Molybdenum Disulfide as an Efficient

Catalyst for

Hydrogen Evolution Reaction

Dissertation

By

Abeer Ateeq Alarawi

In Partial Fulfillment of the

Requirements

Doctor of Philosophy

King Abdallah University of Science and Technology

Thuwal, Kingdom of Saudi Arabia

November, 2018
THE THESIS OF ABEER ALARAWI IS APPROVED

BY THE EXAMINATION COMMITTEE

Committee Chairperson: Prof. Jr Hau He

Committee Member: Prof. Enzo Di Fabrizio, Prof. Yu Han, and Prof. Song Jin.
ABSTRACT

Molybdenum Disulfide as An Efficient Catalyst For Hydrogen Evolution Reaction

Abeer Alarawi

Hydrogen is a carrier energy gas that can be utilized as a clean energy source instead of oil and natural gas. Splitting the water into hydrogen and oxygen is one of the most favorable methods to generate hydrogen. The catalytic properties of molybdenum disulfide (MoS$_2$) could be valuable in this role, particularly due to its unique structure and ability to be chemically modified, enabling its catalytic activity to be further enhanced or made comparable to that of Pt-based materials. In general, these modification strategies may involve either structural engineering of MoS$_2$ or enhancing the kinetics of charge transfer, including by confining to single metal atoms and clusters or integrating with a conductive substrate.

We present the results of synergetic integration of MoS$_2$ films with a Si-heterojunction solar cell for generating H$_2$ via the photochemical water splitting approach. The results of the photochemical measurements demonstrated an efficient photocurrent of 36.3 mA cm$^{-2}$ at 0 V vs. RHE and an onset potential of 0.56 V vs. RHE. In addition to 25 hours of continuous photon conversion to H$_2$ generation, this study points out that the integration of the Si-HJ with MoS$_2$ is an effective strategy for enhancing the internal conductivity of MoS$_2$ towards efficient and stable hydrogen production.

Moreover, we studied the effect of doping an atomic scale of Pt on the catalytic activity of MoS$_2$. The electrochemical results indicated that the optimum single Pt atoms loading amount demonstrated a distinct enhancement in the hydrogen generating, in which the overpotential
was minimized to -0.0505 V to reach a current density of 10 mA cm\(^{-2}\) using only 10 ALD cycles of Pt. The Tafel slopes of the ALD Pt/ML-MoS\(_2\) electrodes were in the range of 55–120 mV/decade, which indicates a fast improvement in the HER velocity as a result of the increased potential. Stability is another important parameter for evaluating a catalyst. The same (10 ALD cycles) Pt/ML-MoS\(_2\) electrode was able to continuously generate hydrogen molecules at for 150 hours.

These superior results demonstrate that the low conductivity of semiconductive MoS\(_2\) can be enhanced by anchoring the film with Pt SAs and clusters, leading to sufficient charge transport and a decrease in the overpotential.
ACKNOWLEDGMENTS

I would like to express my overwhelming gratitude to my research guide, Prof. Jr Hau He, for his expertise shown in guiding my work and the willingness to share his knowledge and experience. Also, I deeply thank my committee members Prof. Di Fabrizio, Prof Yu Han and Prof. Song Jin for their positive advising and comments.

Also, I would like to thank all the scientists in KAUST core labs for the support at all levels of the research. I find immensely enjoyable working with my dear lab colleagues. The discussion, experiments and lab time have all bonded us as lifetime friends.

A very special thanks and appreciation go out to my beloved husband Nayef for his patience, and support. My deep and utmost gratitude to my parent and my kids Melaph, Mayer and Yamin for their love and care during my PhD research period. Finally, I thank all my well-wishers and friends who have supported me in this thesis, especially Norah and Idris.

Above all, I thank God Almighty.
# TABLE OF CONTENT

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>TITLE PAGE</td>
<td>1</td>
</tr>
<tr>
<td>EXAMINATION COMMITTEE</td>
<td>2</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>3</td>
</tr>
<tr>
<td>ACKNOWLEDGMENT</td>
<td>5</td>
</tr>
<tr>
<td>TABLE OF CONTENT</td>
<td>6</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>10</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>14</td>
</tr>
<tr>
<td><strong>CHAPTER 1: INTRODUCTION AND BACKGROUND</strong></td>
<td>15</td>
</tr>
<tr>
<td>1.1 Introduction</td>
<td>15</td>
</tr>
<tr>
<td>1.2 General Background</td>
<td>18</td>
</tr>
<tr>
<td>1.2.1 HER mechanism</td>
<td>20</td>
</tr>
<tr>
<td>1.2.2 Free energy hydrogen adsorption</td>
<td>20</td>
</tr>
<tr>
<td>1.3 Primary Criteria for Evaluating Catalyst</td>
<td>21</td>
</tr>
<tr>
<td>1.3.1 Total electrode activity</td>
<td>21</td>
</tr>
<tr>
<td>1.3.2 Tafel plot</td>
<td>22</td>
</tr>
<tr>
<td>1.3.3 Stability</td>
<td>22</td>
</tr>
<tr>
<td>1.3.4 Faradic efficacy</td>
<td>22</td>
</tr>
<tr>
<td>1.4 MoS$_2$ as A Catalytic Material</td>
<td>23</td>
</tr>
<tr>
<td>1.4.1 Structural properties</td>
<td>23</td>
</tr>
<tr>
<td>1.4.2 MoS$_2$ for electrochemical HER</td>
<td>24</td>
</tr>
<tr>
<td>1.4.3 MoS$_2$ for photochemical HER</td>
<td>24</td>
</tr>
<tr>
<td>1.5 Synthesis Methods</td>
<td>26</td>
</tr>
<tr>
<td>1.5.1 Top-down methods</td>
<td>26</td>
</tr>
<tr>
<td>I. Mechanical cleavage</td>
<td>26</td>
</tr>
<tr>
<td>II. Liquid phase exfoliation</td>
<td>26</td>
</tr>
<tr>
<td>1.5.2 Bottom-up methods</td>
<td>27</td>
</tr>
<tr>
<td>I. Chemical vapor deposition</td>
<td>27</td>
</tr>
<tr>
<td>II. Hydrothermal synthesis</td>
<td>28</td>
</tr>
<tr>
<td><strong>CHAPTER 2: RESEARCH OBJECTIVES AND APPROACH</strong></td>
<td>30</td>
</tr>
<tr>
<td>2.1 OVERVIEW</td>
<td>30</td>
</tr>
<tr>
<td>2.2 State-Of-The Art</td>
<td>32</td>
</tr>
</tbody>
</table>
2.2.1 Strategies for improving MoS$_2$ catalytic activity for HER
   I. Thinning layers
   II. Create active sites

2.2.2 Strategies for enhancing electron transport of MoS$_2$ for HER
   I. Strain engineering
   II. Heteroatom doping
   III. Nonmetal atom doping
   IV. Metal atom doping
   V. Designing synergetic composites
   VI. Designing nanostructure
   VII. Coupling effect
   VIII. Employing metallic candidates

2.3 Recent Advances in Emerging Single Atom Confined MoS$_2$ for HER

2.3.1 Synthesis of SACs
   I. Atomic layer deposition (ALD)
   II. Wet chemistry synthesis
   III. High temperature pyrolysis
   IV. Metal-organic framework (MOF) derived SACs
   V. Metal/acid leaching
   VI. Mass-selected soft-landing

2.3.2 Characterization of SACs
   I. HADDF- STEM for SACs
   II. XANES and EXAFS for SACs

2.3.3 Single atom-2D support interactions
   I. SACs on MoS$_2$

2.4 Conclusion

CHAPTER 3: HYDROTHERMAL GROWTH AND CHARACTERIZATION OF MoS$_2$

3.1 Introduction

3.2 Synthesis of MoS$_2$

3.3 Characterization of MoS$_2$ Thin Films
   3.3.1 Raman spectroscopy
   3.3.2 Photoluminescence (PL)
3.3.3 X-ray photoelectron spectroscopy (XPS) 63
3.3.4 X-ray diffraction (XRD) 64
3.3.5 Scanning electron microscopy (SEM) 65

3.4 Electrochemical Studies 66
3.4.1 Linear sweep voltammetry (LSV) 66
3.4.2 HER mechanism (Tafel Slope) 67
3.4.3 Stability 67

CHAPTER 4: SYNERGISTIC HETEROSTRUCTURE OF MoS₂/Si-HJ 70
TOWARD PHOTOCHEMICAL HER

4.1 Introduction 70
4.2 Fabrication Details 73
   4.2.1 Synthesis of MoS₂ 73
   4.2.2 Si-HJ Photoelectrochemical cell fabrication method 73
4.3 Characterization Details 74
4.4 Characterization of MoS₂/Si-HJ Electrode 75
   4.4.1 SEM and TEM microscopies 75
   4.4.2 Photoelectrochemical measurements 77
4.5 Conclusion 82

CHAPTER 5: SINGLE Pt ATOMS CONFINED INTO MoS₂ TOWARD AN 83
EFFICIENT HYDROGEN EVOLUTION REACTION

5.1 Introduction 83
5.2 Electrode Fabrication Methods 85
   5.2.1 Synthesis of MoS₂ 85
   5.2.2 Doping of single Pt atoms into MoS₂ 85
5.3 Electrode Characterization Methods 86
   5.3.1 X-ray photoelectron spectroscopy (XPS) 86
   5.3.2 High resolution transmission electron microscope (HR-TEM) 88
5.4 Electrochemical Studies 91
5.5 Conclusion 98

CHAPTER 6: SUMMARY AND OUTLOOK 99

APPENDICES 102
   1. Publications 102
   2. Conferences and presentations 102
LIST OF FIGURES

**Figure. 1.1.** Various routes of energies are utilized for driving the water-splitting reaction including thermal, electrical, biochemical, and photonic, or their combination 16

**Figure. 1.2.** Schematic diagram of water splitting components, including the cathode, anode, and electrolyte 19

**Figure. 1.3.** A volcano plot shows the relation between the measured exchange current density and the DFT-calculating Gibbs free energy of the hydrogen on the catalyst surface. 21

**Figure. 1.4.** (a) Photograph image of MoS$_2$ crystal in the bulk shape. (b) 2D TMDC stacking layers. (c) A 2H, and 1T polytopes of MoS$_2$ 24

**Figure. 1.5.** Band edge position of the selected monolayers of TMDCs, calculated by density functional. The horizontal red dashed line is the redox potential of water splitting at pH = 0 and the green dashed line is at pH = 7; adapted from reference 25

**Figure. 1.6.** (a, b & c) Top-down methods of producing MoS$_2$, including mechanical, liquid, and electrochemical exfoliation, respectively. (d & e) Bottom-up methods of producing large-area MoS$_2$ 29

**Figure. 2.1.** Summary of the strategies for improving the catalytic performance of 2D nanomaterials for HER. 31

**Figure. 2.2.** A scheme illustrates the ALD deposition of Pt single atoms on graphene nanosheets 42

**Figure. 2.3.** A scheme of the synthesis of the Fe/NG catalyst by high-temperature pyrolysis 44

**Figure. 2.4.** Schematic of the synthetic procedure for MOF-derived W-SACs 45

**Figure. 2.5.** Schematic illustration for the fabrication of single Sn atom-doped N-doped CFs 46

**Figure. 2.6.** (a-f) HAADF-STEM images of single Ni, Co, Mo, Fe, Pt and Ru atoms anchored on graphene-based supports. (g) HAADF-STEM image of single atom Pt on MoS$_2$. (h&j) HAADF STEM image and EELS elemental analysis of single Fe atom doped graphene 48
**Figure 2.7.** (a) XANES and (b) FT-EXAFS spectra of A-Ni-NG, A-Ni-NSG, and NiPc catalysts

**Figure 2.8.** (a) EXAFS spectra of Mo$_1$Ni$_1$C$_2$. (b&c) High resolution N1s XPS and EXAFS spectra of Co atoms confined on an N-doped graphene (Co-NG) catalyst. (d) EXAFS spectra of Co–$^5$MoS$_2$. (e) HAADF-STEM images of Co–$^5$MoS$_2$. (f&g) HAADF image simulation and atomic model of Co–$^5$MoS$_2$

**Figure 2.9.** (a) TEM image of pure MoS$_2$. (b, c) HAADF-STEM images of Pt single atoms (red circles) confined in a MoS$_2$ plane. (d) Magnified view of the marked square region of (c), demonstrating that the Pt single atoms are substitutionally doped for Mo atoms (marked by red arrows). (e) EXAFS and (f) Pt L$_3$-edge XANES spectra of Pt-MoS$_2$, Pt foil, and commercial 40% Pt/C catalyst. (g-j) HAADF-STEM image and the corresponding EDX mapping images of the Pt-MoS$_2$ catalyst. (k) HER polarization curves of Pt-MoS$_2$, bulk MoS$_2$, few-layered MoS$_2$ (FL-MoS$_2$), and commercial Pt/C catalysts. (l) Corresponding Tafel slopes and (m) HER polarization curves of Pt-MoS$_2$ before and after 5000 CV cycles between -0.13 V and +0.57 V (vs. RHE) at 100 mV s$^{-1}$

**Figure 2.10.** Volcano plot of different configurations of various SACs confined in MoS$_2$ either if bonded with four (left) or six (right) S atoms. In the ball and stick molecular structures shown, the green balls refer to Mo atoms, yellow balls to S, and blue and purple balls represent the doped SACs

**Figure 3.1.** The hydrothermal decomposition synthesis method steps of producing MoS$_2$ thin films

**Figure 3.2.** (a) Raman-active frequency modes of MoS$_2$. (b) The corresponding Raman spectrum shows the frequencies of $E_{1g}^{1}$ and $A_{1g}$ Raman modes.

**Figure 3.3.** PL spectrum of multilayer MoS$_2$ in the photon wavelength range from 300 nm to 900 nm

**Figure 3.4.** (a) Chemical composition analysis spectra by XPS of the Mo 3d, S 2s and (b) S 2p peak regions for a multilayer film of MoS$_2$

**Figure 3.5.** (a) XRD pattern of the polycrystalline 2H-MoS$_2$ where the sharp peak centered at $2\theta = \sim 14.6^\circ$ corresponds to the (002) Bragg reflection plane

**Figure 3.6.** A top view SEM image of the multilayer MoS$_2$ film

**Figure 3.7.** (a) LSV curves of ML-MoS$_2$ and Pt electrodes measured in 0.5 M of H$_2$SO$_4$ at a scan rate of 100 mV/s. (b) Tafel plots for various electrodes in 0.5 M
H$_2$SO$_4$. (c) An illustration of the relation between the precursor concentration, overpotential, and Tafel slope. (d) Chronoamperometric electrolysis test of 1 M ML-MoS$_2$ over 66.6 h

**Figure. 4.1.** Schematic diagram illustrates the synergistic integration of the ML-MoS$_2$ film with the Si-HJ (PEC) cell

**Figure. 4.2.** (a) Top view SEM image of the multilayer MoS$_2$ film. (b) Top view of the pyramidal micro-structuring Si-HJ cell. (c & d) Cross section image of the dropped casting MoS$_2$ film above the Si-HJ PEC cell surface. (e&f) HR-TEM for the MoS$_2$ and Si-HJ interface area

**Figure. 4.3.** (a) LSV curves for ML-MoS$_2$/Si-HJ cell and 5 nm Pt/ Si-HJ cell photocathodes measured in 0.5 M H$_2$SO$_4$ under simulated 1 Sun irradiation. (b) The ML-MoS$_2$/Si-HJ photocathode’s response to on/off illumination. (c) The corresponding impedance spectroscopy (Nyquist plot) curves of ML-MoS$_2$/Si-HJ cell and MoS$_2$. (d) Stability photoelectrochemical test of ML-MoS$_2$/Si-HJ cell for 25 h of operation

**Figure 5.1.** XPS spectra of ALD Pt SAs/ MoS$_2$ electrodes with different ALD cycles ranged from 0 to 10: (a) Mo 3d spectrum; (b) S 2P spectrum; and (c) Pt 4f spectrum

**Figure. 5.2.** HR-TEM images of pure MoS$_2$ (a), 3 cycles ALD Pt/MoS$_2$ (b), 5 cycles ALD Pt/MoS$_2$ (c), 7 cycles ALD Pt/MoS$_2$ (d), 10 cycles ALD Pt/MoS$_2$ (e) and 30 cycles ALD Pt/MoS$_2$ (f) 30cycles ALD Pt/MoS$_2$

**Figure. 5.3.** (a) LSV curves of commercial Pt wire, ML-MoS$_2$, and different ALD cycles of Pt SAs and clusters confining MoS$_2$. (b) Tafel plots for commercial Pt, 2H-MoS$_2$, and of ALD Pt/MoS$_2$

**Figure. 5.4.** (a&b) EIS was used to analyze the charge transport of ML-MoS$_2$ and ALD Pt/MoS$_2$ (different cycles) electrodes. (c) XRD pattern of the polycrystalline ML-MoS$_2$ and 10 cycles ALD Pt/MoS$_2$ where the sharp peak centered at 20 = ~14.6° corresponds to the (002) Bragg reflection plane

**Figure. 5.5.** (a) I-t measurement of 10 ALD cycles Pt/MoS$_2$ electrode demonstrates a continuous HER process to generate hydrogen molecules. (b) Cyclic voltammetry for measuring 10 ALD cycles Pt/MoS$_2$ electrode stability before and after 150 hours.
Figure 5.6. XPS spectra of 10 ALD cycles Pt SAs/ MoS$_2$ electrode after LSV measurement (a) Mo 3d spectrum; (b) S 2P spectrum and (c) Pt 4f spectrum

Figure 5.7. (a-f) demonstrate the CV curves of bare MoS$_2$ and (different ALD cycles) of Pt/MoS$_2$ electrodes in the potential region of 0.1-1 V vs RHE

Figure 5.8. The $C_{dl}$ plots of bare MoS$_2$ and ALD Pt/MoS$_2$ electrodes, with different ALD cycles ranging from 3 to 10
LIST OF TABLES

Table 2.1: Summarizes the electrochemical performance values toward HER for different 2D materials support various single metal atoms kinds.

Table 3.1. Summary of the electrocatalytic characteristics of different MoS$_2$-based electrode structures.

Table 4.1. Literature summary based on MoS$_2$/Si photocathodes for PEC systems toward HER.

Table 5.1. The overpotential and Tafel slopes of commercial Pt, ML-MoS$_2$, and different ALD cycles of Pt confining the MoS$_2$. 
1.1 Introduction

By the middle of this century, energy consumption will have doubled compared to today due to world population growth, which is predictable to reach more than nine billion people. Nonrenewable energy sources, such as fossil fuels, will eventually exhausted; therefore, it is essential to develop alternative resources [1]. A potential substitute energy source is hydrogen, which is produced annually worldwide at a rate of more than 500 billion cubic meters (or 44.5 million tons). It is widely utilized in different industrial applications, for example, refining petroleum, generating ammonia, and chemicals preparation [2].

Unlike oil and natural gas, which are available on the earth, hydrogen does not be available naturally and must be manufactured. A variety of energy resources can be utilized to generate hydrogen, such as solar, nuclear, wind, hydro-electric, and geothermal powers and fossil fuels. Another way is by employing the water splitting reaction, in which there are different routes that can be used to produce hydrogen, such as by utilizing thermal, electrical, photonic, or biochemical energies [2]. These energies can be used alone or in combination for producing hydrogen, as summarized in Fig. (1.1) [7]. Once synthesized, hydrogen applied as an energy carrier gas for different storing and transporting applications [1].

Delving into more details, there are many ways of producing hydrogen, at various yields and purities. The thrombolysis method involves the production of hydrogen and oxygen by the chemical dissociation of water when thermal energy is applied at a temperature higher than 2500 K. Examples of this method include steam methane reforming (i.e., \( \text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2 \)).
3H₂) and coal gasification (i.e., 3C + O₂ + H₂O → H₂ + 3CO). Thermal energy is used to produce around 95% of the world’s hydrogen [1, 2]. In contrast, the electrochemical method of hydrogen synthesis relies on an electric current passing through water to chemically decompose it into hydrogen and oxygen at the respective electrodes. This method produces only 4% of the world’s hydrogen, though with high purity (100%) [3]. Meanwhile, photolysis of water means using the photonic energy to chemically break water into hydrogen and oxygen. Theoretically, around 70% of the sun’s radiation has a wavelength of 1008 nm (matches infrared light) which allow it to be eligible for producing H₂ from the water-splitting reaction that requires the potential of 1.23 eV [1]. Lastly, the biochemical energy that appears in microorganisms, such as green microalgae and cyanobacteria, can be combined with photonic energy (through the capture of solar light) to produce the hydrogen ions and oxygen from water splitting process. By the hydrogenase enzyme, the produced hydrogen ions are converted into hydrogen (i.e., 2H₂O + solar → 2H₂ + O₂) [1].

![Figure 1.1](image_url)

**Figure. 1.1.** Various routes of energies are utilized for driving the water-splitting reaction including thermal, electrical, biochemical, and photonic, or their combination [1].
Water electrolysis is a technique that can produce H₂ in an environmentally friendly way. Nevertheless, the main disadvantage of this method is its expensive cost. To solve this issue, incessant technological enhancement and new catalytic material innovation are required to significantly minimize the generation process cost. Particularly, the noble metal group is the best (however are the most expensive) hydrogen evolution catalysts for electrochemical water splitting. Therefore, involving earth-abundant catalysts can be considered as one of the best candidates for reducing the total cost of the hydrogen generation. [2].

Moreover, one of the most sustainable techniques for generating hydrogen is the photoelectrochemical water splitting method by direct solar-to-hydrogen conversion. To date, many photoactive materials have been investigated for use in this application. However, until now there is no known catalyst or combination of catalysts that meet the requirements for this process [4]. For example, most of the reported catalytic compounds exhibit either a small conversion efficiency or low stability, such as oxides [5], nitrides [6], carbides, and cadmium-based materials [7]. Also, some catalytic materials have a negative impact on the environment. Furthermore, even if noble metals exhibit acceptable efficiency, their scarcity rise the hydrogen fuel cost and prevent the large-scale production [4].

This thesis presents our research in an attempt to address these problems, specifically focusing on the adoption of electrolysis and photonic energy approaches for obtaining hydrogen via water splitting. Chapter 1 is an introduction to the research presented in this work. We then provide a brief background of water splitting fundamentals, the mechanism, the characteristics of using MoS₂ as a catalyst material and its synthesis methods. In Chapter 2, we present an overview of the research motivation and objectives. Additionally, Chapter 2 discusses state-of-the-art strategies applied in MoS₂ for enhancing its electrocatalytic and photocatalytic water splitting performance. Moreover, the literature review of recent advances in emerging single metal atom confined two-dimensional materials for water splitting applications is also
presented in Chapter 2. Discussion of the current work and obtained results are demonstrated in Chapters 3, 4 and 5. The thesis is concluded with Chapter 6, which addresses the research work summery, future prospects, and implications.

1.2 General Background

In general, the water splitting reaction consists of two half-reactions: the water oxidation reaction (OER) and the hydrogen evolution reaction (HER). The total reaction is described by Equation (1.1).

\[ \text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2} \text{O}_2 \]  

\[(1.1)\]

There are three required components of the electrochemical water splitting cell: the electrolyte (a solution, such as \(\text{H}_2\text{O}\)), the cathode, and anode. HER occurs on the cathode, while the OER takes place upon the coated anode, as illustrated in Fig. (1.2) [2]. For speeding the water splitting reaction, an external voltage are passed to the electrodes for separating the water molecules into hydrogen and oxygen. The following equations illustrate the chemical reaction at each electrode [2]:

Cathode \[ 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2 \]  

\[(1.2)\]

Anode \[ \text{H}_2\text{O} \rightarrow 2\text{H}^+ + \frac{1}{2} \text{O}_2 + 2\text{e}^- \]  

\[(1.3)\]

The thermodynamic voltage of water splitting is 1.23 V at 25 °C, regardless of media in which the water splitting takes place. In reality, to achieve electrochemical water splitting we need to exceed the intrinsic activation barriers that exist on both the anode (\(\eta_a\)) and cathode (\(\eta_c\)), in addition to other resistances (\(\eta_{other}\)) by applying voltages higher than the thermodynamic potential. This excess potential is known as the overpotential (\(\eta\)), and the sources of added resistance include the solution resistance and contact electrode resistances [2]. Therefore, the practical operational voltage (\(E_{op}\)) for water splitting can be described as:
\[ E_{op} = 1.23 \ V + \eta_a + \eta_c + \eta_{other} \quad (1.4) \]

**Figure 1.2.** A Schematic diagram of water splitting components, including the cathode, anode, and electrolyte [2].

As presented in Equation (1.4), efficient water splitting requires reducing the total over-potential in one of four ways. First, optimizing the design of the electrolytic cell helps reduce \( \eta_{other} \). Second, minimizing the values of \( \eta_a \) and \( \eta_c \) by selecting an active catalytic material (catalyst) for oxygen and hydrogen evolution, respectively. Third, optimizing the method of electrode preparation can lead to a larger effective active area. Finally, reducing the bubbles that are appeared on the electrode surface helps to increase the exposed effective active area, which helps lower the reaction over-potential [2]. This thesis focuses only on the HER process. Therefore, the OER mechanism will not be covered in the following discussions.
1.2.1 HER mechanism

In fact, the HER mechanism in the alkaline electrolyte is quite unclear; however, in the acidic electrolyte, the HER mechanism generally involves two reaction steps.

Firstly, in the Volmer step, the electron and proton generates an adsorbed hydrogen atom (H_{ads}) on the electrode surface (H^{+} + e^{-} → H_{ads}). The second step after H_{ads} generation is the HER process, which can be accomplished either by the Tafel step (2 H_{ads} → H_{2}), or the Heyrovsky step (H_{ads} + H^{+} + e^{-} → H_{2}), or by both. In both paths, adsorbed hydrogen atoms at the electrode surface govern the HER process regardless of which route reaction taking place [2].

1.2.2 Free energy of hydrogen adsorption (ΔG_{H})

The Gibbs free energy of hydrogen adsorption (ΔG_{H}) on the electrode catalyst material has been utilized as a respectable descriptor of the intrinsic activity of the catalyst for HER [8]. Hydrogen surface bonding always controls the adsorption step and affects the overall reaction rate. Fig. (1.3) displays a volcano shaped plot of the connection between the exchange current density (a measure of catalytic activity) and ΔG_{H}. Pt metal occupies the top of the volcano plot with the best known activity and almost zero hydrogen absorption energy. The metals located on the left side of Pt bind H_{ads} strongly to the electrode surface, which can block the active sites and fail to evolve hydrogen. This leads to a relatively facilitated initial Volmer step, but difficult subsequent Tafel or Heyrovsky steps, and results in a small and positive ΔG_{H}. In contrast, the metals on the right side of Pt have a weak H_{ads} bond to the electrode surface, which fails to stabilize the intermediate state and prevent any reaction from occurring. As a result, a slow Volmer step will occur, which borders the overall turnover rate and therefore ΔG_{H} can be large and negative [2, 9]. The perfect catalyst material must have a hydrogen adsorption energy close to ΔG_{H} = 0 and bind hydrogen neither too weakly nor too strongly [8].
Figure 1.3. A volcano plot shows the relation between the measured exchange current density and the DFT-calculating Gibbs free energy of the hydrogen on the catalyst surface [9].

1.3. Primary Criteria for Evolution Catalysts

To measure, calculate, and elucidate the HER catalytic activity of a given catalyst material, there are some significant parameters that can be used, including the total electrode activity, the Tafel slope, stability, and faradic efficiency.

1.3.1 Total electrode activity

Even though there is no specific manner of judging the activity of catalysts for HER, there are two special overpotentials in the reaction that are repeatedly provided to compare the total electrode catalyst activity between materials. The first one is the “onset potential” (Ƞₒ), which is indicated at a catalytic current density of -1 mA cm⁻². The second is the “overpotential” (Ƞ) that is measured at an electrocatalyst current density of -10 mA cm⁻². At this current density value, the expected solar energy to water-splitting device efficiency is 12.3% [2]. We can calculate those overpotentials by applying cyclic voltammetry (CV) or linear sweep voltammetry (LSV).
1.3.2 Tafel plot

A Tafel plot demonstrates a logarithmic relation between the electrochemical current density \( j \) and a variety of overpotentials, as indicated by the Tafel equation \( \eta = a + b \log j \). Two important parameters can be derived from this equation, including the Tafel slope \( (b) \) or the exchange current density \( (j_0) \) at a zero value of \( \eta \). The Tafel slope indicates the intrinsic catalytic activity of the used catalyst. In general, a high \( j_0 \) and a small Tafel slope are required for an efficient catalytic material [10, 11].

1.3.3 Stability

The catalyst’s stability in the harsh media at pH extremes (pH 0 or 14) provides an estimate of whether the structural and catalytic properties of the electrode will be stable for HER. To characterize the electrocatalytic electrode stability, we can either measure how the current varies with time (I–t curve) or perform CV. For the I–t curve, the current density has to be larger than 10 mA cm\(^{-2}\) for more than 10 hours to indicate the catalyst is stable, while for CV measurements the number of cycles have to be more than 5000 cycles [2, 11].

1.3.4 Faradic efficiency

Faradic efficiency for electrochemical HER is expressed as the ratio of the experimentally measured \( \text{H}_2 \) produced to the theoretical amount, which can be calculated from the current density based on a 100% Faradaic yield. Also, it describes the electrons efficiency that involved in HER reaction [11]. In summary, low overpotential, low Tafel slopes, and a high exchange current density are preferred in hydrogen water splitting.
1.4 MoS$_2$ as a Catalytic Material

1.4.1. Structural properties

Molybdenum disulfide (MoS$_2$); Fig. (1.4.a) is a transition metal dichalcogenide (TMDs), a class of materials that feature the formula MX$_2$ and layered structures that form X–M–X. In this formula, M is a transition metal from group IV (e.g., Ti, Zr, Hf, etc.), group V (e.g., V, Nb, or Ta) or group VI (e.g., Mo, W, etc.). Chalcogen elements, such as S, Se, or Te, make up the X element of the compound. These materials form stacking layers where the chalcogen atoms are in two layers separated by a layer of metal atoms, in which each layer features a thickness of ~6–7 Å, as shown in Fig. (1.4.b) [8]. The intra-layer M–X bond is composed of a covalent bond while the layers are bonded by weak van der Waals forces [11].

In general, MoS$_2$ is similar to other TMDCs in that their crystal coordination structure is either hexagonal or rhombohedral. Also, the metal atoms have octahedral or trigonal prismatic symmetry. Moreover, the electronic property of MoS$_2$ ranges from metallic (1T) to semiconducting (2H). The band gap can be modified by changing the number of layers and therefore the thickness of the material. For example, MoS$_2$ in the bulk phase (Fig. (1.4.a, c)) has an indirect bandgap of 1.3 eV, which converts to a direct bandgap of 1.8 eV in the mono-layer form [8].
Figure 1.4. (a) Photograph image of MoS$_2$ crystal in the bulk shape [8]. (b) 2D TMDC stacking layers [8]. (c) A 2H and 1T polytopes of MoS$_2$ [8].

1.4.2. MoS$_2$ for electrochemical HER

We believe MoS$_2$ is a favourable candidate for replacing the noble-metal-based catalysts for HER due to the following reasons. First, based on its free energy of hydrogen adsorption (Fig. (1.3)), MoS$_2$ demonstrates a modest $\Delta G_H$ value which close to zero, and demonstrates a high $j_0$, both of which suggest its ability to efficiently generate H$_2$ [12]. Second, MoS$_2$ has an ultra-large specific surface area, where the number of the exposed active sites on the surface can be comparable to the total number of atoms. Third, the ultrahigh specific surface area permits this material to be coupled with other substrates. Fourth, the catalytic activity can be easily enhanced by chemical modification, such as by regulating defects [12], strain [13], and doping with a single atom [14].

1.4.3. MoS$_2$ for photochemical HER

As demonstrated in Fig. (1.5), the majority of single-layer MX$_2$ materials have band edge energies that are uncomplimentary for photocatalytic water splitting without applying an external bias potential. Even though MoS$_2$ has the ability to split water, because of its band edge positions and Fermi level that can align with the redox potentials of the electrolyte (0 eV for H$^+/H_2$ and 1.23 eV for O$_2$/H$_2$O) [4], it has a Fermi level position that is slightly more
positive than that required for HER, which suggests using MoS$_2$ as a candidate for a tandem approach to catalyzing this reaction.

By considering the mechanism of photocatalytic water splitting, the photocatalytic process can be described through two approaches. In the first approach we must consider the exciton (electron-hole pair) binding energy that needs to overcome the conduction and valence band energies and then must be well aligned energetically with the water redox potentials [15]. As a result, the exciton can split into an electron in the conduction band maximum (CBM), and a hole in the valence band minimum (VBM) and then diffuse separately to react with the electrolyte. The second approach is controlled by the excitons which directly react with water. The exciton binding energy must not reduce the CBM and VBM levels too much as to make the redox reaction unfavorable [15].

![Figure 1.5](image)

**Figure 1.5.** Band edge position of the selected monolayers of TMDCs, calculated by density functional. The horizontal red dashed line is the redox potential of water splitting at pH = 0 and the green dashed line is at pH = 7; adapted from reference [15].
1.5 Synthesis Methods

Like other TMDCs, MoS$_2$ exists in a bulk form in which the structural stacking arrangement allows for exfoliation of the material into individual and atomically thin layers [16]. Therefore, this section discusses the available synthetic methods for producing ultra-thin layers of MoS$_2$, which can either be categorized as top-down exfoliation techniques from bulk materials or bottom-up growth methods (Fig. 1.6) [17].

1.5.1 Top-down methods

I. Mechanical cleavage

Micromechanical cleavage (using adhesive tape) has been used to peel the thin flakes of MoS$_2$ from their parent bulk crystals. This method produce very pure and clean single-crystal flakes that appropriate for using in the fundamental characterization and devices fabricating. The disadvantage of this method is not suitable for the large-scale applications and the difficulty with controlling the size and thickness [16].

II. Liquid-phase exfoliation

The liquid phase exfoliation method involves intercalation of ionic species to exfoliate layered materials. One example of this method involves submerging MoS$_2$ powder in a solution of n-butyl lithium to intercalate between the layers, followed by exposing the material to water. The water reacts vigorously with the lithium to evolve H$_2$ gas, which rapidly separates the layers [18]. In this exfoliation method, the resulting material has different structure and electronic from its bulk counterpart. In this exfoliation method, the resulting material has different structure and electronic from its bulk counterpart. In particular, MoS$_2$ electronic structure converts from the semiconducting (trigonal) to metallic phase (octahedral). Annealing at 300 °C can retain back the 1T-MoS$_2$ phase to 2H-MoS$_2$, rearranging the Mo atom coordination and the semiconducting bandgap [19]. The current challenges in this method involve controlling
the location and amount of the 1T phase through controlled exposure of single-layer MoS$_2$ to Li. Also, the experiment is required to high temperature (100 °C) for a long time duration (three days) [16]. This method enables additional and more scalable applications of layered compounds, such as composites and hybrids, and thin films and coatings [19].

1.5.2 Bottom-up methods

Inventing new methods for synthesizing MoS$_2$ that has the large-scale and uniform layer's thickness is an important stage for several industrial applications. Chemical vapor deposition (CVD) and hydrothermal synthesis are two effective bottom-up methods of producing MoS$_2$.

1. Chemical vapor deposition (CVD)

This method can be applied to a wafer-scale substrate, such as graphene, Cu foil, and insulating and epitaxial growth on SiC substrates. In general, it requires solid precursors and high-temperature heating. Using CVD, MoS$_2$ has been synthesized by several approaches, such as vaporizing sulfur and MoO$_3$ powders to directly deposit MoS$_2$ onto a nearby substrate [20]. Sulfurization of a thin layer of Mo metal that was previously sputtered onto a heated wafer is another CVD-based method [21]. Moreover, dip coating a substrate in a solution of (NH$_4$)$_2$MoS$_4$ and then heating the material will decompose the precursor to MoS$_2$ [22]. Moreover, the final MoS$_2$ film thickness is dependent on either the precursor concentration or initial precursor thickness. Particularly, the CVD method is appropriate for the synthesis of high-quality and uniform MoS$_2$ sheets with controllable size and thickness. However, the inflexible experimental conditions, such as high temperature, high vacuum, and specific substrates, limit practical applications of the MoS$_2$ sheets [19, 23].
II. Hydrothermal synthesis

Preparing MoS$_2$ nanosheets by hydrothermal synthesis required chemical reaction between the metal-salts precursors. Utilization of the low-cost precursors (for example metal salts or earth-abundant MoS$_2$ powders) is an advantage of this method comparing to other methods. In addition, hydrothermal synthesis is a scalable technique that can be used for the production of good quality MoS$_2$ nanosheets with desirable size and thickness. Also, It is a relatively easy method in which it enables the MoS$_2$ products to be conveniently transferred onto other substrates using a simple exfoliation process [23].

Figure 1.6. (a-c) Top-down methods of producing MoS$_2$, including mechanical, liquid, and electrochemical exfoliation, respectively. (d & e) Bottom-up methods of producing large-area MoS$_2$ [17].
CHAPTER 2
RESEARCH OBJECTIVES AND APPROACH

2.1. OVERVIEW

Air pollution and global warming are correlated with the current hydrogen production methods that utilize fossil fuels. Therefore, adopting new renewable technologies for generating H\textsubscript{2}, such as electrochemical water splitting, is undoubtedly important for the future of this clean energy source. Noble metals catalyst based are the best known efficient catalysts for HER; however, they limit water splitting applications due to their cost value and relative scarcity on Earth. Accordingly, substitution of Pt with low-priced, abundant catalysts would be massively promising for the sustainable production of hydrogen [12, 24].

Currently, involving 2D nanomaterials that have low cost, such as Transition metal dichalcogenides (TMDs) [25, 26], transition metal carbides [27], transition metal oxides [28], transition metal nitrides [29], transition metal selenides [30], and transition metal phosphides [31], have received significant attention for catalyzing hydrogen production. As discussed in Chapter 1, the unique characteristics of MoS\textsubscript{2} make it preferable as a catalytic material for achieving the high performance necessary for catalyzing HER [32, 33]. The basal surface of MoS\textsubscript{2} is catalytically inert, however, it can be chemically modified to improve its performance. Consequently, many research groups have spent effort on enhancing the use of MoS\textsubscript{2} as a catalyst for HER under the guidance of the fundamental mechanism (Fig. 2.1)) and based on its unique plenary structure and electrical characteristics [12].

There are several strategies that can be applied to enhance the catalytic activity of MoS\textsubscript{2} toward HER (Fig. 2.1) [12]. These strategies can involve either increasing the number of active sites on the surface of the material or increasing its electrical conductivity. Obtaining more active
sites has been examined by exposing more edges or creating active defects using plasma [34] or thinning the layers by exfoliation [35]. In contrast, accelerating the kinetics of charge transfer and enhancing the conductivity can be achieved by using approaches such as heteroatoms doping [36], applying strain in the basal plane [13], or coupling with conductive materials or substrates [37].

**Figure. 2.1.** Summary of the strategies for improving the catalytic performance of 2D nanomaterials for HER [12].
In this thesis, we elaborate the results of some strategies for enhancing the HER performance of MoS$_2$ based on its superior characteristics and features. The main two proposed strategies that we used to improve the hydrogen evolution performance of MoS$_2$ are:

- **Coupling MoS$_2$ with a conductive substrate, such as a Si heterojunction solar cell.**
- **Anchoring a single metal atom, such as Pt, into MoS$_2$.**

We believe this thesis will provide deep insight into MoS$_2$ nanomaterial catalysts for HER and will help establish a new research direction in the electrocatalytic field.

**2. 2. STATE-OF-THE-ART**

**2. 2. 1. Strategies for enhancing the MoS$_2$ catalytic activity for HER**

It is important for the catalysts in electrochemical hydrogen evolution to have abundant active sites and high catalytic ability. The active sites in ultrathin 2D TMDC materials originate at the unsaturated metal or nonmetal edges, therefore, thin layers can help expose these active edges that were originally embedded in the bulk phase. For the inert basal plane, creating more active sites by applying edge and defect engineering has also been reported to improve the HER activity of the material [38, 39]. As this thesis will focus mainly on enhancing the internal conductivity of the MoS$_2$, we briefly review the literature of strategies for increasing the catalytic active edges.

**1. Thinning layers**

There are two methods for reducing the thickness of MoS$_2$ layers, including exfoliation [35] and CVD [20]. The weak van der Waals forces between the MoS$_2$ layers facilitate exfoliation to generate ultrathin sheets. In contrast, the advantage of using direct CVD growth lies in controlling the thickness of the layers. However, the effect of the layer-dependent mechanism in the electrochemical HER method is incomprehensible due to the complexity of the reaction...
in the electrolyte [12]. In addition to exfoliation and CVD methods, ball milling route [40] and the template method (for example utilizing a template contains mesoporous silica) [41] are other examples of methods for thinning the layers of MoS$_2$. In summary, decreasing layer numbers to the monolayer leads to an increase in the active sites which possibly can expose more edges and enhance the catalytic performance for HER [12].

**II. Creating active sites**

As mentioned previously, the catalytically active sites on MoS$_2$ are located at the edges of the material, whereas the basal surfaces do not feature any obvious catalytic activity. Consequently, creating more active sites is a viable strategy for improving the HER activity, which can be accomplished by edge and defect engineering of the basal plane. The key influence on HER performance by defect engineering is to generate more catalytic edges at the catalyst surface by introducing structural defects such as pores, terraces, low coordinated atoms, kinks, and corner atoms. The number of defects is considered important in the catalytic ability of MoS$_2$ [12]. On the other hand, the physical defects are produced by using an argon or O$_2$ plasma for changing the electronic characteristics of MoS$_2$ and activate the insert in-plane sulfur atoms [34].

**2. 2. 2. Strategies for increasing the electron transport of MoS$_2$ for HER**

In aiming to create a perfect catalyst for HER, sufficient active sites and fast charge transfer is needed. MoS$_2$ is categorized as either being intrinsically metallic, with fast electron transport properties that can help increase the catalytic activity of the material, or semiconducting, in which poor conductivity limits the HER kinetics. Therefore, researchers have been studying ways of enhancing the electron transport for improved HER catalysis. Strain engineering [13], heteroatom doping [42], synergetic composites [43], and employing metallic candidates [44] are all example strategies for accelerating the kinetics of charge transfer in MoS$_2$. 
I. Strain engineering

Because of the 2D materials atomic thickness and high elasticity, the strain has been readily applied to produce a lattice deformation. The strain has an impact on the d-band electronic structure, making it nearer to the Fermi level and, thus, leading to improved electron transfer rates of hydrogen adsorption. Therefore, the dissimilarity in gap states due to the strain is a key factor for improving HER performance. Researchers have grown MoS$_2$ on a curved surface of nonporous gold to introduce external strain [45]. In another example, Zheng et al. doped S vacancies into monolayer 2H-MoS$_2$ to introduce strain, resulting in creating a new valence band near to the Fermi level that facilitates charges transferring and bonding with hydrogen atoms [13].

II. Heteroatom doping

Doping heteroatoms into MoS$_2$ can deform the basal plane or expand the interlayer spacing. This doping strategy can be utilized to modify the d-band electronic properties of the material and decrease the hydrogen adsorption free energy, which leads to improve the HER process. In general, there are two approaches to doping: nonmetal [46, 47] and metal-based [48], both of which can boost the rate of charge transfer.

III. Non-metal- atoms doped

Many kinds of non-metals have been doped in MoS$_2$ to produce unique characteristics that improve the efficiency of hydrogen water splitting. For example, Xiang et al. reported modulating the band gap of MoS$_2$ nanosheets by controlling the proportion of Se content in semiconducting MoS$_2$$_{(1-x)}$Se$_{2x}$ alloys ($x = 0.39$, 0.51, 0.61). Doping Se atoms into ultrathin MoS$_2$ nanosheets can help achieve a more appropriate $\Delta G_H$ than that of pure MoS$_2$ or MoSe$_2$, resulting in an efficient hydrogen separation from the surface of monolayer MoS$_2$$_{(1-x)}$Se$_{2x}$ [49]. Alternatively, T, S, O, and H atoms can also be doped in MoS$_2$ to enhance its HER performance
by reducing its bandgap [12]. For example, Yan et al. synthesized ultrathin S-doped MoSe$_2$ nanosheets to create extra donor levels in the forbidden gap. The doped defects and residual strain produce a narrowing band gap, which increases the electrical conductivity of the material and improves the catalytic performance of S-doped MoSe$_2$ compared to intrinsic MoSe$_2$ [50].

**IV. Single metal atoms doping**

Single metal atoms can be also introduced into 2D TMDCs (as co-catalyst) for achieving an efficient H$_2$ generation process. It has been proposed that doping vanadium (V) into the semiconductor phase of MoS$_2$ transforms the material into a semimetal. Subsequently, the defect sites produced by V doping can enhance the carrier concentration and enhance the electron transferring process between the overlapping nanosheet edges [51]. Moreover, to promote the initial discharge of the alkaline or acid solutions, Co$^{2+}$ and Mo$^{4+}$ centers have been proposed by Markovic et al., in which he synthesized a highly robust CoMoS$_x$ catalyst by combining higher activity CoS$_x$ with the higher stability of MoS$_x$. It was proposed that in the active sites the defects take place by dissolving Co and Mo cations. Particularly, this doping type has the ability to solve the instability of CoS$_x$ materials issue and generate H$_2$ in both alkaline and acid media [52].

**V. Designing synergetic composites**

For accelerating the electrons transport process in electrochemical HER, some synergetic composites have been explored to take advantage of the intrinsically high catalytic activity of 2D nanomaterials, such as MoS$_2$, while addressing their poor conductivity. Synergy with C-based substrates has feature particular promise, as the excellent conductivity and perfect stability of the conductive carbon materials, such as graphene, carbon nanotubes, and other carbon-based compounds, that have been employed in combination with 2D TMDC catalysts to increase the total HER activity. In this regard, to enhance the electrochemical current density
to a large degree, Coleman et al. reported the combination of MoS\textsubscript{2} nanosheets with single-walled carbon nanotubes, which helped to activate otherwise inaccessible MoS\textsubscript{2} sites and build more conductive channels for charge transfer [53]. In general, utilizing nanostructures and employing active material/substrate coupling effects are effective ways of designing synergetic composites.

**VI. Designing nanostructures**

Depositing stacked 2D TMDC layers on conductive substrates limits the charge transport to the active sites. Accordingly, appropriate nanostructure design is needed to improve the electron transfer process for higher catalytic performance of HER. With this in mind, Chen et al. employed porous metallic MoO\textsubscript{2} as a substrate for MoS\textsubscript{2} to create a MoS\textsubscript{2}/MoO\textsubscript{2} catalyst, which also featured high electrical conductivity [54]. In addition, Liu’s group proposed coupling of 2D tiny MoS\textsubscript{2} nanoplates with graphene sheets. As result, the conductivity was increased due to the rapid electron transfer in the whole atomic basal plane [55]. In addition, vertically oriented core-shell MoO\textsubscript{2}/MoSe\textsubscript{2} nanosheet arrays grown on insulating SiO\textsubscript{2}/Si wafers or conductive carbon cloth have also shown promise. This core-shell nanostructure array exhibits synergistic effects that generate superior HER performance, in which high-density defects and disorder on the shell created by a large crystalline mismatch between MoO\textsubscript{2} and MoSe\textsubscript{2} provide abundant active sites for HER while the metallic MoO\textsubscript{2} inside the core accelerates charge transport for H\textsubscript{2} production [56].

**VII. Coupling effects**

Coupling the conductive substrate with the catalyst leads to reduce the contact resistance, accelerate charge transfer kinetics, and minimize the energy of hydrogen adsorption, that resulting in efficient HER performance. From this respect, Chhowalla and his group reported the electronic coupling between the substrate and 2H-phase MoS\textsubscript{2} nanosheets for reducing the
contact resistance between the supports and the active catalysts [37]. Consequently, the coupled structure demonstrated an excellent HER performance, which had never previously been achieved for the intrinsic 2H-phase of MoS$_2$ and where SiO$_2$ on Si wafers were utilized to load the MoS$_2$ catalysts [37]. Briefly, fabricating a composite by coupling two or more different materials has been considered a convenient and exciting strategy to maximize the advantages and minimize the drawbacks of each individual component to accomplish significant improvements to the HER process.

VIII. Employing metallic candidates

The chemical composition and phases of TMDC materials govern their electronic properties, being either semiconducting, metallic, or superconducting. Taking MoS$_2$ as an example, it has two phases: 2H-MoS$_2$ (semiconductor) and 1T-MoS$_2$ (metallic) [44]. These two MoS$_2$ phases exhibit a quite different HER catalytic activity. For 2H-MoS$_2$, the active sites originate only from uncoordinated S atoms at the edges of the material, while for 1T-MoS$_2$, the basal surface is also catalytically active. Therefore, metallic TMDCs can be employed as competitive candidates for catalyzing HER. Simultaneously, more faster charge transfer could be achieved by utilizing this phase due to the intrinsic metallic characteristic of 1T-MoS$_2$ [57].

2.3 Recent Advances in Emerging Single Atom Confined MoS$_2$ for HER

Tremendous efforts have been devoted to developing heterogeneous catalysts based on noble metals, non-noble metals, non-metals, and metal oxides to improve the performance of various electrochemical reactions [58]. Among them, noble-metal-based catalysts have been extensively investigated due to their unique electronic and catalytic properties [59-62]. However, the high cost and scarcity of precious metals greatly hampers their usage for various catalytic applications. As a result, significant efforts have been taken to replace noble metals with different inexpensive non-noble metals and metal-free catalysts [63]. Unfortunately, these
materials tend to suffer from poor conductivity and diminished catalytic properties compared to that of noble metals [64]. Therefore, increasing studies have been devoted toward the development of catalysts that utilize a minimal amount of noble metal resources. It is well known that the heterogeneous catalytic process usually occurs at the surface of the catalyst [65]. In the case of metal-nanoparticle-based catalysts, only the small portion of the metal atoms that are exposed to the reactants can act as catalytically active centers while the remaining material is not involved in the reaction and thereby simply wasted [7]. In addition, metal catalysts with irregular morphologies, non-uniform distribution, and different particle sizes can produce multiple active sites that affect the selectivity toward specific products [66]. Reducing the size of the metal nanoparticles to sub-nanometer or atomic-scale can address these issues by significantly increasing the number of catalytic active sites on the surface of the catalyst where virtually all isolated metal atoms are ideally accessible to reactants [67]. Atomic-sized metal catalysts have the following interesting properties, including: i) atomically dispersed metal centers [68]; ii) coordinatively unsaturated metal active sites [69-71]; iii) electron confinement/quantum size effects [72-75]; and iv) metal-solid support interactions [76, 77]. These interesting properties of metal atom catalysts could simultaneously improve both the catalytic activity and selectivity of the materials for various electrochemical reactions.

Zhang and his co-workers first proposed the concept of single atom catalysts (SACs) in 2011 through the development of individual Pt atoms incorporated in iron oxide (Pt/FeO₅) to form a catalyst for CO oxidation [78]. SACs consist of isolated single atoms that are uniformly dispersed on a solid support and are prepared using different techniques, such as atomic layer deposition (ALD), mass selected soft landing, high temperature thermal annealing, wet chemistry, etc., [79, 80]. For example, Pt single atoms on nitrogen-doped graphene nanosheets were synthesized using ALD [81], in which Pt atom sizes were controlled by limiting the number of ALD cycles. SACs have shown extraordinary catalytic activity compared to their
nanoparticle or bulk-metal counterparts toward various electrochemical reactions, including the hydrogen evolution reaction (HER) [82], oxygen evolution reaction (OER) [83], oxygen reduction reaction (ORR) [84], and CO₂ reduction [85], etc. Moreover, density functional theory (DFT) simulations have revealed the potential and unique catalytic nature of SACs. Such theoretical simulation studies can further help to design efficient catalysts with tunable catalytic activity and selectivity [86].

In SACs, the type of solid support plays a significant role in stabilizing the metal atoms, preventing their aggregation, minimizing the metal usage, and enhancing the catalytic activity [87]. In fact, different types of materials, such as graphene, transition metal dichalcogenides (TMDs), traditional bulk metal oxides (e.g., MgO₂, Al₂O₃, SiO₂, TiO₂, FeOₓ, ZnO, CeO₂), zeolites, and metal-organic frameworks (MOFs) have been widely used as supports for single atoms [82, 88]. It is important to choose the appropriate support for the specific SAC to achieve the desired catalytic activity and selectivity. The metal species can chemically interact or bond with the neighboring atoms in the support, which in turn not only stabilizes the single atom catalyst but also enhances its intrinsic catalytic activity [89]. In addition, the chemical interaction between the single atom and solid support can enhance charge transfer. Moreover, the use of different supports can provide increased metal-support active sites or improve the redox properties, which are generally responsible for attaining better catalytic performance [90].

Recently, two dimensional (2D) materials with interesting physical and chemical properties have gained substantial attention as a new class of promising supports for SACs. In particular, the unique properties of graphene make it an ideal material for this application. Graphene is composed of a one-atom-thick layer of sp²-bonded carbon atoms that are closely arranged in a hexagonal crystal lattice structure with alternating C–C and C≡C bonds [91]. Moreover, graphene has a large specific surface area (theoretical value of 2630 m²/g), which helps to
support high catalyst loading and provide good stability and high electrical conductivity. It also has the potential for low manufacturing costs [23]. Due to its attractive properties, graphene has been widely utilized as a support material for water splitting applications [91, 92]. 2D graphene nanosheets with large specific surface area offer more anchoring sites and defects to trap single metal atoms on the surface. The doping of various heteroatoms, such as nitrogen (N), sulfur (S), boron (B), and phosphorous (P) onto graphene can also alter the electronic properties of the material. Most importantly, the heteroatoms in graphene, especially N and S, can act as binding sites for single metal atoms because of their tendency to coordinate with metals. Single metal atoms incorporated in graphene can also effectively alter the electronic structure of adjacent carbon atoms, which can then serve as additional active sites for different catalytic applications [93]. In addition to graphene, the catalytic activity of the inert basal plane surface of MoS$_2$ can be activated by confining Pt single atoms on the 2D surface, in which Mo atoms are replaced by Pt atoms [94]. Because of their promising catalytic activity and stability, SACs incorporated into 2D materials have been extensively investigated for water splitting applications.

In this literature review, we aim to focus on different types of single atoms confined on 2D supports for electrocatalytic (HER) process. We highlight the recent progress on the synthesis and characterization of SACs and SAC-MoS$_2$ support interactions, and also investigate the HER mechanism of single metal atoms confined to 2D supports.

### 2.3.1 Synthesis of SACs

SACs on a variety of supports have been synthesized using different experimental preparation methods, such as ALD, various wet chemistries, high temperature pyrolysis, metal/acid leaching, and mass-selected soft-landing methods [95]. The fabrication of SACs is a challenging task due to the tendency of metal atoms to aggregate, and metal clusters to form.
Most SAC synthesis methods are not scalable and tend to be quite challenging and complex [88]. In this section, we briefly discuss the different synthesis methods adopted for SAC preparation.

I. Atomic layer deposition (ALD) of SACs

ALD can be used to deposit catalytic materials on large surface area supports with precise, atomic-scale control in terms of thickness and composition [96]. In this process, the support material (substrate) is alternately exposed to pulsed vapors of different reactive precursors. The key characteristic of the ALD method is its self-limiting nature by depositing materials in an atomic layer-by-layer fashion. Most recently, the ALD method has been used to deposit SACs onto graphene and other solid supports [81]. Sun and his co-workers have synthesized isolated single Pt-atom doped graphene using the ALD process, which is shown schematically in Fig. (2.2) [97]. The existence of oxygen-rich functional groups on the surface of the graphene sheets react with the MeCpPtMe₃ precursor, causing a Pt-containing monolayer to be formed on the graphene surface [Fig. (2.2.a&b)]. Furthermore, the Pt-containing monolayer reacts with the subsequent oxygen pulse and forms new adsorbed oxygen molecules on the Pt surface [Fig. (2.2.c&d)]. These two steps form the complete ALD cycle. Similarly, Cheng et al. adopted the same ALD technique to prepare Pt single atoms on N-doped graphene for HER application [81].
II. Wet Chemistry Synthesis

Wet chemistry is the most widely used technique to synthesize nanomaterials because of its relatively facile and sustainable nature [87]. Wet chemistry approaches include co-precipitation and wet impregnation processes, which have been successfully employed to prepare SACs [87]. For example, an incipient wetness method was adopted to synthesize Pt single atoms anchored to titanium nitride (TiN) and titanium carbide (TiC) catalysts [98]. In this technique, Pt precursor and supports are mixed together in an ethanol solution and dried in a vacuum oven. The obtained powders are then heated at 100 °C under H$_2$ atmosphere to produce Pt single atoms on the TiN and TiC supports. The final Pt loading was calculated to be less than 1 wt% and clearly showed the formation of Pt SACs [98]. Likewise, isolated Pt single atoms anchored
on a graphitic carbon nitride (g-C$_3$N$_4$) support were prepared using a wet impregnation method [27].

III. *High temperature pyrolysis*

Single atom Co, Ru, Fe, Mo, and Ni on heteroatom-doped graphene sheets have been synthesized using high temperature pyrolysis methods [89, 99-102]. For example, Zhang *et al.* synthesized single Fe atoms confined on nitrogen-doped graphene (NG) using a simple high temperature thermal annealing process [103]. Fig. (2.3) shows the schematic illustration for the synthesis of an isolated single atom Fe/NG catalyst, in which graphene oxide (GO) and a Fe precursor are homogenously mixed together using ultra-sonication. The oxygen-rich functional groups, such as epoxy, hydroxyl and carbonyl, present on the surface of GO exhibit strong interactions and adsorption towards Fe ions in the solution phase, which stabilize the Fe ions on the GO surface. Subsequent lyophilization is carried out on the homogenous solution to remove the water molecules and prevent the GO nanosheets from restacking, which further results in the formation of Fe ions distributed throughout a GO foam. Subsequent thermal annealing is performed on the Fe ion-GO foam at high temperature (750 °C) under an Ar/NH$_3$ gas flow. As a result, N is doped with graphene (forming NG) while isolated single Fe metal atoms are simultaneously anchored to the surface of the NG material. The isolated single Fe atoms are further stabilized via the formation of coordination bonds with the N atoms of the NG sheets [103]. Recently, Yuan Pan and his coworkers designed a single Co atom-N-doped carbon sphere catalyst using a similar high temperature pyrolysis method under an Ar atmosphere [104].
IV. Metal organic framework (MOF)-derived SACs

SACs derived from MOFs have gained considerable attention in different electrochemical applications. Very recently, Chen et al. synthesized single tungsten atoms (W-SAC) anchored on MOF-derived N-doped graphene for electrochemical HER application (Fig. (2.4)) [105]. In this work, tungsten chloride (WCl₅) was encapsulated with a UiO-66-NH₂ MOF, followed by a pyrolysis at high temperature (950 °C) under an inert atmosphere. Finally, the pyrolyzed sample was treated with HF to remove the zirconia metal to obtain the resulting W-SAC. Likewise, Jiao et al. employed a similar approach to prepare single Fe atoms anchored on N-doped porous carbon catalyst (FeSA-N-C) derived from MOF-545 via a pyrolysis to achieve a maximum single Fe atom loading of ~1.76 wt% [106].

Figure 2.3. Schematic illustration for the synthesis of the Fe/NG catalyst by high temperature pyrolysis [48].
V. Metal/Acid Leaching

The Flytzani-Stephanopoulos’s group first demonstrated the use of a metal leaching technique for the preparation of SACs. Using an established metal leaching process originally used to recover Au from Au-containing ores, the authors were able to produce Au single atom-metal oxide [107]. Similarly, Fig. (2.5) depicts a schematic illustration for the synthesis of single Sn atoms on N-doped carbon fibers (Sn-CFs) using the acid leaching method [108]. The synthesis of single atom Sn on CFs involves electrospinning a precursor solution containing SnCl₂, polyacrylonitrile (PAN), and poly(methyl methacrylate) (PMMA), followed by pyrolysis. Finally, the pyrolyzed sample undergoes the acid leaching process, in which unreacted metal species are removed to obtain the single Sn atom-doped CFs. Though the metal leaching method is fast and selective, it is not environmentally friendly, nor scalable for industrial applications.
Figure. 2.5. Schematic illustration for the fabrication of single Sn atom-doped N-doped CFs [53].

VI. Mass-Selected Soft-Landing

The mass-selected soft-landing method has been used to deposit complex ions from the gas phase onto the surface of a substrate with accurate control of the material composition, charge state, kinetic energy, and coverage, thereby producing uniform multicomponent films on surfaces with tailored properties. This soft-landing method is based on the physical deposition method, in which different types of flat substrates can be used to produce any metal clusters or single atoms at low kinetic energies and with an accurate number of atoms dispersed onto the surface. This method is helpful for performing fundamental studies, such as determining the structure-function relationships of deposited clusters and quantifying the effect of the surface on the charge state, structure, and reactivity of the supported ions [109-111].

2.3.2 Characterization of SACs

After SAC fabrication, it is necessary to characterize the material in order to confirm the formation of isolated single metal atoms, as well as to study the chemical oxidation states and coordination environment of the single atoms with their support and determine their spatial distribution. However, characterizing SACs is a challenging task because it requires powerful tools with high spatial resolution to probe single atoms and atomic scale morphologies.
Currently, highly sophisticated characterization tools are employed to study SACs, including high angle aberration corrected dark field-scanning transmission electron microscopy (HAADF-STEM). In addition to microscopic techniques, spectroscopic methods such as X-ray absorption near edge structure (XANES), X-ray absorption fine structure (XAFS), and extended X-ray absorption fine structure (EXAFS) have been used to study the morphological, electronic, and chemical properties of SACs. In this section, we briefly discuss the characterization techniques used to analyze these materials.

I. HAADF-STEM for SACs

HAADF-STEM can be used to confirm the existence of single atoms on various solid supports. Additionally, it helps to identify the location of single atoms with respect to the surface structure of the support [76]. HAADF-STEM takes advantage of Rutherford scattering of electrons to detect heavy metal atoms on low atomic number (Z)-based supports [76]. Fig. (2.6.a-f) shows HAADF-STEM images of single atoms, including Ni [102], Co [99], Mo [101], Fe [103], Pt [81], and Ru [89] incorporated onto graphene supports, while Fig. (2.6.g) displays Pt single atoms on MoS$_2$ [94]. The small bright dots indicate the existence of single atoms, which are uniformly dispersed on the support. In addition, electron energy loss spectroscopy (EELS) can be used to study SACs. As shown in Fig. (2.6.h&i), EELS atomic spectra of the bright dot indicates the presence of Fe and N, which further suggests the formation of Fe-N$_x$ bonding [112]. However, HAADF-STEM cannot distinguish single atoms from the support when the materials’ atomic numbers are similar. The main drawback of this approach is the inability to detect electronic states of single atoms within a reaction environment or the oscillation of catalysts. Additionally, the sample can be damaged under the high-energy beam or probe current [113].
Figure 2.6. (a-f) HAADF-STEM images of single Ni [47], Co [44], Mo [46], Fe [48], Pt [24] and Ru [32] atoms anchored on graphene-based supports. (g) HAADF-STEM image of single atom Pt on MoS$_2$ [38]. (h&j) HAADF STEM image and EELS elemental analysis of single Fe atom doped graphene [57].
II. XANES and EXAFS for SACs

XANES and EXAFS can evaluate the active sites, local atomic structure, chemical state, and coordination structure of SACs [78, 114, 115]. In particular, XANES is sensitive to the oxidation state and coordination chemistry of single metal atoms. In contrast, EXAFS can provide information about the coordination number and chemical bonding between the single metal atom and the neighboring atoms of the support. For example, using EXAFS, Yang et al. confirmed the local coordination environment and oxidation state of single Ni atoms doped on a N and S-co-doped graphene catalyst (A-Ni-NSG; Fig. (2.7)) [102]. The oxidation state of Ni in A-Ni-NSG was identified to be +1 with the electronic configuration of 3d⁹ and S = 1/2 [Fig. (2.7.a)]. Furthermore, the chemical interaction between the single Ni atom and the NSG support was studied using Fourier transform-EXAFS spectroscopy, as displayed in Fig. (2.7.b). A high intense peak at 1.45 Å corresponds to the Ni-N bond, while a small peak at 1.81 Å is assigned to the Ni-S bond, indicating the successful chemical coordination of single atom Ni with the neighboring N and S atoms in the graphene sheets.

Figure. 2.7. (a) XANES and (b) FT-EXAFS spectra of A-Ni-NG, A-Ni-NSG, and NiPc catalysts [47].
2.3.3 Single atom-2D support interactions

The catalytic performance of SACs not only depends on the nature of the single atom but also on the support and the metal-support interactions [116]. 2D carbon-based supports have gained significant attention due to the materials’ high stability, large surface area, and high electrical conductivity. [117]. N- and S-doped graphene nanosheets are considered especially promising supports for SACs as the heteroatoms can act as binding sites for single atom metals, which helps to stabilize the atoms to serve as catalytic active sites [102].

To take advantage of this synergistic reactivity, various research groups have studied the effects of depositing SACs on doped carbon supports. For example, Chen and his co-workers designed Mo SACs anchored to an N-doped carbon catalyst for HER [101]. As can be clearly seen from the FT-EXAFS spectra, the Mo$_1$N$_1$C$_2$ exhibits a coordination peak at 1.3 Å that corresponds to the Mo-N bond. [Fig. (2.8.a)]. Similarly, Fei et al. confined atomic Co metal onto N-graphene(Co-NG) and demonstrated it as an efficient catalyst for HER applications [99]. As shown in Fig. (2.8.b), a binding energy peak centered at 398.4 eV is assigned to Co-pyridinic N-bonding. Furthermore, a small peak identified at 3.5 Å in the FT-EXAFS spectrum confirms the formation of the Co-N bond [Fig. (2.8.c)]. Similarly, single Ni atoms were coordinated with N and S sites of graphene, which further acted as active sites for electrocatalytic CO$_2$ reduction [102].

In addition to graphene, SACs can also be incorporated onto other 2D supports, such as MoS$_2$, g-C$_3$N$_4$, and layered double hydroxides, etc. Recently, isolated single Co atoms were doped in a monolayer MoS$_2$ (Co–$^8$MoS$_2$) [14]. EXAFS shows the formation of Co-S with a coordination peak of 2.21 Å [Fig. (2.8.d)]. As shown in Fig. (2.8.e), the HAADF-STEM image of the Co–$^8$MoS$_2$ material clearly reveals the presence of single atoms of Co, which are located on the Mo side. Based on the experimental results, the HAADF image was
simulated using a DFT-optimized atomic structure [Fig. (2.8.f&g)]. The simulated HAADF image shows good agreement with the experimental result in Fig. (2.8.e).

Figure. 2.8. (a) EXAFS spectra of Mo$_1$N$_1$C$_2$ [46]. (b&c) High resolution N1s XPS and EXAFS spectra of Co atoms confined on an N-doped graphene (Co-NG) catalyst [44]. (d) EXAFS spectra of Co–$^8$MoS$_2$ [63]. (e) HAADF-STEM images of Co–$^8$MoS$_2$ [63]. (f&g) HAADF image simulation and atomic model of Co–$^8$MoS$_2$ [63].

I. SACs on 2D MoS$_2$

MoS$_2$ has been considered a promising catalyst for HER due to the following advantages. First, MoS$_2$ has an optimal $\Delta$G$_{\text{H}_2}$ value, which is close to that of Pt, as illustrated from the Gibbs free energy volcano plot in Fig. (1.3) [118]. Second, 2D MoS$_2$ has an ultra-large surface area that possesses a large number of active sites, comparable to the total number of surface atoms. Third, the ultrahigh surface area that arises from the 2D nanostructure allows MoS$_2$ to serve as an ideal platform to couple with other substrates. Finally, the unique surface of MoS$_2$ can be
easily activated and optimized for achieving high HER activity by simple chemical modification methods, such as by introducing defects, strain, and doping single atoms [12].

There are several strategies that can be applied to improve the catalytic activity of MoS$_2$ towards SACs for HER [12]. The strategies can involve either increasing the active sites on the surface of the material or enhancing the MoS$_2$ electrical conductivity. Obtaining more active sites has been achieved by exposing more edges or creating active defects using plasma [119], or thinning the layers using an exfoliation process [120]. In addition to doping with single atoms [94], accelerating the kinetics of charge transfer and enhancing the conductivity can be performed by introducing strain in the basal plane [13] or coupling with other conductive materials or substrates [121]. In this section, we will elaborate on single atom doped MoS$_2$ for HER applications.

The catalytic active sites of MoS$_2$ occur at unsaturated S or Mo atoms along the material’s edges while the in-plane area is inert [38, 122]. Therefore, introducing single atoms to the MoS$_2$ lattice can trigger the catalytic activity of in-plane S atoms. Based on this strategy, Deng Jiao and co-workers confined Pt single atoms in few-layered MoS$_2$ lattices (Pt-MoS$_2$) using a direct chemical synthesis method [94]. The characterization results demonstrated that pure MoS$_2$ has a layer distance of 0.62 nm, as shown in the inset of Fig. (2.9.a). Additionally, HAADF-STEM images confirmed the confinement of Pt single atoms in the pure MoS$_2$ lattice, as demonstrated in Fig. (2.9.b-d). The Pt atoms tend to substitute for Mo in the lattice and are uniformly dispersed in the MoS$_2$ plane.
**Figure 2.9.** (a) TEM image of pure MoS\(_2\). (b, c) HAADF-STEM images of Pt single atoms (red circles) confined in a MoS\(_2\) plane. (d) Magnified view of the marked square region of (c), demonstrating that the Pt single atoms are substitutionally doped for Mo atoms (marked by red arrows). (e) EXAFS and (f) Pt L\(_3\)-edge XANES spectra of Pt-MoS\(_2\), Pt foil, and commercial 40% Pt/C catalyst. (g-j) HAADF-STEM image and the corresponding EDX mapping images of the Pt-MoS\(_2\) catalyst. (k) HER polarization curves of Pt-MoS\(_2\), bulk MoS\(_2\), few-layered MoS\(_2\) (FL-MoS\(_2\)), and commercial Pt/C catalysts. (l) Corresponding Tafel slopes and (m) HER polarization curves of Pt-MoS\(_2\) before and after 5000 CV cycles between -0.13 V and +0.57 V (vs. RHE) at 100 mV s\(^{-1}\) [38].
Furthermore, EXAFS spectra confirmed the existence of Pt single atoms by the fact that no Pt-Pt bond peak was observed. In contrast, the peak corresponding to Pt–S appeared at 2.2 Å [Fig. (2.9.e-f)]. The HAADF-STEM image and corresponding EDX maps of Pt-MoS₂ indicates the homogeneous distribution and existence of Mo, S, and Pt elements [Fig. (2.9.g-j)]. As shown in Fig. (2.9.k), the HER electrochemical results demonstrated that the bulk MoS₂ has poor HER activity, while the pure few-layered MoS₂ without Pt SACs showed improved activity but is still much inferior to the 40% Pt/C catalyst. In contrast, the Pt-MoS₂ material displayed a distinct enhancement of HER activity, with an overpotential of 60 mV to reach a current density of 10 mAcm⁻². The Tafel slope value of Pt-MoS₂ was 96 mV/dec, which is quite deviated from the Tafel slope value of the Pt/C electrocatalyst (32 mV/dec), indicating that the enhancement in the catalytic HER activity of Pt-MoS₂ not only originates from Pt but also arises from the S atoms in MoS₂ [Fig. (2.9.l)]. In addition, Pt-MoS₂ was found to be stable up to 5000 CV cycles without any significant degradation in activity [Fig. (2.9.m)].

DFT calculations were carried out to investigate the HER catalytic properties of Pt-MoS₂. Pt-doped S-sites were found to be the catalytically active sites and demonstrated a ΔG_H⁺ value of close to 0 eV while the ΔG_H⁺ of the S edges of pure MoS₂ was ~0.1 eV, which is consistent with previous reports in the literature [123]. Moreover, the presence of Pt SACs in the lattice enhances the S in-plane catalytic activity towards HER compared to that of S atoms at the edge of the material. As demonstrated by the calculated total DOS, pure MoS₂ has a significant band gap while the position of the valence band moves downward for Pt-MoS₂. Additionally, some hybridized electronic states occur near the Fermi level of the Pt-MoS₂ structure, which activate the S-edge atoms and thereby enhances their HER activity. Consequently, introducing Pt single atoms to the MoS₂ lattice produces a significant change in the electronic properties and atomic structure of MoS₂, resulting in the improved HER activity [94].
Based on the improvement in the HER activity of Pt-MoS$_2$, the authors also studied the HER activity of different metallic single atoms confined in MoS$_2$ using DFT calculations [94]. As illustrated from the volcano plot in Fig. (2.10), when metal atoms are substituted for Mo in the MoS$_2$ lattice, the metal atoms located on the right side of the volcano plot, such as V, Ti, Fe, Mn, and Cr, tend to remain in the middle of the lattice to bond with six S atoms. Keeping the surrounding six S atoms occupied results in low HER activity due to their weak binding ability with H$^+$. Meanwhile, the metals on the left side of the volcano plot (e.g., Pt, Ag, Pd, Co, and Ni) prefer to shift towards one side of the MoS$_2$ lattice and bond with only four S atoms, which helps to adsorb H$^+$ atoms and connect to the neighboring unsaturated S atoms [94].

**Figure. 2.10.** Volcano plot of different configurations of various SACs confined in MoS$_2$ as coordinated with four (left) or six (right) S atoms. In the ball and stick molecular structures shown, the green balls refer to Mo atoms, yellow balls to S, and blue and purple balls represents the doped SACs [38].
Shi Yi and his group [124] proposed a method to engineer the electronic density of MoS$_2$ for accelerating HER by introducing a transition metal atom into the lattice, such as Zn. The Zn single atom confinement process was achieved using a solvothermal method to produce Zn-doped MoS$_2$ (Zn-MoS$_2$), which exhibited superior electrochemical HER activity, with an onset potential of 130 mV and a turnover frequency of 15.44 s$^{-1}$ at 300 mV. Compared to pure MoS$_2$, Zn-MoS$_2$ XPS spectra showed a negative shift in the binding energies of Mo 3d and S 2p, indicating an increase in the electronic density of MoS$_2$ after introducing Zn SACs, which the authors attributed to the good HER performance. Meanwhile for other transition metals, introducing Fe atoms to MoS$_2$ significantly decreased the HER activity, while Ni atoms had a negligible effect [94].

To enhance the HER activity of the MoS$_2$ basal plane, Zhaoyan Luo and co-workers [125] introduced Pd (1 wt%) to the MoS$_2$ lattice. They found that single Pd atoms substituted at Mo sites simultaneously created sulfur vacancies in the basal plane. Consequently, a phase conversion from 2H MoS$_2$ to the stabilized 1T structure was observed, enabling more electrons to access absorbed H$^+$ atoms at the electrode/electrolyte interface. The theoretical calculations indicated that S atoms located next to the Pd sites featured a $\Delta G_{H^+}$ value of approximately -0.02 eV, which was far better than the reported Gibbs energy value of most favorable edge sites [123, 126]. The resultant Pd-doped MoS$_2$ showed an exchange current density of 805 $\mu$A cm$^{-2}$ and an overpotential of 78 mV to achieve a current density of 10 mA cm$^{-2}$. Additionally, the catalyst exhibited excellent long-term stability up to 100 h of continuous reaction time.

The results obtained from the previously discussed studies demonstrate the influence of single atoms in enhancing MoS$_2$ HER activity by altering the intrinsic catalytic activity of the MoS$_2$ surface. We believe that this mechanism can be expanded to other 2D TMD materials, such as WS$_2$, MoSe$_2$, WSe$_2$, and MoTe$_2$. Moreover, SACs confined onto the MoS$_2$ support can be applied to other catalytic processes, such as hydride-sulfurization [127] and syngas conversion.
to higher alcohols [128]. Table. (2.1) below summarizes the electrochemical performance values toward HER for different 2D materials supporting various single metal atoms kinds.

Table 2.1: Summarizes the electrochemical performance values toward HER for different 2D materials support various single metal atoms kinds.

<table>
<thead>
<tr>
<th>2D Support</th>
<th>SA</th>
<th>Synthesis Method</th>
<th>Overpotential mV vs. RHE @ 10 mA cm$^{-2}$</th>
<th>Tafel slope mV dec$^{-1}$</th>
<th>TOF S$^{-1}$</th>
<th>Stability</th>
<th>Electrolyte</th>
<th>REF</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-doped graphene</td>
<td>Co</td>
<td>Chemical synthesis</td>
<td>~ 147</td>
<td>82</td>
<td>0.022 - 1.189</td>
<td>10 h</td>
<td>0.5 M H$_2$SO$_4$</td>
<td>[99]</td>
</tr>
<tr>
<td>N-doped graphene</td>
<td>Pt</td>
<td>ALD</td>
<td>50</td>
<td>29</td>
<td>NA</td>
<td>1000 CV cycles</td>
<td>0.5 M H$_2$SO$_4$</td>
<td>[81]</td>
</tr>
<tr>
<td>NG/CdS</td>
<td>Co</td>
<td>Chemical synthesis</td>
<td>210</td>
<td>126</td>
<td>8.8</td>
<td>15 h</td>
<td>10 Vol % lactic acid aqueous solution</td>
<td>[129]</td>
</tr>
<tr>
<td>Graphene</td>
<td>Ni</td>
<td>Chemical exfoliation</td>
<td>50</td>
<td>45</td>
<td>0.8</td>
<td>1000 CV cycles</td>
<td>0.5 M H$_2$SO$_4$</td>
<td>[130]</td>
</tr>
<tr>
<td>CN</td>
<td>Mo</td>
<td>Combining templated &amp; pyrolysis methods</td>
<td>132</td>
<td>90</td>
<td>0.05</td>
<td>1000 CV cycles</td>
<td>0.1 M KOH</td>
<td>[101]</td>
</tr>
<tr>
<td>Graphdiyne</td>
<td>Ni</td>
<td>Electrochemical deposition</td>
<td>88</td>
<td>66</td>
<td>45.8</td>
<td>5000 CV cycles</td>
<td>0.5 M H$_2$SO$_4$</td>
<td>[82]</td>
</tr>
<tr>
<td>MoS$_2$-Few layers</td>
<td>Pt</td>
<td>Chemical synthesis</td>
<td>60</td>
<td>96</td>
<td>NA</td>
<td>5000 CV cycles</td>
<td>0.1 M H$_2$SO$_4$</td>
<td>[94]</td>
</tr>
<tr>
<td>MoS$_2$</td>
<td>Zn</td>
<td>Solvothermal methods</td>
<td>NA</td>
<td>51</td>
<td>15.44</td>
<td>1000 CV cycles</td>
<td>0.5 M H$_2$SO$_4$</td>
<td>[124]</td>
</tr>
<tr>
<td>MoS$_2$</td>
<td>Pd</td>
<td>Spontaneous interfacial redox technique</td>
<td>78</td>
<td>62-80</td>
<td>0.15-21.15</td>
<td>100 h &amp; 5000 CV cycles</td>
<td>0.5 M H$_2$SO$_4$</td>
<td>[125]</td>
</tr>
</tbody>
</table>
2.4 Conclusion

SACs with unique properties, such as low coordination active sites, quantum confinement effects, and metal-support interactions have significantly improved the catalytic activity, stability, and selectivity of these materials for various catalytic applications. Unlike metal nanoparticles or bulk metal catalysts, SACs are identical in size and uniformly dispersed on a solid support, enabling all the isolated metal atoms to be actively involved in the catalytic reaction, and as a result SACs have shown improved catalytic activity compared to their metal nanoparticle counterparts.
CHAPTER 3

HYDROTHERMAL GROWTH AND

CHARACTERIZATION OF MoS$_2$

3.1 Introduction

In general, two-dimensional (2D) materials are the ideal material for utilizing in various devices due to their superior electronic and structural characteristics such as high conductivity, fast carrier motilities, high optical transparency, excellent mechanical flexibility, and their good stability in the chemical media. Particularly, MoS$_2$ has recently gained much attention because of its amazing electronic property including direct-gap that can be increased with increasing the layer numbers. However, still finding a synthetic approach for producing a high-quality with large-scale MoS$_2$ atomic thin layers is still difficult. In this chapter, we a report simple, scalable, and applicable synthetic approach to prepare MoS$_2$ where the films obtained with using thermal decomposition of ammonium tetrathiomolybdate [(NH$_4$)$_2$MoS$_4$], annealed with moderate temperature at different annealing times. Detailed microscopic and spectroscopic characterizations were provided. The structure and growth mechanism of MoS$_2$ thin layers were investigated.

3.2 Synthesis of MoS$_2$

Fig. (3.1) displays a schematic illustration for the synthesis of MoS$_2$ thin films via the thermal annealing method. We first prepared different concentrations, that ranged from 0.5 to 1.5 M of Ammonium tetrathiomolybdate (NH$_4$)$_2$MoS$_4$, in dimethylformamide (DMF) and ultra-
sonicated the solutions for 30 minutes [131]. Then, each solution was spin coated (500 rpm for 30 s and then 1500 rpm for 45 s [132]) on a fluorine-doped tin oxide (FTO) substrate, which was then heated at 80 °C for 20 min. Afterwards, the spin-coated film was transferred to a tube furnace and heated at 450 °C for 1 hour under argon and hydrogen (8:2) atmosphere to obtain the MoS$_2$ thin film [131]. Importantly, the introduced hydrogen plays a critical role to avoid creating MoO$_3$ during the growth process and improves the MoS$_2$ film quality. Equation 3.1 shows the thermal decomposition reaction involved with this synthesis of MoS$_2$ from the initial precursor [131].

$$(\text{NH}_4)_2\text{MoS}_4 + \text{H}_2 \rightarrow 2\text{NH}_3 + 2\text{H}_2\text{S} + \text{MoS}_2$$  \hspace{1cm} (3.1)

**Figure. 3.1.** The steps of the hydrothermal decomposition synthesis method of producing MoS$_2$ thin films [131].
3. 3. Characterization of MoS$_2$ Thin Films

3. 3. 1. Raman spectroscopy

Raman spectroscopy measurements were carried out using a micro-Raman spectrometer. The samples were excited with a visible light laser (wavelength ($\lambda = 473$ nm)). An objective lens at 100x magnification was applied to focus the excitation laser on the desired spot of the MoS$_2$ thin film. In general, there are three characteristic Raman-active frequency modes of MoS$_2$, as illustrated in Fig. (3.2. a). These modes include the A$_{1g}$ mode, which corresponds to an out-of-plane optical vibration of the sulfur atoms, the E$_{12g}$ mode, which represents the in-plane vibration of sulfur atoms moving in one direction and the molybdenum atom in the other, and finally, the shear mode, which is a rigid-layer oscillation of adjacent layers [133].

Fig. (3.2.b) displays the Raman spectrum of our synthesized MoS$_2$ thin film. Two characteristic Raman peaks can be identified at $\sim 379.3$ cm$^{-1}$ and 406.82 cm$^{-1}$, which are assigned to the E$_{12g}$ and A$_{1g}$ mode of MoS$_2$. The peak positions confirmed that the MoS$_2$ film structure can be formed at a thermolysis temperature higher than 300 °C [134, 135]. Additionally, the 27.52 cm$^{-1}$ separation between the A$_{1g}$ and E$_{12g}$ peaks indicated we had obtained a multilayer film of MoS$_2$ [136]. The absence of vibrational peaks at 150 cm$^{-1}$, 219 cm$^{-1}$, and 327 cm$^{-1}$, which are characteristic of the metallic 1T-MoS$_2$, indicates we obtained the semiconductor phase (2H-MoS$_2$) [44].
3.3.2. Photoluminescence (PL)

In order to investigate the semiconducting phase of the obtained 2H-MoS$_2$ multilayer film, we evaluated the photoluminescence (PL) properties of the material using a Lab RAM micro-PL spectrometer. Fig. (3.3) illustrates the PL emission spectrum of the MoS$_2$ film excited at 373 nm at room temperature. Thermal annealing of the MoS$_2$ precursor at 450 °C leads to a high intensity PL feature at around 610 nm that is characteristic of 2H-MoS$_2$ excitons. The emission spectrum for the multilayer film reflects the semiconductor phase of MoS$_2$, with a direct band gap of around 2 eV [36, 136]. The peak at 610 nm reflects the energy of an exciton radiatively recombining from the direct band gap. Moreover, it indicates that the detected photoluminescence peak arises from the direct band gap of the multilayer MoS$_2$ and not due to the formation of structural defects or chemical impurities [136].
**Figure. 3.3.** PL spectrum of multilayer MoS$_2$ in the photon wavelength range from 300 nm to 900 nm.

### 3.3.3. X-ray Photoelectron Spectroscopy (XPS)

We additionally studied the manifestation of the ML-MoS$_2$ semiconducting phase by X-ray photoelectron spectroscopy (XPS). The high-resolution Mo 3d and S 2p spectra of the MoS$_2$ thin film are shown in Fig. (3.4.a&b). The Mo 3d spectra consists of binding energy peaks at around 229.28 eV and 232.4 eV, which correspond to Mo 3d$_{5/2}$ and Mo 3d$_{3/2}$ orbitals, respectively, both of which are components of ML-MoS$_2$ [137]. Additionally, we assigned a small binding energy peak centered at 226.8 eV to S 2s. Likewise, in the S 2p region of the spectra, the peaks appeared around 163eV. Moreover, the almost complete absence of an Mo$^{6+}$ 3d$_{5/2}$ signal at around 236 eV confirmed no Mo oxidation had occurred on the MoS$_2$ lattice during the thermal annealing process. The same holds true for the S 2p orbitals, in which there was no signal at around 168 eV due to oxidized sulfur [137].

The peaks at 163.5 eV and 161.97 eV that are assigned to S 2p$^{1/2}$, and S 2p$^{3/2}$ orbitals, respectively, are directly related to the 2H-phase of MoS$_2$ [124, 137]. The outcome of the XPS results strongly supports the notion that the semiconducting 2H-phase of MoS$_2$ is preserved
when the thermal annealing process is carried out at 450 °C. Finally, the Mo and S binding energies are identical to the previously reported values in the literature [138].

![Figure 3.4](image)

**Figure 3.4.** (a) Chemical composition analysis spectra by XPS of the Mo 3d, S 2s and (b) S 2p peak regions for a multilayer film of MoS\(_2\).

### 3. 3. 4. X-Ray Diffraction (XRD)

The X-ray diffraction (XRD) spectrum of the 2H-MoS\(_2\) film is shown in Fig. (3.5.a). The results demonstrate one sharp peak and many smaller peaks, indicating the formation a polycrystalline ML-MoS\(_2\) film. The sharp peak centered at \(\theta = \sim 14.6^\circ\) corresponds to the (002) Bragg reflection plane of the hexagonal 2H-MoS\(_2\) structure [139]. The peaks appearing between 20° and 80° could be related to the typical peak structure of the MoS\(_2\).
Figure. 3.5. (a) XRD pattern of the polycrystalline 2H-MoS$_2$ where the sharp peak centered at $2\theta = \sim 14.6^\circ$ corresponds to the (002) Bragg reflection plane.

3. 3. 5. *Scanning Electron Microscopies (SEM)*

A scanning electron microscopy (SEM) image (Fig. 3.6) shows the MoS$_2$ film is continuous, featuring grains that cover all the FTO glass substrate.

Figure. 3.6. A top view SEM image of the multilayer MoS$_2$ film.
3.4. Electrochemical Studies

We evaluated the HER activity of the 2H-MoS$_2$ thin film at 25 °C in an electrolyte solution of 0.5 M H$_2$SO$_4$ (pH = 0) using a standard three electrode system, containing a 2H-MoS$_2$ electrode as the working electrode, Pt wire as the counter electrode, and Ag/AgCl (1 M KCl) as the reference electrode. All electrode potentials are represented with respect to the RHE, according to Equation (3.2):

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.230 \text{ V.}$$  \hspace{1cm} (3.2)

3.4.1 Linear sweep voltammetry studies (LSV)

LSV was achieved to measure the HER catalytic activity at a scan rate of 20 mV/s. Fig. (3.7.a) demonstrates the LSV curves of ML-MoS$_2$ on FTO electrodes prepared at various precursor concentrations, in which the current density is defined as the measured current normalized by the geometrical area of the FTO substrate. Also, all the curves were iR corrected to reflect the intrinsic behaviors of the catalysts.

The LSV curve of the multilayer-MoS$_2$ electrode, made with a 1 M (NH$_4$)$_2$MoS$_4$ precursor, indicates an overpotential of -0.180 V vs. RHE at -10 mA cm$^{-2}$, as illustrated in Fig. (3.7.a). The observed overpotential is almost equivalent to that of previously reported metallic MoS$_2$ nanosheets [140]. However, the current density is higher compared to mechanically activated MoS$_2$ and nanostructures MoS$_2$ [44, 141]. Additionally, the overpotential of the 1 M MoS$_2$ sample is consistent with previous reports, as illustrated in Table. (3.1). In contrast, the 0.5 M and 1.5 M electrodes demonstrated high overpotentials, as shown in Fig. (3.7.c).
3.4.2 HER mechanism (Tafel slope)

The Tafel plots constructed for the different ML-MoS\textsubscript{2} precursor concentration electrodes are presented in Fig. (3.7.b). We fitted the linear portions under different overpotential regions for comparison. The Tafel slope was found to be 64 mV/decade for the 1 M ML-MoS\textsubscript{2} electrode. This Tafel value is consistent with previous reports of MoS\textsubscript{2} crystals, which range from 55–60 mV/decade [38]. Moreover, the mechanism of hydrogen adsorption/desorption is close to the Heyrovsky reaction regime (40 mV/decade) and the rate-limiting step here is the electrochemical desorption step [142]. However, the observed Tafel slope is less than that of previously reported MoS\textsubscript{2} materials, such as mechanically activated MoS\textsubscript{2}, MoS\textsubscript{2} sheets, MoS\textsubscript{2} spheres, MoS\textsubscript{2} and MoSe\textsubscript{2} films, and MoS\textsubscript{2} particles [132].

3.4.3 Stability studies

Stability considers as an important parameter to examine the catalyst performance. Fig. (3.7.d) shows a chronoamperometric test that was applied to analyze the stability period of the 1 M MoS\textsubscript{2} electrode at an overpotential of -0.5 V vs. RHE. A plot of the current density versus time demonstrates a negligible decrease in the current density (approximately -5 mA cm\textsuperscript{-2}) for 20 hours. Based on this result, it would appear that the semiconductor phase of MoS\textsubscript{2} is a very promising catalyst for electrocatalytic H\textsubscript{2} production. However, its performance is still far from the Pt metal groups. Table. (3.1) summarizes the HER electrocatalytic performance of 1 M ML-MoS\textsubscript{2} and other types of MoS\textsubscript{2} electrodes published in the literature.
Figure 3.7. (a) LSV curves of ML-MoS$_2$ and Pt electrodes measured in 0.5 M H$_2$SO$_4$ at a scan rate of 100 mV/s. (b) Tafel plots for various electrodes in 0.5 M H$_2$SO$_4$. (c) Diagram illustrating the relation between the precursor concentration, overpotential, and Tafel slope. (d) Chronoamperometry electrolysis test of 1 M ML-MoS$_2$ over 20 hours.

In order to consider ML-MoS$_2$ multilayer film as a potential catalyst material to replace Pt, several enhancement approaches can be applied. Here, we will discuss the preliminary results of these approaches, with the general focus being improving the MoS$_2$ conductivity (Fig. 2.1)). In the first project, we investigated the effect of the integrating MoS$_2$ into a Si heterojunction solar cell. In the second project, we studied the performance of MoS$_2$ after anchoring to Pt SAs and clusters.
Table 3.1. Summary of the electrocatalytic characteristics of different MoS\(_2\)-based electrode structures.

<table>
<thead>
<tr>
<th>MoS(_2) structure</th>
<th>Electrolyte</th>
<th>Overpotential mV vs. RHE @ 10 mA cm(^{-2})</th>
<th>Current Density (mA cm(^{-2}))</th>
<th>Tafel Slope (mV/decade)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Multilayer</strong></td>
<td>0.5 M H(_2)SO(_4)</td>
<td>180</td>
<td>10</td>
<td>65</td>
<td>This work</td>
</tr>
<tr>
<td>Amorphous</td>
<td>0.5 M H(_2)SO(_4)</td>
<td>200</td>
<td>10</td>
<td>53</td>
<td>[143]</td>
</tr>
<tr>
<td>Defect-rich ultrathin nanosheets</td>
<td>0.5 M H(_2)SO(_4)</td>
<td>300</td>
<td>70.5</td>
<td>50</td>
<td>[144]</td>
</tr>
<tr>
<td>Metallic nanosheets</td>
<td>0.5 M H(_2)SO(_4)</td>
<td>187</td>
<td>10</td>
<td>43</td>
<td>[44]</td>
</tr>
<tr>
<td>Single layer MoS(_2) coating on carbon nanotubes</td>
<td>0.1 M H(_2)SO(_4)</td>
<td>236</td>
<td>10</td>
<td>63</td>
<td>[145]</td>
</tr>
<tr>
<td>MoS(_2) on Au electrode</td>
<td>0.5 M H(_2)SO(_4)</td>
<td>150</td>
<td>0.92</td>
<td>69</td>
<td>[146]</td>
</tr>
<tr>
<td>Li doped MoS(_2) nanoparticles</td>
<td>0.5 M H(_2)SO(_4)</td>
<td>200</td>
<td>200</td>
<td>62</td>
<td>[147]</td>
</tr>
<tr>
<td>MoS(_2)/RGO (Reduced graphene oxide)</td>
<td>0.5 M H(_2)SO(_4)</td>
<td>150</td>
<td>9</td>
<td>41</td>
<td>[43]</td>
</tr>
<tr>
<td>Mo(_1)Soy (humble-soybeans) /RGO</td>
<td>0.1 M HClO(_4)</td>
<td>177</td>
<td>10</td>
<td>62.7</td>
<td>[148]</td>
</tr>
</tbody>
</table>
CHAPTER 4
SYNERGTIC HETROSTRUCTURE OF MoS$_2$/Si-HJ

TOWARD PHOTOCHEMICAL HER

4.1 Introduction

Solar-driven water splitting is an auspicious approach to utilizing renewable energy to produce hydrogen fuel [149, 150]. The water splitting method can be categorized into two types, the electrochemical and the integrated photoelectrochemical cells (PEC) [1, 151]. A PEC system consists of two critical components: a material that is able to absorb the light to generate electron-hole pairs upon illumination and a co-catalyst to smooth the charge transfer and therefore minimizes the resultant overpotential toward gas production [152]. Among the wide range of light absorbing materials, Si-based photocathodes have been widely adopted because of their low cost in the conventional solar industry [153, 154]. Moreover, many theoretical studies have illustrated that silicon has one of the best band gaps that can be aligned with the water oxidation–reduction potential levels [155].

In tandem photoelectrochemical (PEC) systems, p-type Si has been widely used as the photocathode for HER due to its earth abundance, inexpensive, suitable band gap (around 1.1 eV), and capability of efficient sunlight absorption [156, 157]. However, the p-Si/H$_2$O junction causes an intrinsically low open circuit voltage ($V_{oc}$), which can limit the energy-conversion efficiency in PEC for HER application [157]. In contrast, substituting the p-Si/liquid junction with a built-in p-n junction by adding an n$^+$-layer to the p-Si can improve the photovoltage [157]. For example, Lewis demonstrated that the HER onset potential can be improved to about
0.56 V when Pt is used as a co-catalyst and p-Si is used that features a high level of n⁺ surface doping. This is because the n⁺-layer provides a built-in depletion region of the semiconductor-liquid junction [157]. Therefore, combining an additional p⁺-Si layer with the n⁺-p Si junction leads to facilitate collecting the majority carrier, improving the device fill factor (FF) and increasing the total efficiency [158].

In this respect, the Si-heterojunction solar cell (Si-HJ) is applied as a photocathode due to its high open circuit voltages (V_{OC}), high-circuit current density (J_{SC}), and excellent photon management to avoid recombination by the surface structuring. Moreover, the Si-HJ cell has a high efficiency due to its periodic micro-pyramid (MP) structure, which has the omnidirectional broadband ability to trap light [159]. Furthermore, the Si-HJ cell features a high minority carrier lifetime and superior carrier collection efficiency because of the passivation of the MP structure with a 5 nm thick amorphous Si film [160]. Despite these superior characteristics of the Si-HJ, Si is not stable and readily corrodes under aqueous electrolytes [154, 161].

In contrast, platinum and other noble metals catalyst based are the greatest electrocatalysts for HER but their expensive price and the shortage in resources have been limited their usage [162, 163]. Consequently, intensive researches have been devoted to fabricating a catalyst that possesses characteristics such as an earth-abundant, inexpensive, non-toxic and a highly efficient catalytic characteristic toward HER. For example, metal alloys [164], chalcogenides [165], nitrides [166], phosphides [167], borides [168], and carbides [169] have been studied for producing H₂. Nonetheless, their stability and efficiency to serve as a co-catalyst still need to be improved. In fact, most of these catalysts have only been applied as electrocatalysts, and only a few of them have been utilized for the photoelectrochemical HER due to several imperfections, including chemical mismatch between semiconductor/co-catalyst and low stability during the operation. Furthermore, the appearance of interfacial defect states cause
charge recombination sites due to the unappropriated band alignment of the light absorber/co-catalyst/electrolyte bands [44]. In addition, there are fabrication issues related to the morphology, thickness and full covering when using the direct synthesis method for co-catalyst on the light absorbent substrate [170]. In contrast, semiconducting multilayer molybdenum disulfide film (2H-MoS$_2$, ML) is the best co-catalyst candidate for coupling with Si-HJ cell photocathodes due to its electrochemical stability in the acidic environment, the direct synthesis method, and a favourable band-gap alignment with Si solar cell [171], despite the fact that that MoS$_2$ suffers from low internal conductivity due to its natural semiconducting feature, which makes it not comparable to the Pt catalytic performance toward HER [136].

Building on these features, here we illustrate the effect of synergistic heterostructure integration ML-MoS$_2$ and Si-HJ cell as a photocathode for H$_2$ evolution. The ML-MoS$_2$/Si-HJ cell photocathode shows an ability to address the shortcoming of each component. We have successfully exhibited a solar-to-hydrogen conversion efficiency of 7.5% under one sun illumination (AM 1.5G) and 25 hours of continuous H$_2$ production, in addition to a high saturation photocurrent density of 38.7 mAcm$^{-2}$ at 0 V vs RHE and a positive onset potential of 0.5 V. More importantly, the electrochemical impedance spectroscopy (EIS) elucidates the improvement in the MoS$_2$ conductivity after the Si-HJ integration which reflects the smooth charge transport within the heterostructure interfaces. Accordingly, the integration of a perfectly designed Si cell (excellent light harvesting) and the MoS$_2$ (HER catalytic ability, and chemical protection) result in fabricating of an earth-abundant photocathode that has an efficient and stable hydrogen production characteristic.
4.2 Fabrication Details

4.2.1 Synthesis of MoS$_2$

The MoS$_2$ synthesizing method via the thermolysis annealing (described in details in section (3.1)) was used.

4.2.2 Si-HJ photoelectrochemical cell fabrication method

The HJ photoelectrode includes several components. Firstly, n-type layers of (100) Si wafer with a thickness of 150 μm contains a dopant concentration of $5 \times 10^{15}$ cm$^{-3}$ that were fabricated on both sides of the cell by using an electrodeless chemical etching process [Solution of potassium hydroxide (KOH, 45 vol. %) and isopropyl alcohol (IPA)] to create a micro-pyramidal surface structure. Secondly, an emitter layer includes a 300 nm of p$^+$-Si with a dopant concentration of $9 \times 10^{19}$ cm$^{-3}$ which is formed by utilizing the thermal diffusion of BCl$_3$. Thirdly, the back surface field layer contains a 300 nm of n$^+$-Si with the dopant concentration of $3 \times 10^{20}$ cm$^{-3}$ that is fabricated by the thermal diffusion process of POCl$_4$. By utilizing the techniques of atomic layer deposition and plasma-enhanced chemical vapor deposition, the 7 nm of Al$_2$O$_3$ and 50 nm of Si$_3$N$_4$ were deposited on the top of the emitter layer, respectively. Finally, both Al$_2$O$_3$ and Si$_3$N$_4$ layers were etched by HF, and then the photolithography and lift-off processes were applied to both materials, to deposit 300 nm of Ag on the top side of the cell. Furthermore, the p$^+$-layer side function is to harvest the light (light harvesting layer), due to its nearest location to the interface of the p$^+$-n junction position.

Prior to MoS$_2$ deposition, Si HJ cell was treated with hydrofluoric (HF) acid to remove the native oxide layer. MoS$_2$ film on Si HJ photocathode was prepared by drop-casting MoS$_2$ precursor solution on the n$^+$ side of Si and subsequently thermal annealing process was carried out as followed in MoS$_2$ synthesis in section 4. 2.1.
For packing MoS₂/Si HJ photocathode, Ga-In eutectic alloy (Sigma-Aldrich) was deposited on the electrode to make ohmic contact. The photocathode was subsequently connected with a Cu wire using silver paste. Samples then were embedded in Epoxy (Hysol 11C), and the only part that was covered with MoS₂ was exposed to the electrolyte. Epoxy then was dried at 80 °C for 30 min. The sample areas were then measured through the digital images using Photoshop before the PEC measurements.

4.3 Characterization details

Raman spectroscopy measurements were carried out using a micro-Raman spectrometer. The samples were excited with a visible light laser [wavelength (λ = 473 nm)]. An objective lens at 100x magnification was used to focus the excitation laser on the desired spot of the MoS₂ thin film. Photoluminescence (PL) spectra of MoS₂ film was obtained using a Lab RAM micro-PL spectrometer. X-ray photoelectron spectroscopy (XPS) studies were carried out in a Kratos Axis Supra DLD spectrometer equipped with a monochromatic Al Ka X-ray source (hv = 1486.6 eV) operating at 150 W, a multi-channel plate and delay line detector under a vacuum of ~10⁻⁹ m bar. X-ray diffraction patterns (XRD) were collected at room temperature using a Bruker D8 Advance powder diffractometer (German Bruker) equipped with a Lynx- Eye detector and a Cu source. We used a field-emission scanning electron microscope (FE-SEM, Magellan and FEI) to observe the surface morphology. The TEM instrument used for this study was a probe Cs corrected FEI-ST Titan 80–300 kV (ST) microscope. The high angle annular dark field-scanning electron microscopy (HAADF-STEM) were obtained using Titan Themis-Z TEM (TFS) at an operating voltage of 300 kV.

We evaluated the HER activity of the MoS₂ thin film at 25 °C in 0.5 M H₂SO₄ electrolyte using a standard three electrode system, consists a MoS₂ electrode as the working electrode, Pt wire
as the counter electrode, and Ag/AgCl (1 M KCl) as the reference electrode. All electrode potentials were converted with respect to RHE scale, according to Equation (4.1): Also, all the HER curves were iR corrected to reflect the intrinsic behaviors of the catalysts.

\[ E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.197 \text{ V}. \]  

(1)

The electrochemical impedance spectroscopy (EIS) of the samples were measured at a frequency changing from 200 KHz to 100 MHz. For photoelectrochemical measurements, AM 1.5G illumination was achieved with a 150 W halogen-lamp-based solar simulator. The chronoamperometry measurement was carried out at -0.8 V vs RHE, within a three-electrode cell under 1 sun illumination in 0.5 M H$_2$SO$_4$.

### 4.4 Characterization of MoS$_2$/Si-HJ Electrode

#### 4.4.1 SEM and TEM microscopies

A top view scanning electron microscopy (SEM) image of MoS$_2$ film reveals a continuous, ordered and compressed, featuring grains that cover entire n$^+$ side of Si-HJ cell (Fig. 4. 1. a).

As shown in Fig. 4. 1. b, SEM image of the front side of Si HJ cell shows micro-pyramidal structure. Fig. 4.1.c shows the SEM image of MoS$_2$/Si HJ PEC cell in which a conformal and smooth MoS$_2$ thin film catalyst is uniformly covered the Si micro-pyramidal surface with a thickness of ~ 1–1.5 µm. Fig. 4. 1. (d-f) depicts the HR-TEM images of MoS$_2$/Si HJ. The lattice fringes values of 0.607 nm and 0.31 nm noted in Fig. 4. 1 (d, e) indicates the successful integration of MoS$_2$ with Si. Also, the HR-TEM images confirm the nanosheets layer-by-layer growth mode on the faceted n$^+$-Si layer where the interface area clearly appeared between the two materials. Fig. 4. 1 (g, h) depicts the HR-TEM image and its corresponding EDX mapping image at the interface between MoS$_2$ and Si. The HAADF-STEM image and its EDX mapping
further reconfirms the integration of MoS\textsubscript{2} with Si. Furthermore, the mapping images confirm the existence of Mo, S and Si elements in MoS\textsubscript{2}/Si HJ (Fig. 4. 1. i-l).

**Figure. 4.1.** (a) Top view SEM image of MoS\textsubscript{2} film, (b) SEM image of front surface of Si, (c) SEM image of MoS\textsubscript{2} coated Si, (d-f) HR-TEM images of MoS\textsubscript{2}/Si HJ, (g, h) TEM image and its corresponding mapping and (i-l) HAADF-STEM mapping images of Mo, S and Si elements in MoS\textsubscript{2}/Si HJ.
4.4.2 Photochemical characterization

The PEC H₂ production performance of the photocathode was evaluated in 0.5 M H₂SO₄ using a three electrode assembly. Illumination of the working electrode was simulated by solar irradiance and calibrated to “one sun” based on the AM 1.5G standard [172]. Fig. (4. 3. a) illustrates the schematic structure of MoS₂/Si HJ photocathode for PEC H₂ production. As shown in Fig. (4. 3. b), MoS₂/Si HJ photocathode exhibits an excellent PEC H₂ production performance with a positive onset potential of 0.56 V vs RHE, which is similar to the V_{oc} of the Si-MP solar cell. Impressively, MoS₂/Si HJ photocathode has achieved a maximum photocurrent density of 36.33 mA cm⁻² at 0 V vs. RHE, indicating exceptional PEC H₂ production activity of MoS₂/Si HJ photocathode. Moreover, the achieved current density and open circuit overpotential values are higher than most of the literature reported on MoS₂/Si-based photocathodes (Table. 1). Because of the superior characteristics of the Si-HJ cell since it possesses the ability to minimize the charge reduction and improve the light harvesting. In addition, integration MoS₂ to this Si-HJ cell leads to reduce the charge transfer resistance and provide a complete corrosion protective layer thereby enhanced the solar to H₂ conversion performance. Most importantly, the high saturation current density values that can be obtained from the MoS₂/Si HJ photocathode is close to the J_{sc} for Si MP solar cells, suggesting a minimal optical loss due to the efficient light-trapping properties of the Si MP structure. Fig. (4. 3. c) displays the MoS₂/Si HJ photocathode response to ON/OFF light illumination. Besides, Fig. (4. 3. d) demonstrates the stability measurement of MoS₂/Si HJ photocathode in which the MoS₂/Si HJ photocathode is found to be stable up to 600 min of reaction time.

To explain the excellent performance of the HJ photocathode, we carried out EIS to elucidate the charge-transfer resistance. Fig. (4. 3. e) demonstrates the Nyquist impedance plots for MoS₂/Si HJ and the bare MoS₂ photocathodes measured under one sun. The MoS₂/Si HJ photocathode has two distinguishable semicircles which are smaller than the semicircle
presented for the bare MoS\textsubscript{2} photocathode. The semicircles shape confirmed the reduction of the kinetics transport resistivity in MoS\textsubscript{2}/Si HJ photocathode. Furthermore, the semicircles proved the positive impact of the integration of the MoS\textsubscript{2} with Si, since more irreversible electrons can travel from the Si heterojunction to MoS\textsubscript{2} increasing its conductivity. Moreover, the HJ cell structure increased the charge separation and decreased the recombination probability within the MoS\textsubscript{2}/Si inference area. All of these factors played a role in increasing the MoS\textsubscript{2} electrons contribution to the hydrogen evolution process towards producing an efficient PEC performance.
Figure. 4.2. (a) Schematic illustration of MoS$_2$ integrated Si photocathode for PEC H$_2$ production (b) LSV curve of MoS$_2$/Si HJ photocathode in 0.5 M H$_2$SO$_4$ at a scan rate of 20 mV/s upon AM 1.5G illumination, (c) MoS$_2$/Si HJ photocathode response to ON/OFF illumination, (d) Stability curve of MoS$_2$/Si HJ photocathode in 0.5 M H$_2$SO$_4$ and (e) EIS spectra of MoS$_2$ film and MoS$_2$/Si HJ photocathode.
Table. 4.1. Literature summary based on MoS$_2$/Si hetrostructure for photochemical toward HER.

<table>
<thead>
<tr>
<th>Photocathode structure</th>
<th>Electrolyte</th>
<th>Photocurrent onset potential (V vs RHE)</th>
<th>Photocurrent density (mA cm$^2$ at 0 V)</th>
<th>Stability (h)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>ML-MoS$_2$/Si-HJ cell</td>
<td>0.5 M H$_2$SO$_4$</td>
<td>0.56</td>
<td>36.33</td>
<td>25</td>
<td>This work</td>
</tr>
<tr>
<td>MoS$_2$/n$^+$p Si</td>
<td>0.5 M H$_2$SO$_4$</td>
<td>-0.20 to -0.10</td>
<td>17</td>
<td>100</td>
<td>[173]</td>
</tr>
<tr>
<td>MoS$_2$/Al$_2$O$_3$/n$^+$p-Si</td>
<td>0.5 M H$_2$SO$_4$</td>
<td>0.35</td>
<td>34.5</td>
<td>40</td>
<td>[174]</td>
</tr>
<tr>
<td>1T-MoS$_2$/p-Si</td>
<td>0.5 M H$_2$SO$_4$</td>
<td>0.25</td>
<td>17.6</td>
<td>3</td>
<td>[171]</td>
</tr>
<tr>
<td>MoS$_x$/Ti/n$^+$p-Si</td>
<td>1.0 M HClO$_4$</td>
<td>0.33</td>
<td>16</td>
<td>1</td>
<td>[175]</td>
</tr>
<tr>
<td>MoS$_2$/TiO$_2$/NW-Si</td>
<td>0.5 M H$_2$SO$_4$</td>
<td>0.30</td>
<td>15</td>
<td>75</td>
<td>[176]</td>
</tr>
<tr>
<td>Co-MoS$_x$/Si</td>
<td>Phosphate solution pH= 4.25</td>
<td>0.25</td>
<td>17.5</td>
<td>3</td>
<td>[177]</td>
</tr>
<tr>
<td>MoS$_2$/p-Si (wafer scale)</td>
<td>0.5 M H$_2$SO$_4$</td>
<td>0.79</td>
<td>24.6</td>
<td>2.78</td>
<td>[178]</td>
</tr>
<tr>
<td>MoS$_2$/Al$_2$O$_3$/n$^+$p-Si</td>
<td>1 M HClO$_4$</td>
<td>0.4</td>
<td>35.6</td>
<td>120</td>
<td>[179]</td>
</tr>
<tr>
<td>MoS$_2$/NWs-Si</td>
<td>0.5 M H$_2$SO$_4$</td>
<td>0.26</td>
<td>16.5</td>
<td>48</td>
<td>[180]</td>
</tr>
</tbody>
</table>
Finally, the half-cell solar-to-hydrogen conversion efficiency ($\eta_{\text{STH}}$), which refers to the relationship between the input energy (solar irradiation) to the output energy (electric or chemical energy via hydrogen evolution subtracted from the input applied potential) has been calculated using the following equation [172].

$$\eta_{\text{STH}} = \left[ J_{\text{sc}} \text{ (mA cm}^{-2} \right) \times (1.23 \text{ V}) \times \eta_f / P_{\text{total}} \text{ (mW cm}^{-2} \right) \text{]}_{\text{AM 1.5G}} \tag{4.3}$$

The output energy ($P_{\text{out}}$) is equal to the measured current density ($J_{\text{sc}}$) times the effective potential ($V_{\text{redox}}$) required to run the desired reaction (in our case this is reflected in the potential required to exceed the 1.23 V needed to split water to H$_2$) times the faradic efficiency of the hydrogen evolution reaction ($\eta_f$) [172]. Based on Equation (4.3), the MoS$_2$/Si HJ photoelectrode indicates a half-cell $\eta_{\text{STH}}$ of 5.5 %.

### 4.5 Conclusion

In conclusion, MoS$_2$/Si HJ photocathode reported herein exhibited a maximum half-cell $\eta_{\text{STH}}$ of 5.5 % with a high photocurrent density of 36.33 mA/cm$^2$, an open circuit potential of 0.56 V vs. RHE, and stability up to 10 h of continuous reaction time. The EIS measurement demonstrated that the integration of MoS$_2$ significantly reduced the charge-transfer resistances across either the MoS$_2$/Si HJ interface or the MoS$_2$/electrolyte interface and thereby significantly enhance the PEC H$_2$ production efficiency. The excellent PEC H$_2$ production performance of the integrated photocathode provides a promising alternative for non-noble metal co-catalysts toward solar-driven hydrogen production. Importantly, this will also lead to additional research and exploration to employ the semiconducting metal chalcogenides for PEC applications.
CHAPTER 5

SINGLE Pt ATOMS CONFINED INTO MoS2 TOWARD AN EFFICIENT HYDROGEN EVOLUTION REACTION

5.1 Introduction

Nowadays, hydrogen is a renewable and reliable source of clean energy [181]. In fact, most of the H₂ today is produced from the steam-reforming methane which produces environmentally and health hazard gases, such as CO₂ [182]. To address this critical challenge, researchers tend to generate H₂ by utilizing an effective alternative method of the current CO₂-production application, such as electrolysis of water [183].

Pt is a unique catalyst compared to other materials due to its natural HER capability. However, its expensive cost and rare availability in the nature restricts its commercial potential. Therefore, enormous studied have been done to invent a new catalyst with specific features, such as high activity, long-term stability, a frugal cost for evaluating the molecules of hydrogen toward energy storage applications. Therefore, decreasing the Pt loading quantity to the atomic level could be a tool to reduce H₂ generating costs. Unlike metal nanoparticles or bulk metal catalysts, single metal atom catalyst (SACs) are identical in size, uniformly dispersed on the support and all are able to be actively involved in the catalytic reaction, resulting in improvement of the catalytic characteristics including the activity and stability of metals compared to their own nanoparticle counterparts. For example, single Pt atoms confined to FeO₂ demonstrated an efficient catalytic activity for CO oxidation compared to the Pt NPs [78].

Generally, two methods have been reported to reduce the usage of Pt. The first method is to reduce the particle size [184]. An example of this method was reported by Jordanov et al., in which they reduced the Pt particle size from 11 nm to 4 nm, which led to greatly increased
surface area and active sites for hydrogen evolution [184]. The second method is based on developing support materials that feature large surface areas and high chemical stability [184]. Various substrates, such as carbon supports [185], copper foam [186], and nanoporous gold films [187] have been suggested as ideal substrates aimed at reducing the amount of Pt used while maintaining the high HER activity.

Although SACs have been demonstrated to be efficient catalysts for different catalytic applications, the catalytic performance of SACs is not yet superior to the large-scale catalysts synthesis, due to their nature tending to diffuse and aggregate creating nanoparticles. It is essential to obtain scalable, controllable, and facile synthetic methods to achieve efficient SACs with high loading of metal atoms on the substrate especially method that are suitable for large scale applications. In this work, we used atomic layer deposition (ALD) as a synthesizing technique because of its ability for large-scale growth [188]. In addition to its precise control of the metal atom size and distribution on the support material due to its feature of self-limiting growth nature (an atomic layer-by-layer fashion) [189].

On the other hand, MoS$_2$ is an effective catalyst for generating hydrogen from water via either electrochemical or photochemical approaches, due to the H-S bond formation feature at its S-edges. [1, 3, 5, 190]. In the HER process, MoS$_2$ electrons can transfer across the layers to bond with the pre-absorbed protons (in the electrolyte) and reduce them to form H$_2$ gas. Therefore, the HER activity of MoS$_2$ depends on its conductivity and the number of exposed S-edges. To contribute to this area of study, we explore the effect of confining Pt SAs into MoS$_2$ (ALD Pt SAs /ML-MoS$_2$) for enhancing the MoS$_2$ conductivity toward the H$_2$ evolution application. The obtained electrochemical results emphasize the positive influence of the Pt SAs and clusters on improving MoS$_2$ conductivity that resulted in almost zero overpotential and 150 hours of continuous stability.
5.2 Electrode Fabrication Methods

5.2.1 Synthesis of MoS₂

We synthesized MoS₂ thin films via the thermolysis annealing method as described in details in section (3.1). The thickness of the MoS₂ ranged between 50–70 nm.

5.2.2 ALD doping of Pt SA into MoS₂

The Pt SAs and clusters deposition were performed in the Atomic Layer Deposition (ALD) chamber. Based on the growth details reported in reference [97], we used solid MeCpPtMe₃ and oxygen as a precursor (99%, Stream Chemicals) while argon was applied as a carrier gas and nitrogen as a purge gas. The holding time was 20 seconds and with a growth rate of 0.05 nm/cycle. The growth chamber temperature was 250 °C and the precursor container (MeCpPtMe₃) temperature was kept at 69 °C to avoid precursor condensation. Note, the size, density, and distribution of the Pt SAs and clusters on the MoS₂ thin film rely on the ALD cycle number. Consequently, three ALD cycles were enough to produce a single Pt atom while clusters formed with seven ALD cycles.

5.3 Electrode Characterization Methods

X-ray photoelectron spectroscopy (XPS) studies were accomplished by utilizing a Kratos Axis Supra DLD spectrometer equipped with a monochromatic Al Ka X-ray source (hv = 1486.6 eV) operating at 150 W, a multi-channel plate and delay line detector under a vacuum of a ~ 9-10 m bar, while X-ray intensity data were achieved at room temperature using a Bruker D8 Advance powder diffractometer (German Bruker) equipped with a Lynx- Eye detector and a Cu source. Moreover, the ALD Pt SAs/ML-MoS₂ internal structures were morphologically examined by highly resolution transmission electron microscopy (HR-TEM), high-angle annular dark-field scanning transmission electron microscopy (HADDAF) and aberration-corrected scanning transmission electron microscopy (AC-EM). The ALD Pt SAs/ML-MoS₂
heterostructure were synthesized on the Au grid that coated with carbon film using the previous synthesis method previously mentioned in section (3.1) for preparing MoS$_2$, followed by utilizing an ALD technique to confine the Pt SAs and clusters.

We examined the HER activities for the ALD Pt SAs /ML-MoS$_2$ electrodes by using standard three-electrode electrochemical cell setup in 0.5 M H$_2$SO$_4$ electrolyte. The Ag/AgCl and Pt wire were utilized as the reference and the counter electrode, respectively. To employ it as a reference point, we also measured the catalytic activity of the commercial Pt wire. All the potentials reported in this work were normalized against that of the RHE. The HER activity of the electrodes was evaluated by measuring linear sweep voltammetry (LSV) by sweeping the potential from 0 to -0.5 V versus RHE at room temperature at the scan rate of 20 mV/s. To estimate the Tafel plot values for assessing the HER kinetics of each electrode, the polarization potential curves were replotted as overpotential ($\eta$) versus log current density. The Tafel equation ($\eta = b \log (j) + a$) can be utilized to estimate the Tafel slope (b). Furthermore, electrical impedance spectroscopy (EIS) was collected using the FRA impedance potentiostatic modules. The amplitude of the AC signal was 10 mV and the impedance ranged from 200 KHz to 100 MHz with 10 points/decade. The stability measurement was examined by applying a chronoamperometry technique to record the change in current density with the time at the fixed applied potential of 0.2 V and at a scan rate of 20 mV/S. Also, cyclic voltammetry (CV) was performed at various sweep rates to calculate the double layer capacitor ($C_{dl}$) values in a potential range of (0.1-1 V) versus RHE at room temperature.

5.3.1 X-Ray photoelectron spectroscopy (XPS)

XPS was applied to identify the chemical components presented in the electrodes and their related oxidation states. As illustrated in the spectra in Fig. (5.1 a-c), the elements of Mo, S, and Pt can be obviously identified in the ALD Pt SAs/ML-MoS$_2$ electrodes. For the bare MoS$_2$ control sample, we attribute the binding energies of Mo 3d$_{5/2}$ and Mo 3d$_{3/2}$ observed at 229.14
eV and 232.38 eV to the presence of Mo in the $4^+$ oxidation state [8]. Also, the binding energies of the S 2p$_{3/2}$ and S 2p$_{1/2}$ states were observed at 162.07 eV and 163.25 eV, respectively, the binding energy located at 226.9 eV is attributed to the S 2s state.

For (different ALD cycles) Pt/MoS$_2$ electrodes, two peaks are presented at 72.82-72.71 eV and 76.119-76.02 eV which belong to Pt 4f$_{7/2}$ and 4f$_{5/2}$ states. These Pt binding energy values confirm the existence of Pt (in the electrode) in its metal phase and no oxides were formed during the ALD synthesis process [191]. As clearly shown in Fig. (5.1 b-c), increasing the ALD cycles from 0 to 10 leads to negative shifting in the S binding energy peaks compared to the corresponding S-peak of the control sample. Also, the Pt binding energy peaks are negatively shifted due to increasing the Pt loading amount with increases in the ALD cycles. The Pt loading amount was estimated to be 0.78, 0.9, 1.4 and 1.6 wt% for the 3, 5, 7 and 10 ALD cycled samples, respectively. Latterly, XPS data confirm Pt SAs and cluster formation and subsequent their anchoring into the MoS$_2$ film.

![Figure 5.1](image.png)

**Figure 5.1.** XPS spectra of ALD Pt SAs/ MoS$_2$ electrodes with different ALD cycles ranged from 0 to 10: (a) Mo 3d spectrum; (b) S 2P spectrum, and (c) Pt 4f spectrum.
5.3.2 High resolution transmission electron microscopy (HR-TEM)

HR-TEM imaging techniques is considered a key method for investigating local structure information and the metal species (either single atoms or clusters) distribution on the support, because of the high spatial resolution allow to precisely indicate the size and distribution of each individual metal atoms [192]. Comprehensively, we examined the size, density, and distribution of the Pt SAs and clusters anchored into the MoS$_2$ film by applying HAADF-STEM microscopy.

Particularly, Fig. (5.2. a-e) illustrates HR-TEM and HAADF-STEM images of (different ALD cycles) Pt/ML-MoS$_2$ samples. Fig. (5.2.a) clearly displays the typical MoS$_2$ structure that has plentifully exposed (002) basal planes with a calculated interlayer fringe distance of 0.69 nm [193]. Moreover, Fig. (5.2. b-c) demonstrate the effect of the atomic number (Z) on the atoms contrasted in HADDAF-TEM images. Numerous individual Pt atom (bright spots due to larger Z) distributed along the MoS$_2$ lattice (darker color) for the samples ALD cycles of 3 and 5. In contrast, fig (2.5.d-e) exhibit the HAADF-STEM images of the 7 and 10 ALD cycles samples, where Pt atoms (ranging from 2-3 atoms) bonded together to form a mini-cluster shape that uniformly dispersed and were confined into the MoS$_2$ lattice. Moreover, increasing the ALD cycles to 30 leads to aggregation of Pt atoms and creation of large size clusters that may form NPs [81, 97], as illustrated in fig (2.5.f). Interestingly, the obtained HAADF-STEM images reflect the z-dependent contrast for detecting the location of heavy single metal atom sites, such as Pt and Au that are confined on the surface or within the lattice of lighter Z materials, such as graphene or MoS$_2$ [189]. Particularly, these images confirm the capability of the ALD technique for fabricating different morphological metal shapes on the MoS$_2$ surface by only controlling the number of ALD cycles.
Figure 5.2. (a) HR-TEM images of bare MoS$_2$. HADDAF-TEM images of (b) 3 cycle ALD Pt/MoS$_2$, (c) 5 cycle ALD Pt/MoS$_2$, (d) 7 cycle ALD Pt/MoS$_2$, (e) 10 cycle ALD Pt/MoS$_2$ and (f) 30 cycle ALD Pt/MoS$_2$. 
5.4 Electrochemical Studies

Jaramillo et al [194] suggested that the electrode overpotential at 10 mAcm$^{-2}$ is a crucial parameter for evaluating different catalyst performance. Accordingly, we measured the catalytic activity of a commercial Pt wire (a reference point). The Pt exhibits high HER catalytic performance with an overpotential near 0 V vs RHE. The LSV results elucidated in Fig. (5.3.a) displaying the bare ML-MoS$_2$ catalytic activity for HER with an overpotential of around -0.273 V. vs RHE at 10 mA cm$^{-2}$. In contrast to bare ML-MoS$_2$, the ALD Pt/MoS$_2$ electrodes featuring different Pt ALD cycles show distinctly enhanced HER activity in which the overpotential is reduced to -0.0505 V vs RHE to reach a current density of 10 mA cm$^{-2}$ using only 10 ALD cycles. Decreasing the overpotential values reflects the improvement on the catalytic activity of ALD Pt/MoS$_2$ electrodes towards the HER compared to the MoS$_2$. This is likely attributed to improved MoS$_2$ electronic conductivity and enhanced the charge carrier transportation with increased the Pt loading amount. To explain the obtained results, MoS$_2$ can be considered a low conductive material compared to the metal catalyst such as Pt due to its natural semiconductor behavior, which leads to insufficient charge transport. However, when the Pt SAs and clusters are confined into MoS$_2$, the overpotential is decreased (due to increase MoS$_2$ conductivity) to a value that can be comparable to the corresponding commercial Pt electrode value. Table. (5.1) presents the overpotential values of commercial Pt, bare MoS$_2$, and (different ALD cycles) Pt/MoS$_2$ electrodes at 10 mA cm$^{-2}$.

Furthermore, a smaller Tafel slope reflects the faster increasing the HER rate with increasing potential. Therefore, the linear portion of the Tafel plots in Fig. (5.3.b) were fit to the Tafel equation to determine the Tafel slope of each electrode ($I = b \log J + a$, in which $J$ is the current density and $b$ is the Tafel slope). We calculated the Tafel slope of the commercial Pt wire as 41.5 mV/decade, which is near to the 40 mV/decade of the Volmer-Heyrovsky reaction, while the Tafel slope is 144 mV/decade for the bare ML-MoS$_2$ and 78 mV/decade for the 10 ALD
cycle Pt/MoS$_2$ electrode. The Tafel slopes of the ALD Pt/MoS$_2$ electrodes ranged from 78-137 mV/decade, which indicates a fast improvement to the HER velocity with increasing potential [195]. The value of 78 mV/decade for the 10 ALD cycle Pt/MoS$_2$ electrode in this work is close to that of Li-MoS$_2$ nanoparticles [147] and carbon nanotubes coated with a single layer of MoS$_2$ [145], this value also suggesting a Volmer-Heyrovsky mechanism of the HER process [43, 57, 196]. Table 5.1 illustrates the Tafel slope values for all the electrodes.

**Table 5.1.** The overpotential and Tafel slopes of commercial Pt, bare ML-MoS$_2$ and (different ALD cycles) of Pt/MoS$_2$ electrodes.

<table>
<thead>
<tr>
<th>Electrode conditions</th>
<th>Overpotential (V vs RHE) at -10 mA cm$^{-2}$</th>
<th>Tafel slope (mV/decade)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt</td>
<td><strong>-0.023</strong></td>
<td><strong>41.5</strong></td>
</tr>
<tr>
<td>MoS$_2$</td>
<td>-0.237</td>
<td>144</td>
</tr>
<tr>
<td>3 cycle ALD Pt/MoS$_2$</td>
<td>-0.136</td>
<td>137</td>
</tr>
<tr>
<td>5 cycle ALD Pt/MoS$_2$</td>
<td>-0.127</td>
<td>104</td>
</tr>
<tr>
<td>7 cycle ALD Pt/MoS$_2$</td>
<td>-0.074</td>
<td>90</td>
</tr>
<tr>
<td>10 cycle ALD Pt/MoS$_2$</td>
<td><strong>-0.0505</strong></td>
<td><strong>78</strong></td>
</tr>
</tbody>
</table>
Figure 5.3. (a) Plot presents the LSV curves of commercial Pt wire, bare ML-MoS$_2$ and (different ALD cycles) of Pt/MoS$_2$. (b) The corresponding Tafel slope curves.

We also applied the Nyquist plots for evaluating the charge transport improving with increasing ALD cycles of the bare MoS$_2$ and ALD Pt/MoS$_2$ electrodes. Fig. (5.4.a) illustrates the semicircles in the low-frequency mode where as expected, the ALD Pt/MoS$_2$ electrode (10 cycles) showed a lower charge-transfer impedance ($R_{ct}$) of (~13.06 Ω cm$^2$) than that of the bare MoS$_2$ multilayer film (~78.75 Ω cm$^2$). As expected, the impedance $Z_{lm}$ values decreased with an increase the Pt ALD cycles from 0 to 10 cycles. Consequently, the electrons transport is faster in the ALD Pt/MoS$_2$ electrodes than the bare MoS$_2$ catalyst. Also, the proposed explanation of these idealistic results is that MoS$_2$ in its original form is a semiconductor material with low conductivity compared to the Pt metal. As a consequence, loading an atomic amount of Pt led to improvement of the MoS$_2$ electronic semiconductor behavior and enhancement of the internal charge transport, which led to the excellent HER performance. Moreover, XRD pattern exhibits no obvious change in MoS$_2$ hexagonal structure that maybe caused by anchoring Pt SAs and clusters, Fig. (5.4. b).
Figure 5.4. (a) EIS was used to analyze the charge transport of bare ML-MoS$_2$ and (different ALD cycles) Pt/MoS$_2$ electrodes.

Furthermore, stability is a significant parameter for evaluating the catalyst. Chronoamperometry (j-t) shown in Fig. (5.5. a), for the 10 ALD cycle Pt/MoS$_2$ electrode, demonstrates a constant HER process to generate hydrogen molecules at an overpotential of -0.230 V. Remarkably, the cathodic current density remained stable at approximately -8 mA cm$^{-2}$ for over 150 hours, suggesting the highest stability of the MoS$_2$ based catalysts in the reported literature. Moreover, we applied an extra stability test in which CV plots were measured before and after the stability measurement, Fig. (5.5. b). We did not observe any obvious shift in the onset potential or curve shapes before or after the stability measurement. This excellent durability of the 10 ALD cycle Pt/MoS2 electrode confirms that it has a strong potential to replace the noble metals -based electrodes for HER application.
Figure 5.5. (a) I-t measurement of 10 ALD cycle Pt/MoS$_2$ electrode demonstrates a continuous HER process to generate hydrogen molecules. (b) Cyclic voltammetry for measuring 10 ALD cycle Pt/MoS$_2$ electrode stability before and after 150 hours.

To confirm the excellent stability result, XPS was applied after the LSV measurement to investigate the change in the chemical composition of the 10 ALD cycle Pt/MoS$_2$ electrode. Fig (5.6.a-c) illustrates the binding energy spectra of Mo, S and Pt elements without any obvious change of the elements binding energy compared to that obtained before the electrochemical measurement, as illustrated in Fig. (5.1.a-c), demonstrating that the 10 ALD cycle Pt/MoS$_2$ is a stable electrode for HER in the acidic solution.
The surface area and the catalytic active site amounts are factors that have an important impact on the HER performance. Therefore, to evaluate the effective surface area of the electrodes, the cyclic voltammetry measurement was carried out to calculate the double-layer capacitance ($C_{dl}$) which is defined as a gauge for the interfacial area between the electrode surface and an electrolyte. In fact, it is difficult to precisely determine the catalytic active surface area because of the ambiguous capacitive behavior of the MoS$_2$ electrode [197], however, we can safely calculate the relative surface areas by using the current density response that was presented in the cyclic voltammetry curves. Fig. (5.7.a-f) indicates the CV curves of bare MoS$_2$ and Pt/MoS$_2$ electrodes with 3, 5, 7 and 10 ALD cycles in the potential region of 0.1–1 V vs RHE. In more detail, the $C_{dl}$ values are estimated by plotting the DJ ($J_{\text{anode}} - J_{\text{cathode}}$) at fixed potential of 0.4 V vs. RHE against the scan rate, where the slope is twice $C_{dl}$. 

**Figure. 5. 6.** XPS spectra of 10 ALD cycle Pt SAs/ MoS$_2$ electrode after LSV measurement (a) Mo 3d spectrum; (b) S 2P spectrum and (c) Pt 4f spectrum.
Figure 5.7 (a-f) demonstrate the CV curves of bare MoS$_2$ and (different ALD cycles) of Pt/MoS$_2$ electrodes in the potential region of 0.1-1 V vs RHE.

Fig. (5.8) displays the $C_{dl}$ slope plots of MoS$_2$ and ALD Pt/MoS$_2$ electrodes, with different ALD cycles, where the bare MoS$_2$ electrode shows a smaller $C_{dl}$ ($3.61 \times 10^{-3}$ mFcm$^{-2}$) while the 10 ALD cycle Pt/MoS$_2$ value is $10.9 \times 10^{-3}$ mFcm$^{-2}$. These results point to increasing the Pt loading amount which leads to increasing the electrode active edge sites which has a positive impact in improving the HER activity. Also, there is a proportional relation between increasing $C_{dl}$ values and catalytic active sites densities toward HER with increasing the ALD cycles, due to the impact of increasing the Pt SAs and cluster loading amount.
Figure 5.8. The $C_{dl}$ plots of bare MoS$_2$ and ALD Pt/MoS$_2$ electrodes, with different ALD cycles ranging from 3 to 10.

5.4 Conclusion

In electrochemical HER, decreasing the Pt loading amount and increasing its utilization efficiency are important characteristics for producing large scale HER-based products, since Pt nanoparticles cannot promote the HER activity where only the surface atoms are fully involved in the electrochemical reaction while the bulk atoms are inert. To solve this challenge, confining single Pt atoms and clusters into an efficient catalyst, such as MoS$_2$, would be an ideal idea. In this work, the ALD technique shows the ability to solve the Pt tendency for agglomerating and forming nanoparticles. Therefore, The ALD Pt/ML-MoS$_2$ electrodes demonstrate an excellent catalytic activity and long-term stability which results from improving the MoS$_2$ electronic conductivity toward the HER application.
CHAPTER 6

SUMMARY AND OUTLOOK

In conclusion, we have demonstrated that 2H-MoS$_2$ is a promising candidate for catalyzing photo/electrochemical HER. The superior nature of its planar surface, which maximizes the number of exposed active sites while providing an ultra-short diffusion path, ensures high HER catalytic performance comparable to that of Pt catalysts. Moreover, due to the atomic thickness and the chemical accessibility of 2H-MoS$_2$, its catalytic activity could be further enhanced by several modification strategies. In general, two main approaches are being pursued: the first involves engineering the structure of MoS$_2$ to improve its intrinsic catalytic activity, including thinning the layers, exposing the edges, and incorporating defects to create more active sites. The second approach aims to enhance the kinetics of charge transfer, including strain engineering, doping the substrate with heteroatoms, and designing synergetic composites, all of which can efficiently facilitate charge transfer in the electrochemical system.

In this thesis, we have demonstrated fabrication of multilayers of MoS$_2$ using the hydrothermal decomposition technique and characterized the material for HER applications. We have also focused on enhancing the internal conductivity of ML-MoS$_2$ using the following strategies:

I. **Integrating MoS$_2$ into Si-HJ solar cell to serve as synergetic heterostructure for photoelectrochemical H$_2$ production.**

II. **Anchoring single metal atoms and clusters such as Pt in MoS$_2$ to electrochemically generate H$_2$.**

For the synergetic heterostructure of ML-MoS$_2$/Si-HJ cell studies, we believe that the extra conductivity improvement will result in higher photoelectrochemical efficiency that can be
comparable to the efficiency of coupling a Si heterojunction solar cell to Pt. For the Pt-SAs and clusters anchoring into MoS$_2$ studies, we have demonstrated excellent HER performance with a low overpotential of -0.05 V vs. RHE and a small Tafel slope of 78 mV/decade in addition to the long-term durability of the HER electrocatalyst (150 hours). As a result, we have proven the 2H-MoS$_2$ electrocatalyst can survive corrosion during the electrolysis process.

In future work, we will continue studying the HER catalytic activity and stability of 2H-MoS$_2$ after integration into the Si-triple junction solar cell. Though Pt-SACs/ML-MoS$_2$ have been demonstrated as efficient catalysts for different catalytic applications. However, the catalytic performance of transition metal dichalcogenide monolayers/single metal atoms (SACs/TMD) is not yet superior to all conventional catalysts. There are many challenges that remain and need to be addressed to develop highly efficient and robust SACs/TMD.

I. More scalable, controllable, and facile synthetic procedures are particularly needed to achieve efficient metal SACs with a high loading of metal atoms on the substrate, especially methods that are suitable for large scale applications.

II. The stabilization of atomic single metal atoms on the support such as a monolayer of TMDs, is another critical challenge as single atoms have a very high surface energy, which tends to promote aggregation and the formation of nanoparticles. Therefore, more attention should be paid to developing a viable route to stabilizing SACs that can withstand prolonged reaction times under harsh environments.

III. SACs/TMD interactions are one of the most important parameters that play a vital role in achieving the desired catalytic activity and selectivity. The conceptual mechanism underlying the metal-TMD interactions needs to be further supported with experimental results to understand how single metal atoms interact with TMD to enhance the catalytic properties. Moreover, real time in situ analysis would be helpful to probe the structural and dynamic changes that occur on SACs during catalytic reactions. In such studies, it
would be ideal to have the capability to identify the specific active sites responsible for the catalytic reactions.

IV. Other than carbon supports, recently developed 2D materials, such as MXene and LDH, etc., may also be employed as potential supports to anchor single atoms. In addition, dual single atom doping is a novel, developing approach involving the addition of two different single atoms onto two different heteroatom sites of the same support, which could enhance the catalytic activity of SACs for water splitting applications.

To date, SACs/TMD hetrostructure have been used either as HER or OER catalysts. Further studies should be focused on designing bi-functional SACs/TMD to drive both HER and OER simultaneously. Considering the interesting SACs properties, we also foresee that the development of SACs confined on 2D supports may be further extended to advanced sustainable energy conversion and storage applications.

TMDs combined with single metal atoms have been utilized as composites for photocatalytic H₂ evolution. We believe that there is still a need for more research in this field to fully understand how SACs are involved in enhancing the solar to hydrogen conversion efficiency. Our aim in combining the rich structure of MoS₂ with numerous engineering strategies is to boost its performance so that it will enable the highly efficient, renewable, and affordable large-scale production of hydrogen.
APPENDICES

1. Publications


2. Conference and presentations

I. The 4th Saudi International Nanotechnology Conference. **Abeer Alarawi** and Jr Hau He. King Fahd University of Petroleum and Minerals (KFUPM), (October 25-27, 2016), Dhahran, KSA.

II. Electrochemistry Society, 232$^{nd}$ ECS Meeting. **Abeer Alarawi** and Jr Hau He, (October 1-5, 2017), National Harbor, MD (greater Washington, DC area), USA.

REFERENCES


