{2.5} (4.3), e) Pt_{0.2}MoS_{0.6} (3.2) and f) Pt_{0.3}MoS_{0.8} (2.6) where the concentration (in mM) of Pt precursor used is denoted in brackets.

Figure 10.S8 a) Magnified region of Nyquist plots of electrodeposited MoS₂ and Pt-MoS_x composites. b) Randles-modified circuit utilized to model electrochemical impedance spectra for hydrogen evolution reaction. R_b refers to the resistance of electrolyte solution, R_{ct} is charge transfer resistance and CPE denotes constant phase element. Conditions: background electrolyte, H₂SO₄ (0.5 M).

Figure 10.S9 Magnified linear sweep voltammograms for hydrogen evolution reaction (HER) on electrodeposited MoS₂, Pt and their co-deposited Pt-MoS_x composites. Conditions: background electrolyte, H₂SO₄ (0.5 M); scan rate, 2 mV s⁻¹; all measurements are performed relative to the Ag/AgCl reference electrode and corrected to reversible hydrogen electrode (RHE) potential.

Figure 10.S10 Cyclic voltammograms of electrodeposited a) Pt_{0.1}MoS_{2.5} and b) Pt_{0.2}MoS_{0.6} to examine catalytic stability in acid. Conditions: background electrolyte, H₂SO₄ (0.5 M); scan rate, 100 mV s⁻¹.

Figure 10.S11 HER polarisation curves before and after 1000 cyclic voltammetric scans for a) Pt_{0.1}MoS_{2.5} and c) Pt_{0.2}MoS_{0.6}. Tafel slopes before and after 1000 cyclic voltammetric scans corresponding to b) Pt_{0.1}MoS_{2.5} and d) Pt_{0.2}MoS_{0.6}. Conditions: background electrolyte, H₂SO₄ (0.5 M); scan rate, 2 mV s⁻¹; all measurements are performed relative to the Ag/AgCl reference electrode and corrected to reversible hydrogen electrode (RHE) potential.

Figure 10.S12 Scanning electron micrographs of Pt_{0.1}MoS_{2.5} a) before and b) after 1000 cyclic voltammetric scans, and for Pt_{0.2}MoS_{0.6} for c) before and d) after 1000 cyclic voltammetric scans.

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Chapter 11

Electrochemical Tuning of Group 6 Transition Metal Dichalcogenides for Electrocatalysis

11.1 *Introduction*

11.2 *Results and Discussion*

11.2.1 *Inherent Electrochemistry*

11.2.2 *Post-Electrochemical Treatment: Material and Electrochemical Characterisation*

11.2.3 *Post-Electrochemical Treatment: Electrocatalysis*

11.3 *Conclusion*

11.4 *Experimental Section*

11.5 *Supporting Information*

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The thesis author was the primary investigator and first author of the above paper.

11.1 Introduction

The advent of graphene research unearths a host of its remarkable properties; in optical, electronic and mechanical aspects,^{1, 2} and spurred on studies into other two-dimensional (2D) materials. Amidst the 2D materials, the realms of transition metal dichalcogenides (TMDs) have been pursued with great fervor. Akin to graphite, TMDs are layered structures. Each layer consists of a transition metal (e.g. Mo, W) atom sandwiched between two hexagonal lattices of chalcogen (e.g. S, Se) atoms. Within the layers, the atoms are held by strong covalent bonds whereas adjacent layers are weakly bonded by Van der Waals' forces.

In the past, bulk forms of TMDs have been extensively studied for their use as solid state lubricants.³ At present, TMDs in ultrathin layers is all the rage in the scientific community. Contemporary literature has elucidated promising layer-dependent properties of TMDs. One of these properties is the transition in semiconducting nature of TMDs from having an indirect to a direct band gap^{4, 5} when the bulk form is exfoliated into single layers as a result of quantum confinement effects.⁶ Bulk MoS₂, for example, possesses an indirect band gap of 1.2 eV⁷ but once exfoliated into MoS₂ nanosheets, it affords a direct band gap of 1.9 eV⁸ giving rise to novel photoluminescence⁹ and electronic properties.¹⁰ Another important feature is the massive surface area created when the bulk is thinned down into layers. Such large surface area in exfoliated TMD nanosheets carries high density of edges which are potential active sites for electrochemical applications in sensing and energy production, in particular for hydrogen evolution reaction (HER).^{11, 12}

The allure of hydrogen energy boils down to its high energy density¹³ and clean by-

product. Hence, hydrogen may be the panacea to the global concern of rising carbon emissions due to the burning of hydrocarbon to produce energy. Generating hydrogen on a large-scale in a sustainable manner requires a competent catalyst made from materials that are abundant. Platinum is widely established as the best HER catalyst in terms of HER efficiency,^{14, 15} however its major drawback is its low abundance. Existing in relatively high natural abundance compared to platinum, exfoliated TMD nanosheets have generated a great deal of attention as potential electrocatalysts for HER. The HER activity of TMD nanosheets stems from their edges and while their basal planes are deemed inert.¹⁶⁻¹⁸ Efforts are underway to develop TMDs with optimised HER abilities comparable to platinum such as by increasing the number of active sites,^{19, 20} improving electrical conductivity^{11, 21} and enhancing the catalytic capacity of the active sites.²²⁻²⁶

Our previous work reported on the electrochemical tuning of the charge transfer kinetics and HER catalytic properties of bulk and exfoliated MoS₂ nanosheets.²⁷ Electrochemically reduced MoS₂ materials achieved an enhancement in charge transfer kinetics and improved HER. Most intriguing is that the effects of electrochemical tuning were more prominent in exfoliated MoS₂ nanosheets than its bulk form. Inspired by these findings, we extend this present study beyond exfoliated MoS₂ nanosheets, into other layered TMD materials to investigate the impact of electrochemical anodisation or cathodisation on their properties. Herein, we present a fundamental study on the electrochemistry of exfoliated MoS₂, WS₂, MoSe₂ and WSe₂ nanosheets and examine the effect of an oxidative or reductive electrochemical treatment on their electrochemical and HER catalytic behaviour. Characterization of the TMD materials using X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy were also performed to compare the surface

and structural morphologies of the exfoliated TMDs before and after electrochemical treatment. It is also of interest to determine how the type of metal and chalcogen govern the electrochemical and catalytic performance.

11.2 Results and Discussion

We conducted a study on the electrochemical behaviour of exfoliated transition metal dichalcogenides (TMDs) comprising the exfoliated MoS₂, MoSe₂, WS₂ and WSe₂ nanosheets. Cyclic voltammetry measurements on the exfoliated TMD materials were performed over a potential window from -1.8 V to 1.8 V in phosphate buffer solution electrolyte at pH 7.0. These TMD materials were electrochemically oxidized or reduced in an attempt to alter the electrochemical and catalytic properties of materials; in terms of heterogeneous electron transfer (HET) rates, which is studied in the presence of outer sphere classical redox probes such as [Fe(CN)₆]^{4-/3-} and [Ru(NH₃)₆]^{2+/3+}; and as electrocatalysts for hydrogen evolution reaction (HER).

11.2.1 Inherent Electrochemistry

At present, fundamental knowledge on the inherent electrochemistry of exfoliated MoS₂, WS₂, MoSe₂ and WSe₂ nanosheets is inadequate. We first explore this by conducting cyclic voltammetry in two scan directions. The acquired voltammetric profiles of the scans towards positive and negative potentials reveal information about the electroactive surface moieties of the TMD materials. Three consecutive scans were recorded to determine the nature of electrochemical processes in the TMD nanosheets. Figure 11.1 illustrates the cyclic voltammograms of exfoliated MoS₂, WS₂, MoSe₂, and WSe₂ nanosheets at pH 7.0. We also performed cyclic voltammetry under similar conditions for MoO₂, MoO₃, WO₂ and WO₃ to identify the possible electrochemical processes occurring

in the exfoliated TMDs and the voltammograms of Mo and W oxides are captured in Figure 11.S1.

Figure 11.1 Cyclic voltammograms of a) exfoliated MoS₂ nanosheets during the scan to positive potentials and b) the scan to negative potentials, c) exfoliated WS₂ nanosheets

during the scan to positive potentials and d) the scan to negative potentials, e) exfoliated MoSe₂ nanosheets during the scan to positive potentials and f) the scan to negative potentials, g) exfoliated WSe₂ nanosheets during the scan to positive potentials and h) the scan to negative potentials. Conditions: background electrolyte, PBS (50 mM), pH 7.0; scan rate, 100 mV s⁻¹; all measurements are performed relative to the Ag/AgCl reference electrode. Arrow indicates initial scan direction.

The redox peaks are distinctive to various TMD materials. They arise from the type and number of electroactive groups present on the surface of the TMDs. The first scan of exfoliated MoS₂ nanosheets in the positive scan direction resulted in an oxidation peak at *ca.* 0.9 V while the first scan towards the negative potential showed a shoulder reduction peak at *ca.* -1.2 V and a mild oxidation peak at *ca.* 0.8 V as seen in Figure 11.1a and 11.1b. The absence of a reduction peak during the scan to positive potentials indicates that an initial oxidation renders the electroactive moieties on exfoliated MoS₂ nanosheets less susceptible to reduction. During the first scan to positive potentials, exfoliated WS₂ nanosheets possess an oxidation peak at *ca.* 1.2 V of significant intensity at 1000 μA and a shoulder reduction peak at *ca.* -1.6 V. When first swept towards the negative scan direction in Figure 11.1d, two inconspicuous reduction peaks emerged at *ca.* -1.0 V, followed by *ca.* -1.3 V and an apparent oxidation peak appeared at *ca.* 1.0 V of current intensity 570 μA, at nearly half the current intensity of the scan towards positive potentials. The vast disparity between the oxidation current intensities in both scan directions points to the possibility that the initial scan towards negative potentials significantly depletes the number of oxidizable groups on the surface of exfoliated WS₂ nanosheets. Another inference drawn from the immense current intensities of the oxidation peaks relative to

the reduction peaks of exfoliated WS₂ nanosheets in both scan directions depicts majority of the surface groups are oxidizable moieties. As illustrated in Figure 11.1e, two distinct oxidation peaks materialized as a sharp peak at *ca.* 0.8 V and another as a broad peak at a higher potential of *ca.* 1.3 V in the first scan to positive potentials of exfoliated MoSe₂ nanosheets. The oxidation peak at *ca.* 0.8 V is deemed the main oxidation peak because it displayed higher current intensity than the other oxidation peak at *ca.* 1.3 V. The presence of two oxidation peaks indicates 2 different oxidative processes occurring on the surface of exfoliated MoSe₂ nanosheets. There is also a faint reduction peak at -1.2 V. Conversely, two shoulder reduction peaks appeared at *ca.* -0.7 V and *ca.* -1.1 V while a sharp oxidation peak at a potential of *ca.* 0.6 V during the first scan to negative potentials. An initial reduction is necessary for two reductive processes to occur in exfoliated MoSe₂ nanosheets. In exfoliated WSe₂ nanosheets, initial scan for both directions revealed a modest oxidation peak at the same potential at *ca.* 0.7 V. While no reduction peaks were visible in the scan to positive potentials, a reduction peak appeared in the scan towards negative potentials at a potential of *ca.* -1.4 V. Thus, it is deduced that the preceding scan to positive potentials lowers the activity of reducible groups on the exfoliated WSe₂ nanosheets.

Evidence in Figure 11.S1 showcases the inherent electrochemistry of the Mo and W oxides and provides insights into the possible electrochemical processes responsible for the observations in TMDs. The oxidation peak of MoO₂ at *ca.* 0.9 V coincides with the anodic peaks in Mo chalcogenides. Similarly, the reduction peak of MoO₃ at *ca.* -1.0 V lies close to the more negative cathodic peaks in Mo chalcogenides. Hence, this affirms the oxidation of Mo metal centre in Mo chalcogenides to 4+ to 6+ states at *ca.* 0.9 V and the

reduction from 6+ to 4+ states at *ca.* -1.0 V. Unaccounted for redox peaks at *ca.* -0.8 V in MoS₂ and *ca.* 1.3 V in MoSe₂ may stem from the redox behaviour of the chalcogens (S, Se). Reduction of WO₃ occurs at *ca.* -0.8 V and -1.4 V as seen in Figure 11.51h concurs with the 2 cathodic peaks in WS₂ and the peak at -1.4 V coincides with the single cathodic peak in WSe₂. Oxidation of WO₂ manifests as a low and broad peak unlike the sharp anodic peaks in W chalcogenides. Besides the participation of 4+ and 6+ oxidation states in W, the disparity in the peak shape could be a result of the redox processes in the chalcogens.

The electrochemical processes corresponding to the characteristic oxidations and reductions are, to a large extent, chemically irreversible. As supported by the scans of exfoliated MoS₂ nanosheets in Figure 11.1a and 11.1b, the visible peaks observed during the initial scans vanished in the subsequent scans. This observation also applies to exfoliated WSe₂ nanosheets wherein the initially distinct redox peak, illustrated in Figure 11.1g and 11.1h, virtually disappeared from subsequent scans. Clearly, redox processes occurring on exfoliated MoS₂ and WSe₂ nanosheets proceed to completion in the first scan and are regarded as irreversible. Unlike exfoliated MoS₂ and WSe₂ nanosheets, which exhibited immediate decline of the current intensity of their redox peaks after the first scan, peak heights of exfoliated WS₂ and MoSe₂ nanosheets diminish gradually. The reduction peaks of exfoliated WS₂ nanosheets, during initial scans, weakened in current intensity by at least 70 % in the second scans and a marked decrease in the third scans. Analogous to exfoliated WS₂ nanosheets, reduction peaks of exfoliated MoSe₂ nanosheets exhibited decreasing peak current intensities in subsequent scans except for the reduction peak at *ca.* -0.7 V in the scan towards negative potentials that became unnoticeable after the first scan. It may be explained that the reducible moieties on exfoliated MoSe₂

nanosheets were thoroughly consumed during reduction at *ca.* -0.7 V in the initial scan. Likewise, the oxidation peak of the scan towards positive potentials at *ca.* 1.3 V disappeared in subsequent scans; a possibility that the oxidizable moieties on exfoliated MoSe₂ nanosheets at *ca.* 1.3 V were depleted by an irreversible oxidation during the initial scan. The main oxidation peak occurring at *ca.* 0.8 V waned in current intensity by 70 % and shifted to a lower potential at *ca.* 0.5 V in the second scan. The shift in potential is likely ascribed to the reduction process that added moieties prone to oxidation so that oxidation is enabled at earlier potentials. The potential shift was not observed when exfoliated MoSe₂ nanosheets were swept in the cathodic direction first. The current intensity of the sharp oxidation peak at *ca.* 0.6 V plunged by 80 % in the second scan demonstrating that most of the moieties were oxidized in the first scan and few oxidizable moieties were available thereafter. It is also of interest to note that the scan to positive potentials of exfoliated WS₂ nanosheets showcased a single intense oxidation peak at *ca.* 1.2 V in the first scan disintegrated into three minor oxidation peaks at potentials of *ca.* 0.6 V, 1.1 V and 1.6 V subsequently. Therefore, the initial reduction of the moieties on exfoliated WS₂ nanosheets during the scan to positive potentials is a prelude to the 3 separate oxidation processes that arise during the second scan. A similar trend is also noted during the scan to negative potentials with two minor oxidation peaks during the second scan at potentials of *ca.* 0.7 V and 1.0 V wherein *ca.* 1.0 V coincides with the single oxidation peak in the initial scan. In this instance, the presence of two mild oxidation peaks during the scan to negative potentials sheds light on the massive oxidation peak which is deduced to be a merger of the 2 oxidative processes also existing in the first scan to negative potentials. On speculation, the oxidation process at *ca.* 1.0 V involved more

electroactive moieties compared to *ca.* 0.7 V. Thus, oxidation peak at *ca.* 0.7 V in the initial scan to negative potentials was masked by the high current intensity generated by the oxidation process at *ca.* 1.0 V. The two processes become distinguishable during the second scan because the bulk of electroactive moieties on exfoliated WS₂ nanosheets have been oxidized in the initial scan and the remaining oxidizable moieties at these potentials are in comparable quantities.

Based on these findings, the unique oxidative and reductive peaks are inherent to different TMD materials and characteristic of their innate electrochemistry. However, exact mechanisms behind the inherent redox reactions of the TMD nanosheets have not been unveiled and require in-depth studies. We may postulate that the oxidation and reduction processes of exfoliated MoS₂, WS₂, MoSe₂ and WSe₂ nanosheets are largely chemically irreversible. In particular, oxidation of exfoliated MoS₂ and WSe₂ nanosheets proceeded to completion as their respective electroactive moieties were not re-reduced in subsequent scans. Similarly, the reduction of exfoliated MoS₂ and WSe₂ nanosheets were fully reduced in the first scan and did not re-oxidize in subsequent scans.

11.2.2 Post-Electrochemical Treatment: Material and Electrochemical Characterisation

Earlier, we studied the inherent electrochemistry of exfoliated MoS₂, WS₂, MoSe₂ and WSe₂ nanosheets and identified characteristic oxidation and reduction peaks of the TMD materials. For each of the TMD material, we determine a suitable oxidation and reduction potential that lie marginally beyond their characteristic redox potentials for treatment as described in previous section. The oxidation and reduction treatment potentials are determined to be 1.1 V and -1.3 V for exfoliated MoS₂ nanosheets, 1.2 V and -1.6 V for exfoliated WS₂ nanosheets, 1.0 V and -1.2 V for exfoliated MoSe₂ nanosheets and 1.0 V

and -1.3 V for exfoliated WSe₂ nanosheets. At these potentials, it is likely that there is chemical alteration of the surface structure of the TMD materials as a result of redox reactions of the material itself. This knowledge piqued our curiosity about the electrochemical behaviour of the TMD materials after electrochemically oxidizing or reducing them at the chosen potentials. After the exfoliated MoS₂, WS₂, MoSe₂ and WSe₂ nanosheets were subject to chronoamperometric treatment at their respective potentials, we performed surface, structural and morphological characterisation of the materials *via* X-ray photoelectron spectroscopy (XPS), Raman spectroscopy and high resolution transmission electron microscopy (HR-TEM) respectively, followed by cyclic voltammetric measurements to investigate the heterogeneous electron transfer (HET) rate of the oxidized, reduced and untreated TMD nanosheets. Using the Nicholson method,²⁸ the HET rates can be derived from correlating the peak-to-peak separation (ΔE_p) to the charge transfer rate (k_{obs}^0) where larger ΔE_p relates to slower HET rates. With the aid of two different redox probes: ferro/ferricyanide complex ([Fe(CN)₆]^{4-/3-}) and ruthenium(III/II)-hexamine complex ([Ru(NH₃)₆]^{3+/2+}), we are able to acquire electrochemical information about exfoliated MoS₂, WS₂, MoSe₂ and WSe₂ nanosheets as well as their oxidized and reduced forms.

Structural and surface changes of TMDs may result from electrochemical treatment which in turn would be useful towards explaining the electrochemical and catalytic trends of the TMDs. XPS was performed to examine the surface elemental compositions and the high resolution XPS spectra are shown in Figure 11.2. Raman spectroscopy was conducted to evaluate structural information of the TMDs. Raman spectra is illustrated in Figure 11.3.

Figure 11.2 High resolution X-ray photoelectron spectra of the Mo 3d and W 4f regions of exfoliated MoS₂, MoSe₂, WS₂ and WSe₂ nanosheets before and after electrochemical treatment. Metallic 1T phase given in red, semiconducting 2H phase denoted in blue and oxidized (VI) state in green.

The MoS₂ nanosheets seem to preserve the semiconducting 2H phase after the exfoliation as evident in the XPS signals identified at 229 eV and 232 eV for Mo 3d_{5/2} and Mo 3d_{3/2} respectively. Subjecting the MoS₂ nanosheets to electrochemical oxidation or reduction treatment decreases its 2H-phase component. The oxidation of MoS₂ nanosheets is also confirmed by the increase in Mo⁶⁺ 3d_{5/2} and Mo⁶⁺ 3d_{3/2} signals at 233 eV and 236 eV to 28.1 % while in the reduced MoS₂ nanosheets, the extent of oxidation is noted to be slightly lower. Dissimilar to MoS₂ nanosheets, MoSe₂ nanosheets contain a mixture of 2H- and 1T- phase. Redox treatment of MoSe₂ nanosheets elevated the contribution of the 1T-phase Mo 3d_{5/2} and Mo 3d_{3/2} signals to 17.0 % in the oxidized and 12.2 % in the reduced while the 2H-phase components declined to 40.9 % in the

oxidized and further depleted to 31.9 % in the reduced. $\text{Mo}^{6+} 3d_{5/2}$ and $\text{Mo}^{6+} 3d_{3/2}$ signals of electrochemically treated MoSe_2 materials spiked to 42.1 % when oxidized and a surprisingly higher intensity at 55.9 % when reduced.

The WS_2 and WSe_2 nanosheets manifested 2H-phase W $4f_{7/2}$ and W $4f_{5/2}$ peaks at 32 eV and 34 eV. Reduction and oxidation of WS_2 nanosheets increased the amount of 1T-phase to 26.4 % and 10.4 % respectively. However, when WSe_2 nanosheets were subject to electrochemical oxidation or reduction, the 1T-phase was absent and this was accompanied by a higher proportion of 2H-phase at 55.1 % in its oxidized state and 82.3 % in its reduced state. $\text{W}^{6+} 4f_{7/2}$ and $\text{W}^{6+} 4f_{5/2}$ components of WS_2 occurring at binding energies of 36 eV and 38 eV were marginally reduced to 44.0 % in oxidized WS_2 and dropped to 31.5 % in reduced WS_2 . Likewise, there was a minor drop to 44.9 % in oxidized WSe_2 nanosheets and a substantial decline to 17.7 % in reduced WSe_2 nanosheets.

Close inspection of the oxidized M(VI) component across the TMD materials, disregarding the type of electrochemical treatment, reveals the trend of increasing M^{6+} contribution: MoS_2 (8.0 %) < MoSe_2 (22.5 %) < WS_2 (54.2 %) < WSe_2 (57.2 %). This finding coincides with earlier reports on WX_2 (where X= S or Se) are more readily oxidized than MoX_2 ²⁹ and MSe_2 (where M= Mo or W) more vulnerable to oxidation than MS_2 .³⁰

We next explore the effect of electrochemical treatment on the chalcogen-to-metal ratio (Table 11.S1) and deduced that electrochemical treatment varies the chalcogen-to-metal ratio in the Mo chalcogenides whereas the ratio remains relatively unaffected in W chalcogenides. Oxidizing MoS_2 produces a higher chalcogen-to-metal ratio of 2.6 than when untreated. In turn, the high chalcogen-to-metal ratio depicts Mo metal deficiency largely due to the formation of MoO_4^{2-} and; a smaller extent, the SO_4^{2-} species at oxidative

potentials above 1.0 V vs. Ag/AgCl.³¹ Reducing MoS₂ results in a smaller chalcogen-to-metal ratio at 1.9 compared to the previous 2.2 in untreated. There is a dramatic difference in the chalcogen-to-metal ratio of MoSe₂ across its electrochemically treated and untreated states. At an anodic potential of above 1.0 V, MoSe₂ could generate elemental species in their highest oxidation states such as MoO₄²⁻ and SeO₄²⁻ at pH 7. In doing so, the chalcogen-to-metal ratio of MoSe₂ when oxidized is observed to decrease to 1.9 from 3.0 in untreated MoSe₂. Moreover, the further plunge in chalcogen-to-metal ratio of MoSe₂ to 1.1 upon reduction may be attributed to inherent reductions that produce HSe⁻ species³² which deplete the Se chalcogen composition, inducing a Mo-enriched environment in reduced MoSe₂. In the situation of the W compounds, it appears that the chalcogen-to-metal ratio remains relatively stable across the oxidized, reduced and untreated states.

Figure 11.3 Raman spectra of exfoliated a) MoS₂, b) MoSe₂, c) WS₂ and d) WSe₂ nanosheets

before and after electrochemical oxidation or reduction. $\lambda_{\text{exc}} = 514.5 \text{ nm}$.

The Raman spectra in Figure 11.3 depict two predominant signals across all TMD materials: in-plane E_{2g} (shear) and the out-of-plane A_{1g} (breathing) modes. The in-plane E_{2g} mode has the metal and chalcogen atoms moving in opposite directions in-plane and can be distinguished from A_{1g} mode which has the metal atom stationary with chalcogen atoms moving out of the plane in opposite directions. The E_{1g} phonon is also discernible in all TMD materials. Due to its weak diagnostic trait, the E_{1g} mode is not of interest.

The A_{1g} phonon band of exfoliated MoS_2 nanosheets manifested a red shift of 2.0 cm^{-1} and broadened by 2.0 cm^{-1} when electrochemically reduced whereas the E_{2g} band remains relatively unchanged. However, this trend is not replicated for other TMDs. Though it has been discovered that the E_{2g} mode is inert to electron doping, a red shift of the A_{1g} and its broadening are attributes of electron doping.^{33, 34} Such disparity of the phonon signals towards electron doping is explained by the stronger electron-phonon coupling of A_{1g} than E_{2g} . Hence, this observation in the MoS_2 nanosheets verifies that electrochemical reduction has effectively introduced electrons to into the MoS_2 system. Moreover, the decreased in frequency and linewidth broadening of the A_{1g} phonon after redox treatment corresponds to decreased number of layers.³⁵

Raman shifts in exfoliated MoSe_2 nanosheets exhibit a trend contrary to MoS_2 upon electrochemical reduction. The A_{1g} phonon remains fixated at approximately 240 cm^{-1} with a gradual decrease in its full width at half maximum (FWHM) from 10.5 to 9.5 in reduced MoSe_2 . When electrochemically reduced, the E_{2g} mode observes a blue shift and slight broadening (0.8 cm^{-1}). Conversely, oxidized MoSe_2 undergoes a blue shift (1.4 cm^{-1}) in A_{1g} phonon and a sharp decline in FWHM (5.0 cm^{-1}) of the E_{2g} mode. There is also substantial changes to the $I(A_{1g})/I(E_{2g})$ ratio across MoSe_2 materials as a result of electrochemical

treatment which is not noted in other TMDs.

While electrochemically treated WS₂ nanosheets reveal the stiffening of both E_{2g} and A_{1g} modes, we observe broadening in E_{2g} mode and decreased FWHM in A_{1g}. Reported for MoS₂, the linewidth of E_{2g} mode is less sensitive to changes in layer thickness but there is strong layer-dependence of the linewidth in A_{1g} phonon.³⁵ The reduced linewidth in A_{1g} mode after electrochemical treatment translates into presence of thicker layers,³⁶ often the bulk-like inner layers, which dominate the Raman intensity of the treated WS₂. More interestingly, WO₃ Raman signals³⁷ are also observed as illustrated in Figure 11.S4. In untreated WS₂ nanosheets, we notice 2 narrow bands at 715 cm⁻¹ and 807 cm⁻¹ that are typical features of WO₃. However, upon subjecting to oxidation or reduction, the 2 bands vanished and instead a broad signal at 645 cm⁻¹ characteristic of hydrated WO₃ (WO₃·xH₂O) signal is observed. The presence of WO₃ moieties on the surface of WS₂ materials also coincides with significant percentage of W⁶⁺ components from our experimental XPS data and affirmed the presence of solid oxides in all WS₂ materials.

Exfoliated WSe₂ nanosheets are known to exhibit E_{2g} and A_{1g} phonons within close proximity of each other at 248 cm⁻¹ and 250 cm⁻¹ to quote from literature.³⁸ Our experimental Raman band of WSe₂ materials occurring at about 247 cm⁻¹ concurs with literature values.

In addition, the morphological changes of the treated TMDs were investigated by high-resolution transmission electron microscopy (HR-TEM), see Figure 11.S5. After the anodic and cathodic treatment, we could notice the presence of a more extensive amorphous (non-crystalline) phase together with the crystalline one which was prominent in the untreated materials. No other significant differences could be highlighted between

the materials upon the electrochemical treatment. It is crucial to note that HR-TEM probes only a very small portion of the sample and therefore does not provide overall information on the sample properties. Electrochemical behaviour is strongly influenced by the overall chemical and physical properties of the material surface which can be obtained by means of spectroscopic techniques such as XPS and Raman, as discussed above.

Extensive research on $[\text{Fe}(\text{CN})_6]^{4-/3-}$ redox probe in the past has determined its surface sensitivity³⁹ towards various electrode materials. The surface sensitive nature will be advantageous when evaluating HET rates of the exfoliated MoS_2 , WS_2 , MoSe_2 and WSe_2 nanosheets in the presence of $[\text{Fe}(\text{CN})_6]^{4-/3-}$. Figure 11.4 records the voltammetric profiles of $[\text{Fe}(\text{CN})_6]^{4-/3-}$ in 0.1 M KCl on the exfoliated TMD nanosheets and their oxidized or reduced forms resulting from electrochemical treatment.

Figure 11.4 Cyclic voltammograms of 5 mM $[\text{Fe}(\text{CN})_6]^{4-/3-}$ on exfoliated a) MoS₂ nanosheets, b) WS₂ nanosheets, c) MoSe₂ nanosheets and d) WSe₂ nanosheets before and after electrochemical treatment. e) Summary of peak-to-peak separations of treated and untreated TMD materials with their corresponding error bars. Conditions: background electrolyte, KCl (0.1 M); scan rate, 100 mV s⁻¹; all measurements are performed relative to the Ag/AgCl reference electrode.

As reflected in Figure 11.4a (and Table 11.S3), the untreated MoS₂ nanosheets had a ΔE_p of 0.139 V and a k_{obs}^0 calculated to be 2.5×10^{-3} cm s⁻¹. When subject to

electrochemical treatment, oxidized MoS₂ nanosheets had ΔE_p of 0.21 V ($k_{\text{obs}}^0 = 9.5 \times 10^{-4}$ cm s⁻¹) and reduced MoS₂ nanosheets yielded ΔE_p of 0.11 V ($k_{\text{obs}}^0 = 3.6 \times 10^{-3}$ cm s⁻¹). In Figure 11.4c, MoSe₂ nanosheets displayed ΔE_p of 0.22 V ($k_{\text{obs}}^0 = 8.4 \times 10^{-4}$ cm s⁻¹) when not treated, ΔE_p of 0.30 V ($k_{\text{obs}}^0 = 2.8 \times 10^{-4}$ cm s⁻¹) when oxidized and ΔE_p of 0.11 V ($k_{\text{obs}}^0 = 3.5 \times 10^{-3}$ cm s⁻¹) when reduced. Based on these HET rates, we note that both exfoliated MoS₂ and MoSe₂ nanosheets exhibited faster HET rates in their reduced states than when untreated while their oxidized states had slower HET rates. As MoS₂ and MoSe₂ compounds⁴⁰ are usually n-type TMDs, such phenomenon may be supported by the semiconductor band theory.⁴¹ Oxidative treatments of the MoS₂ and MoSe₂ nanosheets at positive potentials at 1.1 V and 1.0 V respectively, which exist above their flatband potential, conduct electrons away from the interface and a depletion region ensues. Deficiency of electrons at the interface hampers electron transfer between the electrolyte and the electrode surface modified with oxidized MoS₂ or MoSe₂. This is evident in the large ΔE_p and low HET rates of the oxidized Mo compounds. In a similar manner, when the MoS₂ and MoSe₂ nanosheets are electrochemically reduced at respective negative potentials of -1.3 V and -1.2 V, electrons gather at the interface which creates an accumulation region. In doing so, the electron rich region at the interface provides a steady stream of electrons for charge transfer and accelerates HET rates of the reduced Mo compounds. WSe₂ nanosheets also comply with same trend as the Mo compounds wherein a higher HET rate of 2.7×10^{-3} cm s⁻¹ was demonstrated in reduced WSe₂ and a slower rate at 2.5×10^{-4} cm s⁻¹ for oxidized WSe₂ nanosheets. Consistent with MoS₂, MoSe₂ and WSe₂ nanosheets, the HET rate of WS₂ nanosheets was slowed down upon oxidation. However, there was negligible improvement of the HET rate of reduced WS₂ nanosheets

from the untreated WS₂ nanosheets unlike enhanced HET performance of reduced MoS₂, MoSe₂ and WSe₂ nanosheets compared to their untreated counterparts. The HET rates of reduced and untreated WS₂ nanosheets are comparable to each other; the reduced at $2.7 \times 10^{-3} \text{ cm s}^{-1}$ and the untreated at $2.8 \times 10^{-3} \text{ cm s}^{-1}$. Perhaps, apart from explanation using the semiconductor band theory, there are other factors inherent to the TMD material that comes into play.

Upon closer scrutiny of Figure 11.4e, we discover that the type of metal and chalcogen are also imperative to the HET rates in TMD materials. Considering the effect of the metal component, we juxtapose treated and untreated MoS₂ with WS₂ nanosheets and MoSe₂ with WSe₂ nanosheets keeping the chalcogen component constant. It is interesting to note that Mo compounds are more effectively activated by electrochemical reduction than W compounds in the aspect of electron transfer rates. Reduced MoS₂ afforded a HET rate that is 1.4 times (42 % increment) faster than its untreated state whereas HET rates of reduced and untreated WS₂ differed by an imperceptible 2 %. Similarly, reduced MoSe₂ yielded a 4.2 times enhancement of HET rates relative to when untreated while reduced WSe₂ was 1.6 times faster than untreated WSe₂. Complementing the findings on the activation of HET rates by reduction, oxidation of MoS₂ and WS₂ nanosheets impeded their electron transfer rates drastically. The deactivation of electrochemical property is more strongly felt in oxidized WS₂ than MoS₂. When oxidized, the HET rate of WS₂ plunged dramatically by 36.7 times its original rate while oxidized MoS₂ had a HET rate 2.6 times slower than its untreated form. Therefore, reduced Mo compounds demonstrate markedly enhanced HET rates relative to W compounds and the deactivation of electrochemical property was more apparent in oxidized W compounds than Mo compounds. We proceed

to investigate how the chalcogen type governs the electrochemical properties of the TMD materials with the metal kept unchanged. Comparisons between MoS_2 and MoSe_2 evince that reduced MoSe_2 portrayed a significantly improved HET rate compared to its untreated state than reduced MoS_2 with its untreated counterpart. Concurring with this trend, the reduced WSe_2 showed enhanced HET rate than when untreated whereas HET rates of reduced WS_2 and its untreated state remained generally the same. From this, we deduce that there is a larger extent of electrochemical activation experienced in Se than S compounds. Among all the TMD materials, MoSe_2 consisting of Mo and Se components is most sensitive to electrochemical activation in the aspect of HET rates because there are crucial differences in the structures of its reduced, oxidized and untreated states. In turn, the active sites available for electron transfer in MoSe_2 materials vary most substantially than the rest of the TMD materials upon electrochemical treatment.

As an experimental control, the measurements were repeated in the presence of $[\text{Ru}(\text{NH}_3)_6]^{2+/3+}$ redox probe to ascertain the findings in $[\text{Fe}(\text{CN})_6]^{4-/3-}$ probe. Unlike $[\text{Fe}(\text{CN})_6]^{4-/3-}$, $[\text{Ru}(\text{NH}_3)_6]^{2+/3+}$ is known to be insensitive to surface functional groups.⁴² After electrochemical oxidation or reduction, Figure 11.5 shows no compelling difference for all the TMD materials. Since the treated and untreated TMD materials exhibited different HET rates in $[\text{Fe}(\text{CN})_6]^{4-/3-}$, we have confirmed that oxidation or reduction treatments had chemically altered the surface composition of the materials.

Figure 11.5 Cyclic voltammograms of 5 mM $[\text{Ru}(\text{NH}_3)_6]^{2+/3+}$ on exfoliated a) MoS₂ nanosheets, b) WS₂ nanosheets, c) MoSe₂ nanosheets and d) WSe₂ nanosheets before and after electrochemical treatment. e) Summary of peak-to-peak separations of treated and untreated TMD materials with their corresponding error bars. Conditions: background electrolyte, KCl (0.1 M); scan rate, 100 mV s⁻¹; all measurements are performed relative to the Ag/AgCl reference electrode.

11.2.3 Post-Electrochemical Treatment: Electrocatalysis

Research into MoS_2 as hydrogen evolution electrocatalyst has garnered much success, prompting scientists to delve into other layered TMDs as sustainable electrocatalysts for hydrogen evolution reaction (HER). Encouraged by the discovery of enhanced heterogeneous electron transfer (HET) performance of Mo compounds and WSe_2 nanosheets after electrochemical reductive pre-treatment, we opted to evaluate the effect of electrochemical pretreatments towards the catalytic HER performance of the TMDs. In particular, we want to determine if the catalytic properties of exfoliated MoS_2 , WS_2 , MoSe_2 and WSe_2 nanosheets can be altered by the application of a reductive or oxidative electrochemical treatment.

Figure 11.6 Linear sweep voltammograms for HER in acidic electrolyte on a) MoS₂ and MoSe₂ nanosheets and their respective oxidized or reduced forms and c) WS₂ and WSe₂ nanosheets and their respective oxidized or reduced forms. Tafel plots for b) Mo compounds and d) W compounds. Presented in bar charts are the averages of e) overpotential at -10 mA cm^{-2} current density and f) Tafel slopes with their corresponding

error bars for all the materials. Conditions: background electrolyte, H₂SO₄ (0.5 M); scan rate, 2 mV s⁻¹; all measurements are performed relative to the Ag/AgCl reference electrode and corrected to reversible hydrogen electrode (RHE) potentials.

Figure 11.6 records the HER polarisation curves of the transition metal dichalcogenide (TMD) materials before and after electrochemical treatment. Often exemplified as the best HER catalyst, Pt/C yields low Tafel slopes of 30 to 40 mV/dec⁴³ and is used as a yardstick in this experiment to gauge the efficiency of HER catalysis by the TMD materials. The experimental Tafel slope of 37.8 mV/dec for Pt/C is in good agreement with literature values. Polarisation curve of bare GC is also included for reference because GC serves as the electrochemical transducer modified with the desired TMD.

Two commonly adopted HER performance indicators are the Tafel slope and the onset potential. The Tafel slope is the increase in overpotential required to elicit a magnitude rise in current density. Smaller Tafel slopes are desirable for HER. Moreover, the Tafel slope elucidates the mechanism for HER on different TMD materials and its rate-determining step. In general, HER consists of two steps.^{44,45} First is the Volmer adsorption step whereby the hydrogen binds to the catalyst (its binding site denoted as M*) as such: $\text{H}^+ + \text{e} + \text{M}^* \rightarrow \text{M-H}$ with a Tafel slope value of 120 mV/dec. Subsequently, it involves a desorption step either *via* the Heyrovsky process: $\text{H}^+ + \text{e} + \text{M-H} \rightarrow \text{M}^* + \text{H}_2$ at a Tafel slope value of 40 mV/dec; or the Tafel process: $2 \text{M-H} \rightarrow 2 \text{M}^* + \text{H}_2$ at a Tafel slope value of 30 mV/dec. The onset potential is understood to be the potential at which the current density begins to fall steeply due to proton reduction. Across literature, the parameters in determining HER onset potentials fluctuate. We measure the onset potential as the potential corresponding to the current density of -0.1 mA cm⁻². The onset values for the TMD materials are

provided in Figure 11.S6 and will not be discussed in detail. Instead of onset potentials, we employ the overpotential at a current density of -10 mA cm^{-2} as a benchmark because the pre-HER waves observed in WS_2 , MoSe_2 and WSe_2 may thwart our evaluation of HER onset potentials.

At a current density of -10 mA cm^{-2} , the overpotentials for the TMD materials are summarised in Figure 11.6e as gathered from the polarisation curves in Figure 11.6a and 11.6c. The HER catalytic trend across untreated TMD materials unveils MoSe_2 as the leading HER catalyst with the lowest overpotential at 0.37 V, followed by WS_2 with overpotential at 0.39 V and MoS_2 at 0.53 V and trailing behind is WSe_2 at highest overpotential at 0.76 V. Their Tafel slope values also reinforce this trend wherein MoSe_2 has the lowest Tafel slope at 86 mV/dec, followed by WS_2 and MoS_2 at higher Tafel slopes of 93 mV/dec and 110 mV/dec. The highest Tafel slope at 169 mV/dec is demonstrated in WSe_2 . Furthermore, a density functional study led by Nørskov *et al*⁴⁶ complements this HER catalytic trend. To quote from this study, MoSe_2 and WS_2 are armed with both their metal and chalcogen edges as active sites for HER. Conversely, MoS_2 and WSe_2 are less privileged; having either metal or chalcogen as active sites and not both. The primary active site for MoS_2 lies at the Mo-edge while WSe_2 utilizes Se-edge. The differential hydrogen free energies, ΔG_{H} , which are suitable markers of HER rate, of Mo- and Se- edge of MoSe_2 are found to be more thermoneutral; with an optimal binding energy approximating zero,⁴⁷⁻⁴⁹ than W- and S- edge of WS_2 . ΔG_{H} of Mo-edge in MoS_2 and Se-edge in WSe_2 are comparable. Hence, the interplay of HER active sites and ΔG_{H} anticipate MoSe_2 to show the highest HER catalytic activity, followed closely by WS_2 . Furthermore, 1T-phase obtained from XPS data may be adopted to account for the more efficient

hydrogen evolution reaction occurring on the MoSe₂ catalyst than the MoS₂ catalyst. MoSe₂ comprises of a higher percentage of 1T-phase compared to MoS₂ which sees the absence of it. By the same token, WS₂ has a higher intensity of 1T-phase than WSe₂ which justifies the behaviour of WS₂ as a better HER catalyst than WSe₂.

However, 1T-phase alone is inadequate to explain the extent of HER activation in the TMD materials because unlike 2H phase, which is thermodynamically stable in TMDs, the 1T phase existing in comparatively low amounts and less stable in atmosphere is prone to oxidation. Hence, chalcogen-to-metal ratio could also be a factor for consideration in such instances.

Out of all the TMD materials, electrochemical activation is found to be successful for MoS₂ material wherein the lowering of HER overpotential is apparent at a current density of -10 mA cm⁻² when MoS₂ is electrochemically reduced. Unlike its untreated form, reduced MoS₂ depicts a smaller Tafel slope value at 95 mV/dec. The catalytic site in MoS₂ is reported to be at the Mo-edge, specifically where the undercoordinated S exists.⁵⁰ Reduced MoS₂ is postulated to contain a marked increase in these HER catalytic zones and hence, displays an improved HER activity. The chalcogen-to-metal ratio derived from the XPS analysis gives credence to this hypothesis whereby reduced MoS₂ has a notably lower ratio than before treatment, indicative of the increase in Mo metal composition in MoS₂ after reduction and likely translates into more Mo-edge sites available for HER which activates the material for HER. Indeed, reduced MoS₂ behaving as a better HER electrocatalyst than when untreated concurs with our earlier electrochemical activation study²⁷ using MoS₂ nanosheets prepared from lithium intercalation with *n*-BuLi. In that study, the reduced MoS₂ nanosheets demonstrated enhanced HER catalysis than its

untreated counterpart. At first sight, oxidized MoS₂ shows little deviation from its untreated counterpart as reflected in the almost overlapping HER polarisation curves. Careful inspection discloses that there is slight increment in its HER overpotential to 0.57 V and a substantial rise in Tafel slope to 161 mV/dec pointing to an imperceptibly weaker HER activity in oxidized MoS₂ than its untreated form. A Tafel slope of 161 mV/dec transforms the HER rate-determining step in MoS₂ from a combination of Volmer-Heyrovsky processes to a Volmer process in its oxidized state. Previous research reports MoO₃ species formation when MoS₂ is electrochemically oxidized.⁵¹ The hydrogen binding site occurring at the Mo-edge of MoS₂ is hindered as a result of MoO₃ which accounts for the imperceptibly lower catalytic behaviour of oxidized MoS₂.

In stark contrast to effective activation of MoS₂ by electrochemical reduction for HER, WS₂ manifests electrochemical deactivation behaviour when reduced and such deactivation occurs at a larger scale when oxidized. Most evident in oxidized WS₂, a high Tafel slope of 164 mV/dec with a corresponding large HER overpotential of 0.59 V is noted. Analogous to oxidized MoS₂, the slow step in HER has morphed from a joint Volmer-Heyrovsky process to the adsorption step in its oxidized state. Oxidation of WS₂ engenders WO_x compounds, predominantly existing as WO₃ due to the conversion of 4+ to 6+ oxidation states in W. WO_x species modifies the W-edge, one of the HER binding site alongside S-edge, and deters hydrogen binding. In doing so, the W-edge sites available for binding are depleted, therefore, impeding oxidized WS₂ as an electrocatalyst for HER. Another reason to justify the poor catalytic performance of oxidized WS₂ is based on XPS data. The 2H-phase of oxidized WS₂ stands at 45.6 % which is more than its untreated state, in turn, weaker HER efficiency is observed for oxidized WS₂. Moreover, the W⁶⁺ factor

appears to be rather significant for oxidized WS_2 at 44.0 % which could influence the catalytic activity of the W-edge.

On the contrary to MoS_2 and WS_2 , the HER catalytic activities of MoSe_2 and WSe_2 materials are less perturbed by electrochemical oxidation or reduction. The Tafel slopes and HER overpotential obtained for reduced, oxidized and untreated MoSe_2 differ marginally from each other by 7 mV/dec and 0.01 V. Tafel slopes of the MoSe_2 materials range from 78 mV/dec to 86 mV/dec indicative of the rate-determining step for HER to be a concerted Volmer-Heyrovsky step regardless of electrochemical treatment. By the same token, WSe_2 materials exhibit relatively constant HER overpotentials of 0.78 V to 0.76 V and Tafel slopes of beyond 120 mV/dec for its treated and untreated forms. Beyond 120 mV/dec, the slow step is predominantly the HER adsorption step for all WSe_2 materials. On the grounds of identical rate-determining steps for the reduced, oxidized and untreated states, the HER catalytic performance of MoSe_2 and WSe_2 materials are impervious to electrochemical activation. Despite the significant changes in chalcogen-to-metal ratio (Table 11.S1) in the oxidized, reduced and untreated MoSe_2 , there is little effect of these differences on the HER efficiency of MoSe_2 materials as both metal and chalcogen edges are HER active.

Notably, there is a correlation between the chalcogen type and its susceptibility to electrochemical activation or deactivation for HER. Electrochemical treatment on TMD materials bearing the S chalcogen, in the case of MoS_2 and WS_2 , influences their catalytic performance for HER. Conversely, TMD materials such as MoSe_2 and WSe_2 which bear the Se chalcogen are less affected by electrochemical treatment on their HER catalytic performance. Since Tafel slopes of the treated and untreated TMD materials lay beyond

or fall within the range of Volmer and Heyrovsky processes, the hydrogen adsorption step contributes to their rate-determining step. The nature and location of the HER active sites in TMD materials govern its effect on electrochemical treatment for HER. Hydrogen binding site occurs at the Mo- and Se-edge for MoSe₂ whereas hydrogen binds solely at the Mo-edge in MoS₂. When subject to electrochemical reduction, Mo (VI) may be reduced to Mo (0) and this possibly improves the hydrogen binding function of the Mo-edge. This effect is more pronounced in MoS₂ because the active site at Mo-edge dominates the catalytic ability for HER. The HER catalytic ability of MoSe₂ comprises of both the Mo- and Se- edge and hence, less activated by electrochemical reduction than MoS₂. Considering WS₂ and WSe₂ materials, the active sites reside at the W- and S- edge for WS₂ and Se- edge in WSe₂. Electrochemical oxidation of WS₂ deactivates its catalytic performance for HER but HER ability of WSe₂ remains relatively unperturbed by oxidation. When electrochemically oxidized, W (IV) becomes W (VI) and WO₃ species⁵² is reportedly formed. Therefore, hydrogen binding at the W-edge is restricted which impairs the HER catalytic ability of WS₂. Disparate from WS₂, W-edge is not the primary active site for HER in WSe₂ and hence WSe₂ is not deactivated by oxidation.

11.3 Conclusion

We explored the inherent electrochemistry of layered transition metal dichalcogenides (TMDs) materials, specifically MoS₂, WS₂, MoSe₂ and WSe₂ nanosheets. It has been determined that electrochemical reduction effectively activates the electrochemical property of MoS₂, MoSe₂ and WSe₂ nanosheets as substantiated by the improved heterogeneous electron transfer (HET) rates in their reduced forms. Among these three TMDs, the enhanced HET rate is most enhanced in reduced MoSe₂.

Antithetical to electrochemical reduction, subjecting all the TMD materials to an electrochemical oxidation deteriorated their HET performance. Of which, the most drastic deactivation is experienced by the oxidized WS₂. The semiconductor band gap theory largely justifies the findings on variations in HET performance upon electrochemical treatment but other factors intrinsic to the TMDs may also contribute. There is also a correlation between the metal and chalcogen type on the extent of electrochemical activation. Considering metal component, Mo prevails over W while in chalcogen type, Se exhibits higher sensitivity to electrochemical activation than S.

Successful electrochemical activation towards hydrogen evolution reaction (HER) is exclusively elucidated in MoS₂. The improved HER efficiency is evident in reduced MoS₂ demonstrating a lower Tafel slope and requiring a smaller HER overpotential at a current density of -10 mA cm^{-2} compared to its untreated counterpart. Conversely, the deactivation of catalytic performance is manifested in the electrochemical oxidation of WS₂ ensuing a higher Tafel slope and larger HER overpotential than when untreated. MoSe₂ and WSe₂ materials indicate that their HER performance is unreceptive to electrochemical oxidation or reduction. In general, electrochemical treatment exerts clout over TMDs containing the S chalcogen but yields no power over the compounds with the Se chalcogen. A comprehensive explanation boils down to density functional theory wherein each TMD possess a characteristic number and type of edge sites for hydrogen binding. Differences in such active sites lead to different HER behaviour. Moreover, the oxidation or reduction processes that the TMDs are subject to may alter these edge sites, hence influencing the catalytic performance.

Therefore, we highlight here that TMDs have distinct responses to electrochemical

treatment. In the aspect of HET, electrochemical treatment can be used to tweak the electrochemical properties of MoS₂, MoSe₂ and WSe₂ nanosheets whereby a reductive process elevates HET and an oxidative process deactivates the charge transfer performance. In the area of HER, electrochemical reduction is a success at activating MoS₂ and an oxidative treatment renders a weaker HER performance in WS₂ nanosheets. Knowledge of the TMD electrochemistry and the effect of electrochemical treatment on TMDs will be pivotal towards achieving desired aims in catalytic and electrochemical applications.

11.4 Experimental Methods

11.4.1 Materials

Potassium ferrocyanide, hexaammineruthenium (III) chloride, potassium chloride, potassium phosphate dibasic, sodium phosphate monobasic, sodium chloride, sulfuric acid and platinum on carbon were purchased from Sigma Aldrich. Pt, Ag/AgCl and glassy carbon (GC) electrodes were purchased from CH Instruments, Texas, USA. Molybdenum disulfide, molybdenum diselenide, tungsten disulfide, tungsten diselenide (< 2 μm), sodium and *tert*-butyllithium (1.7 M in pentane) were obtained from Sigma-Aldrich, Czech Republic. Hexane was obtained from Lach-ner, Czech Republic. Argon (99.9999 % purity) was obtained from SIAD, Czech Republic.

11.4.2 Exfoliation of TMDs

The TMDs were exfoliated using the chemical intercalation method. The intercalation procedure was performed in the glovebox with Ar atmosphere (O₂ and H₂O below 0.1 ppm). Each of the bulk TMD (in powder form, Sigma-Aldrich) was dried at 100 °C for 48 hours before insertion into glovebox which was kept at a constant temperature of 20 °C

using a temperature conditioning system during the entire intercalation process. Li-intercalation process was carried out by stirring 3 g of the bulk TMD powder in 20 mL of 1.7 M *tert*-butyllithium in pentane for 72 h at 20 °C under argon atmosphere. To avoid contamination due to fluorine, a glass-coated magnetic stir bar was used instead of the standard PTFE-coated magnetic stir bar. The flask containing the reaction mixture was capped with a rubber septum with an inserted needle head to prevent the build-up of pressure in the reaction flask and minimize evaporative loss of volatile pentane solvent. Li-intercalated TMD was separated from excess intercalant by suction filtration *via* a 0.45 μm nylon membrane. Filtered material was washed three times with 30 ml of hexane (dried over sodium). The exfoliated material was dispersed in 100 ml of water and ultrasonicated for 15 minutes. Purification and separation were performed by repeated centrifugation (18000 g) and redispersion in water until the conductivity was below 20 μS . Finally, the obtained TMD nanosheets were dried in vacuum oven at 50 °C for 48 hours prior to further use.

11.4.3 Apparatus

X-ray photoelectron spectroscopy (XPS) was performed with a Phoibos 100 spectrometer with a monochromatic Mg K_{α} X-ray source (SPECS, Germany). Survey and high-resolution spectra were obtained for Mo 3d, W 4f, S 2p and Se 3d. The relative sensitivity factors were also adopted for the calculation of chalcogen-to-metal ratios and for deconvolution of oxidized states, 2H and 1T phases in the Mo and W compounds.

Raman spectroscopy was executed on a confocal micro-Raman LabRam HR instrument (Horiba Scientific) in backscattering geometry with a CCD detector, using an argon ion laser at an excitation wavelength of 514.5 nm and a 100 $\times$ objective mounted on an Olympus

optical microscope. The laser spot has a diameter of about 5 μm across. The initial calibration was performed with a silicon reference at 520 cm^{-1} .

High resolution transmission electron microscopy (HR-TEM) was performed using Jeol 2100 TEM (Jeol, Japan) operating at 200 kV.

Voltammetric measurements were recorded on a μ Autolab III electrochemical analyser (Eco Chemie B.V., Utrecht, The Netherlands) with the software NOVA version 1.8 (Eco Chemie). Electrochemical measurements of the transition metal dichalcogenide (TMD) materials were performed in a 5 mL voltammetric cell at room temperature (25 $^{\circ}\text{C}$) in a three electrode configuration. A platinum electrode and an Ag/AgCl electrode functioned as auxiliary and reference electrodes, respectively and a glassy carbon (GC, 3 mm diameter) electrode was adopted as the working electrode.

11.4.4 Procedures

Fundamental electrochemical studies were performed in 50 mM phosphate buffered saline (PBS) as the background electrolyte at pH 7. All cyclic voltammetry experiments were conducted at a scan rate of 100 mV s^{-1} . The voltammetric scan began at 0 V; the potential at which redox processes were not expected to occur,⁵³ and scanned towards 1.8 V followed by a reverse sweep to -1.8 V for the scan to positive potentials, and first towards -1.8 V followed by a reverse sweep to 1.8 V before returning to 0 V for the scan to negative potentials. The exfoliated MoS_2 , MoSe_2 , WS_2 and WSe_2 nanosheets were prepared in concentrations of 1 mg mL^{-1} in ultrapure water and subject to first-time ultrasonication for 1.5 h to attain homogenous dispersions. Prior to each electrochemical measurement, the samples were ultrasonicated for a period of 10 minutes to maintain the well-dispersed suspension of the desired material. 4.0 μL aliquot of the suspension was then drop casted

on a GC electrode and dried to yield an electrode surface modified with 4.0 μg film of the desired material.

Electrochemical activation was performed by applying an oxidation or reduction potential for a period of 300 s to procure their oxidized or reduced forms. For different TMD samples, the treatment was done in PBS pH 7 at a unique potential determined by the redox peaks in the study of their inherent electrochemistry. Exfoliated MoS_2 nanosheets were treated at +1.1 V (oxidation) or -1.3 V (reduction); exfoliated MoSe_2 nanosheets were treated at +1.0 V (oxidation) or -1.2 V (reduction); exfoliated WS_2 nanosheets were treated at +1.2 V (oxidation) or -1.6 V (reduction) and exfoliated WSe_2 nanosheets were treated at +1.0 V (oxidation) or -1.3 V (reduction). After treatment, the electrode was dipped in distilled water to rinse off any adsorbed materials and tested for heterogenous electron transfer (HET) rate using cyclic voltammetry at a scan rate of 100 mV s^{-1} in the presence of potassium ferrocyanide (5 mM) or hexaammineruthenium (III) chloride (5 mM) redox probes in potassium chloride (0.1 M) as the supporting electrolyte.

The k_{obs}^0 values were calculated using the method devised by Nicholson²⁸ that relates ΔE_p to a dimensionless parameter Ψ and consequently into k_{obs}^0 . The roughness of the electrode was not considered in the calculation of k_{obs}^0 . The diffusion coefficient $D = 7.26 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ was used to compute k_{obs}^0 values for $[\text{Fe}(\text{CN})_6]^{4-/3-}$.⁵⁴

The hydrogen evolution reaction (HER) efficiency of TMD materials were tested on glassy carbon (GC) electrodes. The GC electrode surface was renewed before modification with TMD materials using a 0.05 μm alumina particle slurry on a polishing pad and washing with ultrapure water. The desired materials encompassing exfoliated MoS_2 , MoSe_2 , WS_2 and WSe_2 nanosheets and Pt/C were prepared in suspensions of 1 mg mL^{-1} in ultrapure

water. These suspensions were ultrasonicated for 10 minutes to achieve homogeneity. The materials were immobilised on the GC electrode by depositing 4.0 μL aliquot of the suspended materials on the electrode surface. The solvent was left to evaporate at room temperature to yield a randomly distributed film of 4.0 μg of desired materials on the GC electrode surface.

Similar to the HET measurements, activation of the exfoliated MoS_2 , MoSe_2 , WS_2 and WSe_2 nanosheets was performed at pH 7.0 by applying their respective redox potentials for 300 s. HER measurements of these TMD materials were carried out using linear sweep voltammetry at a scan rate of 2 mV s^{-1} in 0.5 M H_2SO_4 electrolyte.

Linear sweep voltammograms are presented *versus* the reversible hydrogen electrode (RHE) using and the measured potentials are calculated using this equation⁵⁵ $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \times \text{pH} + E^0_{\text{Ag/AgCl}}$ where $E_{\text{Ag/AgCl}}$ is the measured potential, pH of 0.5 M H_2SO_4 electrolyte is zero and $E^0_{\text{Ag/AgCl}}$ refers to the standard potential of Ag/AgCl (1 M KCl) at 25°C which is 0.235 V.

11.5 Supporting Information

Figure 11.S1 Cyclic voltammograms of a) MoO_2 during the scan to positive potentials and b) the scan to negative potentials, c) MoO_3 during the scan to positive potentials and d)

the scan to negative potentials, e) WO_2 during the scan to positive potentials and f) the scan to negative potentials, g) WO_3 during the scan to positive potentials and h) the scan to negative potentials. Conditions: background electrolyte, PBS (50 mM), pH 7.0; scan rate, 100 mV s^{-1} ; all measurements are performed relative to the Ag/AgCl reference electrode.

Figure 11.S2 X-ray photoelectron spectra of survey scans of exfoliated MoS_2 , WS_2 , MoSe_2

and WSe_2 nanosheets before and after electrochemical oxidative or reductive treatment.

The survey spectra were calibrated with respect to C 1s peak at 284.5 eV.

Figure 11.S3 High resolution X-ray photoelectron spectra of chalcogen S 2p and Se 3d peak for untreated, electrochemically oxidized or reduced exfoliated MoS₂, WS₂, MoSe₂ and WSe₂ nanosheets.

Table 11.S1 Table of chalcogen-to-metal ratios, 1T, 2H and oxidized M(VI) states of untreated and electrochemically treated TMDs acquired from high resolution X-ray photoelectron spectroscopy. The calculated atomic percentages provide a general view of the relative changes in the TMDs before and after electrochemical treatment and should not be considered in absolute terms.

TMD Material	Chalcogen/Metal Ratio	1T (at. %)	2H (at. %)	M(VI) (at. %)
Ex MoS ₂	2.2	0	92.0	8.0
OX-Ex MoS ₂	2.6	0	71.9	28.1
RED-Ex MoS ₂	1.9	0	79.7	20.3
Ex WS ₂	1.4	6.7	39.1	54.2
OX-Ex WS ₂	1.3	10.4	45.6	44.0
RED-Ex WS ₂	1.4	26.4	42.1	31.5
Ex MoSe ₂	3.0	11.6	65.9	22.5
OX-Ex MoSe ₂	1.9	17.0	40.9	42.1
RED-Ex MoSe ₂	1.1	12.2	31.9	55.9
Ex WSe ₂	2.3	4.8	38.0	57.2
OX-Ex WSe ₂	2.3	0	55.1	44.9
RED-Ex WSe ₂	2.4	0	82.3	17.7

Table 11.S2 Table recording the Raman shifts (specifically, E_{2g} and A_{1g} phonon modes) and the full width at half maximum (fwhm) of the transition metal dichalcogenides before and after electrochemical treatment. Also shown are the relative intensity ratios of A_{1g} to E_{2g} modes.

TMD Material	Peak position of E_{2g} (cm^{-1})	fwhm of E_{2g} (cm^{-1})	Peak position of A_{1g} (cm^{-1})	fwhm of A_{1g} (cm^{-1})	$I(A_{1g})/I(E_{2g})$
Ex MoS_2	382.3	8.2	409.0	7.1	1.9
OX-Ex MoS_2	382.0	8.5	407.1	8.2	2.0
RED-Ex MoS_2	382.3	8.7	407.0	9.1	2.2
Ex WS_2	351.0	10.0	416.1	10.0	1.2
OX-Ex WS_2	351.6	11.1	418.0	9.9	1.3
RED-Ex WS_2	351.6	12.7	417.5	9.6	1.4
Ex MoSe_2	284.4	15.2	239.7	10.5	6.0
OX-Ex MoSe_2	284.9	10.2	241.1	10.3	8.8
RED-Ex MoSe_2	285.1	16.0	239.8	9.5	4.6
Ex WSe_2	246.5*	10.3*			
OX-Ex WSe_2	246.9*	9.4*			
RED-Ex WSe_2	246.7*	10.0*			

*Note: Due to the close proximity of E_{2g} and A_{1g} phonon modes in WSe_2 , the reported values contribute to the observed cumulative peak.

Figure 11.S4 Raman spectra of a wider wavenumber range to demonstrate WO₃ Raman signals also present in exfoliated WS₂ nanosheets before and after electrochemical treatment. $\lambda_{\text{exc}} = 514.5 \text{ nm}$.

Figure 11.S5 High resolution TEM images of exfoliated MoS₂, MoSe₂, WS₂ and WSe₂ nanosheets before (Untreated; left panel) and after anodic (Ox; middle panel) or cathodic (Red; right panel) electrochemical treatment. Scale bars represent 2 nm.

Table 11.S3 Table of heterogeneous electron transfer (HET) rate constant, k^0_{obs} for all the TMD materials before and after electrochemical treatment.

TMD Material	k^0_{obs} (cm s^{-1})
Ex MoS ₂	2.53×10^{-3}
OX-Ex MoS ₂	9.53×10^{-4}
RED-Ex MoS ₂	3.59×10^{-3}
Ex WS ₂	2.81×10^{-3}
OX-Ex WS ₂	7.65×10^{-5}
RED-Ex WS ₂	2.74×10^{-3}
Ex MoSe ₂	8.37×10^{-4}
OX-Ex MoSe ₂	2.80×10^{-4}
RED-Ex MoSe ₂	3.54×10^{-3}
Ex WSe ₂	1.67×10^{-3}
OX-Ex WSe ₂	2.45×10^{-4}
RED-Ex WSe ₂	2.75×10^{-3}

Figure 11.S6 Summary chart of HER onset potentials measured at a current density of -0.1 mA cm^{-2} for untreated, oxidized and reduced TMD materials with their corresponding error bars. GC and Pt/C are also included for comparisons.

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Chapter 12

Conclusion and Epilogue

12.1 Conclusion

12.1.1 *Electrochemistry of layered metal chalcogenides and trends*

12.1.2 *Strategies tailoring electrocatalytic efficiency of transition metal dichalcogenides for hydrogen evolution*

12.2 Epilogue

12.1 Conclusion

As Professor Sir David King has once described climate change – “We are now seeing the biggest opportunity of our age,” imparting the message of capitalising on the challenges that climate change brings; in particular, transforming fossil fuel-driven economies into low-carbon and sustainable economies. Reflecting the zeitgeist of climate change, on-going efforts are aimed at lowering the cost of technologies in clean and renewable energy production. Electrochemical hydrogen evolution reaction (HER) is a reigning champion as the choice of renewable energy production owing to the high energy density of hydrogen, the reliability of electrolysis, and most imperative is the prospective feasible storage and implementation across energy sectors. However, the electrochemical HER process has slow kinetics and relies on expensive platinum-based electrocatalysts. Therefore, this thesis investigates the prospect of a class of materials - layered metal chalcogenides, which are present in higher natural abundance than platinum, as low-cost HER electrocatalysts. The first part (**Part I**) of the thesis explored the electrochemistry of layered metal chalcogenides and establishes the electrochemical and catalytic trends for the wide spectrum of metal chalcogenides in the periodic table. The focus in the second part (**Part II**) of the thesis is Group 6 transition metal dichalcogenide (TMD) electrocatalysts wherein **Part II** examines novel methodologies for their activation as well as their fabrication to yield efficient hydrogen gas production.

12.1.1 Part I: Electrochemistry of layered metal chalcogenides and trends

The advent of molybdenum disulfide (MoS_2) as a promising layered electrocatalyst towards HER has fortified scientific interest in the layered metal chalcogenides. To date, an enormous slice of the research pie on layered metal chalcogenides is inclined towards

Group 6 TMDs; especially that of disulfides and diselenides, while other metal chalcogenides including the ditellurides and non-Group 6 TMDs received little attention. Understanding fundamental electrochemistry and electrocatalytic attributes of layered metal chalcogenides, along with their structure and surface composition, are vital when administering their use in electrochemical applications. **Part I** elucidates the electrochemical trends of the layered metal chalcogenides such as the metal- or chalcogen- dependence and discusses factors that may contribute to the HER performance of layered metal chalcogenides.

The layered metal chalcogenides that are of interest in **Part I** are namely the Group 5 TMDs, layered ditellurides (CoTe_2 and NiTe_2), thallium (I) sulfide (Tl_2S) and tin chalcogenides (SnS and SnS_2). Unlike Group 6 TMDs which are, by nature, semiconducting in the 2H-phase, the Group 5 TMDs (**Chapter 4**) are deemed to be metallic regardless of 1T- or 2H- polymorph. Two members of the ditelluride family; CoTe_2 and NiTe_2 , crystallise in marcasite-, pyrite- and CdI_2 related structures (**Chapter 5**). While NiTe_2 takes on a CdI_2 structure, CoTe_2 adopts an unconventional layered structure that is derived from CdI_2 containing a polymeric cobalt network. Most peculiar is the structure of Tl_2S , a Group 13 chalcogenide, which embraces an anti- CdI_2 type structure such that the chalcogen is sandwiched between metal layers (**Chapter 6**). This structure is the opposite of many TMDs like 1T- MoS_2 . Having different valence states of the metal constituent, the SnS and SnS_2 manifest in distinct structures whereby SnS is orthorhombic and SnS_2 is hexagonal akin to that of MoS_2 (**Chapter 7**). The differences in structures, chemical constituents and electronic properties between TMD families and across classes of metal chalcogenides elicit a point of interest for discussion pertaining to their electrochemistry and

electrocatalysis.

Surface oxides and the intrinsic electrochemical processes occurring on the layered metal chalcogenides account for their distinct inherent electroactivities. The metal chalcogenides are vulnerable to oxidation, resulting in surface metal oxides that are detected during characterisation of the materials. These surface oxides inadvertently participate in the electrochemical process and contribute to the inherent electrochemistry of the metal chalcogenides. The innate electroactive peaks ascribed to the tellurium chalcogen dictate the inherent electrochemistry of all transition metal ditellurides such as VTe_2 , NbTe_2 , TaTe_2 , CoTe_2 and NiTe_2 (**Chapters 4 and 5**). Ti_2S displays multiple inherent signals (**Chapter 6**). Comparing between SnS_2 and SnS , the former possesses higher inherent electroactivity evident in three distinct reductive signals in stark contrast to a single cathodic peak in the latter (**Chapter 7**). SnS is deemed to be generally electro-inactive. The inherent electrochemistry of the layered metal chalcogenides provides a glimpse of their electrochemical window of operation that would be crucial to electrochemical sensing.

The heterogeneous electron transfer (HET) property of the layered metal chalcogenides also delineates their suitability as electrode materials. Equipped with a HET rate (k_{obs}^0) of $3.4 \times 10^{-3} \text{ cm s}^{-1}$ based on measurements performed with $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox probe, TaS_2 stands out amongst Group 5 TMDs with its fast electrode kinetics as an ideal candidate as an electrode material in electrochemical sensing (**Chapter 4**). Chalcogen-dependence is also observed for electrochemical charge-transfer ability in the Group 5 TMDs where HET rates of ditellurides proceed slower than the disulfides and diselenides. In **Chapter 6**, a sluggish k_{obs}^0 as low as $6.3 \times 10^{-5} \text{ cm s}^{-1}$ has been reported for Ti_2S and

points to an unlikely electrode material in electrochemical applications. Between Sn chalcogenides, SnS₂ exhibits faster HET rate than SnS (**Chapter 7**). These findings will have implications on their electrochemical uses.

The electrocatalytic potential of these layered metal chalcogenides towards HER encompasses varying levels of competencies. Propitious Gibbs free energy of the adsorbed hydrogen (ΔG_H) for Group 5 TMDs acquired from past computational studies dubbed them as high-performing HER electrocatalysts with VS₂ at the helm. Tangential to this, **Chapter 4** experimentally documents moderate to mediocre catalytic behaviour of the Group 5 TMDs in bulk form wherein VTe₂ manifested best HER performance evident in its low overpotential of 0.5 V and Tafel slope of 55 mV dec⁻¹. Despite the HER performance of bulk Group 5 TMDs falling below expectations, intriguing chalcogen- and transition metal-dependence are respectively observed for the vanadium dichalcogenides (VS₂, VSe₂, VTe₂) and the Group 5 transition metal ditellurides (VTe₂, NbTe₂, TaTe₂). As revealed in **Chapter 5**, transition metal ditellurides such as CoTe₂ and NiTe₂ demonstrate low overpotentials and small Tafel slopes that are quintessential features of hydrogen evolution electrocatalysts. In particular, the fast HER kinetics of NiTe₂ is able to rival that of platinum as depicted in the almost Pt-like Tafel slope of 44 mV dec⁻¹. On the contrary to MoS₂, the anti-MoS₂ structured TI₂S is a weak electrocatalyst for HER (**Chapter 6**). Besides the poor conductivity of TI₂S, the catalytic performance of TI₂S is also impeded by the exothermic absorption energy that renders the desorption step difficult. Sn chalcogenides fare moderately as HER electrocatalysts; of which, SnS₂ projects stronger HER electrocatalytic behaviour than SnS (**Chapter 7**). The electrocatalytic performance of SnS₂ originated from the favourable ΔG_H at the S edges whereas all edges of SnS are found to be incompatible

for HER. The results communicate fundamental insights to various families of layered metal chalcogenides and provide a preliminary assessment of their inherent HER electrocatalytic property. TMDs discussed in **Chapter 4 and 5** are generally more apposite for HER electrocatalysts as affirmed by the stellar performance of layered CoTe_2 and NiTe_2 . Conversely, there is room for improvement for layered metal chalcogenides such as the Sn chalcogenides.

12.1.2 Part II: Strategies tailoring electrocatalytic efficiency of transition metal dichalcogenides for hydrogen evolution

Layered TMDs are esteemed for their catalytic attributes towards hydrogen evolution. Nevertheless, the electrocatalytic performance of the layered TMDs pales in comparison to that of the platinum electrocatalyst. In a bid to optimise their electrocatalytic properties, **Part II** investigates several innovative approaches, centring on the commonly studied Group 6 TMDs; MoS_2 , WS_2 , MoSe_2 and WSe_2 . These strategies include doping (**Chapter 8**) and electrochemical techniques of fabrication and activation (**Chapters 9-11**).

Doping of TMDs has long been a widespread method to activate their HER performance. Living up to expectations, the doping of WSe_2 with Group 5 transition metals (V, Nb or Ta) in **Chapter 8** showed enhanced HER catalytic efficiency. After doping, an increase number of active sites is observed in all doped WSe_2 . The doping process also appears to induce a phase transition from 2H to 1T phase given the dominance of the 1T-phase in all Group 5 transition metal-doped WSe_2 juxtaposed with the undoped WSe_2 which exists in 2H-phase. Therefore, this Chapter facilitates the understanding of Group 5 transition metal dopants on the electrochemical and catalytic properties of WSe_2 , in relation to their morphological features, and evaluates the efficacy of doping TMDs.

Subsequently, the electrochemical fabrication of TMDs is examined in **Chapters 9 and 10** as a viable alternative to the traditional procedures for synthesis in terms of ease, ecological sustainability and flexibility of deposition on various substrates under ambient conditions. **Chapter 9** demonstrates the successful synthesis of electrocatalytic porous MoSe_x films *via* solid template-assisted electrodeposition by electro-reduction. Depending on the size of the polystyrene bead template used, electro-fabricated porous MoSe_x films contain pores ranging from 0.1 to 1.0 μm diameters. The catalytic activity of the porous MoSe_x films of smaller pore sizes outperforms larger ones and may be reasoned by the tuneable surface wettability as pore sizes vary. Likewise, **Chapter 10** demonstrates a facile one-pot bottom-up synthesis of Pt-MoS_x composite by electrochemical reduction. By adjusting the millimolar concentration of Pt precursors, composites of different surface elemental composition are fabricated. All electrodeposited Pt-MoS_x hybrids showcase low overpotentials and Tafel slopes that surpass MoS_2 as an electrocatalyst. Pt-MoS_x composites are equipped with catalytic performance that closely mirrors that of electrodeposited Pt, in particular the HER kinetics for $\text{Pt}_{1.8}\text{MoS}_2$ and $\text{Pt}_{0.1}\text{MoS}_{2.5}$. Hence, these findings advocate the use of electrodeposition of TMDs as a cost-effective and feasible technique for designing an active electrocatalyst.

The consequence of electrochemical pre-treatment of exfoliated TMDs on the catalytic properties has been evaluated in **Chapter 11**. Towards the goal of activating the electrochemical and catalytic abilities of exfoliated MoS_2 , WS_2 , MoSe_2 and WSe_2 nanosheets, these TMDs are subject to a characteristic reductive or oxidative treatment that lies marginally beyond their inherent electrochemical signals. The HET rates of all TMDs are accelerated after a reductive treatment whereas an oxidative treatment hinders

their charge transfer property. The HER efficiency of MoS₂ is enhanced after a reduction, oxidized WS₂ performed poorly as a catalyst and the catalytic behaviour of diselenides are independent of redox treatment. Hence, this Chapter highlights the effective extent of electrochemical pre-treatment when activating the properties of TMDs for electrochemical applications.

12.2 Epilogue

The twenty-first century is a turning point for electrochemical technologies. Efficiency, versatility, environmentally-benign and sustainability are features that are at the heart of electrochemical systems and they coincide with the values that are increasingly important in society. It is envisioned that these trends will take flight into the future where hydrogen plays the leading role on stage as a clean energy carrier that fulfils the unabated surge in energy consumption and concurrently alleviates the threat of global warming. Despite the growing momentum for hydrogen, the challenge is to improve the economics of hydrogen; that is the production, storage, distribution and use.

While game-changers like the hydrogen-powered transportation provide a glimpse of a world in flux and the nascent paradigm shift, the quest for cost-effective electrocatalysts for the electrochemical hydrogen production remains at the early stage of research. The performance of layered metal chalcogenides as electrocatalysts needs to be further improved to achieve commercialisation. Modifying these materials in a precise and controlled manner by doping, introduction of surface groups and varying the morphology will be critical to the optimisation of the properties. The large-scale synthesis of layered metal chalcogenides is another area of interest to ascertain the uniformity, yield and affordability. To propel the development of advanced electrocatalysts, more studies are

required to establish the trends and factors affecting the catalytic activity by *in situ* characterisations and simulations will lend a hand in strengthening the knowledge of their catalytic nature. With successful efforts, we are one step closer to designing alternative materials that could parallel or even surpass expensive platinum-based electrocatalysts.

Presently, the volume of research channelled into the use of hydrogen in fuel cell applications outweighs the research on integrating hydrogen into the energy system. This disconnect presents a major pillar for future research. The key aspects to be implemented into a hydrogen-based energy system are generally capital-intensive. Besides production of hydrogen, the other elements are the storage, distribution and eventual use. For the widespread deployment of hydrogen to become a reality entails infrastructure design for storage, distribution and utilisation to be durable and resistant to hydrogen embrittlement.

Advancing collective research efforts towards catalytic materials and durable infrastructure to support the hydrogen-based energy system, the hydrogen dream will no longer be a distant future.

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