

Nanostructured Molybdenum Disulfide Thin Film Based Electrocatalysts for Hydrogen Evolution Reaction

Sha Li

Supervised by Professor Jamie H. Warner



*Submitted in conformity with the requirements for the degree of DPhil in
Materials Science*

Department of Materials

Wolfson College

University of Oxford

September 2018

Copyright © 2018 by Sha Li

Dedicated to my parents and my brother

Declaration

The material contained within this thesis has not been previously submitted for a degree at the University of Oxford or any other university. The research reported in this thesis has been conducted by the author unless indicated otherwise.

Copyright Notice

The copyright of this thesis rests with the author. No quotation from it should be published without the prior written consent of the author, and any other information derived from it should be acknowledged.

Abstract

Nanostructured Molybdenum Disulfide Thin Film Based Electrocatalysts for Hydrogen Evolution Reaction

by Sha Li

Wolfson College

In pursuit of DPhil Degree, Trinity Term, 2018

2H-Molybdenum disulfide (2H-MoS₂) with catalytically active edges has emerged as a promising catalyst for the hydrogen evolution reaction (HER), $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$. Towards designing highly active MoS₂ catalyst with maximized edge density and activated basal surfaces, this DPhil project focused on the synthesis of nanostructured MoS₂ thin film based HER electrocatalysts, using chemical vapor deposition (CVD), gas phase treatments and thermal annealing (TA) methods, followed by characterisation and electrochemical testing of their structural and catalytic properties.

Firstly, a reproducible and scalable synthesis method for high-quality 3D edge rich (3D-ER) MoS₂ nanoplatelets utilizing single-step CVD approach was developed. Tailoring CVD parameters resulted in the optimized structure for HER that consists of larger MoS₂ platelets with smaller layered MoS₂ sheets growing perpendicularly, which increases the total number of edge sites within a given geometric area. By systematically controlling the growth temperature, tunable film thickness and surface morphology were achieved, enabling the optimized combination of edge density, inter-planar charge transport and sufficient binding with the substrate as well as fast removal of gas bubbles via a superaerophobic surface.

Subsequently, gas phase treatments for post-growth modification was applied to activate the catalytically inactive basal plane sites of 3D-ER-MoS₂. Hydrogen (H₂) annealing and oxygen (O₂) plasma etching were utilized to generate defects (cracks, pits, holes, and vacancies) that can catalyze HER in the basal surfaces. By controlling O₂ plasma exposure time and H₂ annealing temperature, tunable defect density, surface area, and catalytic activity enhancement can be obtained. Optimum treatment conditions led to dramatic improvements in electrocatalytic activity.

Lastly, a hybrid electrocatalyst was prepared by growing Pt nanocrystals on the surface of 3D-ER-MoS₂ via TA of Pt precursor. By varying synthesis conditions – precursor loading and TA temperature – average size and specific surface area of Pt nanoparticles can be precisely controlled. Results show that higher Pt loading yields better HER performance despite a smaller specific surface area; higher TA temperature delivers a larger average particle size of the Pt crystals and lowers HER activity. Larger average size led to fast sintering and thus poor durability of the catalyst. The outstanding HER activity of Pt/MoS₂ is attributed to highly-dispersed Pt nanoparticles grown on MoS₂ basal surfaces, large MoS₂ edge density and Pt – S bonding effect induced activity improvement of MoS₂ as well as 3D porous network assisted superaerophobic surface.

Acknowledgements

I wish to thank all the people for supporting me during my DPhil research journey at Nanostructured Materials Group, Department of Materials, University of Oxford.

I am grateful to Prof. Jamie H. Warner for providing the opportunity to conduct top-notch research; for providing inspirational ideas, insightful discussions and fruitful criticism; for his constant encouragement and support.

Appreciation should go to my collaborators and colleagues for their knowledge and expertise in related areas: Prof. Mauro Pasta for providing electrochemical testing facilities, incisive criticism and insightful discussion on electrochemical results; Dr. Jakyung Lee, Dr. Xiaochen Wang, and Mr. Si Zhou for their help with high resolution electron microscopy; Dr. Chiara Marletto for her encouragement and helpful advice through my difficult times. I am most grateful to Dr. Shanshan Wang for her mentorship on materials synthesis, Raman spectroscopy, scanning and transmission electron microscope as well as those illuminating conversations, where her exceptional knowledge and integrity have tremendously inspired me.

I am appreciative to my friends for their wholehearted understanding; to those who came along in my pursuit to live the fullness of life for bringing around laughter and tears.

And, to my parents and my brother, with their unconditional love, they are the reason of what I become today.

Publications

The following presents a list of research accomplished during the course of this DPhil project, which has been published. The results and discussion chapters in this thesis are based on the 3 published manuscripts.

Chapter 4

1. **Li, S.**; Wang, S.; Salamone, M. M.; Robertson, A. W.; Nayak, S.; Kim, H.; Tsang, S. E.; Pasta, M.; Warner, J. H. Edge Enriched 2D MoS₂ Thin Films Grown by Chemical Vapor Deposition for Enhanced Catalytic Performance. *ACS Catal.* **2016**.

Chapter 5

2. **Li, S.**; Zhou, S.; Wang, X.; Tang, P.; Pasta, M.; Warner, J. H. Increasing the electrochemical activity of basal plane sites in porous 3D edge rich MoS₂ thin films for the hydrogen evolution reaction. *Mater. Today Energy* **2019**.

Chapter 6

3. **Li, S.**; Lee, J. K.; Zhou, S.; Pasta, M.; Warner, J. H. Synthesis of Surface Grown Pt Nanoparticles on Edge-enriched MoS₂ Porous Thin Films for Enhancing Electrochemical Performance. *Chem. Mater.* **2019**.

Second-Author

4. Xu, W.; **Li, S.**; Zhou, S.; Lee, J. K.; Wang, S.; Sarwat, S. G.; Wang, X.; Bhaskaran, H.; Pasta, M.; Warner, J. H. Large Dendritic Monolayer MoS₂ Grown by Atmospheric Pressure Chemical Vapor Deposition for Electrocatalysis. *ACS Appl. Mater. Interfaces* **2018**.

Co-Author

5. Wang, S.; Sawada, H.; Han, X.; Zhou, S.; **Li, S.**; Guo, Z. X.; Kirkland, A. I.; Warner, J. H. Preferential Pt Nanocluster Seeding at Grain Boundary Dislocations in Polycrystalline Monolayer MoS₂. *ACS Nano* **2018**.
6. Wang, X.; Sheng, Y.; Chang, R.-J.; Lee, J. K.; Zhou, Y.; **Li, S.**; Chen, T.; Huang, H.; Porter, B. F.; Bhaskaran, H.; Warner, J. H. Chemical Vapor Deposition Growth of Two-Dimensional Monolayer Gallium Sulfide Crystals Using Hydrogen Reduction of Ga₂S₃. *ACS Omega* **2018**.

Table of Contents

1	<i>Introduction</i>	1-1
1.1	Project Aims	1-1
1.2	Scope of Thesis	1-1
2	<i>Literature Review</i>	2-4
2.1	Introduction	2-4
2.2	Hydrogen Energy Future	2-5
2.3	Electrochemistry Basics	2-7
2.3.1	Water Splitting	2-7
2.3.2	HER Kinetics	2-10
2.4	Evaluation of Electrocatalytic Activity	2-17
2.4.1	Total Electrode Activity	2-19
2.4.2	Intrinsic Activity by Surface Area Normalization	2-23
2.5	Molybdenum Disulfide	2-28
2.5.1	Crystal Phases	2-28
2.5.2	Catalytic Properties	2-32
2.6	Design of MoS ₂ Based Nanostructured Electrocatalysts	2-38
2.6.1	Principles for Electrocatalyst Design	2-38
2.6.2	Edge Enrichment in 2H-MoS ₂	2-41
2.6.3	Basal Plane Activation in 2H-MoS ₂	2-45
2.6.4	Pt/MoS ₂ Composites	2-58
2.7	Conclusion	2-65
3	<i>Methodology</i>	3-67
3.1	Introduction	3-67

3.2	Synthesis of MoS₂ Thin Film based Electrocatalysts.....	3-67
3.2.1	CVD Growth of 3D-ER-MoS ₂ Porous Thin Film	3-67
3.2.2	Defect Engineering of CVD 3D-ER-MoS ₂ Porous Thin Film	3-73
3.2.3	Surface Growth of Pt Nanoparticles on CVD 3D-ER-MoS ₂ Porous Thin Film	3-74
3.3	Raman Spectroscopy	3-75
3.4	Scanning Electron Microscopy	3-76
3.5	(Scanning) Transmission Electron Microscopy	3-76
3.6	Three Electrode Electrochemical Measurements.....	3-77
3.6.1	HER Measurement	3-79
3.6.2	Cottrell Measurement	3-79
4	<i>Edge Enriched 3D MoS₂ Thin Films Grown by Chemical Vapor Deposition for Enhanced Catalytic Performance</i>	<i>4-81</i>
4.1	Introduction	4-81
4.2	Results and Discussion	4-83
4.3	Conclusion.....	4-111
5	<i>Activating Basal Plane Sites in 3D Edge Rich MoS₂ Thin Films for the Hydrogen Evolution Reaction</i>	<i>5-112</i>
5.1	Introduction	5-112
5.2	Results and Discussion	5-113
5.3	Conclusion.....	5-133
6	<i>Synthesis of Surface Grown Pt Nanoparticles on Edge-enriched MoS₂ Porous Thin Films for Enhancing Electrochemical Performance</i>	<i>6-135</i>
6.1	Introduction	6-135

6.2	Results and Discussion	6-137
6.3	Conclusion.....	6-161
7	<i>Conclusion and Outlook.....</i>	7-163
7.1	Conclusion.....	7-163
7.2	Outlook.....	7-167
	<i>Appendix</i>	169
	<i>References</i>	180

1 Introduction

1.1 Project Aims

The objective of this doctorate project was the design and synthesis of nanostructured molybdenum disulfide (MoS_2) thin film based electrocatalysts for hydrogen evolution reaction (HER) by chemical vapor deposition (CVD), post-growth gas phase treatments and thermal annealing (TA) approaches and subsequent systematic investigation of structural, chemical and electrocatalytic properties of the resultant products via a series of characterisation techniques and electrochemical testing methods.

1.2 Scope of Thesis

This thesis covers research executed over the course of 3.5 years of a UK DPhil degree at the Department of Materials, University of Oxford. The overall structure of this thesis is illustrated in **Figure 1–1**. Guided by catalyst design principles, my research is on identifying the active catalytic structures in MoS_2 , setting out a proper strategy for optimizing MoS_2 based catalysts and synthesizing the catalysts using appropriate experimental methods so that high electrocatalytic performance can be achieved.

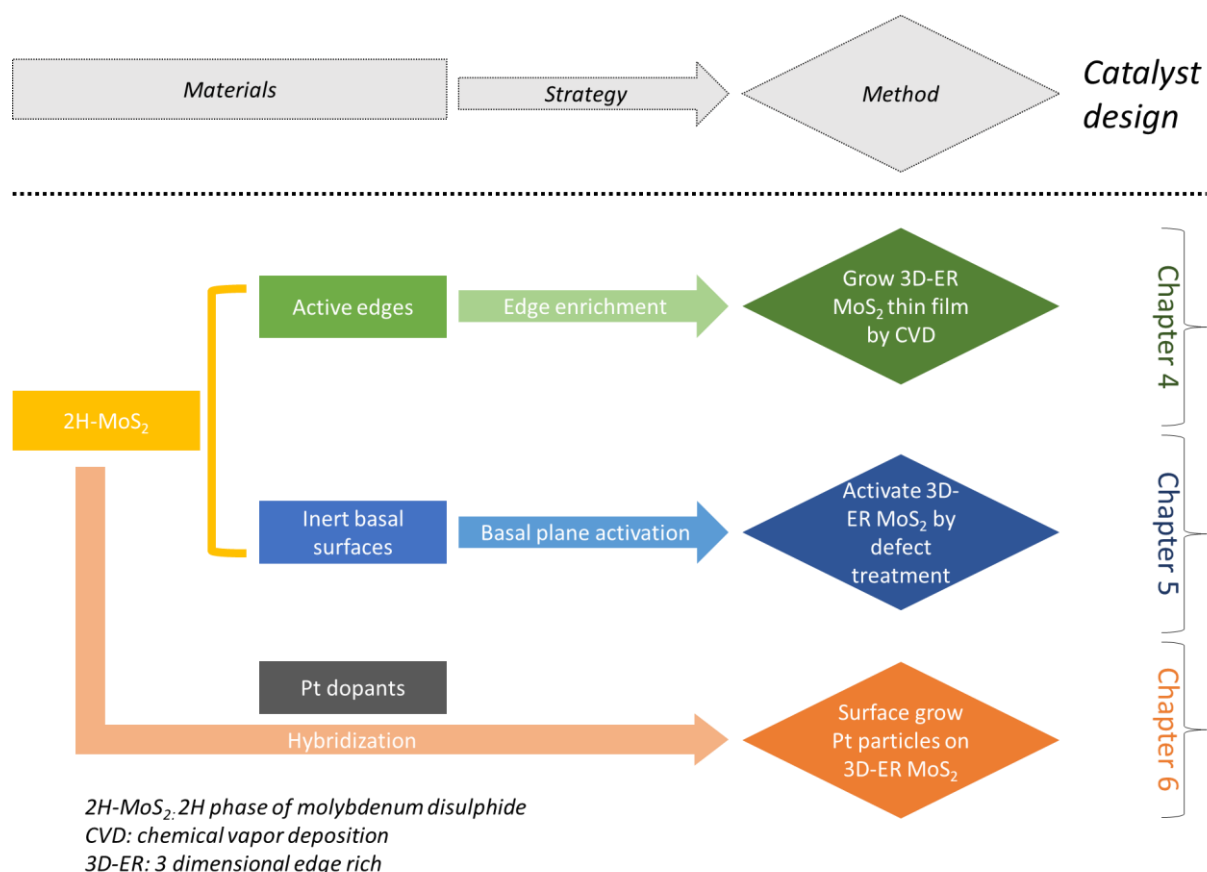


Figure 1–1. Schematic illustration of the overall structure of this thesis constructed under a catalyst design paradigm (as indicated in grey blocks).

First of all, a comprehensive literature review (**Chapter 2**) is provided from the following aspects: the critical role of electrocatalysts in a sustainable energy future, electrochemistry basics and an evaluation framework for HER electrocatalyst, crystallographic structure and catalytic properties of MoS₂, as well as catalyst design strategies and state-of-the-art MoS₂ based electrocatalysts.

The first problem I have tackled was to establish a scalable single-step atmospheric pressure CVD (APCVD) approach to produce 3D edge rich (3D-ER) MoS₂ thin films with a highly porous network on a wide range of substrates to be readily integrated into different electrochemical device architectures, corresponding to **Chapter 4**. The

porous network of vertical aligned MoS₂ nanoplatelet was systematically characterized and tested to provide a correlation between morphology, microstructure and electrochemical performance, in order to identify the critical parameters that improve catalytic performance and can potentially help guide the optimization of industrial MoS₂ electrocatalysts.

Subsequently, I provide a feasible solution to activate basal plane sites by the generation of defects via post-growth gas phase treatments. Hydrogen (H₂) annealing and oxygen (O₂) plasma etching were employed to further improve the HER activity of 3D-ER MoS₂ thin film by making use of the huge amount of catalytic inactive basal surfaces. As a result, **Chapter 5** was on tunable defect modification by controlling gas phase treatment conditions. Furthermore, the quantitative correlation between defect modulation and catalytic improvement was explored.

Apart from being a promising electrocatalyst with high edge density, the 3D-ER branched MoS₂ with high surface area holds potential as a 3D networked scaffold, to deposit highly dispersed Pt nanocrystals on the surface of its vertically standing nanoplatelets, where the electrocatalytic active surface area and sintering resistance of Pt crystals are expected to be improved. In **Chapter 6**, a facile and scalable approach to synthesize Pt/MoS₂ hybrid catalyst directly on the glassy carbon (GC) electrode via the CVD – TA method was demonstrated. The impact of Pt content and nanocrystal size on activity and stability of the hybrid HER catalyst was systematically studied.

The final chapter was to recapitulate and conclude the aforementioned studies and envision the potential problems and gaps in the study that can be further improved.

2 Literature Review

2.1 Introduction

It's believed that in the development of sustainable energy and environment H_2 plays a central role.(1, 2) The development of efficient and inexpensive non-noble-metal based HER catalysts is highly desirable for practical H_2 production using water-splitting devices. Improvement of both activity and stability of such catalysts remains a key challenge.(3)

Recent theoretical(4) and experimental(5) efforts have demonstrated the promise of nanostructured layered MoS_2 and its derivatives (molybdenum sulfides, MoS_x) as a great alternative to expensive platinum (Pt) metals for electrocatalytic HER, due to their high catalytic activity and affordable price.

In this review, the electrochemistry basics of water splitting will be firstly introduced identifying the critical factors that determine HER rate, followed by a thorough insight into the accepted evaluation system (methodology as well as parameters) of electrocatalytic performance for HER. The next part will then focus comprehensively on the crystal phases and catalytic properties of MoS_2 . Lastly, state-of-the-art nanostructured (2H-) MoS_2 based electrocatalysts will be discussed in terms of the synthesis route, morphology, structure, catalytic activity as well as structure-property-function relationships.

2.2 Hydrogen Energy Future

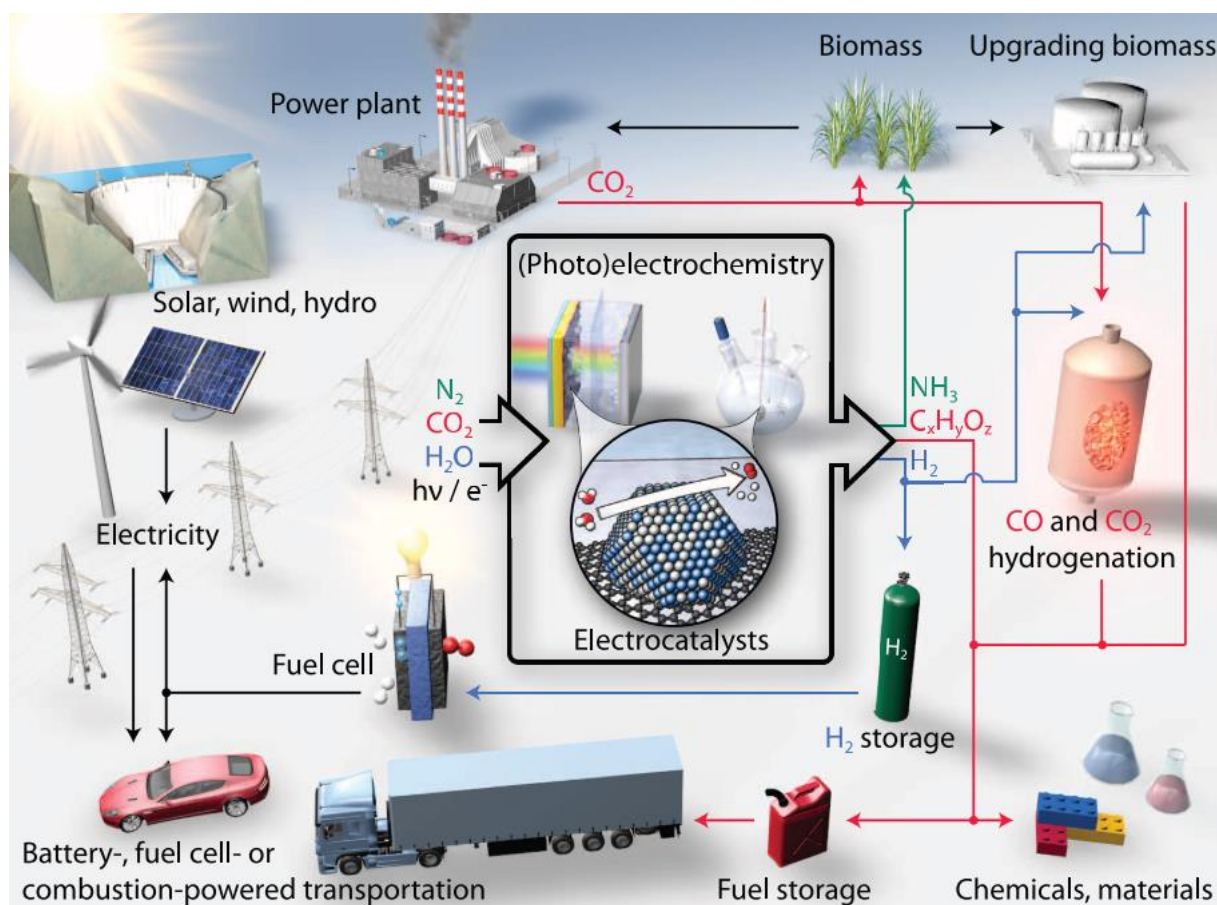


Figure 2-1. Sustainable energy future. Schematic of a sustainable energy landscape based on electrocatalysis. [Reproduced with permission from (6)]

Energy gets energy as life thrives on life.(7) The world's growing population and inflated living standards have posed great challenges to the global energy supply. Rapid depletion and greenhouse gas emission from the burning of oil, gas, and coal render the urgent need to reduce the dependency of society's energy consumption on fossil fuels. Energy options based on natural resources such as solar, hydro and wind are therefore attractive.(8) However, natural energy is intermittent with time and location. Conversion techniques from primary energy to secondary energy, such as electricity, are crucial for developing clean and low-cost energy resources.(9) Hydrogen (H_2) has emerged as a

promising energy carrier to store the intermittent energy. It provides higher energy density than battery systems and a carbon-emission-free byproduct (water) when burnt.(1) Moreover, it can be integrated into various hybrid energy systems, and hence provides versatile solutions for both domestic and industrial applications.(2)

Under such background, sustainable production of H_2 becomes vital. Electrolysis and photolysis water splitting are two feasible approaches to store primary natural energy in the form of H_2 . In a solar powered water electrolyzer, water is split into H_2 and O_2 gases, then the as-generated gases are stored and transported to a fuel cell or combustion system to convert the stored chemical energy into electricity supplied through the power grid. Such a H_2 energy cycle is completely pollution free as the only effluent is pure water.(10)

Figure 2-1 depicts potential pathways for sustainable fuel (such as H_2 , hydrocarbons, oxygenates and ammonia CH_4) production coupled to renewable energy resources through electrochemical conversion processes.(6) For the implementation of H_2 energy technologies, one of the most critical requirements is to advance the development of highly active, stable and cheap catalysts for HER in water-splitting devices, which typically uses catalysts such as Pt-group metals.(11) However, although Pt metals are the most effective electrocatalytic catalyst for water splitting, they are expensive due to scarcity. Therefore developing earth-abundant materials based HER catalysts is essential for the long-term future of H_2 involved green energy conversion purposes.(3)

2.3 Electrochemistry Basics

2.3.1 Water Splitting

Water splitting can be realised in a variety of device configurations. A common approach is the electrochemical water splitting process, including electrolysis, photo-electrochemical water splitting, and photocatalytic water splitting.

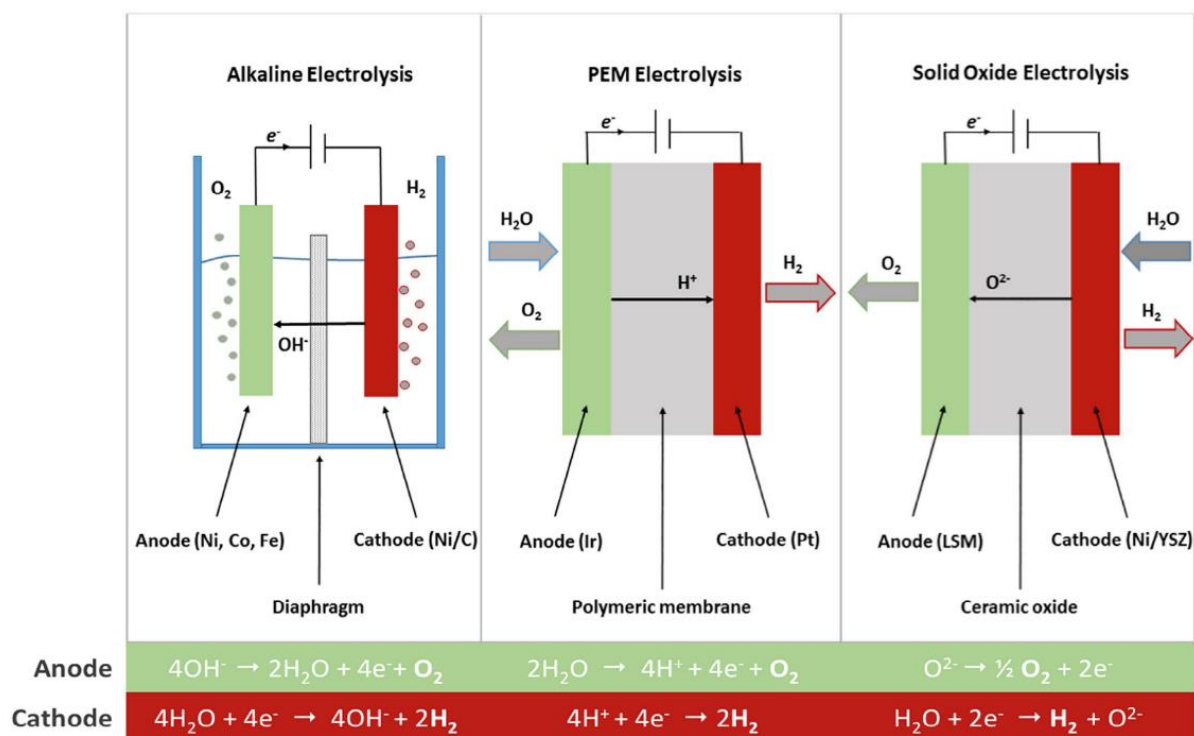


Figure 2-2. Operation principles of alkaline, proton-exchange membrane (PEM) and solid oxide water electrolysis (SOE). The overall reaction is $\text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2}\text{O}_2$. Oxygen evolution reaction (OER) and HER occur at the anode and cathode, respectively. [Reproduced with permission from (12)]

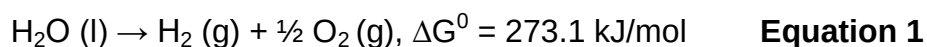
Electrolysis is the splitting of water into O₂ and H₂ gases driven by external electric current passing through the cell. Depending on the type of electrolyte material and thus the type of ionic agent, as well as operating temperature, water electrolyzers are classified into three main categories: alkaline, polymer-electrolyte membrane (PEM) and

solid oxide electrolyzers (SOE). Device configurations and operating principles are illustrated in **Figure 2-2**.⁽¹³⁾

The photoelectrochemical (PEC) method splits water by electrolysis but the electricity is supplied by photovoltaic systems using semiconductor material absorbing sunlight and generating excited charge carriers.⁽¹⁴⁾

This process can be further simplified into a single step water dissociation by the assistance of photocatalyst suspended directly in water rather than a photovoltaic or an electrolytic system, which is termed as photocatalytic water splitting.⁽¹⁵⁾

According to Physical Chemistry by Atkins,⁽¹⁶⁾ despite different device configurations, however, the overall water splitting reaction remains the same as following:



At standard condition, the reaction is non-spontaneous because of a positive ΔG^0 value. The thermodynamic standard cell potential E_{cell}^0 can be obtained from ΔG^0 using the following equation

$$\Delta G^0 = -nFE_{\text{cell}}^0 \quad \textbf{Equation 2}$$

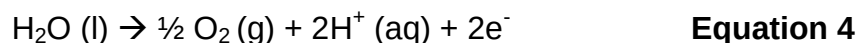
If neglecting the kinetic barriers and resistance losses, the standard potential of water electrolysis cell is -1.23 V.

The reduction and oxidation processes responsible for the overall reaction are separated in space via two half-reactions in acid media.

Reduction of H^+ ions takes place at the cathode (hydrogen evolution reaction – HER; reverse of HER is the hydrogen oxidation reaction – HOR):



Oxidation of water takes place at the anode (oxygen evolution reaction – OER; reverse of OER is the hydrogen oxidation reaction – ORR):



Each half-reaction possesses its own specific redox potential under equilibrium. The zero-current potential E in terms of composition is expressed by Nernst equation:

$$E = E^0 + (RT/nF)\ln(a_{\text{O}}/a_{\text{R}}) \quad \text{Equation 5}$$

Where E^0 is the standard potential of the redox couple, a_{O} the activity of reactant in an oxidized state, a_{R} the activity of product in the reduced state. In the case of HER, a_{O} is the concentration of H^+ in aqueous solution and a_{R} is the pressure of the H_2 gas. The HER/HOR redox couple on Pt surface, $\text{Pt}|\text{H}_2(\text{g})|\text{H}^+(\text{aq})$, is defined to have the standard potential of 0 V under standard conditions (1 M H^+ concentration, 1 atm H_2 gas) at all temperatures and thus called the Standard Hydrogen Electrode (SHE). Every other redox potential is then assigned on that basis by constructing a cell with the SHE. The OER/ORR redox potential, for instance, under the standard condition is 1.23 V. The chemical potentials discussed above are theoretical values and only meaningful when the reaction is under equilibrium where the forward and reverse rates are equal – net current flow is zero.

By applying a voltage that deviates from the thermodynamic potential, the reaction equilibrium will be broken and the rates of the forward and reversed reactions will be different. Thus, the net reaction is driven towards a particular direction and there is a net current flow. In other words, the applied potential must exceed the zero-current potential

by at least an overpotential η , to achieve a detectable rate of reaction (net current flow). The working cell potential E' is the sum of zero-current cell potential ΣE , overpotentials at the electrodes $\Sigma \eta$ and the ohmic drop (iR_S , R_S is the internal resistance of the cell) due to the current flowing through the electrode. Both η and iR_S increase with net-current and may be regarded as the inefficiency in electrolysis.

$$E' = \Sigma E + \Sigma \eta + iR_S \quad \text{Equation 6}$$

This is the scenario that applies to a practical electrolysis cell where electrochemical *kinetics* aspects need to be taken into consideration. Catalysts are essential at both cathode and anode surfaces to decrease the activation energy barriers, and consequently, lower the overpotential and increase the cell efficiency. This thesis will focus on electrocatalyst for HER at the cathode side – the reaction of interest to generate H_2 gas.

2.3.2 HER Kinetics

Let me use the following elementary reaction as an example to explain electrochemical reaction kinetics in details:



the rate of the forward reaction ($\text{mol/m}^2\text{s}$) is

$$v_f = k_f C_O = j_c / F \quad \text{Equation 8}$$

the backward reaction rate is defined as

$$v_b = k_b C_R = j_a / F \quad \text{Equation 9}$$

where k_f and k_b are the reaction rate constants in s^{-1} . j_c and j_a are the cathodic and anodic current density in A/m^2 . The net reaction rate is then expressed as

$$\begin{aligned} v_{net} = v_b - v_f &= k_b C_R - k_f C_O = j_a / F - j_c / F = (j_a - j_c) / F \\ &= j / F \end{aligned} \quad \text{Equation 10}$$

and the net current density j is formulated as the following:

$$j = j_a - j_c = F[k_b C_R - k_f C_O] \quad \text{Equation 11}$$

Following the Arrhenius equation, the rate constants are given by

$$k_f = A_f \exp(-\Delta G_c / RT) \quad \text{Equation 12}$$

$$k_b = A_b \exp(-\Delta G_a / RT) \quad \text{Equation 13}$$

If under dynamic equilibrium, the kinetic energy barriers are ΔG_c^0 and ΔG_a^0 , then the standard rate constant is

$$k_0 = k_f = k_b = A_f \exp(-\Delta G_c^0 / RT) = A_b \exp(-\Delta G_a^0 / RT) \quad \text{Equation 14}$$

with equilibrium potential E complying with the Nernst equation and $C_O^* = C_R^*$.

If an overpotential $\eta = E' - E$ is present, the relative energy of the electron resident on the electrode is changed by $-F\eta$, which will subsequently change the cathodic and anodic free energy barriers by fractions of total energy change. This fraction is defined as $1 - \alpha$. α is known as the transfer coefficient, a measure of the symmetry of the energy

barrier.

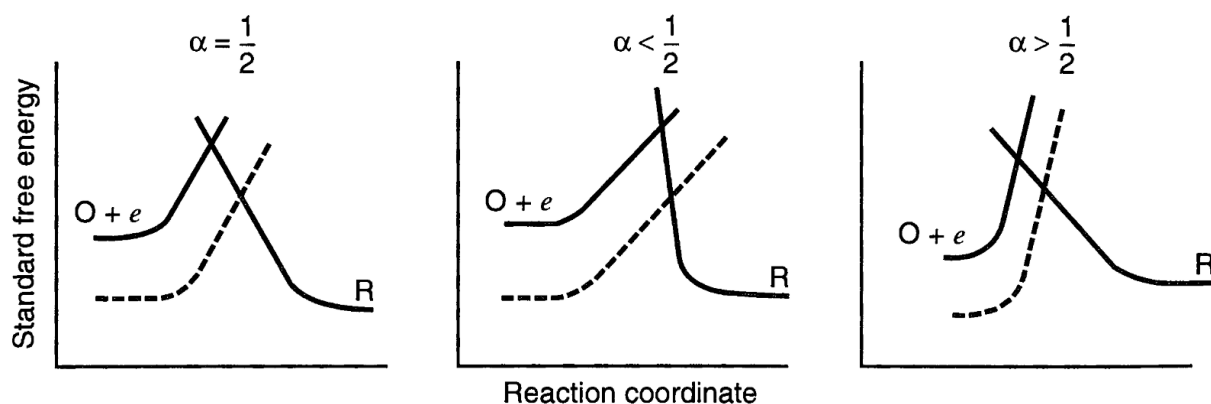


Figure 2-3. The transfer coefficient as an indicator of the symmetry of the barrier to reaction. The dashed lines show the shift in the curve for $O + e^-$ as the potential is made more positive. [Reproduced with permission from (17)]

The changes in free energy barriers are given as:

$$\Delta G_a = \Delta G_a^0 - (1 - \alpha)F\eta \quad \text{Equation 15}$$

$$\Delta G_c = \Delta G_c^0 + \alpha F\eta \quad \text{Equation 16}$$

Combining **Equation 11**, **Equation 14**, **Equation 15** and **Equation 16**, under non-equilibrium potential conditions, the relationship between reaction rate (i.e. net current density) and overpotential is obtained and expressed by the Butler–Volmer equation:

$$j = Fk_0[C_R e^{(1-\alpha)\eta f} - C_O e^{-\alpha\eta f}] = j_0 \left[\frac{C_R}{C_R^*} e^{(1-\alpha)\eta f} - \frac{C_O}{C_O^*} e^{-\alpha\eta f} \right] \quad \text{Equation 17}$$

where $f = F/RT$ (F is the Faraday constant, R is the gas constant and T is the temperature in Kelvin). $j_0 = Fk_0 C_O^{(1-\alpha)} C_R^\alpha$ is the exchange current density, which corresponds to the characteristic current density at equilibrium potential. It represents the electrocatalytic properties of the electrode for a given reaction and is a measure of

the degree of the electron transfer activity when the forward and reverse reactions are balanced.

When the solution is well stirred so that the concentrations of reactants and products are quasi-constant, the Butler-Volmer equation is

$$j = j_0[e^{(1-\alpha)\eta f} - e^{-\alpha\eta f}] \quad \text{Equation 18}$$

For the HER at the cathode, η is negative and the anodic current $j_0e^{(1-\alpha)\eta f}$ will be exponentially decayed. As a result, the cathodic current will dominate the overall current

$$j = -j_0e^{-\alpha\eta f} \quad \text{Equation 19}$$

Specially, for a large overpotential ($\eta < -0.12$ V), the Butler–Volmer equation can be simplified as the well-known Tafel equation

$$\eta = a + b \log |j| \quad \text{Equation 20}$$

where j_0 is again the exchange current density and b is the Tafel slope. The Tafel slope represents the indirect height of the kinetic barrier of the reaction.

In acid media, where plenty of protons are available, the HER is facile and proceeds through three possible reaction steps via two different mechanisms, as shown in **Figure 2-4**.

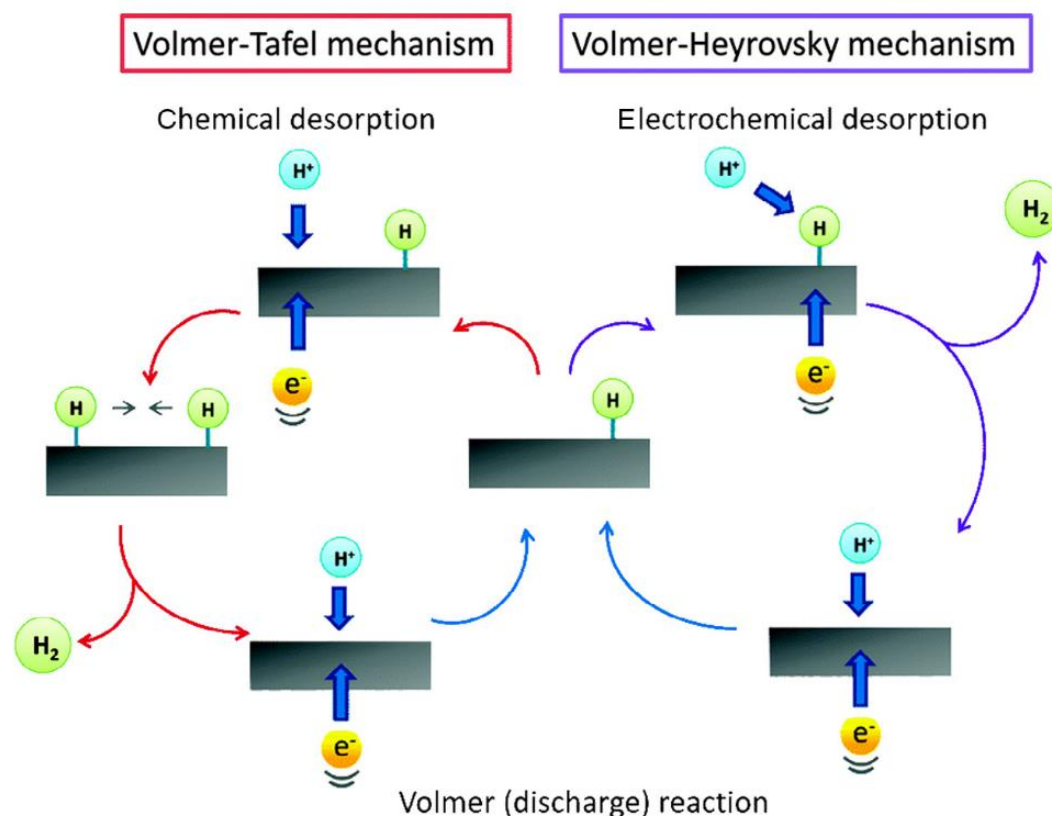


Figure 2-4. HER pathways. The mechanism of hydrogen evolution on the surface of an electrode in acidic solutions. [Reproduced with permission from (18)]

As indicated in **Figure 2-4**, it is believed that HER may occur through the Volmer-Heyrovsky and Volmer-Tafel mechanisms, respectively.(18, 19) In both cases, the first step is the Volmer reaction, which is the electrochemical hydrogen adsorption – the discharging and adsorption of H^+ on the catalyst active sites and formation of an intermediate absorbed hydrogen H_{ads} , $H^+ (aq) + e^- \rightarrow H_{ads}$. The Tafel slope for the Volmer reaction can be expressed as:

$$b_{1,V} = 2.303 RT / \alpha F$$

Equation 21

where R – ideal gas constant; T – absolute temperature; F – Faraday constant; α symmetry factor (0.5).

Depending on the coverage of absorbed hydrogen - H_{ads} , the HER can then proceed via either electrochemical desorption (Heyrovsky reaction) or chemical desorption (Tafel reaction). When the coverage of H_{ads} is low and there are sufficient active sites near the H_{ads} sites at the electrode surfaces, the H_{ads} will preferably join with a proton and an electron simultaneously to evolve a molecule of H_2 , $H_{ads} + H^+ (aq) + e^- \rightarrow H_2(g)$, known as the Heyrovsky reaction. The Tafel slope of this reaction can be expressed as:

$$b_{2,H} = 2.303 RT / (1 + \alpha)F \quad \text{Equation 22}$$

If H_{ads} is high enough, two adjacent H_{ads} will join together chemically and evolve a molecule of H_2 , $2H_{ads} \rightarrow H_2(g)$, known as the Tafel reaction. Its Tafel slope can be expressed as:

$$b_{2,T} = 2.303 RT / 2F \quad \text{Equation 23}$$

The corresponding Tafel slopes for Volmer, Heyrovsky and Tafel reactions under standard condition (298 K) are calculated to be 118 mV/dec, 39 mV/dec, and 29 mV/dec, respectively. The experimentally obtained Tafel slope value can be utilized to determine the HER rate-determining step (RDS) and indicate the HER mechanism.(13) A Tafel slope of 69 mV/dec implies that hydrogen evolution behavior occurring on the surface follows a Heyrovsky-dominated Volmer–Heyrovsky mechanism.(20)

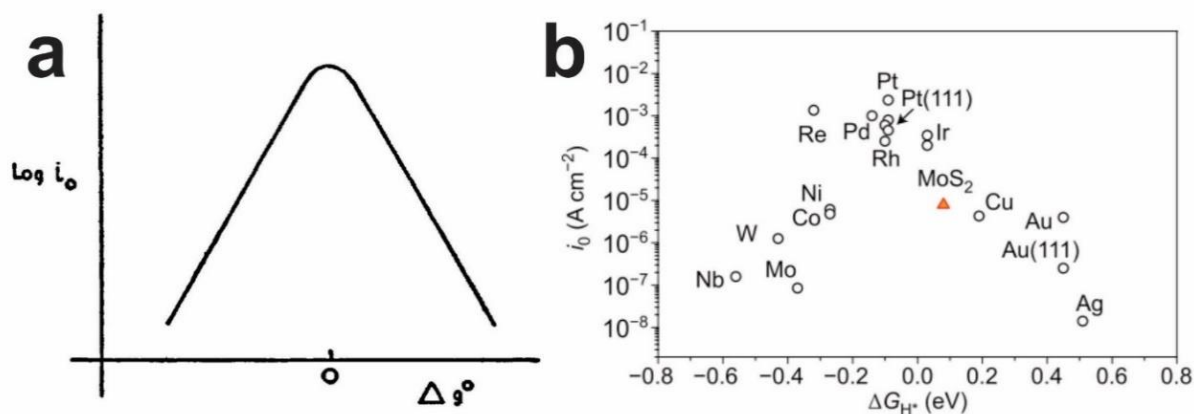


Figure 2-5. HER volcano plot for metals and MoS_2 . (a) A form of $j_0 - \Delta G_H$ relation assuming that the adsorbed H atoms obey a Langmuir adsorption isotherm [Reproduced with permission from (24)]. Experimentally measured $\log(j_0)$ plotted as a function of DFT-calculated ΔG_H for (b) different metal surfaces [Reproduced with permission from (4)] and nanoparticulate MoS_2 [Reproduced with permission from (5)].

Based on the above discussion on HER pathways, the overall reaction rate is largely determined by the hydrogen adsorption free energy ΔG_H at the catalyst surface sites, which is determined by the electronic structure of the catalyst material.(21) If ΔG_H is very positive where the electrode surface binds hydrogen atoms too weakly, failing to stabilize the intermediate state and preventing the HER to take place, the adsorption (Volmer reaction) step tends to limit the overall reaction rate; whereas if ΔG_H is very negative where the electrode surface binds hydrogen atoms too strongly, blocking the active sites and failing to continue to evolve hydrogen, the desorption (Heyrovsky or Tafel reaction) step will limit the overall rate although the initial Volmer step is easy.(22, 23) Therefore, ΔG_H is a good descriptor for HER catalyst. An optimal HER electrocatalyst is generally recognized to bind the reaction intermediate H_{ads} neither too strongly nor too weakly, by providing catalytic surfaces that exhibit a $\Delta G_H \approx 0$, using H_2 as a reference. Originally proposed by Parsons back in 1958,(24) the volcano

relationship has emerged as a powerful tool to evaluate the variation of exchange current density j_0 (catalytic activity) as a function of adsorbed hydrogen free energies, by plotting the experimentally measured j_0 against density functional theory (DFT)-calculated ΔG_H at the appropriate coverage as shown in **Figure 2-5**.⁽⁶⁾ In order to maximize the rate of the HER, a catalyst with appropriate surface properties must be employed.

It is not surprising that Pt group metals are the most commonly chosen catalyst for the HER since they lie at the top of the curve as shown in **Figure 2-5**, with very large j_0 as well as near neutral ΔG_H . More importantly, the j_0 value of MoS_2 surpasses those of the common metals and is only slightly lower than those of the Pt metals. When plotted as a function of ΔG_H , MoS_2 follows the volcano trend perfectly, indicating the potential of MoS_2 materials as an alternative to Pt for HER,⁽⁵⁾ details of which will be discussed in **section 2.5.2**.

2.4 Evaluation of Electrocatalytic Activity

The commonly used evaluation characteristics for the performance of electrocatalysts include catalytic activity, stability, selectivity, cost, and optical or mechanical properties. It is important to be aware that there's no universally agreed methodology or approach to access the electrocatalytic property. It is therefore vital and challenging to choose from a variety of strategies an appropriate one for a given catalytic system based on the relevant performance metrics since each approach has its own merits and demerits. Hereafter we will discuss and justify a useful evaluation framework for a MoS_2 based catalyst system.⁽²⁵⁾

$$j(\eta) = \frac{i(\eta)}{A} = \left[\sum_{x=1}^S TOF_x(\eta) \right] \cdot \frac{nF}{AN_A} = S \cdot \overline{TOF}(\eta) \cdot \frac{nF}{AN_A} \quad \text{Equation 24}$$

j catalytic current density ($A/cm^2_{\text{electrode}}$)

i catalytic current (A)

η overpotential (V)

A geometric surface area ($cm^2_{\text{electrode}}$)

S number of surface sites

n number of electrons transferred per molecule, 2 for HER

F Faraday constant, 96458 (C/mol electrons)

N_A Avogadro's number, $6.022 \cdot 10^{23}$ (mol^{-1})

TOF_x turnover frequency of site x (s^{-1})

$\overline{TOF}$ average turnover frequency of all sites (s^{-1})

When assessing a specific kind of catalyst, catalytic activity is the most critical one, however, there is no universal method for assessing the activity of HER catalysts. Broadly speaking, there are two primary categories of activity measurements of interest, which are “total electrode” activity (i.e., geometric electrode area normalized measurements) and “intrinsic” activity (i.e., per-site turnover frequency, TOF). Total electrode activity provides important information on practical device performance. However, it is not powerful enough for fundamental investigation of novel catalyst materials since it does not reveal the physical or chemical origins of catalytic activity. Intrinsic activity, on the other hand, reveals a catalyst’s activity on a per-site basis, hence is more helpful for catalyst development through determination of the molecular-level structure-property-function relationships.(26) As revealed in **Equation 24**, the two categories of activity measurements are fundamentally related. The total electrode

activity of HER catalyst is basically the product of two factors: the number of active sites and the intrinsic activity (TOF) of each catalytic site.⁽²⁵⁾ The widely recognized parameters for evaluating and comparing total electrode activity and intrinsic activity will be discussed in **section 2.4.1** and **2.4.2**.

2.4.1 Total Electrode Activity

In the evaluation of a certain HER catalyst system, the first step is typically to measure the total electrode activity. This represents the performance of the complete electrode and thus reveals the device-oriented information. In order to conduct such measurements, the catalyst is often supported on an inert and conducting substrate, and cyclic voltammetry (CV) or linear sweep voltammetry (LSV) is performed to measure the catalytic current response as a function of applied overpotential (j - η). For HER activity measurement, calibration of the applied overpotential scale to the reversible hydrogen electrode (RHE) and normalization of measured current to geometric electrode area are essential in order to facilitate appropriate comparison between catalysts tested under different experimental conditions. Representative LSV cathodic polarization curves are shown in **Figure 2-6**. To evaluate the overall electrode performance, ***onset overpotential***, ***Tafel slope***, ***exchange current density*** and ***stability*** are widely considered as the mandatory parameters when reporting the performance of HER catalysts.

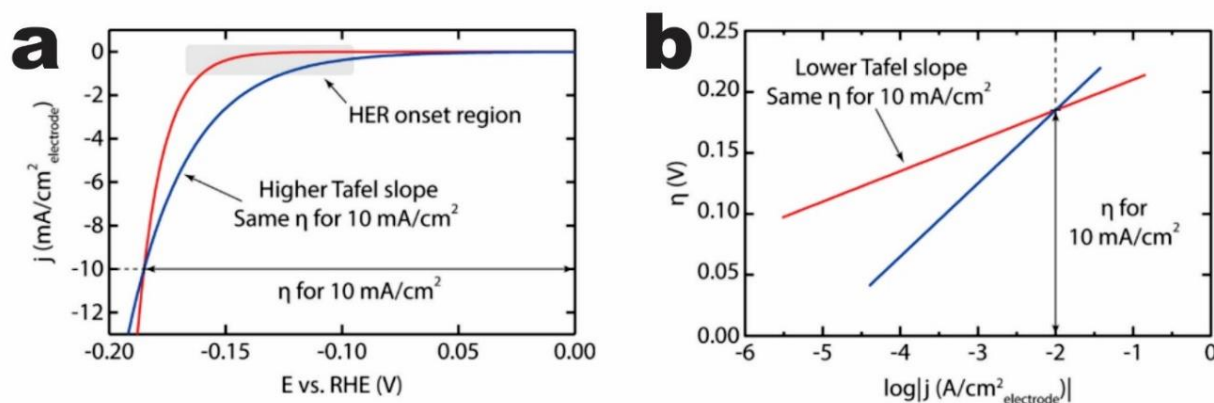


Figure 2-6. Exemplar total HER activity of two theoretical catalysts. Representative LSV plotting (a) cathodic polarization curves (j - η) and (b) Tafel plots (η - $\log|j|$). [Reproduced with permission from (25)]

Onset overpotential. It should be noted that for an electrochemical reaction to proceed in a real system, there are always a number of barriers to overcome and therefore an additional amount of driving force (η) is required other than the theoretical/thermodynamic value (see **section 2.3.1**). For HER, three barriers should be taken into consideration: the activation overpotential, the concentration overpotential and overpotential due to uncompensated resistance (the resistance exerted by the electrochemical interfaces).(13) The activation overpotential is the most important one for HER as it represents the energy to overcome activation energies of the hydrogen formation reaction on the electrode surface. It is the inherent barrier that depends on the surface activity of the catalyst materials and determines the HER kinetics.(27) The onset is defined as the potential at which catalytic current is first observed and can be practically determined by j - η polarization curves using the LSV technique.

According to the literature, the onset overpotential is actually a poorly defined term,(28) there are generally two methods for its determination. 1) As per its definition 'when current is first observed' the onset potential can be determined on the basis of reaching

a specific current density. Depending on the surface area of the catalyst and the scan rate of the LSV, a suitable current value for the onset ($0.05 \sim 5 \text{ mA/cm}^2$, e.g., 0.1 mA/cm^2) should be clarified when reporting in a research paper in order to avoid ambiguity.(29) 2) Determined from a semi-log plot of the current density response (Tafel plot: $\eta\text{-log}|j|$), the onset is the overpotential point where two linear portions of the plot intersect.(30) This method has been applied to determine the onset overpotential for all the samples reported in this thesis. Another commonly used figure of merit is the overpotential for $10 \text{ mA/cm}^2_{\text{electrode}}$, which is the current density expected in a 12.3% efficient solar to hydrogen device.(31) It's on the order of the efficiency that would be required for cost competitive photoelectrochemical water splitting. In this perspective, the $10 \text{ mA/cm}^2_{\text{electrode}}$ metric can be used to compare MoS_2 based electrocatalysts.(25, 26, 29)

Although the onset overpotential for HER is negative, in literature people always report its absolute value to indicate the amplitude of the electrical energy required to generate hydrogen. In this thesis, to avoid confusion, all the onset overpotentials will be reported as absolute values: a smaller absolute onset overpotential value means HER starts with smaller electricity input, which is favourable.

Exchange current density (j_0) and Tafel slope (b). Tafel plot of an electrochemical process depicts the relationship between the steady-state current density and the applied overpotential. It can be generally obtained by replotting the polarization curve of η logarithmically related to j .(29) The linear portion on the larger current density side fits into the Tafel equation as discussed in **section 2.3.2** ($\eta = a + b \log |j|$). Frequently used two metrics for accessing total electrode activity, b and j_0 , can be then obtained. b reveals the reaction mechanism and RDS of the HER. Practically, it tells the additional

voltage required to increase the current density by an order of magnitude, with units commonly reported in mV/decade.⁽²⁵⁾ Ultimately, all electrodes are judged by the overpotential required to reach an operating current density, which is determined by both b and the onset overpotential. j_0 reveals the rate of reaction at the reversible potential ($\eta = 0$ by definition) and is an indicator of the intrinsic catalytic activity of the electrode material under equilibrium conditions, which is dependent on the charge transfer efficiency inside the catalyst.⁽³²⁾ It is generally obtained from Tafel plots by extrapolation. Therefore, smaller b and larger j_0 are desirable, especially for high current applications such as water electrolyzers.

Stability. Another aspect worth considering in a practical sense is the stability of catalyst materials, both structurally and catalytically, especially because of the harsh working condition of the HER catalyst at pH extremes (pH 0 or 14). Two approaches can be considered for stability investigation. One route is chronoamperometry (*i.e.* under a fixed overpotential) or chronopotentiometry (*i.e.* under a fixed current density) technique of the HER electrocatalyst and it is been well accepted to keep a current density larger than 10 mA/cm^2 for a period longer than 12 h.⁽¹³⁾ Another route is to perform the overpotential cycling using the LSV or CV technique for several thousands of cycles to elucidate the stability of the catalyst. In this thesis work, the cycling method has been utilized to evaluate the durability of MoS_2 thin film based HER electrocatalysts.

It is worth noting that when justifying a catalyst system, it's essential to take the current range into consideration. For instance, the two catalysts shown in **Figure 2-6** appear the same regarding total electrode performance as both require the same overpotential for -10 mA/cm^2 . Whereas different HER mechanisms are likely to be present for both

catalysts based on their Tafel slopes – the blue one will perform better in low current applications ($<10 \text{ mA/cm}^2$) and red in high current applications ($>10 \text{ mA/cm}^2$).

2.4.2 Intrinsic Activity by Surface Area Normalization

Although total electrode activity reveals the performance of the catalyst loaded on the electrode as a whole, which holds significance in practical device development, the insights into the intrinsic activity of each catalytic site are fundamental and more ideal for understanding the origins of the catalytic activity and thus helping develop highly intrinsically active catalyst.

Unfortunately, the current limitations in experimental techniques have presented difficulties in accurate determination of the per-site activity. The most common approach to probe the intrinsic per-site activity is to first measure the total electrode activity, and then separately measure the total number of active sites. Combining both pieces of information then enables us to infer average per-site activity. Although being relatively imprecise, such method still provides reasonable insights into the comparative specific activity of a catalyst material and further guide the design and optimization of highly active systems.

The total number of active sites in most cases is determined by its related parameters such as mass adding, total surface area (SA) or electrochemically active surface area (ECSA). It should be noted that these approaches only give an approximate rather than exact values. In the case of precious-metal-free materials like MoS_2 , the catalyst mass is not as critical to the cost of the device, mass normalization of the total electrode activity is much less common and therefore will be not discussed in this review. Rather, surface area normalization in MoS_2 is explicitly discussed.

For MoS₂ catalyst, SA or ECSA (as opposed to the geometric electrode area) is one of the most common measurements for estimating the number of catalytic sites because the number of active sites often scales with the catalyst surface area. Both gaseous adsorption and electrochemical techniques have been employed to probe the active surface area. Gaseous adsorption techniques such as BET tend to overestimate the active surface area, by adsorbing some materials that may be electrocatalytically inert, resulting in a conservative estimate of the intrinsic activity. ECSA is used to determine the electrochemically active surface sites; however, the values obtained from CV and impedance analysis (EIS) differ significantly from one another and lead to potential error. 2H-MoS₂, especially, with HER active edge sites and inert basal planes, has complicated the case furthermore due to the fact that the number of active sites may not scale directly with SA or ECSA. Under such circumstances, the direct determination of the total number of active sites is preferred to surface area measurements. To this end, scanning tunneling microscopy (STM), transmission electron microscopy (TEM) imaging and electrochemical oxidation of the MoS₂ have been applied to estimate the total number of edge sites in MoS₂. All these aforementioned techniques could provide a reasonably useful estimation of the total number of active sites and thus allow us to gain an idea of the intrinsic activity of the catalyst material. Development and employment of novel methodologies for the determination of the total number of active sites still remain an open question in this area.

In this thesis work, Cottrell measurement, an electrochemical method based on the analysis of time-dependent diffusional flux of molecular species to an electrode surface,(33, 34) has been employed for the accurate determination of the real surface area of MoS₂ based electrocatalysts. The Cottrell equation describes the change in

electric current with respect to time in a controlled overpotential experiment, such as chronoamperometry.⁽³³⁾ For a simple redox event, such as the ferri-ferrocyanide couple (**Figure 2-7b**), the current measured depends on the rate at which the analyte diffuses to the electrode. That is, the current is said to be 'diffusion controlled'. The Cottrell equation is only valid when the following conditions hold:

1. At $t = 0$, the overpotential jump is applied and the electroactive substance becomes reactive; at $t > 0$, charge transfer rate is infinitely high. The electroactive substance is depleted at the electrode surface to the extent that its concentration drops to zero (*i.e.* the proviso that at the electrode surface: $c(t = 0) = c$; $c(t > 0) = 0$). The overall rate of the electrode reaction is controlled by diffusion of the analyte from the bulk of the solution to the interface.
2. The solution resistance is negligible so that the voltage drop in the solution is close to zero.
3. The transport of the electroactive substance is limited by diffusion; migration and convection are neglected.
4. The electrode surface is planar so that the diffusion proceeds only along one spatial coordinate.

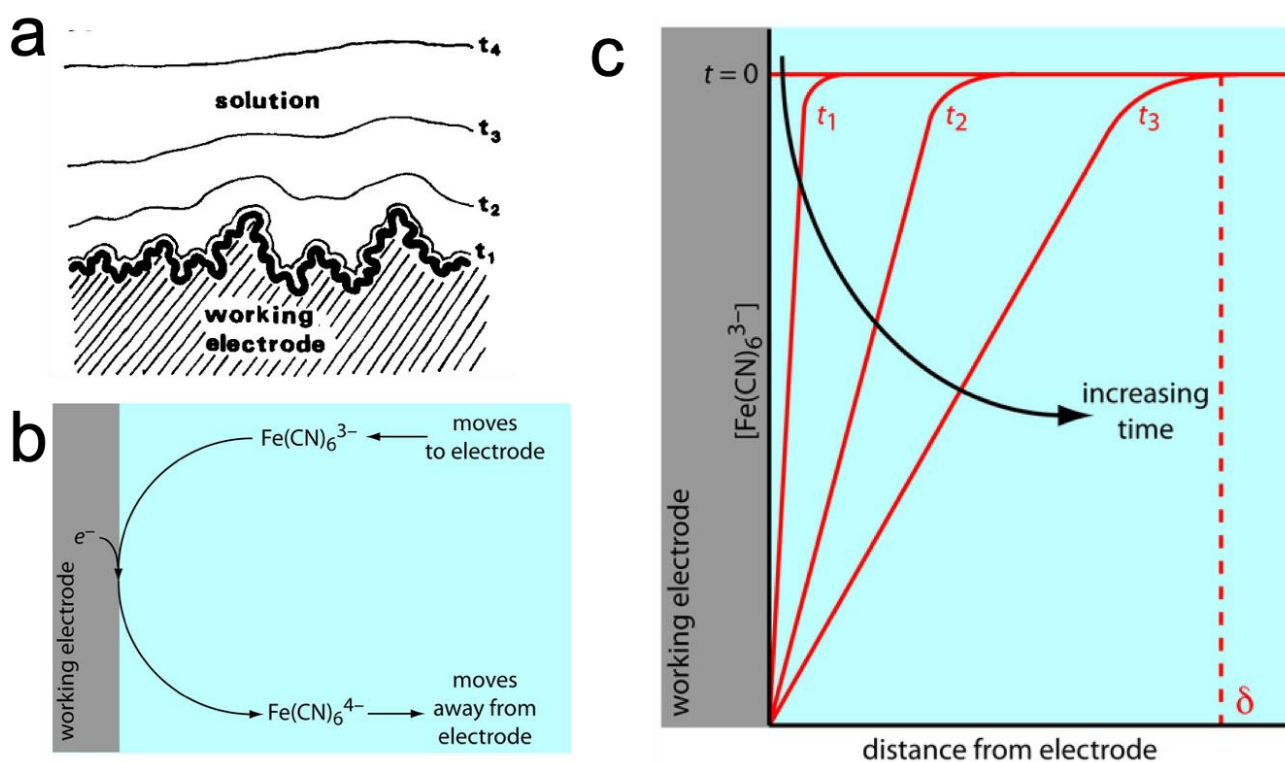


Figure 2-7. Diffusion controlled flux of molecular or ionic species to an interface. (a) Concentration profiles as a function of time ($t_1 < t_2 < t_3 < t_4$) in the vicinity of a rough (fractal) working electrode following a potential jump. The lines represent the border of the depleted zones. [Reproduced with permission from (33)] (b) Schematic showing the transport of Fe(CN)_6^{4-} away from the electrode's surface and the transport of Fe(CN)_6^{3-} towards the electrode's surface following the reduction of Fe(CN)_6^{3-} to Fe(CN)_6^{4-} . (c) Concentration gradients (in red) for Fe(CN)_6^{3-} following the application of a potential that completely reduces it to Fe(CN)_6^{4-} . [Reproduced with permission from online [source](#)]

At a given time t , the current is described by Cottrell equation:

$$i(t) = nFADc/\delta \quad \text{Equation 25}$$

where D is the diffusion coefficient (cm^2/s), c is the concentration of an electroactive substance in bulk solution (mol/cm^3), A is the surface area of the electrode (cm^2), F is the Faraday's constant, t is the time (s) and n is the number of electrons transferred.

Before applying the potential ($t = 0$), the concentration of $\text{Fe}(\text{CN})_6^{3-}$ is the same at all distances from the electrode's surface. After applying the potential, its concentration at the electrode's surface decreases to zero and $\text{Fe}(\text{CN})_6^{3-}$ diffuses to the electrode from bulk solution. The longer the potential is applied, the greater the distance over which diffusion occurs. The dashed red line shows the extent of the diffusion layer at time t_3 . These profiles assume that convection and migration do not significantly contribute to the mass transport of $\text{Fe}(\text{CN})_6^{3-}$. (See **Figure 2-7c**) The thickness of Nernst diffusion layer is $\delta = \sqrt{(\pi Dt)}$ at time t . It generalizes Cottrell equation into

$$i(t) = nFAc \sqrt{(D/\pi t)} \quad \text{Equation 26}$$

where, specifically, the current of the electrode is inversely proportionally to $\sqrt{\pi t}$; the rapid current decay is seen within a short period of time before reaching a limited value.

The surface area can be determined by measuring the current as a function of time $i(t)$. By extracting the slope of Cottrell plot (current vs. time^{-1/2}: $i(1/\sqrt{t})$), A can be calculated based on $\frac{i}{1/\sqrt{t}} = nFAc \sqrt{\frac{D}{\pi}}$ using already-known values – n , c and D of the molecule involved in the redox reaction.

From the above discussion, it can be known that the area measured from Cottrell equation is the fraction of the surface where the ferri-ferrocyanide redox reaction can occur. It does not accurately represent the total area of edges that are catalytically active for HER. It tends to overestimate HER catalytically active area and underestimate the HER intrinsic activity because a certain degree of basal surfaces is counted. Overall, it still provides a fair idea of the 3D-ER rough surface area. In this thesis, all the MoS_2 samples are measured by Cottrell method and the resultant surface area will be noted

as Cottrell surface area – A. The specific HER activity of the MoS₂ catalysts can be then calculated by normalizing the total electrode activity by A. This information affords us a rational approach for assessing intrinsic activity of the catalyst.

2.5 Molybdenum Disulfide

2.5.1 Crystal Phases

MoS₂ is in the group of transition metal dichalcogenides (TMDs, *i.e.*, MX₂, where transition metal M = Mo or W and chalcogen X = S, Se, or Te). Bulk MoS₂ has a layered structure with interlayer van der Waals (vdW) forces similar to graphite.⁽³⁵⁾ A single MoS₂ layer contains three layers of atoms (S-Mo-S atomic planes), with Mo in the middle and S atoms on top and below, where the Mo and S atoms are bonded by strong ionic-covalent bonds. The coordination between Mo and its six surrounding S atoms in individual monolayer MoS₂ are found to be either trigonal prismatic (D_{3h} point group) or octahedral (D_{3d} group), that is commonly referred to as monolayer 1H or 1T phase, respectively (**Figure 2-8a,b**). The most common and thermodynamic stable configuration at room temperature is the 1H phase; the 1T phase possesses higher energy and thus less commonly found in the natural form of monolayer MoS₂.⁽³⁶⁾

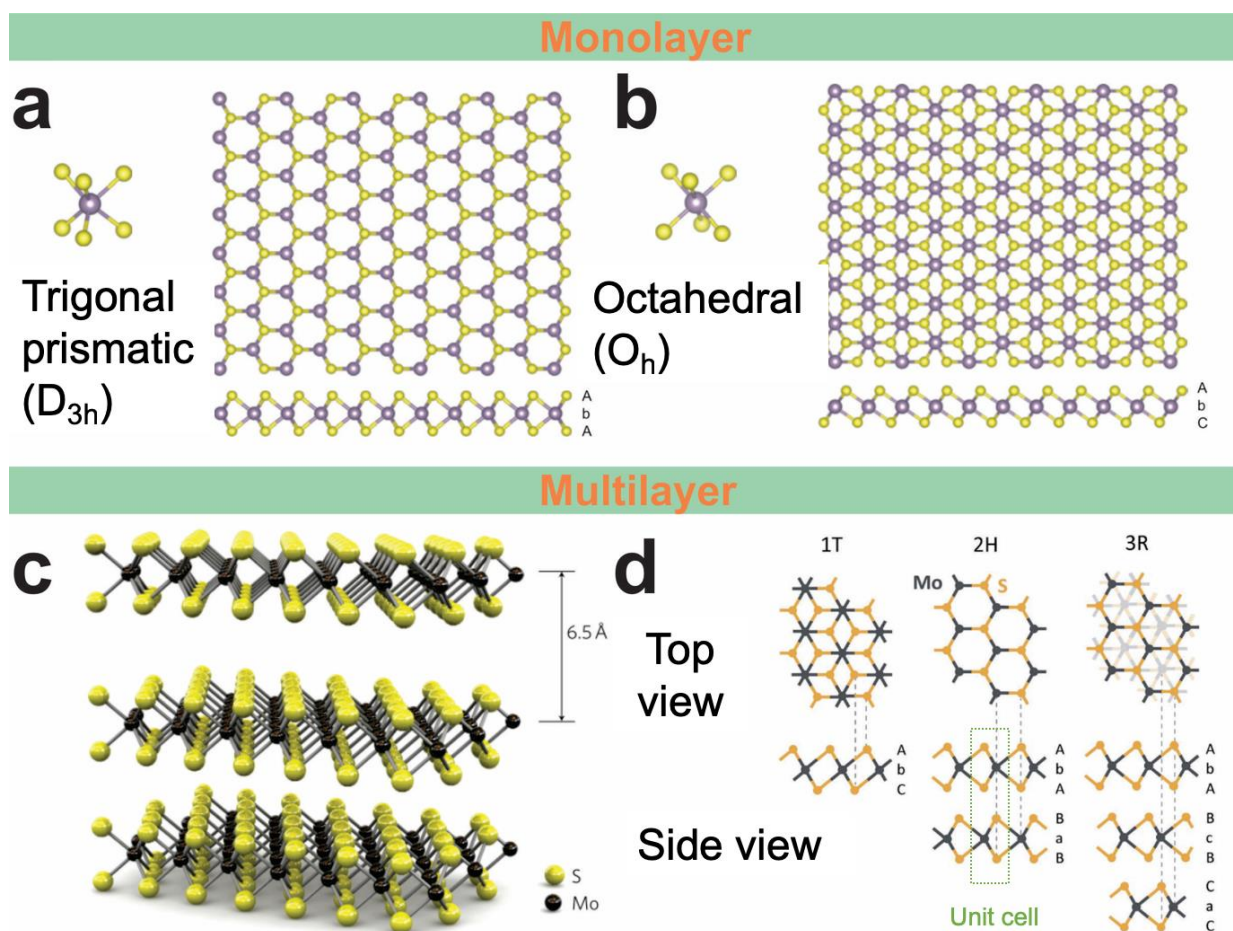


Figure 2-8. Structural models of various MoS_2 crystal phases. Atomic models showing (a) 1H and (b) 1T phases of monolayer MoS_2 , respectively. [Reproduced with permission from (37)] (c) 3D schematic illustration of multilayer MoS_2 . [Reproduced with permission from (35)] (d) Atomic models displaying three different phases, 1T, 2H and 3R, in multilayer MoS_2 , respectively. [Reproduced with permission from (38)]

Depending on the metal coordination of monolayer and stacking sequence of the layers, enriched polytypes are exhibited in the multilayer or bulk phase MoS_2 , which are 1T, 2H, and 3R, where the digit denotes the number of layers within a single crystallographic unit cell, and the letter describes the crystallographic symmetry systems for trigonal, hexagonal, and rhombohedral structure (**Figure 2-8c,d**). Note that it is a convention to denote the polytype as the prefix to MoS_2 , if specified, as following: 2H- MoS_2 stands for the 2H polytype of MoS_2 . The 2H and 3R phases are stable and commonly found in

nature and synthetic forms, respectively (2H as a majority, 80%); whereas 1T is metastable. The intralayer configuration of 2H and 3R phases are the same, but the interlayer stacking orders are different. 2H exhibits the stacking order of AbA BaB AbA..., while that of 3R is AbA BcB CaC AbA... where the upper and lower cases represent the relative position of Mo and S atoms, respectively. The crystallographic parameters are the same with regard to 2H and 3R polytypes: the distance between a Mo atom and its nearest S atom is 2.41 Å. The thickness of each S-Mo-S layer is ~3.15 Å and the distance between adjacent layers is ~3.49 Å, indicating the interlayer vdW interaction is weaker than intralayer covalent bonding.

The electronic structure of MoS₂ strongly depends on the coordination environment of the transition metal and its *d*-electron count. The diverse electronic properties of MoS₂ polytypes arise from the progressive filling of the non-bonding *d* bands. When the orbitals are partially filled, as in the case of 1T phase, metallic conductivity is shown. When the orbitals are fully occupied, as in 2H phase, the material is semiconducting.(37)

The physical and chemical properties of the 3R polytype are almost identical to those of the 2H polytype, such as the Raman spectrum and the electronic band structure. 3R will transform to 2H upon heating. 2H-MoS₂ is a diamagnetic semiconductor with an indirect bandgap of 1.29 eV. In Raman scattering two characteristic vibration modes are typically revealed: E¹_{2g} mode (383 cm⁻¹, strong) and A_{1g} mode (409 cm⁻¹, strong), which are widely used as fingerprints of MoS₂. E¹_{2g} corresponds to the in-plane opposite vibration of two S atoms with respect to the Mo atom sitting in between them and is therefore preferentially excited for a terrace-oriented surface. A_{1g} corresponds to the out-of-plane vibration of S atoms in opposite directions, which is believed to be more influenced by the long-range interlayer Coulombic interactions with its neighboring materials compared

with the E_{2g}^1 mode and thus is preferential for the edge-oriented surface. Therefore, the intensity ratio A_{1g}/E_{2g}^1 provides information on the texture of MoS_2 multilayered thin films and will be employed as descriptor for degree of vertical alignment of the MoS_2 thin films in this thesis: A_{1g}/E_{2g}^1 is found to be close to 1 for terrace- and larger than 1 for edge-oriented surface, as illustrated in **Figure 2-9**.(39–41)

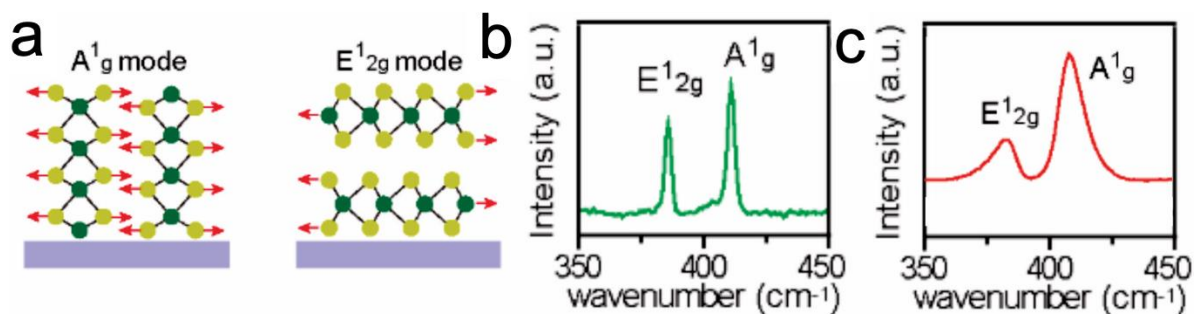


Figure 2-9. Vibrational properties of MoS_2 characterised by Raman spectroscopy. (a) Schematics of preferentially excited A_{1g}^1 Raman mode for an edge-terminated film, and E_{2g}^1 mode for the terrace-terminated film. Raman spectrum from (b) terrace-terminated and (c) edge-terminated surface of MoS_2 . [Reproduced with permission from (39)]

1T- MoS_2 is metastable, metallic, paramagnetic and is a synthetic form of MoS_2 .(42) The new peaks at 150, 219 and 327 cm^{-1} in the Raman spectrum are associated with the 1T phase formation. Practically the phase transformation from 2H to 1T can be triggered by alkali intercalation,(43) rhenium (Re) doping or electron dosing (irradiation of electron beams), where the electron transfer from intercalated or doped metals destabilizes the original trigonal-prismatic 2H structure and favors octahedral coordination of Mo atoms;(44) while selective growth of large-scale 2D 1T- MoS_2 has not been achieved.(38) The 1T phase is susceptible to the transformation to the 2H polytype when annealing up to 95°C or even simple aging. The metallic nature of 1T- MoS_2 has triggered its promise in electrocatalytic applications. Catalytic properties of different crystal phases will be detailed in **section 2.5.2**.

2.5.2 Catalytic Properties

MoS₂ possesses many interesting properties, allowing it to be utilized in the fields of lubrication,(45–48) 2D transistors,(35, 38, 49) hydrodesulfurization catalysis and lithium batteries.(50–54) This review will focus on the catalytic properties of MoS₂ for HER.(10, 55–57) Tributsch *et al.* (1976) have suggested that the MoS₂ layer crystals are poor HER catalysts.(58) However, nanostructured MoS₂ has emerged as a promising catalyst system due to its enhanced concentration of active sites and thus improved HER activity.(18) It is therefore critical to identify the most active site in MoS₂ in order to design and develop a high-performance electrocatalyst in place of Pt metals.

Due to its unique layered crystal structure, there are generally two types of atomic sites of interest in MoS₂ – edge sites on the side surfaces and thermodynamically favorable terrace sites on the basal planes.(25) The electron and hole mobility along the basal plane is ~ 2200 times faster than perpendicular between the sheets. The distinctive metallicity of 1T phase from 2H or 3R phase will also have an impact on the electrocatalytic activity. Therefore, to screen the catalytic properties of MoS₂, surface termination (basal planes and edges), as well as crystal phases (2H and 1T), should be considered.(59, 60)

The structural models in **Figure 2-10** show all the sites of interest, including Mo and S edges in pristine 2H-MoS₂, sulphur vacancies (SVs) in 2H-MoS₂ as well as 1T-MoS₂.

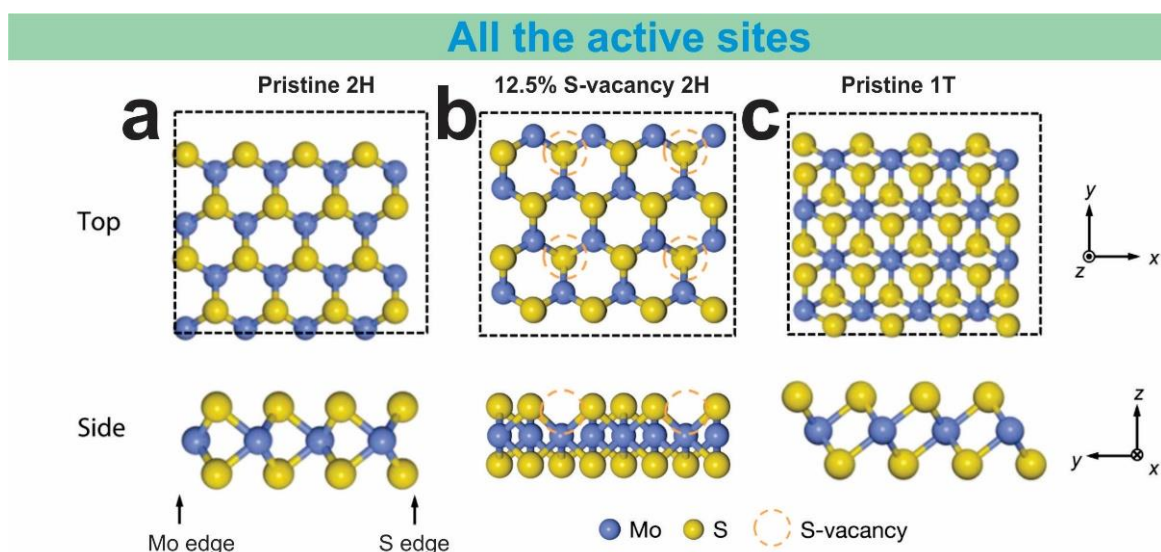


Figure 2-10. Structural model of different types of electrocatalytic active sites in MoS_2 . Top and side views of unit cells showing structures of (a) pristine-2H indicating Mo and S edges, (b) 12.5% S-vacancy (SV)-2H and (c) 1T MoS_2 , respectively. [Reproduced with permission from (60, 61)]

There have been extensive studies on identifying the catalytic properties and the active site of 2H- MoS_2 . It is agreed in the industrial heterogeneous hydrodesulfurization (HDS) that the active centers of MoS_2 are coordinately unsaturated metal sites at the edge surfaces and the reactivity is further enhanced by the vacancies created at the neighboring sulfur sites.(62, 63)

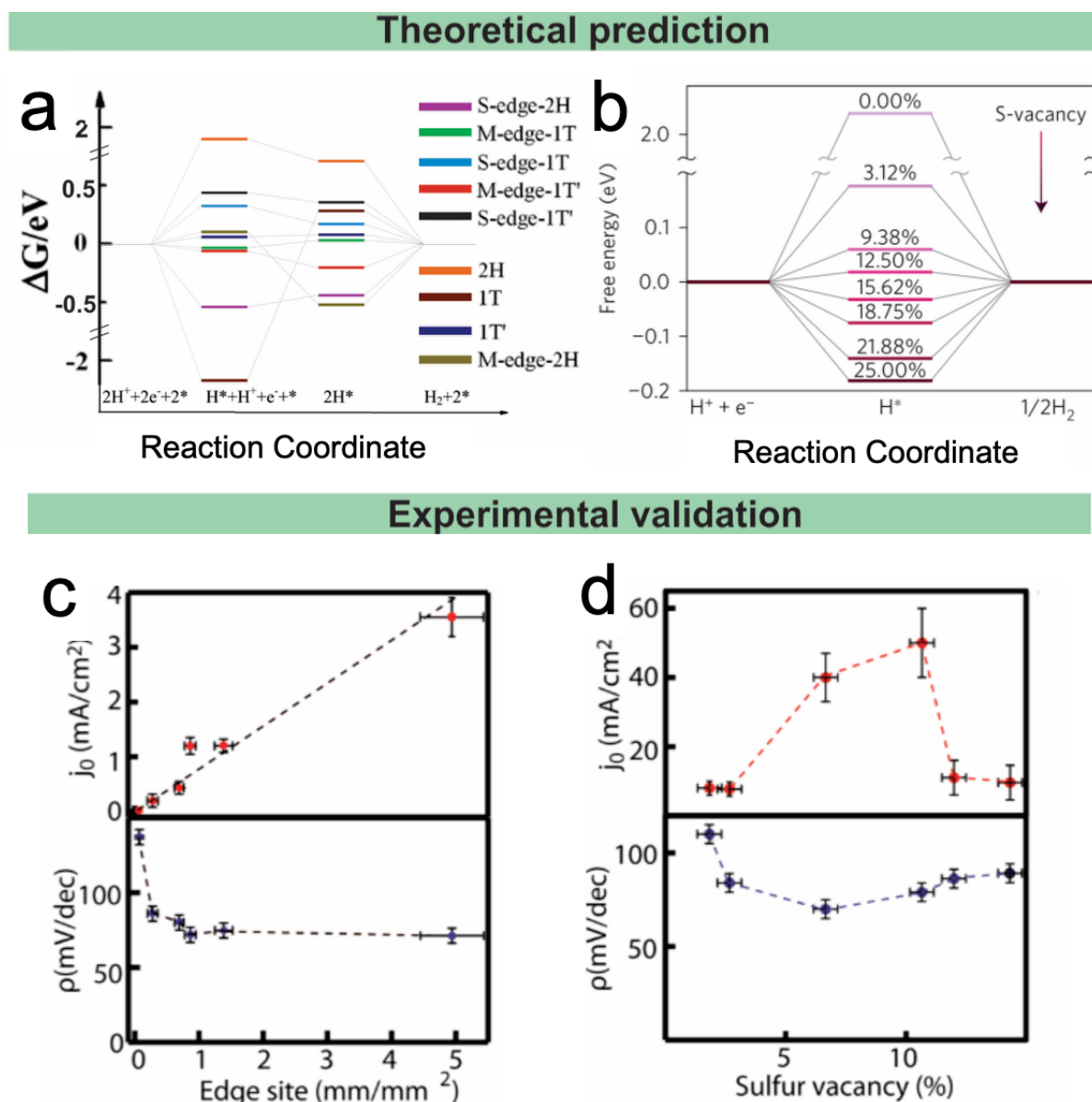


Figure 2-11. Theoretical prediction and experimental validation of different types of electrocatalytic active sites in MoS₂. Free energy versus the reaction coordinate for the HER of (a) pristine 2H and 1T, and (b) SV(0~25%)-2H MoS₂. [Reproduced with permission from (59, 61, 64, 65)] Exchange current densities and Tafel slopes of 2H-MoS₂ thin films as a function of (c) edge length per unit area and (d) density of the SVs. [Reproduced with permission from (32)]

Inspired by highly active hydrogen evolving enzymes (nitrogenase and hydrogenase), which contain Mo, Ni, and Fe with under-saturated sulfur at the active sites, using DFT calculations, Hinnemann *et al.* built a theoretical model using ΔG_{H} as descriptor to

identify the suitability of a certain material system for HER electrocatalysis. By comparison with metallic (Au, Pt, Ni and Mo) and biological (nitrogenase and hydrogenase) catalysts, it was found computationally that the Mo-edge (10-10) of 2H-MoS₂ obeys the criterion of possessing $\Delta G_H \sim 0.08$ eV (**Figure 2-11a**) at 50% H coverage, which is close to the optimum value of 0 V and similar to the highly active Pt metals, nitrogenase and hydrogenase catalysts. Furthermore, guided by the prediction of MoS₂ edges as catalytic active sites, MoS₂ nanoparticles supported on graphite were successfully prepared and fabricated with standard Pt electrode and Nafion proton exchange membrane into a membrane electrode assembly (MEA). Such as-designed MoS₂/graphite with a large number of nanostructuring exposed edges was proved to be quite reasonable material for HER with an overpotential of 175 mV at 10 mA/cm², verifying their theoretical prediction of active Mo-edge.⁽⁶⁶⁾ DFT calculation on the basal planes of 2H-MoS₂ revealed, in stark contrast, that those terrace sites exhibit ΔG_H of 1.92 eV (**Figure 2-11a**), which explains the poor catalytic activity of bulk MoS₂ crystals.⁽⁶⁰⁾

The above computational studies provided a powerful theoretical model to search for potential active catalyst systems and served as a good demonstration that increased edge density by nanostructuring can enhance HER activity. Significant experimental efforts have stemmed from the theoretical consideration that the Mo-edges of 2H-MoS₂ are catalytically active whereas the basal surfaces remain inert towards HER; however no quantified correlation between the number of edges and catalytic activity has been established.

The study by Jaramillo and co-workers in 2007 experimentally confirmed that sulfurized Mo-edges are the dominant edge structure and are responsible for the HER catalytic

activity in 2H-MoS₂.⁽⁶⁷⁾ They deposited nanoparticulate MoS₂ onto a clean Au(111) substrate using physical vapor deposition (PVD) with deliberately chosen morphologies in order to achieve a systematically varied fraction of terrace and edge sites. The area and edge length of different samples were quantified using STM. The measured electrocatalytic activity was discovered to correlate linearly with the number of edge sites (perimeter length) rather than the area of the MoS₂ catalysts (**Figure 2-11c**). TOF of the MoS₂ edge was calculated to be 0.02 s⁻¹ and fell onto the higher end of the TOFs spectrum for metals (although ~ 50 times lower than Pt).

Most recently, Li *et al.* (2016) have demonstrated the first activation and optimization of inactive basal plane sites of 2H-MoS₂ for HER by introducing SVs and strain. They have first theoretically predicted, using DFT calculations, that strained SVs in 2H-MoS₂ basal planes serve as a new type of highly active catalytic site with near neutral ΔG_H (**Figure 2-11b**). Guided by this theoretical prediction, optimized 2H-MoS₂ with strained (1.35%) SV (12.5%) sites were experimentally prepared using a mild argon (Ar) plasma and capillary force method and tested to have a TOF of 0.08 – 0.31 s⁻¹, exceeding those of best-characterized MoS₂ edge sites and 1T metallic basal surfaces, the best reported at that time (**Figure 2-11d** showing the impact of SV on catalytic activity).⁽⁶¹⁾ Following this study, an unambiguous study on all the catalytic active sites of MoS₂ further validated that, in addition to well-known edges, SVs provide another type of active sites in 2H-MoS₂.⁽³²⁾ Followed by the discovery of active SV, Tsai's work in 2017 has demonstrated a scalable route for the generation of SVs using electrochemical desulfurization of 2H-MoS₂ for enhanced HER activity, which is promising to directly improve industrial 2H-MoS₂ catalysts.⁽⁶⁴⁾

Theoretical study has revealed that the MoS₂ basal surfaces inside 1T phase are metallic and therefore show ΔG_H close to neutral (**Figure 2-11a**), which suggests they could be active HER catalysts.⁽⁶⁵⁾ 1T edges are metallic and catalytic active just as in the 2H phase and thus 1T-MoS₂ are electrocatalytically active regardless of basal planes and active edges.^(60, 68) Although the majority of natural and synthetic MoS₂ is in 2H or 3R phase, a stable 2H $\rightarrow$ metastable 1T phase transformation can be triggered by lithium intercalation process. This intriguing and effective approach can be utilized to prepare 1T-MoS₂ HER catalysts with high performance.^(69–72) The transition from semiconducting to metallic polymorphs has been shown to be positive for the electrocatalytic performance of MoS₂.⁽⁵²⁾ Apart from the increased density of active site rising from the active basal planes, metallicity facilitated facile electrode kinetics and low-loss electrical transport enables the superior HER activity of 1T-MoS₂.⁽⁷²⁾

To summarize, for the basal planes, the most significant parameter in determining the catalytic activity is the metallicity; the semiconducting 2H phase has catalytically inactive basal surfaces whereas metallic 1T phase is suggested to have active basal planes. The edges, in contrast, are found to be metallic regardless of the metallicity of the basal planes of the 2H and 1T polymorphs.⁽⁶⁰⁾ Additionally, the pristine 2H basal planes can be activated by (strained) SVs, which serve as another major type of active sites in MoS₂ catalyst, apart from edge and terrace sites.

Amorphous molybdenum sulfide has also been demonstrated to possess high HER activity owing to the high surface area morphologies. However, the surface composition tends to transform to MoS₂ when subject to reducing overpotentials in an electrochemical cell and thus long-term stability becomes an issue.⁽⁷³⁾ In addition, the amorphous phase is often synthesized by solution-based methods, leading to low yield,

poor quality, and difficult control of morphology and layer number.(73, 74) CVD, which has been extensively employed in this thesis work, normally yields the 2H phase of MoS₂. Hence, in the following discussion of state-of-the-art MoS₂ catalysts, we will be focusing only on 2H-MoS₂.

2.6 Design of MoS₂ Based Nanostructured Electrocatalysts

2.6.1 Principles for Electrocatalyst Design

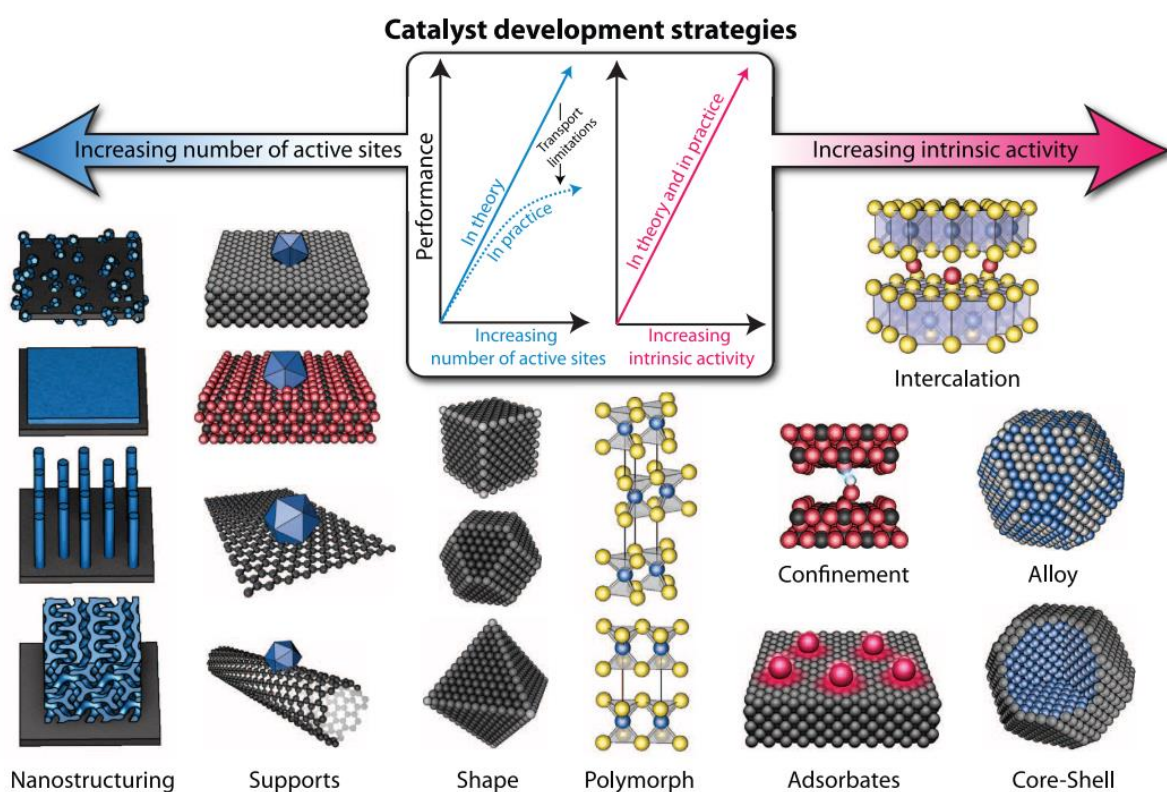


Figure 2-12. Catalyst development strategies. Schematic of various catalyst development strategies, which aim to increase the number of active sites and/or increase the intrinsic activity of each active site. [Reproduced with permission from (6)]

Demand for HER catalyst is driven by a lowered overpotential while remaining affordable and earth abundant. The development of non-noble-metal based hydrogen-evolving

catalysts is vital to the practical application of water-splitting devices. Improvement of both the activity and stability of such catalysts remains a key challenge. Having understood the HER reaction pathways and identified catalytic active sites of MoS₂, I will then discuss the strategies in the development of MoS₂ HER electrocatalysts for improved activity in water splitting applications.

In order to optimize HER catalyst, guided by **Equation 24**, where the two fundamental factors contributing to the total electrode activity are indicated, there are accordingly two basic strategies to improve the catalytic activity of a system. *Route 1* is to increase the active site density (number of the active site per geometric area of the electrode) by increasing the total surface area or enhancing preferential exposure of active sites in the surface termination; effective approaches are for instance higher loading or nanostructuring of active material to expose more active sites. *Route 2* is to improve the intrinsic per-site activity of the catalyst by modifying the physical or chemical properties of the material; to this end efforts include doping with a transition metal,(75) strain engineering,(76) substrate interaction,(77) Li intercalation and transformation to the 1T phase.(72) The schematic illustration of these two routes are shown in **Figure 2-12**.(6) The observed plateau corresponds to the charge and mass transport limitation with a heavily-loaded electrode,(25) whereas an increase of intrinsic activity leads to direct improvement of electrode activity that mitigates transport issues. It is notable that quite often these two strategies are addressed simultaneously, intentionally or unintentionally, leading to the greatest improvement of catalytic activity, in a single material system.(29) In the following survey, I aim to classify previous studies based on the predominant HER enhancing factor/s in their systems, if there is a combination of several factors contributing to the activity enhancement at all.

In this thesis, materials were synthesized by the CVD method, as being promising for high quality, controllable and large-scale production of MoS₂. It is agreed that such gaseous phase sulphurization normally yields crystalline 2H polymorph.⁽²⁵⁾ Therefore, hereafter we will be focusing on a review of 2H-MoS₂ edge density enhancement by nanostructuring methods, as well as utilization of basal surfaces by introducing additional active edges and SVs through post-growth treatments. In addition to acting as a cheap and abundant HER electrocatalyst, the as-designed 3D porous architecture obtained via CVD also holds promise as scaffold towards constructing a nanoparticulate Pt supported hybrid catalyst system, thus related studies in developing highly performed Pt-based catalyst with minimized metal loading will be also reviewed.

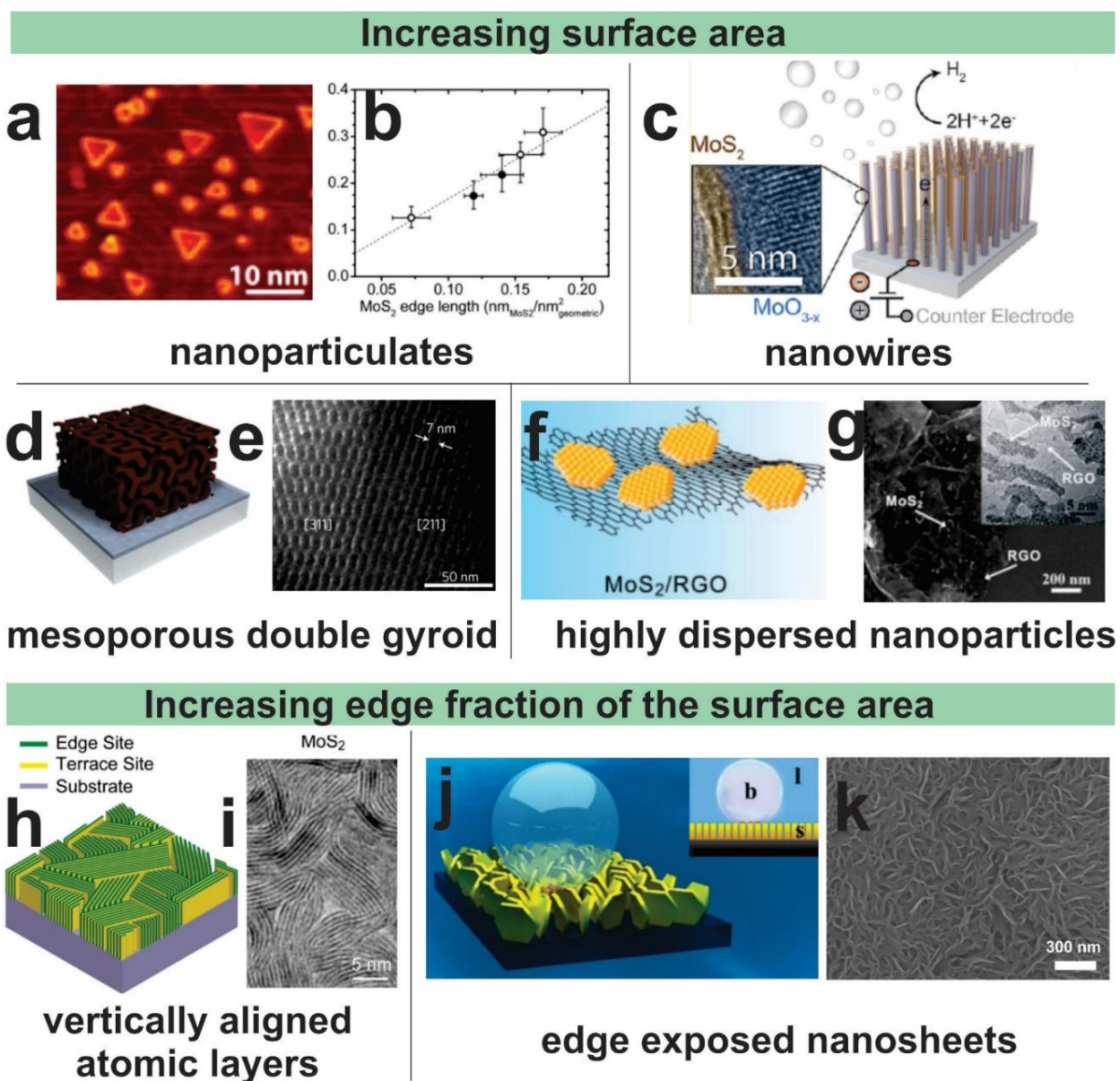
2.6.2 Edge Enrichment in 2H-MoS₂

Figure 2-13. Edge enrichment in pristine 2H-MoS₂ HER catalysts. Increased total surface area achieved by (a,b) nanoparticulate, [Reproduced with permission from (67)] (c) nanowires, [Reproduced with permission from (78)] (d,e) mesoporous double gyroid, [Reproduced with permission from (79)] and (f,g) highly dispersed nanoparticles on reduced graphene oxide (rGO). [Reproduced with permission from (80)] Preferential edge exposure in the form of (h, i) vertically aligned atomic layers [Reproduced with permission from (81)] and (j,k) edge exposed nanosheets. [Reproduced with permission from (82)]

As discussed in **section 2.5.2**, edge sites of 2H-MoS₂ have been shown to be catalytic active for HER, while the basal surfaces remain inactive. Researchers have been attempting to increase the total number of accessible edges of the catalysts by making nanostructured layered MoS₂.^(5, 40, 83–85) Attractive strategies to increase edge density of the electrode include 1) to increase the total surface area of the loaded catalyst (**Figure 2-13a-g**) and/or 2) to enhance the preferential exposure of edges in the surface termination (**Figure 2-13h-k**).

2.6.2.1 Increasing total surface area

As a layered material with atomic layers stacked together by weak interlayer interactions, MoS₂ often crystallizes to form atomically smooth thin films, nanotubes and platelets or fullerene-like nanoparticles due to the anisotropic bonding. There have been extensive studies on MoS₂ nanowires, mesoporous nanostructure and nanoparticles with improved HER activity. These nanostructured catalysts possess high total surface area and substantial density of exposed edges and thus holds great potential in the application as highly active HER electrodes.^(39, 69, 79, 82, 83, 86–93)

For example, in the work on identification of catalytic active edge sites by Jaramillo (**Figure 2-13a,b**), nanoparticulate MoS₂ was successfully deposited on a Au(111) surface and shown to exhibit TOF of 0.02 s⁻¹ (in the higher range of TOFs for metals).⁽⁶⁷⁾ However, due to the sparse distribution of the monolayer domains, the physical area of the electrode had not been fully utilized. The total electrode activity was therefore poor despite the good per-site activity.

Core-shell structure of MoS₂-MoO₃ nanowires was prepared by sulfidising MoO₃ in H₂S (10%)/H₂ (90%) atmosphere to develop the high surface area (**Figure 2-13c**). The

conductive reduced MoO_3 core assists fast charge transport along the length of the nanowire. 250 mV was observed to achieve $10 \text{ mA/cm}^2_{\text{electrode}}$. The total surface area was achieved by the as-designed core-shell structure, however, the edge density was shown to be low compared to the basal surfaces, which emphasized the significance of higher exposure of edge density over basal planes rather than the mere increase of total surface area.(78)

Another novel morphology – a three dimensional mesoporous MoS_2 double gyroid – was investigated for purpose of increasing surface area(**Figure 2-13d,e**). The formation of extended basal surfaces was constrained by nanoscale curvature and therefore a higher degree of edges was exposed, along with high surface area.(79) This double gyroid structure achieved $10 \text{ mA/cm}^2_{\text{electrode}}$ at 220 mV. The fraction of edge sites at the surface was found to be 2-4 times higher than the aforementioned nanowires. One drawback of such MoS_2 structure is the increased resistive loss due to slow electron transport from the surface to the substrate because the electron mobility perpendicular to the basal planes is much slower than for the in-plane direction (3 orders of magnitude).(25)

Moreover, reduced graphene oxide (rGO) was employed as support to synthesize MoS_2 nanoparticles on for a better dispersion and reduced agglomeration (**Figure 2-13f,g**), which led to the larger number of accessible active edges and leads to improved HER activity at the same catalyst loading. Moreover, the underlying rGO support facilitates fast charge transport from the MoS_2 to the conductive substrate. The coupled structure showed $10 \text{ mA/cm}^2_{\text{electrode}}$ at 150 mV.

2.6.2.2 Preferential edge exposure

Although HER activity can be advanced to a certain extent by increased total surface area, higher surface area alone is still insufficient as the basal plane sites in the surface remain catalytically inactive. Therefore, preferential exposure of MoS₂ edges is ultimately effective to maximize the density of active sites and thus can lead to greatly enhanced catalytic performance. To realise this goal, structures can be classified into two categories depending on the scale of vertical alignment: 1) vertically aligned atomic layers produced by sulfurizing elemental metal (Mo) seed layers,(39, 94, 95), and vapor sulfurization of sponge-like molybdenum oxide layers(81); (2) edge exposed nanoplatelet synthesized by hydro-sulfurization of Mo-coated substrates,(96) solvothermal conversion,(77, 97, 98) chemically exfoliation,(99) CVD,(100–102), and surfactant-assisted low-temperature solution process.(103)

In the pursuit of preferential exposure of edges, progress was seen by synthesis of MoS₂ thin films with vertically aligned atomic layers, thereby maximally exposing edges on the film surface, as reported by Kong (**Figure 2-13h,i**).(81) This novel morphology was prepared by exposing a 5 nm electron beam evaporated Mo film to 100 mTorr elemental S vapor for 10 min at 550 °C. The resultant edge-terminated films are promising for catalysis with maximal edge density and reduced resistive loss of electron transport from support to active surface sites benefitting from the vertical alignment of individual layers. An exchange current density as high as $2.2 \times 10^{-6} \text{ A/cm}^2_{\text{electrode}}$ (corresponds to TOF of $\sim 0.013 \text{ s}^{-1}$) was achieved, but the Tafel slope was high (120 mV/dec). It is worth noting that the overall device performance on the geometric area aspect is not that good, with $10 \text{ mA/cm}^2_{\text{electrode}}$ at 440 mV, due to the low catalyst loading and small surface area. Moreover, the morphology of such atomic layered thin film is

almost flat, where a large number of H_2 gas bubbles accumulates during the reaction, leading to decreased effective electrode area.

Vertically-oriented MoS_2 nanosheets synthesized via hydrothermal method exhibit excellent HER activity (**Figure 2-13j,k**), even higher than Pt/C at higher potentials.(82) The unique oriented growth of MoS_2 nanosheets brings about maximally exposed edges that serve as active sites in HER catalysis. Moreover, edge exposed nanoplatelets are favorable for constructing a “superaerophobic” surface due to the reduced adhesion of as-formed gas bubbles on the electrode surface by an order of magnitude compared to its counterparts.(82) This enables quick removal of small bubbles and provides a constant working area, resulting in an improved electrocatalytic performance. The porous structure can also have importance in the electrocatalytic water splitting. Self-assembled porous MoS_2 thin films show high real surface area and a 3D open framework that enable efficient mass transport, for example, H^+ and H_2 in the case of HER, through the high-surface-area thin-film network. Electrochemical durability was also observed, attributed to the strong bonding between the nanosheets and the substrate as well as the self-removal of the as-formed H_2 bubbles from the nano-porous electrode surface.(79, 93)

2.6.3 Basal Plane Activation in 2H- MoS_2

Aforementioned efforts have revolved around increasing the edge density, which has allowed enhancement of HER activity, the inactive basal planes that are under-utilized, however, strongly impede the optimization of fully active MoS_2 catalysts.(61, 104) The semiconducting nature confined charge transport resistance of 2H- MoS_2 remains another key limitation of increasing HER rate.

To activate the catalytically inactive basal surfaces and circumvent the slow charge transport issues, triggering the 2H $\rightarrow$ 1T phase transformation could be potentially considered. For example, the solution approach by Li-intercalation has been proved effective in further enhancing the electrocatalytic performance by modifying the electronic structure of the MoS₂ to have active edges and basal sites. (71) 2H $\rightarrow$ 1T transformation is not viable in the CVD process, which has been utilized in this thesis for the sake of wafer scale, high quality and clean production of the controllable 3D porous network. Therefore, for the CVD approach the focus will still be on how to artificially generate active sites in 2H-MoS₂ basal planes to improve HER activity.

As discussed in **section 2.5.2**, recent work has revealed that in 2H-MoS₂ basal SVs serve as active sites for HER, along with edges. Defect treatment holds potential for introducing additional active edges and SVs by forming cracks, holes, incorporating foreign atoms or removing S atoms in the inert MoS₂ basal planes as well as pre-existing edges. In this way, the number of active sites can be increased and the catalytic activity of 2H-MoS₂ will be consequently enhanced.(83, 92, 105–110) Based on their dimensions, defects can be categorized into two main types: microscopic defects including cracks, holes and termination of domains (**section 2.6.3.1**); point defects including oxygen incorporation (**section 2.6.3.2**) and sulphur vacancies (**section 2.6.3.3**).

2.6.3.1 Cracks, Holes and Additional Edges

In previous studies, in order to etch MoS₂ to generate cracks and holes that can serve as additional active edges for HER, in-situ generation of edges during the growth process, as well as post-growth treatments such as electron beam (EB) irradiation,(36)

plasma (Ar, O₂ and H₂) etching,(110, 111) acid (HNO₃) etching(89) and oxidative (air or O₂/Ar mixture) etching(112) have been deployed.

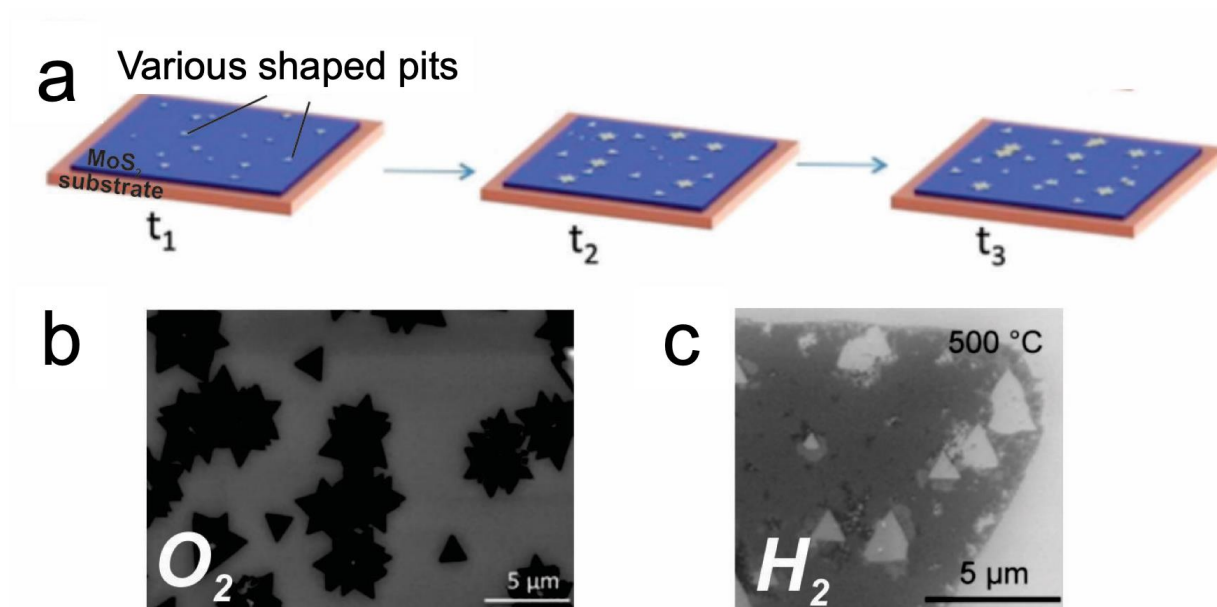


Figure 2-14. Gaseous phase annealing generated holes and additional edges in MoS₂. (a) Schematic of gaseous annealing process showing time ordered evolution of etched patterns. SEM images of etched pattern by gaseous (b) O₂ [Reproduced with permission from (112)] and (c) H₂ [Reproduced with permission from (111)].

O₂ annealing of monolayer and thick MoS₂ has been reported to be an effective way to introduce randomly oriented and controllable triangular etched shapes, forming pits with uniform etching angles.(45, 92, 110, 113, 114) The etching process was typically conducted by exposing MoS₂ sample simply to air or Ar/O₂ mixture for a specific period at controlled temperature from 300 to 400 °C (**Figure 2-14a**).(115) The initiation triangular pits are likely to come from extended lattice defects such as edges or grain boundaries between layers. The etching process then continues by pits growing into triangles and other geometric forms that contain pseudo-hexagonal shaped branched nerves, which hold potential for acting as active HER edges. The resultant pattern is

demonstrated by SEM images in **Figure 2-14b**. The Mo and S atoms at the edges are converted to MoO_3 and SO_2 gas molecules at high annealing temperatures.(112) Raman spectroscopy confirms that oxygen annealing process does not produce MoO_3 below 340 °C;(112) whereas at 400 °C the same process results in conversion of MoS_2 to MoO_3 .(116)

Researchers have conducted anisotropic etching by **H_2 annealing** resulting in hexagonal holes with zigzag edge structure on graphene and WS_2 .(117, 118) Such an annealing process can be similarly conducted using H_2/Ar gas on MoS_2 to create holes on the basal surfaces in order to increase the exposed edges for HER catalysis. As evidenced in Ye's work,(92) the H_2 annealing approach was shown to be effective in introducing small triangular holes in the basal planes of the monolayer MoS_2 , which is revealed in **Figure 2-14c**. As a result, the edge density was significantly increased and HER activity was enhanced compared to the pristine monolayer. Since there was only one atomic layer of active materials deposited onto the surface, the number of edges was limited and thus the usage of physical area of the electrode was not maximized.

The resultant features from both O_2 and H_2 gas phase annealing provide numerous newly exposed edges inside MoS_2 bulk that can catalyze HER. Further tuning of etching parameters such as temperature, time and gas flow resulted in various ordered structures and fascinating displays.(112)

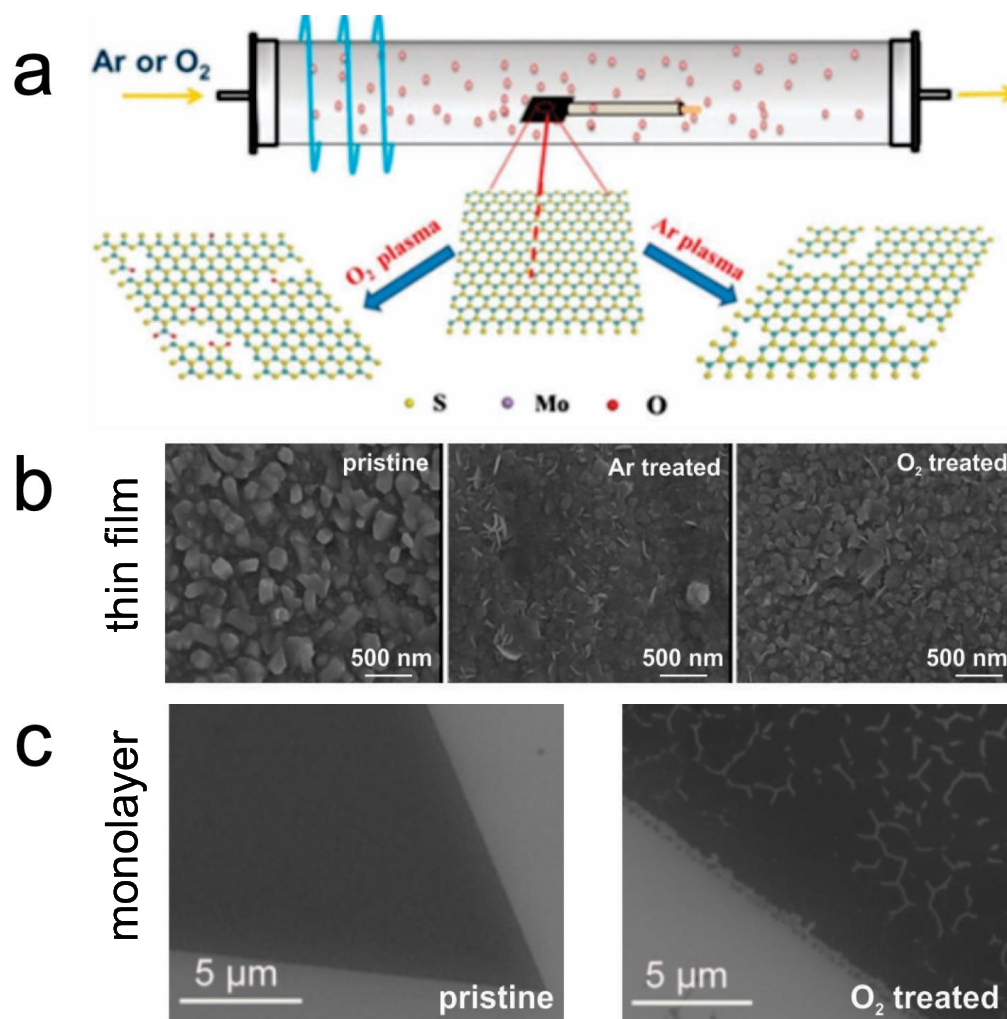


Figure 2-15. Plasma etching generated cracks and additional edges in MoS_2 . (a) Schematic of plasma etching of pristine MoS_2 . (b) SEM images of MoS_2 thin films before and after Ar and O_2 plasma etching. [Reproduced with permission from (110)] (c) SEM images of MoS_2 monolayer before and after O_2 plasma etching. [Reproduced with permission from (111)]

Plasma etching is a general technique for etching and cleaning. It is capable of tuning the structure and functionality of materials by introducing physical and chemical defects. The generation of various etched patterns can introduce additional edges for HER catalysis. Previous work has explored Ar and O_2 plasma etching on MoS_2 thin film as well as monolayer HER catalysts.(110, 111) The process flow chart is illustrated in **Figure 2-15a**. It was demonstrated that after Ar and O_2 plasma exposure, the MoS_2 thin

film was maintained but the particle size was slightly decreased compared to the pristine sample, indicating more edges are exposed (**Figure 2-15b**).⁽¹¹⁰⁾ In the case of monolayer MoS₂, O₂ plasma treatment created a large number of cracks with certain angles (120°) and irregular shapes, which leads to substantial increase in open edges (**Figure 2-15c**).⁽¹¹¹⁾

Oxygen-containing plasma produces two main types of by products that influence HER activity oppositely. One is a MoO₃ phase, which brings about a negative impact on HER catalysis due to increased resistivity and slower charge transport.⁽¹¹⁹⁾ Another is incorporated O into the MoS₂ lattice through substitution or absorption of O atoms on top of S atoms, in which case the band gap of MoS₂ will be decreased and the catalytic activity can be positively tuned. O-incorporation effects will be further discussed in **section 2.6.3.2**.

The third method to generate cracks in the MoS₂ basal plane is **electron beam (EB) exposure**. The process has been demonstrated by Wang *et al.* as in **Figure 2-16a**.⁽³⁶⁾ The continuous EB radiation caused loss of Mo and S atoms, together with residual stress from the transfer process, lead to the formation and propagation of the crack (**Figure 2-16b**). ACTEM imaging analysis showed that the crack propagates along the zigzag direction after rupturing the MoS₂ monolayer. The newly exposed edges exhibit almost perfect zigzag Mo and S terminations (**Figure 2-16c**).

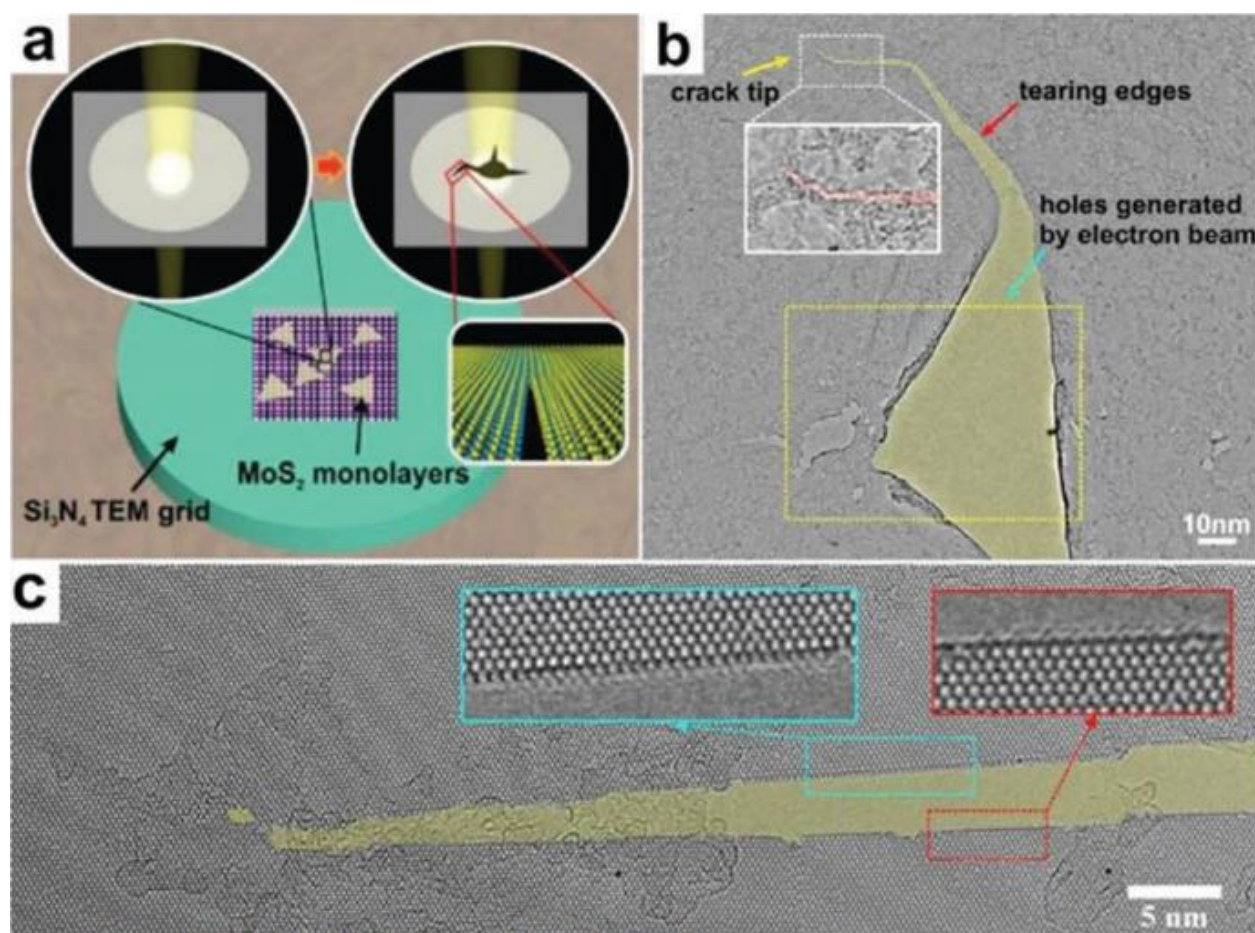


Figure 2-16. Electron beam irradiation generated cracks in MoS₂. (a) Schematic illustration of crack formation process on MoS₂ monolayer by electron beam (EB) irradiation. ACTEM images of (b) popped area of monolayer MoS₂ by focused EB and the resultant crack emission, with the zigzag lattice propagation direction of the crack tip shown in (c). [Reproduced with permission from (36)]

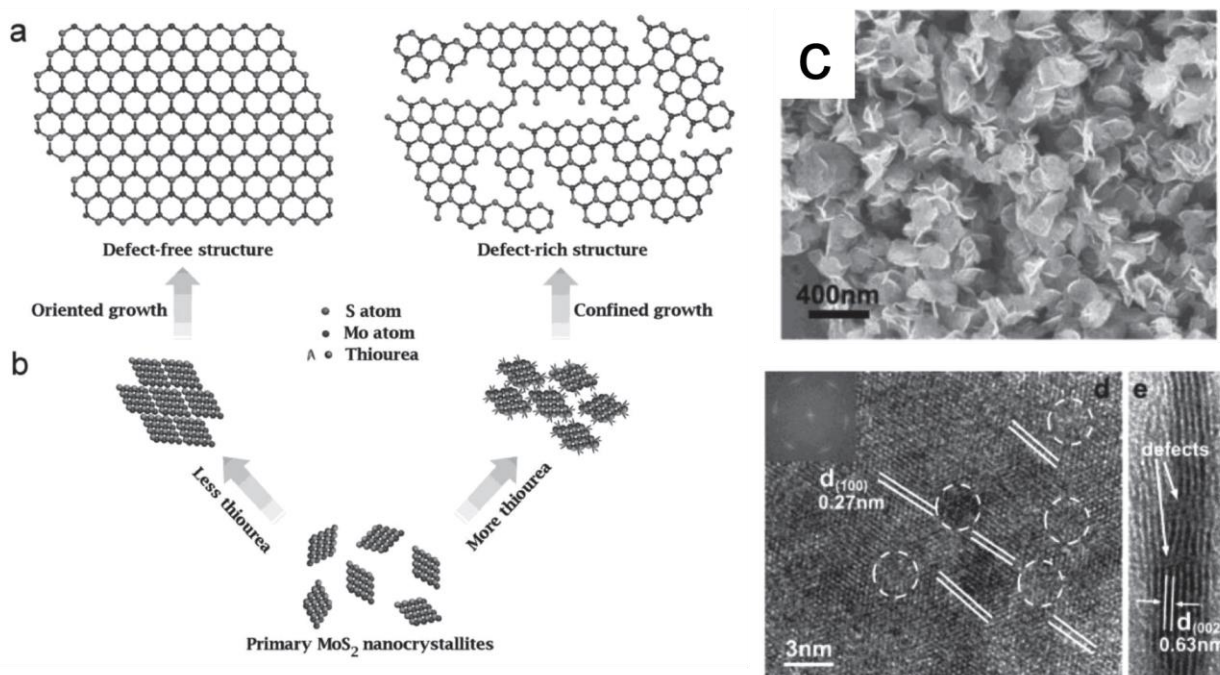


Figure 2-17. In-situ generation of defects in MoS₂. (a) Structural model and (b) as-designed pathways to obtain defect-free and defect-rich structures by tuning the precursor amount during synthesis, with (c) SEM showing the edge exposed morphology and (d,e) HRTEM images depicting two different defect-rich regions. [Reproduced with permission from (90)]

In addition to the post-growth methods discussed above, defects and additional edges can also be enriched during the synthesis process, in an *in-situ generation approach*. This strategy has been highlighted in the synthesis of defect-rich MoS₂ nanosheets using hydrothermal methods (**Figure 2-17a,b**). The defect-rich structure with additional edges (**Figure 2-17c**) was synthesized by using an excess amount of the reaction precursor thiourea, to not only reduce Mo (VI) to Mo (IV), but also stabilize the nanosheet morphology. Thiourea will be adsorbed on the surface of primary nanocrystals so that oriented crystal growth is partially inhibited, which leads to the defect-rich structure formation with quasiperiodic configuration, exposing a large number of additional edges by defect-induced cracks on the basal surfaces. The defect-rich structure is further verified by HRTEM images (**Figure 2-17d,e**). The slight rotation of

each individual (100) plane indicates the disordered atomic arrangement, which results in the basal plane crack and formation of additional edges. The six arcs in the FFT correspond to the quasiperiodic structure as a result of the presence of rich defects in the structure. Such structure is shown to be advantageous for HER with a small onset overpotential of 120 mV, benefitting from the 13 times higher number of edges than the bulk counterpart.(90)

2.6.3.2 Oxygen Incorporation

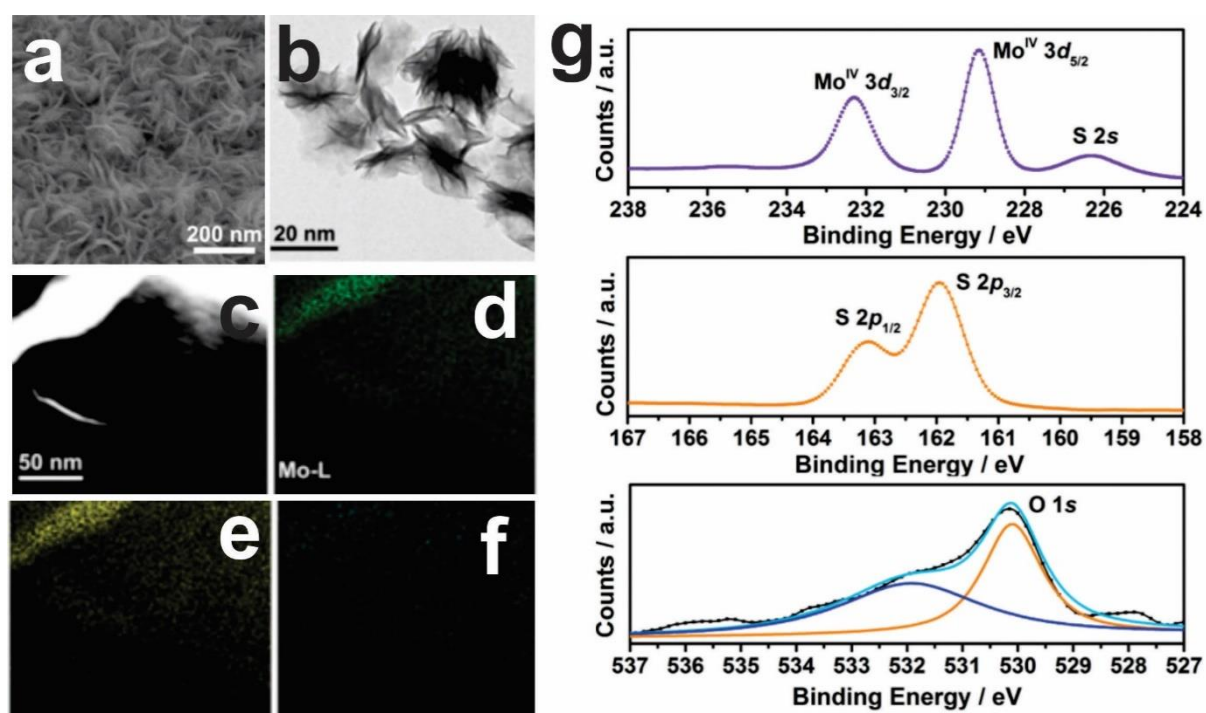


Figure 2-18. O-incorporated MoS₂ vertically aligned nanosheets. (a,b) SEM and TEM images of the nanosheets exhibiting vertical alignment. (c) STEM image of an individual O-incorporated MoS₂ nanosheet and (d-f) corresponding EDS maps showing that Mo, S, and O elements are homogeneously distributed in the whole nanosheets. (g) XPS data of O-doped MoS₂ on carbon cloth. The binding energies of Mo showing no oxidation of Mo^{IV} occurs, spectra of S indicating the chemical state is -2, and binding energies of O suggesting the existence of two different chemical states in the samples that correspond to Mo^{IV}-O bonds and absorbed water molecules. [Reproduced with permission from (120)]

Although the HER activity of MoS₂ based catalysts can be enhanced by increasing the active site density, the poor intrinsic conductivity of 2H-MoS₂ due to its large bandgap still impedes the overall HER rate.

Theoretical calculations have shown that O-incorporation into the MoS₂ lattice by substitution of S atoms or adsorption on top of S atoms will decrease the bandgap of monolayer MoS₂ from 1.86 to 1.64 eV or more, respectively.⁽¹⁰⁶⁾ O-incorporation is proposed as an effective approach for bandgap modulation. For example, O₂ plasma has been extensively employed to tune the electrical properties of MoS₂.^(119, 121, 122) This finding holds promise for regulating the conductivity of the 2H-MoS₂ and thus boosting the HER catalysis.

A low-temperature hydrothermal synthesis method has been successfully demonstrated to produce O-incorporated MoS₂ with boosted conductivity and edge density that leads to enhanced HER performance.^(91, 105, 120) In recent work,⁽¹²⁰⁾ vertically aligned nanosheets incorporated with O were successfully prepared using the aforementioned solution-based synthesis route. The vertical alignment of the nanosheets can be clearly observed in **Figure 2-18a,b**. STEM images and energy-dispersive spectroscopy (EDS) mapping were performed and revealed that the nanosheets are comprised of uniformly distributed Mo, S and O elements (**Figure 2-18c-f**). Owing to the low synthesis temperature, the reaction tends to be incomplete, leading to remaining Mo-O bonds inherited from the precursor, thus resulting in O-incorporation. X-ray photoelectron spectroscopy (XPS) data in **Figure 2-18g** reveals a O 1s peak at 530.1 eV, corresponding to the binding energy of oxygen in Mo^(IV)O₂, indicating the presence of Mo(IV) – O bonds. The binding energies of Mo suggest the dominance of Mo^{IV}, which further verifies the successful incorporation of oxygen into MoS₂ lattice rather than

surface oxidation of MoS₂. Benefitting from the synergistic regulation of both controllable edge enrichment and modified intrinsic conductivity, the HER activity is dramatically improved, exhibiting 120 mV onset overpotential (10 mA/cm²) as well as excellent stability.

2.6.3.3 Sulfur Vacancies

An alternative approach to making use of catalytically inert basal surfaces is to modulate the type of active sites and generate basal SVs in order to further enhance the HER activity.

Electron microscopy investigations (**Figure 2-19a-c**) have revealed that under EB irradiation,(123, 124) S atoms can be removed from the lattice to form SVs – the most common vacancy in TMDs, confirming the possibility of enhancing the HER activity by forming catalytic active SVs.(36)

The first study on activation and optimization of 2H-MoS₂ basal planes for catalytic purposes was demonstrated by introducing SVs and strain using *Ar plasma* exposure and capillary force (**Figure 2-19d**).(61) ACTEM imaging clearly shows the existence of SVs in the 2H-MoS₂ (**Figure 2-19e**). DFT calculations indicated that SVs introduce gap states that favor hydrogen adsorption and straining the SVs shifts the gap states even closer to the Fermi level which will result in optimal ΔG_H . SVs are new active sites on the basal planes and straining the surface can further fine tune the catalytic activity of 2H-MoS₂. HER activity of MoS₂ can be enhanced by both strain and SV as seen from the LSV curves in **Figure 2-19f**. An optimized combination of 1.35% strain and 12.5% SV SITES was shown to have a TOF of 0.08 – 0.31 s⁻¹, exceeding those of best-characterized MoS₂ edge sites and 1T metallic basal surfaces, the best reported at that time.

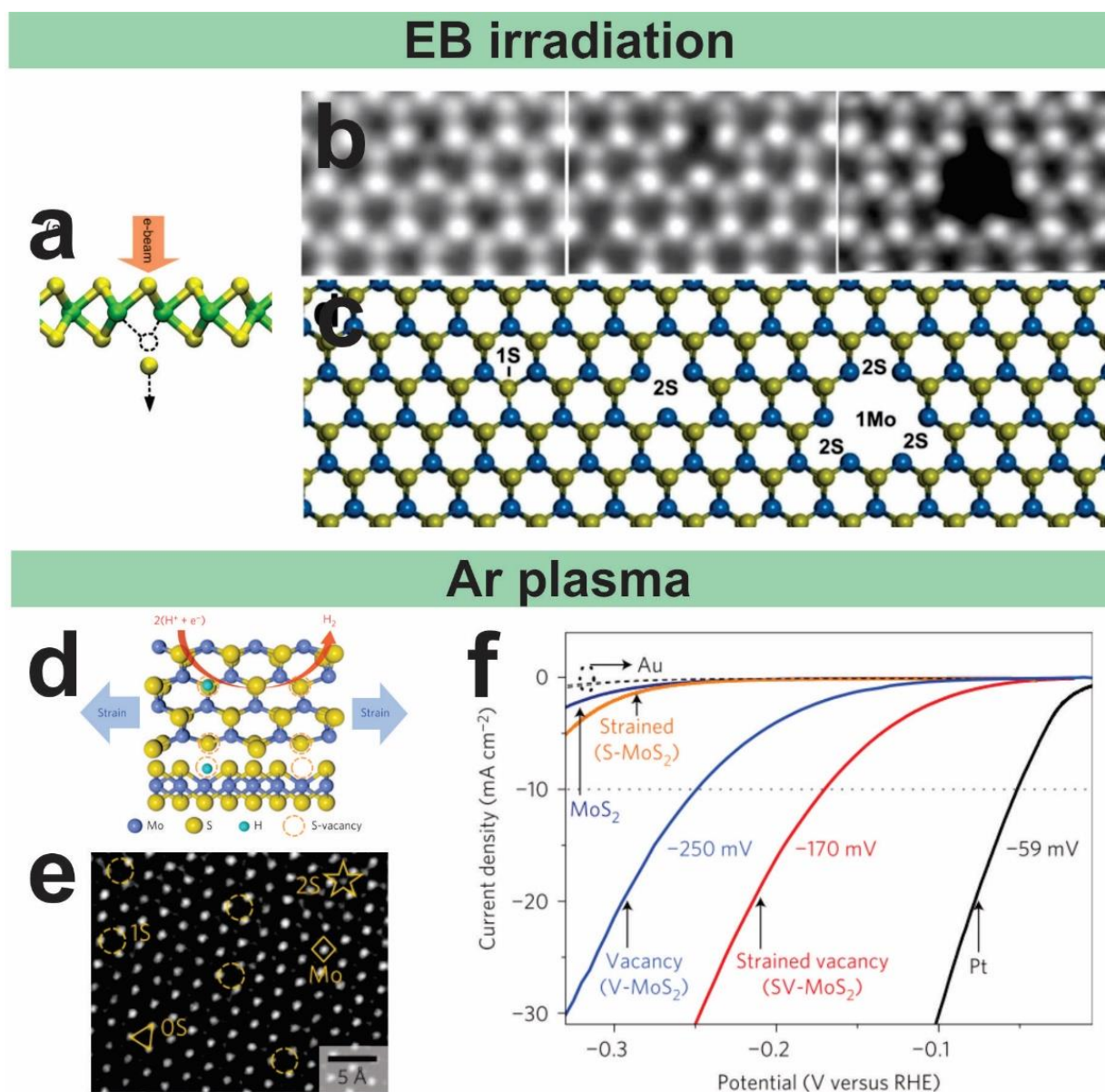


Figure 2-19A. Generation of SVs in MoS₂. (a) Atomic model of S atom sputtering under EB irradiation, [Reproduced with permission from (123)] (b) ADF-STEM images of 1S, 2S and 1Mo+2S vacancies in monolayer MoS₂ with corresponding atomic models in (c). [Reproduced with permission from (36)] (d) Schematic of the top and side view of MoS₂ with strained SVs. (e) ACTEM image of monolayer SV(~11.3%)-MoS₂, with big bright dots, small bright dots, small dim dots and dark dots corresponding to Mo atoms, 2S atoms, 1S atom and SVs, (f) LSV curves for Au electrode, Pt electrode, pristine MoS₂, MoS₂ with SV, MoS₂ with strained SV (strain: $1.35 \pm 0.15\%$ and SV: $12.5 \pm 2.5\%$). [Reproduced with permission from (61)]

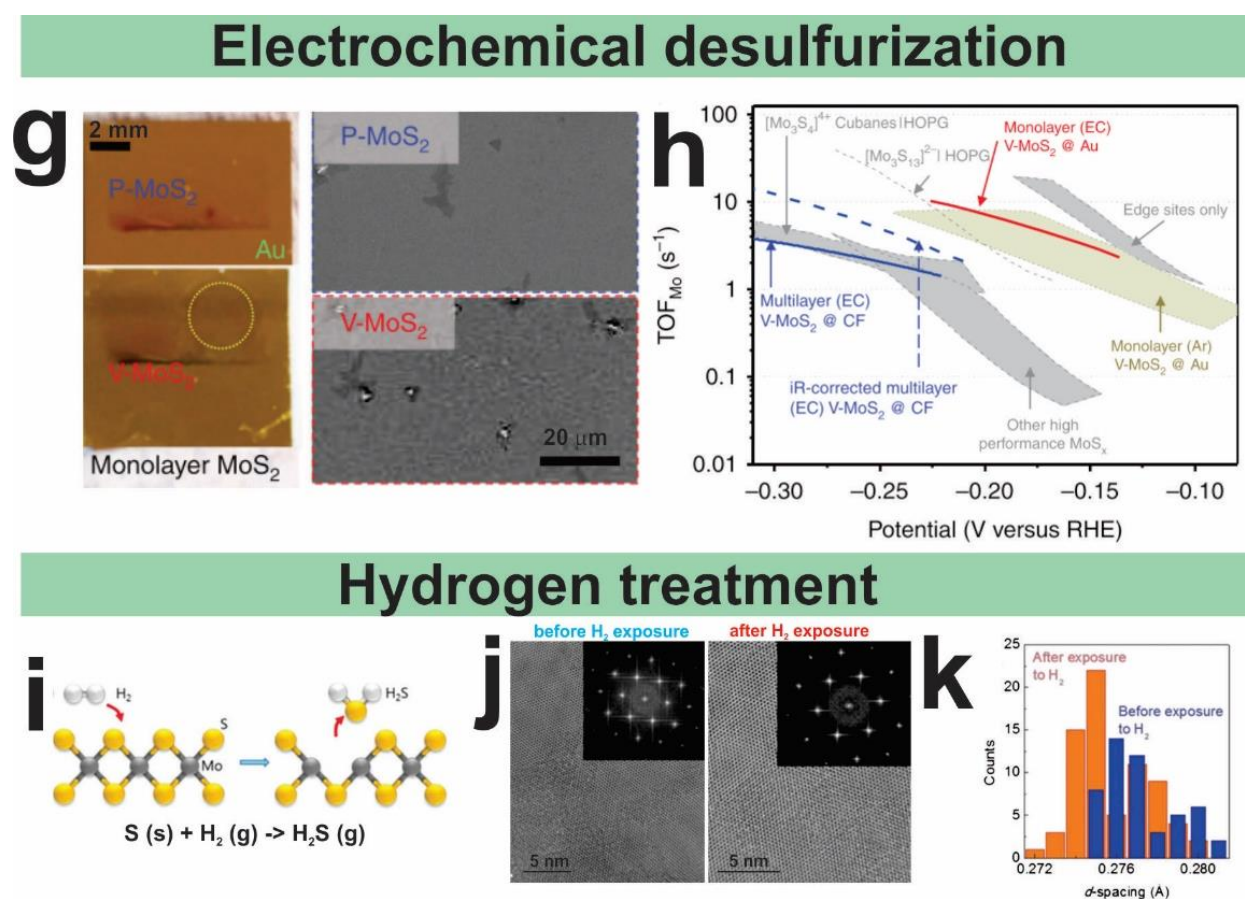


Figure 2-19B. Generation of SVs in MoS₂. (g) Optical and SEM images of pristine (P-MoS₂) and SV (V-MoS₂) monolayer MoS₂ generated by electrochemical desulfurization. (h) Comparison of TOFs per Mo atom between electrochemical desulfurized MoS₂ samples and state-of-the-art MoS_x catalysts. [Reproduced with permission from (64)] (i) Schematic of SV formation by molecule hydrogen treatment. (j) TEM images of multilayer MoS₂ before and after H₂ exposure with corresponding FFT inserted. (k) Histogram suggesting Interlayer spacing $d_{(10-10)}$ is decreased from 2.76 to 2.74 Å after H₂ exposure. [Reproduced with permission from (125)]

However, it remains challenging to industrially implement such plasma exposure method for high-performance 2H-MoS₂ catalysts. More recently, a *electrochemical desulfurization* approach was employed to generate SVs on a facile and scalable basis (Figure 2-19g).⁽⁶⁴⁾ This route is effective in removing S atoms at accessible overpotentials. The resultant SVs exhibited high TOF that is consistent with preciously Ar plasma generated SVs (Figure 2-19h). However, the total electrode activity is limited.

Further investigation needs to be conducted to increase the surface area of the catalyst on the electrode by increasing loading or nanostructuring.

Another feasible approach to modulate the SV density in multilayer MoS₂ to tune the electronic properties was discovered using *molecule hydrogen treatment* at low temperature (22 ~ 77 °C) and low H₂ gas pressure (vacuum ~ 24 bar) (**Figure 2-19i**).⁽¹²⁶⁾ The SV is generated by the dissociated H₂ molecules diffusing and forming H₂S gas with the surface S. It was found that upon exposing to H₂ molecules, MoS₂ went through a redshift (bond softening) as evidenced from Raman spectra and a decrease in d₍₁₀₋₁₀₎ spacing by HRTEM imaging (**Figure 2-19j,k**).⁽¹²⁵⁾ Whereas in high temperature (400 ~ 700 °C) H₂ annealing, despite a slight degree of SV density enhancement in the basal planes as indicated by an atom-by-atom intensity quantification analysis, defects are predominantly generated in the form of etched holes and expose additional edges of the monolayer MoS₂.⁽¹¹¹⁾

These findings demonstrate successful creation of SVs in basal planes and provide various methods that could be potentially effective for activation of basal surfaces by SVs in 2H phase and development of MoS₂ as feasible state-of-the-art HER catalyst. This strategy can be readily transferred onto nearly all MoS₂ catalysts since the industrial bulk MoS₂ surface mainly consists of 2H basal planes.

2.6.4 Pt/MoS₂ Composites

As mentioned in **section 2.2**, Pt metals exhibit the best HER catalytic activity and excellent corrosion resistance in acidic and alkaline environments.⁽¹²⁷⁾ However, the high cost and scarcity of Pt make its use a barrier for mass hydrogen production by the water splitting route.^(128–130) To reduce the cost of water electrolyzers while maintaining acceptable production of H₂,⁽¹²⁷⁾ efforts have been made on reducing Pt

loading without sacrificing the catalytic activity of the system by; (**route-1**) completely replacing Pt with inexpensive non-noble metal alternatives which possess high catalytic activity,(127) (**route-2**) tailoring morphology and microstructure of deposited Pt on its support to enhance the catalytic active surface area and (**route-3**) developing a hybrid catalyst based on noble-metal-free alternatives and Pt for enhanced performance at reduced Pt loading.(127, 131–133)

Following **route-1**, extensive research and progress have been devoted towards the discovery of inorganic catalysts in place of Pt. To date sulfides and phosphides, which usually contain transition metal cations of Mo, Co, Fe, or Ni are reported to be the most effective non-noble metal HER catalysts.(133) The catalytic activity reported for these newly discovered HER alternatives, however, can not be compared with Pt-based catalysts.(133, 134) Taking this into consideration, the optimal choice when designing advanced HER electrocatalyst still appears to be Pt-based catalysts.(133) The challenge lies in achieving similarly high performance at minimized Pt loading.(10, 131)

It is known that Pt electrocatalysts are mostly utilized in the form of supported particles.(127) The architecture of the support exerts great influence on the morphology and microstructure of the Pt particles as well as bonding between metal and support materials that impact particle agglomeration.(133–136) This enables us to modify the particle dispersion and metal-support interaction to enhance the electrochemical active surface area at the same Pt loading,(127, 129, 130, 137) consequently to enhance the catalytic activity economically.(55) This is described as aforementioned **route-2**. An efficient strategy is, for example, to reduce the size of Pt particles to (sub)-nanometer and ultimately atomic scale, which led to dramatic improvement of catalytic activity.(131, 135, 138, 139) Although a catalyst may be deposited on a planar support, only for low

current density applications, for high current density application the Pt catalyst should be incorporated on a high surface area mesoporous or particle-based support.(55, 127) Pt-electrocatalyst supports typically are carbon-based nanomaterials which possess high surface area, good conductivity, and durabilities such as activated carbon, carbon nanofibers, and carbon nanotubes.(10, 131, 135, 137, 140) Recently two-dimensional materials including graphene and MoS₂ have drawn great attention as promising candidate Pt catalyst support due to the extremely high surface area and superior chemical stability.(55, 57, 137, 141–144)

In **section 2.6.2**, I have explicitly discussed the established progress in MoS₂ catalysts with large surface area and enhanced edge density, such as mesoporous structures, vertically standing atomic layers and edge exposed nanosheets *etc.* However, one downside to these structures is the lack of activity on basal surfaces. One possible solution is to utilize high-surface-area MoS₂ as a scaffold to construct Pt/MoS₂ composites, where a small amount of Pt can decorate the inactive MoS₂ basal planes and make use of the full area of MoS₂. (**route-3**) *Firstly*, such high surface area morphology appears promising as a template for well-dispersed Pt atom/nanoparticle surface growth,(55) which is beneficial for the electrochemical active surface area and sintering stability of metal particles. *Secondly*, unlikely carbon-based supports that are catalytic inert, as an effective electrocatalyst, the MoS₂ will act not only structurally as Pt growth template but also provide additional catalytic active edges for the HER. *Thirdly*, synthesizing 0D Pt on 2D MoS₂ to form 0D-2D functional composite may not only enhance the intrinsic properties of individual materials but also trigger synergistic effect bringing novel properties and functions.(57, 127, 130)

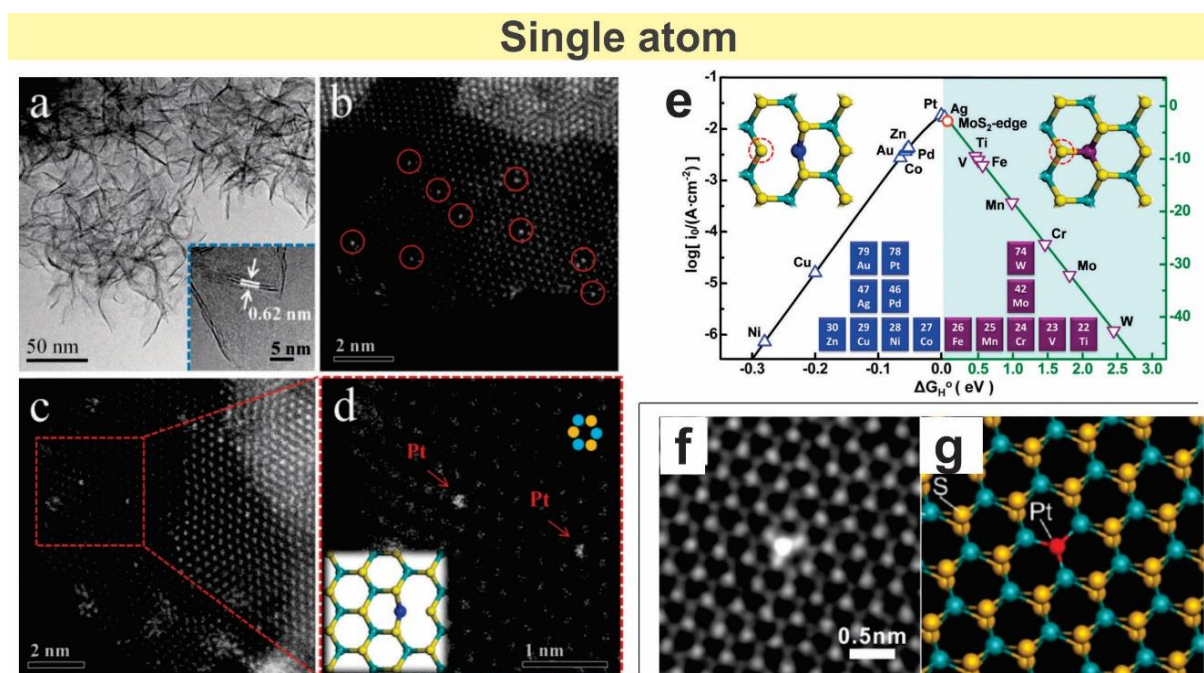


Figure 2-20A. Pt-doped 2D MoS₂. (a) TEM image of single atom Pt-doped MoS₂ nanosheets, inset showing a typical MoS₂ interlayer spacing of 0.62 nm. (b,c) ADF-STEM images of Pt-MoS₂ showing Pt atoms (marked by red circles) uniformly dispersed in the 2D MoS₂ planes. (d) Magnified domain with red dashed rectangle in (c) showing the honeycomb arrangement of MoS₂, with Pt atoms substituting the position of Mo atoms (marked by red arrows). The bottom inset shows the simulated configuration of Pt-MoS₂ with green, yellow and blue balls corresponding to Mo, S and Pt atoms, respectively. (e) HER volcano plot of single metal atom doped MoS₂ nanosheets. The two inset structures indicate different configurations of doped MoS₂ as coordinated with four (left) and six (right) S atoms. The adsorption sites for H atoms are marked by the red dashed circles. Mo, green; S, yellow; doped metal atoms, blue and purple. The bottom inset shows the locations of the metal atoms studied in the periodic table. Two different sets of scales are used on the left and right sides of the volcano plot. [Reproduced with permission from (145)] (f) ADF-STEM image and (g) atomic model of the single Pt atom residing at S site of monolayer MoS₂. [Reproduced with permission from (21)]

Depending on the number of Pt adatoms on MoS₂, two forms of doping can be achieved: single atom (**Figure 2-20a-g**) and nanocrystal (**Figure 2-20h-n**).⁽³⁶⁾ It is found that single heteroatom doping is capable of enhancing the activity of the surface S

atoms;(145) metal nanoclusters can facilitate electron transfer to the 2D crystals and thus modify the surface electronic structure and enhance the reactivity of MoS₂.(144, 146)

Single Pt atom doped few-layer MoS₂ NSs was realised by a direct chemical synthesis method.(145) As can be seen from the TEM images (**Figure 2-20a-d**), Pt single atoms are introduced and dispersed uniformly across MoS₂ basal surfaces by exact substitution of Mo atoms. HER measurement shows enhanced electrocatalytic activity by lowering the overpotential of 60 mV relative to the un-doped counterpart. Furthermore, the catalytic activity remains unchanged after 5000 cycles. DFT calculations revealed that in-plane S atoms neighboring the doped Pt heteroatoms exhibit close to zero ΔG_H (**Figure 2-20e**), which is even lower than that of pristine MoS₂ edge (0.1 eV). This finding confirms S atoms in catalytic inert basal planes of 2H-MoS₂ can be triggered by atomic level doping using Pt, Co and Ni atoms. It is worth noting that on the clean surface of a monolayer MoS₂, the single Pt atoms prefer to locate on the SV sites (**Figure 2-20f,g**), which is energetically favorable as supported by DFT calculations. As a consequence, the HER catalytic activity arising from SVs will be quenched.(21)

In previous studies, utilization of MoS₂ nanosheets (NSs) as a substrate for Pt particles deposition has been reported to achieve higher catalytic activity at reduced Pt loading.(55, 143, 144, 148) Solution phase growth of Pt nanoparticles (NPs) on 2D MoS₂ NSs was demonstrated. The Pt NPs can be synthesized with controllable size and morphology.(144) 2D MoS₂ layers serve as the template to direct the epitaxial growth of Pt NPs. Pt nanostructures were revealed by TEM imaging to exhibit major (111) and (101) orientations on the (001) surfaces of MoS₂ (**Figure 2-20h-j**). In order to track the formation of Pt nanocrystals on the MoS₂ monolayer, an in-situ heating holder was used

to observe the decomposition of Pt precursor at 800 °C in real time (**Figure 2-20k-m**). With the help of a MoS₂ template, ultra-small Pt clusters (~ 20 atoms) were stabilized and formed 2D epitaxial Pt nanocrystals on MoS₂, with a significant lattice strain to match the lattice parameter of underneath MoS₂ template. With the number of Pt atoms rising, the metal atoms start to agglomerate into 3D structures and epitaxy is lost. Interestingly, the 3D nanoparticles can etch the surrounding MoS₂ to increase the edge density for HER catalysis.(147) HER testing suggest that the as-prepared Pt/MoS₂ shows much better HER catalytic activity than the commercial Pt/C catalysts with the same Pt loading as seen in **Figure 2-20n**. The absence of Pt⁰ and the presence of Pt^{δ+} as revealed by XPS are likely from Pt and MoS₂ interaction – electron transfer from Pt NPs to MoS₂ NSs.(149) Moreover, the large surface area provided by the 2D layered MoS₂ network can benefit the capture and transfer of charges in the 3D matrix, hence is desirable for catalysis process with faster charge transfer and ionic interchange.(150) In spite of the excellent HER activity, chemical exfoliation using Li-battery setup has introduced process complexity; monolayer MoS₂ template lacked porous 3D architecture for the size and surface area control of the Pt NPs;(144) moreover, chemically exfoliated MoS₂ sheets are prone to restacking, which will hinder vertical charge transport and limit the number of accessible catalytic active sites(151). The hydrothermal route has been explored to prepare Pt nanospheres on few-layer MoS₂ but the thickness of MoS₂ can not be controlled, therefore lack of transferrable guidelines to other materials system.(148)

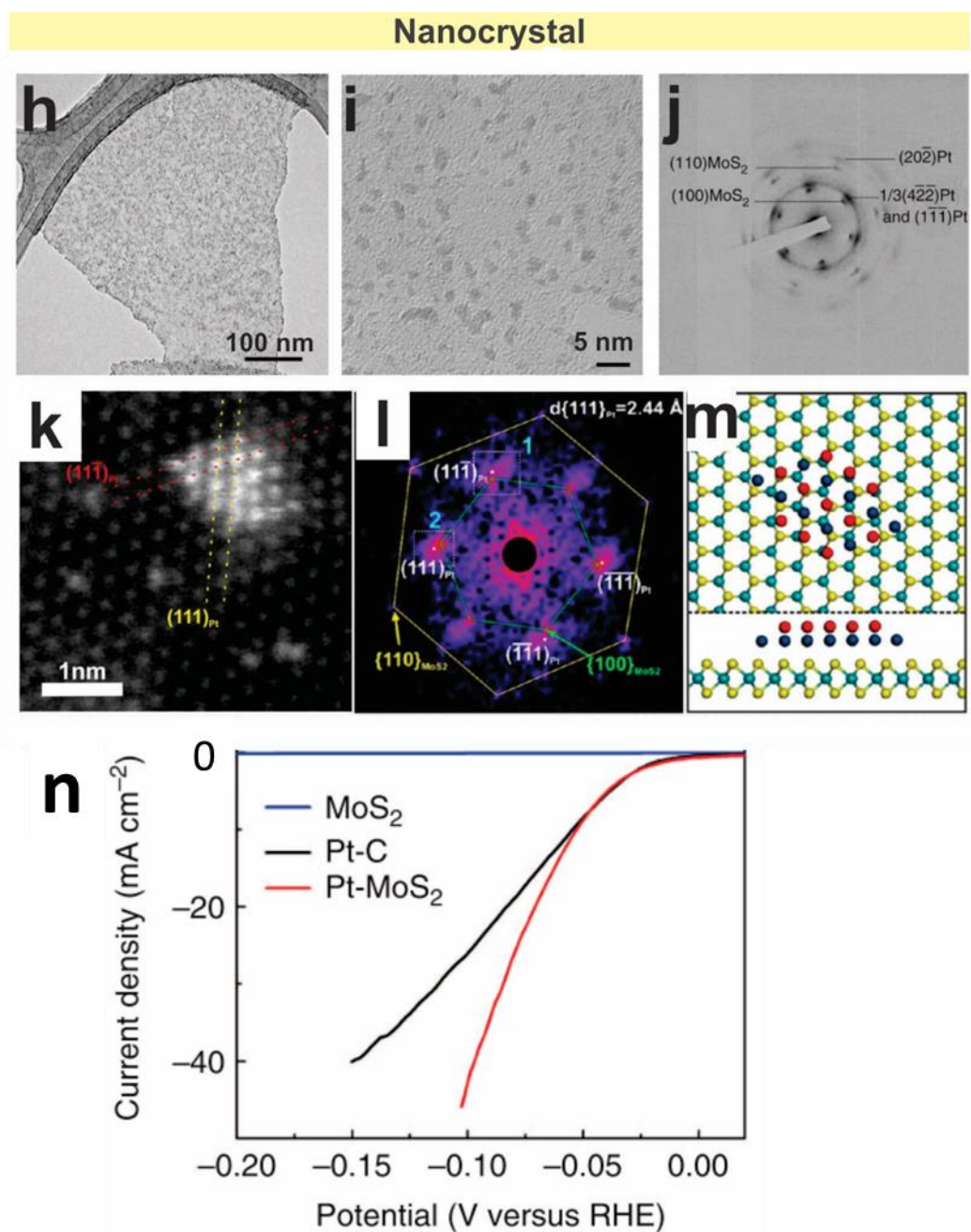


Figure 2-20B. Pt-doped 2D MoS₂. (h) TEM image and (i) magnified TEM image of Pt nanocrystals grown on MoS₂ nanosheet (Pt/MoS₂ hybrid), showing average size of the nanoparticles is 1-3 nm. (j) SAED pattern of Pt/MoS₂ with the electron beam along (001) direction of MoS₂ nanosheets. [Reproduced with permission from (144)] (k) ADF-STEM image, (l) FFT and (m) atomic model of two-atom thick Pt nanocrystal grown on monolayer MoS₂. [Reproduced with permission from (147)] (n) LSV curves of MoS₂, Pt/MoS₂ and Pt/C catalysts, where Pt loading was kept the same for the Pt/MoS₂ and Pt/C electrode (0.027 mg/cm²). [Reproduced with permission from (144)]

2.7 Conclusion

In recent years there have been blossoming efforts in search and development of advanced catalysts for clean energy conversion. MoS₂ is emerging as a promising electrocatalytic alternative to Pt for HER, which relies on exposure of specific active sites (for 2H-MoS₂: edges and basal plane SVs) that are capable of adsorbing and desorbing H with low energetic barriers.⁽³²⁾ In this review, I have highlighted various routes for enhancing HER activity of 2H-MoS₂ catalysts. Effective approaches include nanostructured engineering to increase surface area and edge exposure; generating defects to activate basal planes, as well as Pt heteroatoms/nanocluster doping to modify the reactivity of MoS₂.

- Despite considerable exploration and advancement in the growth of edge-terminated MoS₂ nanostructures, a simple and scalable synthesis route for precise control of 3D edge terminated structure (layer, size, and thickness) with the high surface area is still lacking. Moreover, the structure – catalytic property correlation needs to be quantitatively investigated.
- Defect engineering holds potential for activation of 2H-MoS₂ basal surfaces by introducing cracks, holes, SVs and O-incorporation. However, recent work has been either limited to achieving basal plane activation in monolayered crystals or relying on complex and hard to control solution-based methods. Therefore, basal plane activation in 3D thin films through controllable defect modulation is vital for a high-performance Pt alternative. Correlation of defect modification with HER optimization remains a key challenge due to difficulty in identifying detailed HER active structures.

- Pt heteroatoms or nanocluster doping of MoS₂ serves as an enabling platform for constructing a high-performance composite with minimized Pt loading. Controllable type, content, and distribution of dopants is, however, still a challenge based on current preparation routes. Another limitation is that little attention has been given to the systematic characterisation of Pt-doped MoS₂ hybrid structures, thus the lack of guidelines for efficient hybrid design.

In the following investigations, many of these important aspects will be explored.

3 Methodology

3.1 Introduction

Based on the review of previous work discussed in **Chapter 2** and the available experimental apparatus in our lab, this chapter details the methods of materials synthesis, characterisation as well as electrochemical testing. The purpose of these experiments is to design and optimize the electrocatalysts, to deliver high-performing MoS₂ thin film based catalyst of desirable structural architecture.

The following sections will elaborate in detail: the design of the CVD setup; condition and parameters required for growth of edge terminated nanoplatelets; operational protocols of various characterisation techniques to probe chemical composition, morphology, and microstructure; three electrode electrochemical testing method to investigate electrocatalytic performance.

3.2 Synthesis of MoS₂ Thin Film based Electrocatalysts

3.2.1 CVD Growth of 3D-ER-MoS₂ Porous Thin Film

The CVD synthesis of edge-exposed MoS₂ thin films on different substrates (e.g. silicon wafer, glassy carbon plate (GC), graphite sheet and single wall carbon nanotube sheet) is illustrated in **Figure 3-1**. It consists of three functional parts: (1) two independently controlled tubular furnaces; (2) 4-inch outer and 1-inch inner quartz tubes and (3) gas delivery and exhaust system.

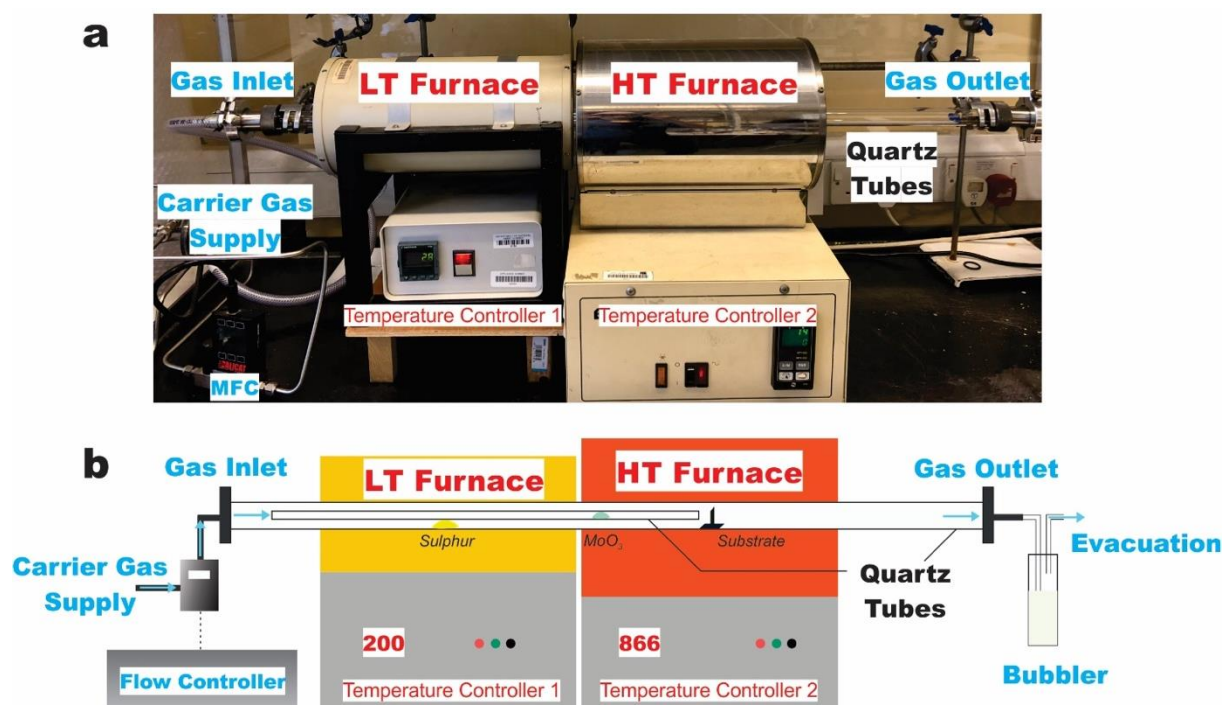


Figure 3-1. (a) Photograph and (b) corresponding schematic illustration depicting atmospheric pressure CVD (APCVD) experimental setup for edge-exposed MoS₂ nanoplatelet growth on various substrates, consisting of three main functional parts: 1) two-furnace system, 2) double-quartz tubes as well as 3) gas delivery and exhaust system.

A two-furnace approach is designed to separately control the temperature of MoO₃ and S precursors as well as substrate and hence, enables tunable CVD reaction parameters, e.g. growth temperature and density of reaction species in the chamber. The low-temperature (LT) furnace is used for controlling the temperature of the S powder, and the high-temperature (HT) furnace of MoO₃ and the growth substrate. The separate temperature control of MoO₃ and substrate is realised by adjusting the positions of MoO₃ powder and the growth substrate in the HT furnace based on the temperature profile as a function of the horizontal position in the tubular furnace with

both open ends (**Figure 3-2**). The influence of temperature gradient on the morphology and thickness of the resultant thin film will be discussed in **Chapter 4**.

The quartz tubes are inserted through the centers of both furnaces for CVD reaction to take place. MoO_3 powder and S powder and the substrate are placed at respective positions inside the quartz tubes (as shown in **Figure 3-1**), which are then coordinated to the positioning relative to the furnaces for temperature control. The double-quartz tube setup is employed to prevent quenching of MoO_3 from S by scattering them into 1-inch and 4-inch tubes, respectively.

The 4-inch quartz tube is connected to a gas delivery inlet on one end and exhaust outlet on the other and properly sealed by vacuum fittings. Pure argon (Ar) gas is employed as a carrier of precursor vapor downstream to the target substrate as well as to ensure inert atmosphere from oxidant and moisture. A mass flow controller (MFC) is used for precise Ar gas delivery. An exhaust pipeline is connected with oil bubbler for monitoring bubbling rate throughout the course of CVD reaction so that overpressure in the quartz tube can be prevented, which can occur because S vapor is prone to solidifying at the cold region of the quartz tube. Hence, it is also necessary to inspect the pipeline prior to each CVD session and replace clogged ones regularly.

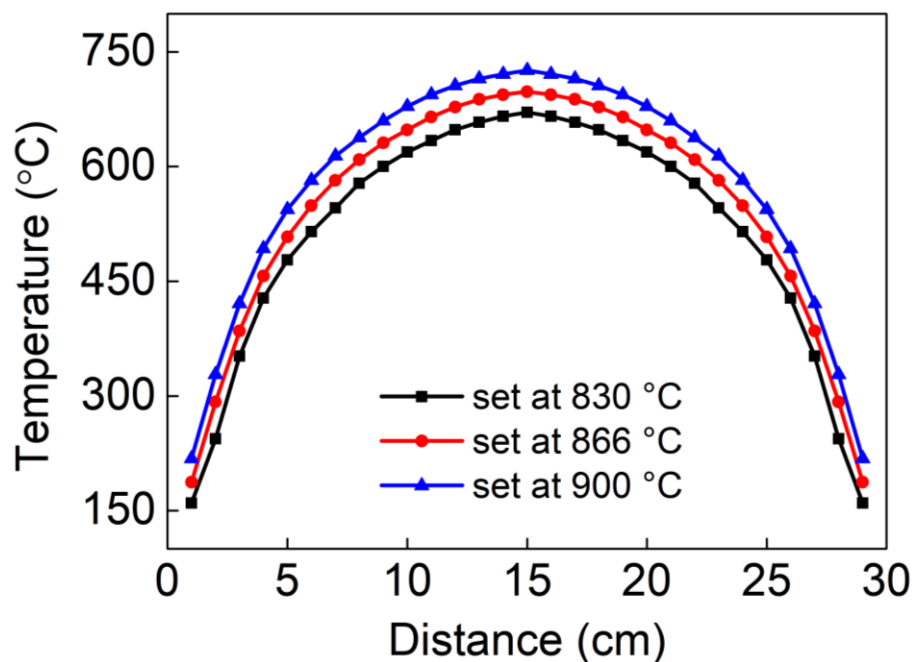


Figure 3-2. Temperature profile inside the HT furnace as a function of horizontal position at set temperature values of 830, 866 and 900 °C, respectively. The temperature gradient enables fine tuning of temperatures at MoO₃ powder precursor and substrate during CVD reaction.

Dedicated efforts have been put into exploring single-step and scalable CVD method to synthesize 3D-ER MoS₂ thin films with tunable morphology and microstructure. This is essential for the investigation of CVD growth mechanisms, and design, optimization of MoS₂ HER electrocatalysts, as well as understanding the governing principles behind the electrochemical transformation. The exact CVD growth recipe that I have developed for 3D-ER MoS₂ thin film is described as follows:

In this thesis, the substrates used for CVD growth included bare silicon wafer (SiO₂/Si - Si with a 300 nm SiO₂ layer), glassy carbon (GC), graphite (G) sheet and single wall nanotube (SWNT) sheet. For the preparation of the growth substrate, acetone was applied to thoroughly clean the substrate. The most gentle and efficient way to carry out this process is to use a cotton bud dipped into acetone, and then gently rubbing

the substrate surface to remove any grease and dirt to avoid contamination during the CVD reaction. The substrate was supported by a three-piece-Si-chip constructed scaffold (homemade with fire cement) so that it can be placed into the quartz tube vertically. The vertical configuration of the substrate eliminates the unfavorable precursor mass depletion problem (*versus* notable concentration gradient of precursor vapor across substrate length when the substrate is configured parallel to Ar gas flow). In addition, it promotes the diffusion and absorption process of reactants onto the substrate through the boundary layer of the gas flow. The scaffold was replaced after each CVD reaction.

After cleaning, the substrate, along with 500 mg molybdenum (VI) oxide (MoO_3) powder ($\geq 99.5\%$, Sigma-Aldrich, melting point 795°C , particle size 100 nm) and 600 mg sulfur (S) powder ($\geq 99.5\%$, Sigma-Aldrich, melting point 115°C , boiling point 445°C) were loaded into the quartz tubes. The substrate was placed vertically at the center of the outer 4-inch quartz tube; S powder (600 mg) was put upstream in the outer 4-inch quartz tube, right at the middle point of the LT furnace where the temperature is 200°C ; MoO_3 powder (500 ~ 1000 mg) was scattered inside the inner 1-inch tube at 2 ~ 3.5 cm from the start point of the HT furnace, which corresponded to a heating temperature at 300°C ~ 400°C . Discussion on the influence of positioning/temperature and precursor quantities of MoO_3 powder on morphology and thickness of final product will be discussed in **Chapter 4**.

Prior to vaporizing the precursors, the CVD chamber was purged with 500 sccm (standard cubic centimeters per minute) of Ar gas for 30 min to flush out O_2 and moisture from the reactor, while both furnaces were kept at room temperature.

Subsequently, the flow rate of Ar gas was adjusted to 150 sccm, while the LT furnace was heated up at 15 °C/min to 180 °C and then at 1 °C/min until it reached 200 °C; the HT furnace to 866 °C at 40 °C/min, dwell upon reaching the target temperature. The total duration of this step was 50 min. The purpose is to fill the reaction chamber with a sufficient amount of S vapor to ensure thorough reduction of MoO₃ into MoS₂ at the subsequent growth stage. Temperatures at the substrate were set to be well above the heating temperature of S to prevent S from solidifying at the substrate as this can cause contamination and disturb the MoS₂ thin film deposition.

For the growth stage, the flow rate of Ar gas was adjusted to 50 sccm to deliver a concentration of precursor species in the vapor phase so that it can form vertically aligned nanoplatelets (the study on the evolution of morphology as a function of carrier gas flow rate is shown in **Chapter 4**). Growth duration between 15 and 120 min was conducted to investigate the growth mechanisms of the edge exposed thin film. S and MoO₃ powders were kept at 200 °C and 300 °C ~ 400 °C to evaporate and migrate to the substrate and deposit and then subsequently grow into a thin film.

When the growth was finished, residual S power was exhausted with 500 sccm of Ar gas for 15 min by quickly ramping the LT furnace up to 420 °C (at 40 °C/min) while the temperature of HT furnace was slightly decreased to 700 °C. In the end, both furnaces were slid sideways to expose the substrate containing quartz tube section to air. Assisted by electric fans, fast cooling of the system was carried out with Ar gas flow at 500 sccm.

After CVD growth, each as-received MoS₂ thin film was checked under SEM to examine whether the 3D-ER morphology was successfully obtained and to

investigate the surface grain size of the MoS₂ domains. This step ensures all the CVD samples used for electrochemical testing and further post-treatments are consistent in morphology.

3.2.2 Defect Engineering of CVD 3D-ER-MoS₂ Porous Thin Film

In order to introduce defects and additional edges to the basal planes of pristine MoS₂ and understand their impact on structural and electrocatalytic properties of the CVD as grown MoS₂, two approaches were employed: H₂ annealing and O₂ plasma etching.

The H₂ annealing process was carried out by placing the CVD as grown MoS₂ edge exposed thin film inside a quartz tube which was then inserted through a tubular furnace. The tube was sealed properly with vacuum fittings and connected with H₂ (25% in Ar) and an Ar supply and exhaust system. Prior to annealing, the tube was purged with 100 sccm of Ar for 30 min to provide a mostly inert atmosphere inside the annealing chamber. During the annealing process, the MoS₂ sample was heated up to 600, 700 and 800 °C (results on temperature-dependent annealing will be discussed in **Chapter 5**) for 2 hours under 50 sccm of H₂ flow. At the end of the annealing process, the quartz tube section of the heated sample was immediately exposed to air by sliding the furnace sideways and rapidly cooling down to room temperature under the protection of 100 sccm of Ar gas.

O₂ plasma treatment is an effective surface modification process which uses short pulses of an oxygen plasma (a partially ionized gas containing free electrons and radicals e.g. O, O⁺ and O²⁺) on the sample. The process relies on the chemical reaction between the elements of the materials etched and the reactive species

generated by plasma, which leads to modification of nanostructure and properties as well as etching effects if the resultant product is volatile. Therefore, the etching process is sensitive to surface morphology and film thickness. Based on a literature survey of plasma etching methods on monolayer and few-layer MoS₂ (summarized in **Table B1**), further investigation of the process has led to a scalable recipe for controllable structural tuning devoted to the 3D-ER MoS₂ nanoplatelets. The process was carried out using a low-pressure plasma system – Zepto Plasma Laboratory Unit (Diener Electronics) with 230 V power supply. The CVD as-grown sample was placed in a ceramic boat and then exposed at a chamber pressure of 0.8~1 mPa with pure O₂ gas for durations of 0, 15 and 30 min. The purpose of this recipe was, on the one hand, be effective enough in introducing defects of interest and on the other, retain a considerable quantity of the active materials.

3.2.3 Surface Growth of Pt Nanoparticles on CVD 3D-ER-MoS₂ Porous Thin Film

Pt nanoparticles grown on 3D-ER MoS₂ was realised via a two-step process: 1) synthesis of substrate/scaffold 3D-ER MoS₂ thin film using CVD and 2) formation of dispersive Pt nanocrystals via thermal annealing (TA) approach. A MoS₂ porous thin film consisting of vertically-aligned nanoplatelets was synthesized via single-step CVD method (as described in **section 3.2.1**) directly on GC substrate in order to be readily employed as a working electrode in the subsequent three electrode electrochemical measurement.

The CVD MoS₂ thin film was drop coated with 10 μ L sonicated H₂PtCl₆·6H₂O:ethanol (Sigma-Aldrich; concentrations of H₂PtCl₆·6H₂O:ethanol were kept at 0.1, 1 and 10

mM, respectively) and then air-dried at room temperature for 20 min. The resultant $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ coated MoS_2 sample was subsequently placed in a ceramic boat and inserted into the center of the tubular furnace. The tube furnace system was properly sealed with vacuum fittings and purged with 200 sccm of Ar for 30 min to get rid of most of the oxygen and moisture. The sample was heated up to 400, 500 and 600 °C for 20, 40 and 60 min with a flow of H_2 (25% in Ar) at 100 sccm, allowing decomposition of H_2PtCl_6 to Pt and surface growth of Pt nanocrystals over MoS_2 surfaces. At the end of the reaction, the sample was rapidly cooled down to room temperature, under the protection of 200 sccm Ar gas, by moving the furnace across to expose the sample containing tube section to air.

3.3 Raman Spectroscopy

Raman spectroscopy is a powerful fingerprinting technique to identify the characteristic vibrational modes of MoS_2 . The ratio of the different modes provides rich information on the texture of MoS_2 layers. JY Horiba Labram Aramis imaging confocal Raman microscope was employed to capture the Raman spectra excited by a 532 nm laser. Before measuring the sample, the Raman spectrometer was calibrated using a standard silicon chip (520.7 cm^{-1}) to exclude any instrumental error. Spectra were typically taken with 50% filtered incident laser intensity from 200 to 600 cm^{-1} with a resolution of 1800 g/mm (1800 grooves per mm grating). The acquisition time of 2 seconds and accumulation number of 2 were applied to deliver a good signal-to-noise ratio whilst preventing sample damage from the laser thermal effects.

3.4 Scanning Electron Microscopy

The main purpose of using scanning electron microscopy (SEM) in this project was to morphologically characterize the sample at micrometer and even down to nanometer scale. For general surface detection of samples, Hitachi S-4300 with an accelerating voltage of 3.0 kV and beam current of 10 μ A was used; Zeiss Merlin Analytical with superior resolution was used only for the H₂-etched MoS₂ sample to identify defect configuration at the sub-domain scale. SEM measurements were carried out on MoS₂ samples grown on SiO₂/Si or carbon-based substrates. For the preparation of SEM specimen, the MoS₂@substrate was pasted onto the SEM stub using carbon conductive tape, to weaken the surface charging issue rising from the semiconducting nature of the sample and SiO₂/Si substrate.

Data on the Zeiss Merlin Analytical was collected by Mr. Xiaochen Wang.

3.5 (Scanning) Transmission Electron Microscopy

Transmission electron microscopy (TEM) is capable of imaging at a significant high resolution that enables the visualization of crystal orientation, lattice structure and even a single column of atoms. An image is formed from the interaction of the electrons with the sample as the beam is transmitted through the specimen, which typically requires the specimen to be an ultrathin section less than 100 nm thick or a suspension on a grid. The as-prepared micrometer-thick MoS₂ thin film needs to be thinned and transferred onto a grid for further TEM characterisation. The TEM specimen was prepared by gently scraping across the surface of as-prepared MoS₂ off the substrate to mechanically detach flakes, and then transferring them to ethanol

for sonication for 30 min to form a dispersive suspension. The suspension was drop-cast onto a lacey carbon TEM grid and air-dried for 20 min to promote adhesion to the grid. TEM characterisation using various instruments were all at room temperature.

Low magnification TEM imaging and selected area electron diffraction (SAED) were conducted on a JEOL JEM-2100 with an accelerating voltage of 200 kV to identify the lattice structure, vertical alignment of the atomic layers and interlayer orientation. Aberration-corrected (AC)-TEM imaging was performed using Oxford's JEOL JEM-2200MCO FEGTEM with a CEOS image corrector and operated at an accelerating voltage of 80 kV, to take high-resolution (HR)-TEM images for studying the atomic configuration of the basal planes and edges. Annular dark-field (ADF) scanning TEM (STEM) imaging was employed on aberration-corrected JEOL ARM200CF STEM equipped with CEOS corrector operated at an accelerating voltage of 60kV, where the lattice structure of surface grown Pt nanocrystals was resolved.

ACTEM imaging was assisted by Mr. Si Zhou; ADF-STEM data was collected by Prof Jamie Warner, Dr. Jakyung Lee and Mr. Si Zhou.

3.6 Three Electrode Electrochemical Measurements

All the CVD grown samples tested for electrochemical properties were freshly prepared and subjected to post-synthesis treatments directly on the GC substrates unless otherwise stated. No additional transfer process was involved. A three electrode electrochemical cell was used for HER testing and Cottrell measurement, to determine the HER activity and Cottrell surface area of the MoS₂ thin film catalysts.

Linear sweep voltammetry (LSV) and chronoamperometry were conducted in a three electrode system to investigate the HER half-reaction of water splitting. The setup (**Figure 3-3**) involved the analyte solution contacting three electrodes: a working electrode (WE), a counter electrode (CE) and a reference electrode (RE). Each of these was connected to a potentiostat, which applied a overpotential difference between the WE (where the electrochemical event of interest occurred) and RE (which acted as a stable reference point against which the overpotentials of WE were measured). The CE completed the circuit, thereby allowing the flow of the current.

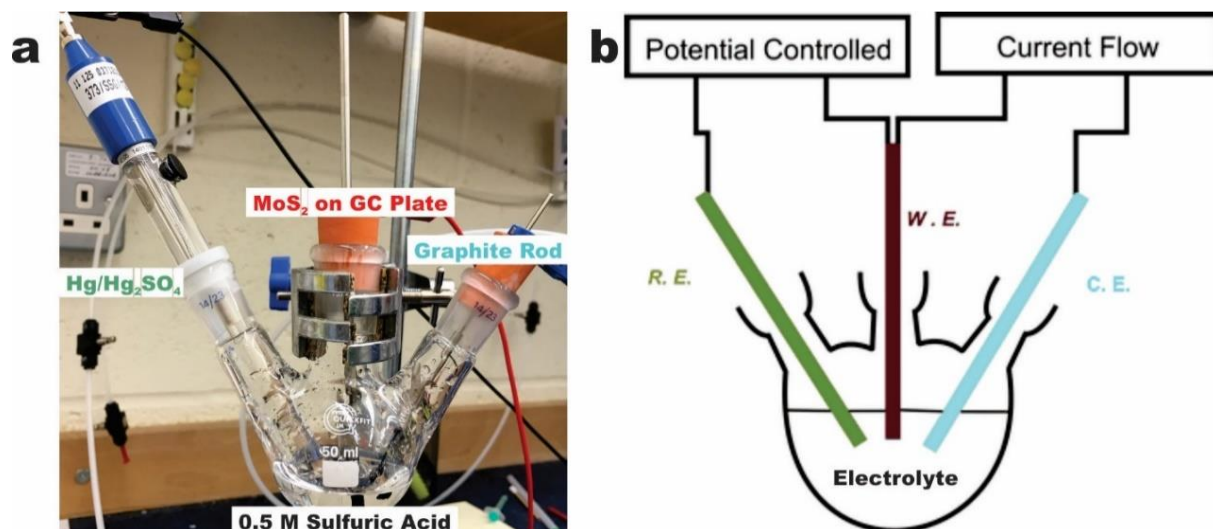


Figure 3-3. (a) Photograph and (b) corresponding schematic illustration showing a standard three-electrode electrochemical cell employed in this study for HER and Cottrell measurements of MoS₂ thin film based catalysts for electrocatalytic activity and Cottrell surface area determination. Essential components include a reference electrode (RE), a working electrode (WE), a counter electrode (CE) and aqueous electrolyte, with the overpotential and current flow on the material of interest (WE) separately controlled or collected through RE and CE.

3.6.1 HER Measurement

HER was performed in 0.5 M H₂SO₄ Ar-purged solution using a three-electrode setup for measurement of electrocatalytic activity of MoS₂ catalysts, with Hg/Hg₂SO₄/K₂SO₄ (sat'd) as RE, $E(\text{RHE}) = E(\text{Hg}/\text{Hg}_2\text{SO}_4/\text{K}_2\text{SO}_4 (\text{sat'd})) + 0.65 - 0.059 \cdot \text{pH}$, and graphite rod as CE. A 1 mm thick GC plate (Sigma-Aldrich Company Ltd.) deposited with MoS₂ thin films was used as the WE. The effective area (1 cm × 0.8 cm) of the WE was defined by applying electrochemically inert hydrophobic wax and pure polytetrafluoroethylene (PTFE) tape. A metal clip was used to connect WE with an external circuit. LSV (scan rate of 1 mV/s) under quasi-equilibrium conditions was recorded by a Biologic VMP3 potentiostat. CV was conducted at 100 mV/s to investigate the long-term stability. The electrochemical impedance spectroscopy (EIS) was carried out from 200000 to 1 Hz with an amplitude of 10 mV.

3.6.2 Cottrell Measurement

Based on the Cottrell equation as explained in **section 2.4.2**, Cottrell measurement was employed to evaluate the Cottrell surface area of the 3D porous MoS₂ thin film.

The chemical solution used for this measurement contained 10 mM K₃Fe(CN)₆ and 100 mM KCl as electroactive substance and inert salt, respectively. The purpose of this concentration configuration was first to have a considerably larger Cottrell current than the charging current,(33) and second to make sure the rate of ferri-ferrocyanide transformation was high enough while keeping the solution resistance low enough.

Chronoamperometry was performed in the three-electrode cell, with the MoS₂ porous thin film on GC as the WE, carbon cloth as the CE and Hg/Hg₂SO₄/K₂SO₄ (sat'd) as the RE. During the measurement, the overpotential was stepped from 0 to 100 mV

(vs. $\text{Hg}/\text{Hg}_2\text{SO}_4/\text{K}_2\text{SO}_4$ (sat'd)) and the corresponding Cottrell current response was recorded for 100 – 150 s, typically, until it reached the limiting value.

4 Edge Enriched 3D MoS₂ Thin Films Grown by Chemical Vapor Deposition for Enhanced Catalytic Performance

4.1 Introduction

MoS₂ shows promise for many catalytic reactions, in particular, the HER.(18) Over the past few years it has been established by both theoretical studies and experimental investigations that the edges of MoS₂ are the main catalytic sites.(4, 5) Advancements have been achieved to grow MoS₂ thin films that are edge rich.

Edge-rich nanostructured MoS₂ catalysts have been synthesized into *vertically aligned atomic layers* by sulfurizing elemental metal (Mo) seed layers,(39, 94, 95) and vapor sulfurization of sponge-like molybdenum oxide layers(81); as well as *edge exposed nanoplatelet* by hydro-sulfurization of Mo-coated substrates,(96) solvothermal conversion,(77, 97, 98) chemically exfoliation,(99) CVD,(100–102) and surfactant-assisted low-temperature solution process.(103) While vertically aligned atomic layers maximize edge exposure, a porous thin film consisting of edge oriented nanoplatelets still holds superiority for providing, firstly, “superaerophobic” surface to enable quick removal of small bubbles and provide a constant working area;(82) secondly, a porous structure with the high real (Cottrell) surface area and 3D open framework that enable efficient mass transport within the bulk.(79, 93) Based on the

discussion above, developing 3D highly porous MoS₂ thin films networked by edge enriched nanoplatelets with the superaerophobic surface is expected to lead to high-performance HER electrocatalysts.

Previous efforts include hydrothermal,(82, 152, 153) or multi-step chemical vapor deposition(93). It is therefore of scientific and technological significance to develop a method with scalability and simplicity to produce the edge rich structure. CVD has proved extremely useful to grow wafer-scale and high-quality MoS₂ thin films on various substrates such as silicon oxide, sapphire, and graphite. Furthermore, CVD synthesis provides adjustment of individual growth parameters and therefore allows precise tuning of the product morphology and structure, which enables optimization of catalytic property and serves as a platform to explore the structure-properties-function paradigm in catalyst design.

In the chapter that follows, I present a scalable single-step APCVD approach to produce 3D-ER 2H-MoS₂ nanoplatelets networked with high porosity on a wide range of substrates including silicon wafers (SiO₂/Si-Si with 285 nm of SiO₂), glassy carbon (GC), graphite (G) and single wall nanotubes (SWNT). The quality of the as-grown thin film is examined by Raman spectroscopy, scanning and transmission electron microscopy techniques, to make sure that it possesses chemical composition of MoS₂, edge-exposed morphology as well as good crystallinity. The supported MoS₂ thin films can be easily integrated into different device architectures for electrochemical applications. The growth of the microporous network is studied carefully to provide correlations between morphology, microstructure and electrocatalytic performance. I

aim to demonstrate the critical parameters that improve catalytic performance and could potentially help guide the optimization of industrial MoS₂ electrocatalysts.

4.2 Results and Discussion

The CVD synthesis of edge-exposed MoS₂ thin films on different substrates is illustrated in **Figure 4-1a**, where a two-furnace double quartz tube system is used (see in **section 3.2.1**). **Figure 4-1b** depicts the temperature profiles of S precursor and the substrate (as stated above MoO₃ powder was placed along with the substrate at different positions in the HT furnace, the MoO₃ powder was heated and cooled simultaneously with the substrate) for the deposition of edge-exposed MoS₂ thin films. S powder was heated for 15 min prior to the introduction of MoO₃ vapor to ensure sufficient supply of S vapor in the reaction system. The CVD synthesis of desirable edge-exposed MoS₂ thin films was optimized by adjusting growth parameters such as carrier gas flow rate (10 s.c.c.m ~ 100 s.c.c.m of Ar gas), growth time (15 min ~ 120 min) and temperature (830 ~ 900 °C), mass amount (500 ~ 1000 mg) and positioning of MoO₃ (2 cm ~ 3.5 cm) as well as substrates (SiO₂/Si, GC, G and SWNT). Optical images of a bare SiO₂/Si substrate and CVD grown edge-exposed MoS₂ thin films on SiO₂/Si at different growth conditions (*i.e.* growth time and temperature) are shown in **Figure 4-1c**, respectively. Longer growth time or higher growth temperature lead to thicker thin film and thus darker optical colour.

4 | Edge Enriched 3D MoS₂ Thin Films Grown by Chemical Vapor Deposition for Enhanced Catalytic Performance

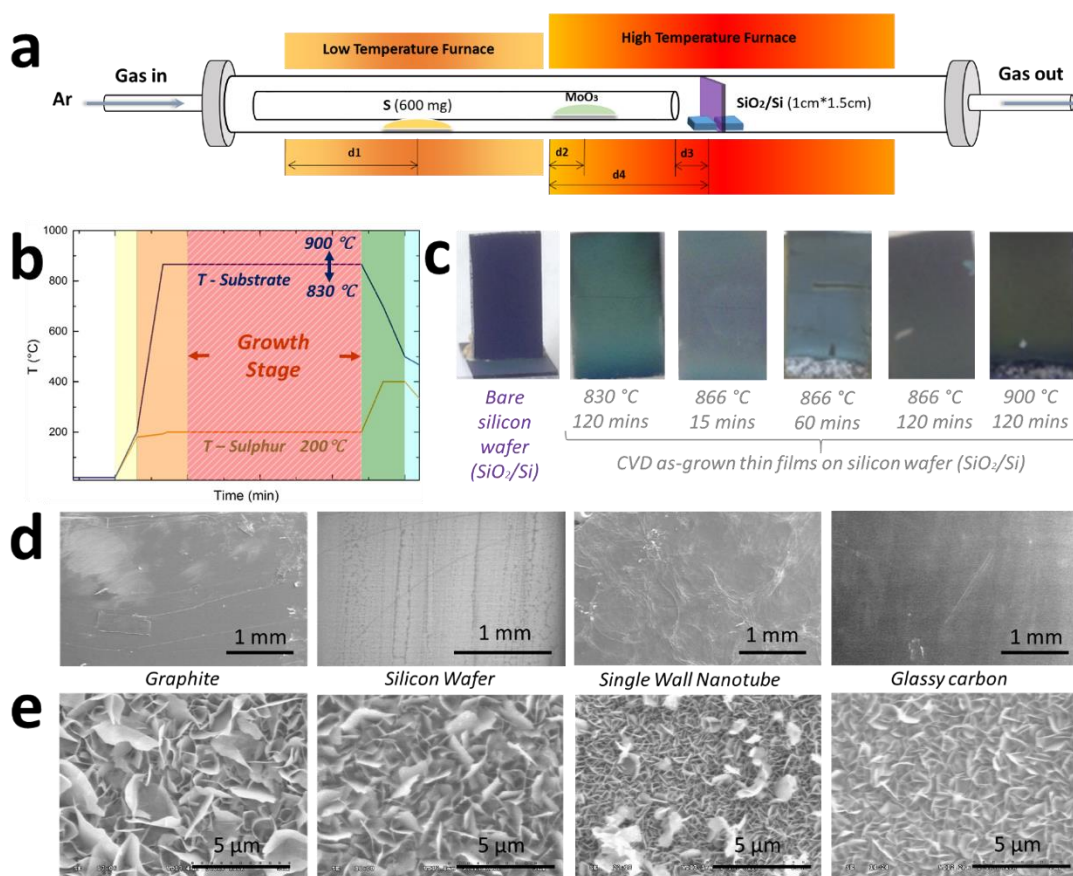


Figure 4-1. Atmospheric pressure CVD synthesis of edge-exposed MoS₂ nanoplatelet network on various substrates. (a) Schematic illustration of the CVD experimental setup ($d_1 = 16$ cm, $d_2 = 2 \sim 3.5$ cm, $d_3 = 1$ cm and $d_4 = 15$ cm). (b) Temperature profiles of sulfur precursor and substrate programmed for the formation of edge-exposed MoS₂ thin film. (c) Optical image of the vertically configured bare SiO₂/Si substrate and CVD as-grown edge-exposed MoS₂ thin films on SiO₂/Si substrate at growth temperature (temperature of the substrate) of 830 °C, 866 °C and 900 °C; growth time of 15 min, 60 min and 120 min, respectively. SEM images (accelerating voltage 3.0 kV) of G, SiO₂/Si, SWNT and GC substrates (d) before and (e) after deposition of edge-exposed MoS₂ thin films grown under the growth condition of 866 °C/60 min with 50 sccm of Ar gas.

At higher deposition temperature and longer growth time, the as-deposited thin films are darker, which means more materials have been deposited onto the substrates.

Figure 4-1e presents scanning electron microscopy (SEM) images of as-grown thin

films on different substrates (various bare substrates under SEM can be seen in **Figure 4-1d**). The comparable platelet size (1 ~ 2 μm) and vertical alignment demonstrate the growth condition is transferrable, proving the generality of the growth process with respect to different substrates.

In order to achieve an edge-rich MoS₂ thin film, flow rates from 10 s.c.c.m to 100 s.c.c.m of Ar gas were employed for CVD synthesis of MoS₂ at 866 °C for 120 min. The products were then examined under SEM as presented in **Figure 4-2a-e**, demonstrating flow rate of carrier gas poses a remarkable effect on both material coverage and product morphology. A clear transformation was observed with increase in carrier gas flow rate: at very low Ar flow rate (10 s.c.c.m), low coverage of nanorods/slabs with a size of ~ 5 μm was formed; as the Ar flow rate increased from 25 s.c.c.m to 50 s.c.c.m, the surface morphology is dominated by small nanoflakes (< 1 μm) and a lower percentage of large nanoparticles (~ 5 μm) are transformed into dense vertically aligned nanoplatelets (2 ~ 3 μm); at even higher Ar flow rates of 75 s.c.c.m and 100 s.c.c.m, deposited material ranges from medium coverage of larger nanoparticles (1 ~ 2 μm) to lower coverage of smaller ones (~ 500 nm).

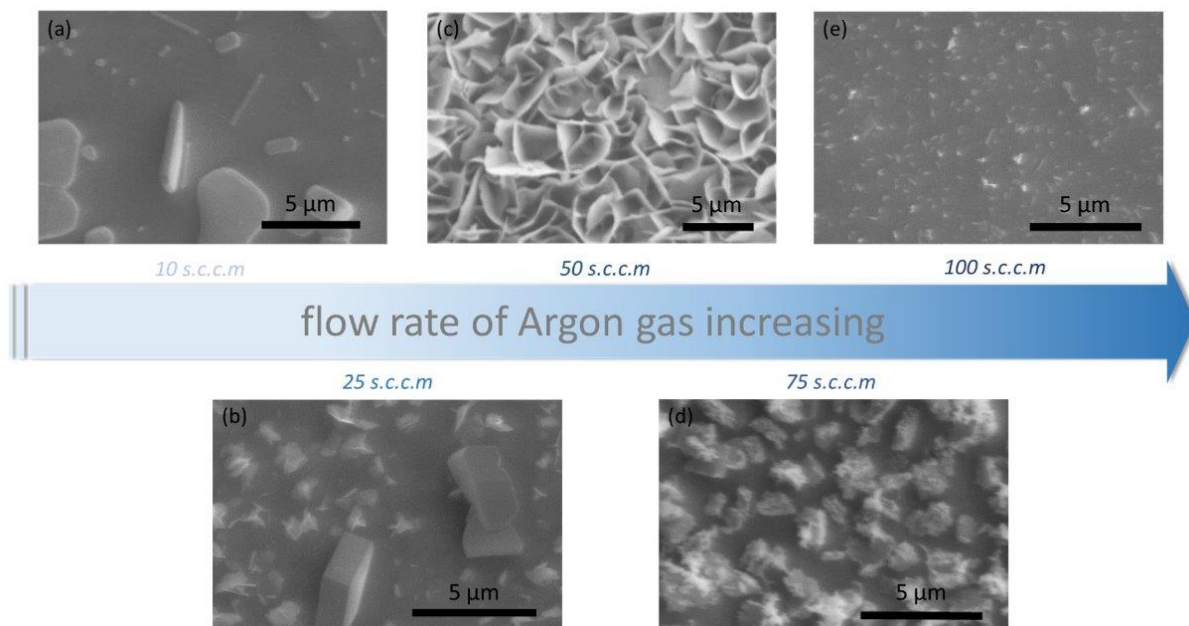


Figure 4-2. Material coverage and morphology of the as-grown MoS₂ thin films with progress in flow rate from 10 s.c.c.m to 100 s.c.c.m of Ar gas at 866 °C for 120 min. SEM images (accelerating voltage 3.0 kV) of the as-deposited samples under (a) 10 sccm, (b) 25 sccm, (c) 50 sccm, (d) 75 sccm and (e) 100 sccm of Ar gas.

Given a fixed deposition temperature (866 °C), at low to moderate carrier gas flow rate (10 s.c.c.m ~ 50 s.c.c.m), the deposition process is considered to be limited by mass transport of precursor species onto reaction sites of the substrate. In this regime, the surface chemical reaction rate is proportional to carrier gas flow rate, *i.e.* given specific growth time and temperature, the higher the gas flow rate is, the larger the amount of deposited products is. The vertical alignment of nanocomponents is more likely to be driven by a kinetic process,⁽³⁹⁾ where concentration of MoO₃ (*i.e.* Mo species in the gas phase) is so large that it has to transport in a fast way along the van der Waals gaps rather than across the layers in MoS₂, leading to the edge-exposed configuration of layers for the fast chemical conversion.

When the gas flow rate continues increasing to 75 s.c.c.m, deposition becomes surface reaction controlled instead, an overdose of precursor species reaches reaction sites on the substrate surface, exceeding the surface reaction rate that the performed growth temperature (866 °C) is capable of transforming. Also, the high concentration of reactants carried by the high gas flow rate leads to undesirable gas phase reaction before those species even reach the substrate sites, depositing particulates on the surface of the substrate. Moreover, the carrier gas transformation from viscous to turbulent flow and disturbance of lamellar gas flow pattern caused by extremely high gas flow rate (100 s.c.c.m) contribute to unstable crystal growth of small nanoflakes, attributing to the fact that the precursor species don't have enough time to settle down for surface reaction or even the chemical conversion in the bulk gas flow.

From the discussion above, Ar flow rate of 50 s.c.c.m is an optimum growth condition between these two aforementioned limiting ones, yielding a dense array of edge-exposed MoS₂ nanoplatelets.

In order to understand the formation and growth mechanism of CVD-synthesized MoS₂ nanoplatelets, the morphological evolution was investigated. The tilted SEM image of the sample grown at 866 °C with 50 s.c.c.m of Ar gas for 120 min in **Figure 4-3b**, shows the material consists of multi-layered nanoplatelets. The observation of nanoplatelets in the perpendicular direction to the substrate suggests that earlier-formed layers of platelets with smaller average size are stacked underneath by the layers of larger nanoplatelets. The film can be roughly divided into three sections: a

bottom layer of very fine crystals (average size, < 0.5 μm), a middle layer formed by slightly larger crystals (average size, 1 ~ 2 μm) and a top layer of very large platelets with a size of ~ 5 μm . The time evolution in **Figure 4-8a** reveals a growth mechanism that involves two steps: 1) formation of primary crystals and 2) growth of secondary crystals off the primary ones. Growth starts with primary nucleation and growth of MoS₂ on the bare substrate until the substrate surface is fully occupied with a layer of MoS₂ fine crystals. These primary-grown crystals then serve as sites for crystallization of the MoS₂ to form new smaller domains with a perpendicular orientation. This growth mechanism is supported by the TEM images in **Figure 4-3c-e** showing abundant vertically orientated layers, which makes the structure promising for catalytic applications by providing a large number of edge sites. Further support of the proposed growth model can be found in **Figure 4-4** and **Figure 4-5**.

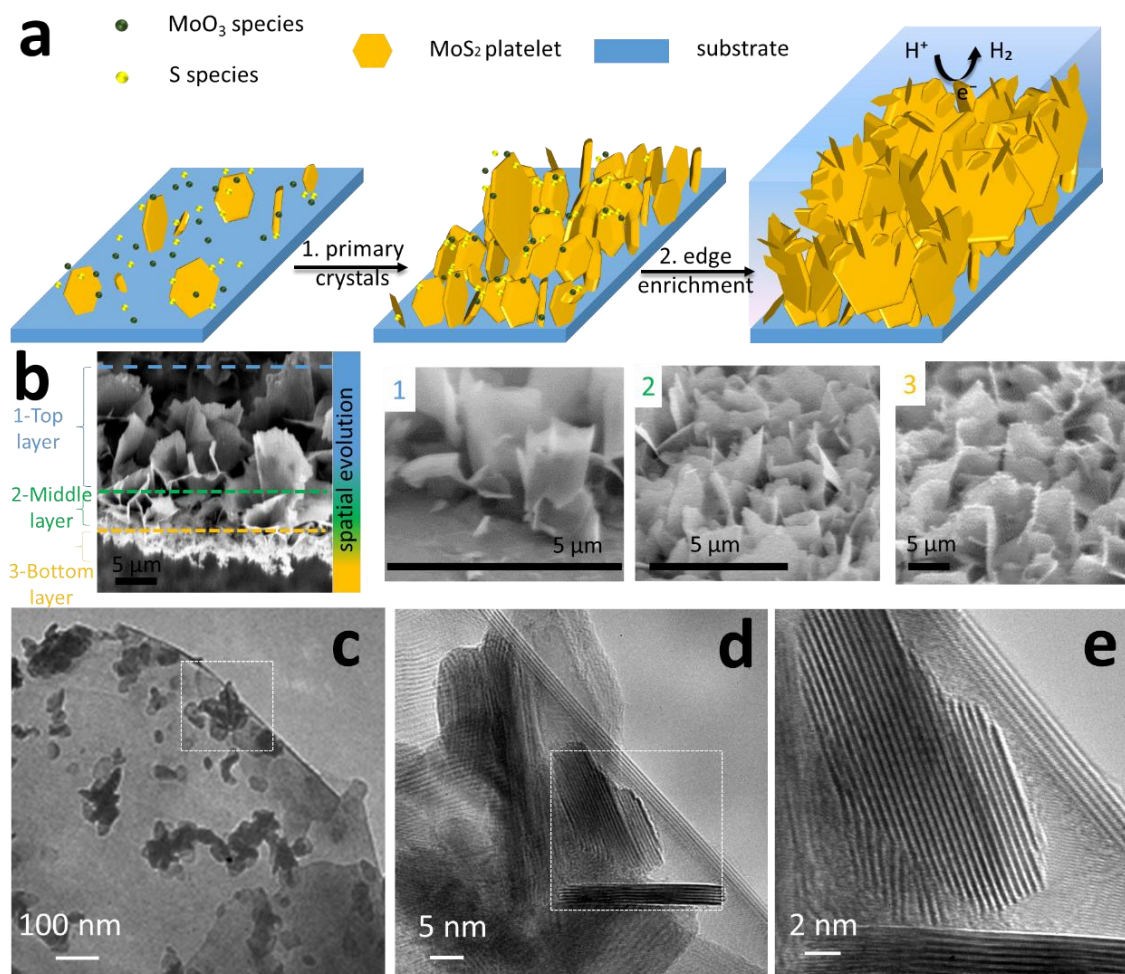


Figure 4-3. Configuration and Edge Enrichment mechanism for the formation of the vertically-aligned MoS₂ network. (a) Demonstration of Edge Enrichment mechanism, comprising (1) primary crystal formation and (2) edge enrichment process. (b) SEM images (accelerating voltage 3.0 kV) showing the spatial evolution of the as-grown MoS₂ thin film in the direction perpendicular to the substrate surface, consisting of three layers in the aspects of different platelet size during growth (as indicated by dashed lines). (c to e) Low to high magnification TEM images (accelerating voltage 200 kV) of the petal site from top-layer crystals, on which vertically-aligned nanoflakes are nucleated. (Growth condition: 866 °C under 50 s.c.c.m of Ar gas for 120 min with MoO₃ positioned at 3.3 cm)

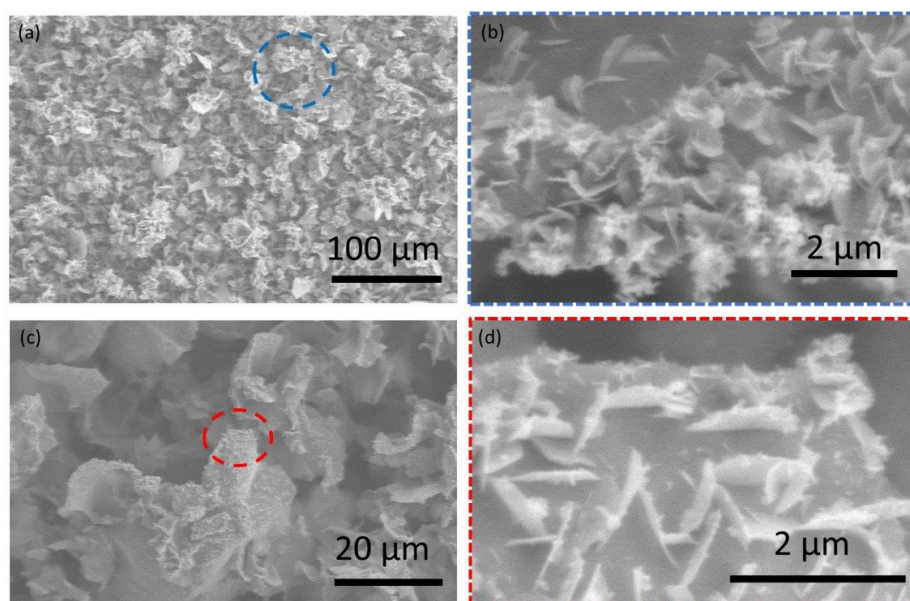


Figure 4-4. Crystal nucleation and growth on the edge sites of primary crystals revealed by SEM images (accelerating voltage 3.0 kV) from samples grown at 866 °C with 50 s.c.c.m of Ar gas for 120 min with the positioning of MoO₃ at 3.5 cm.

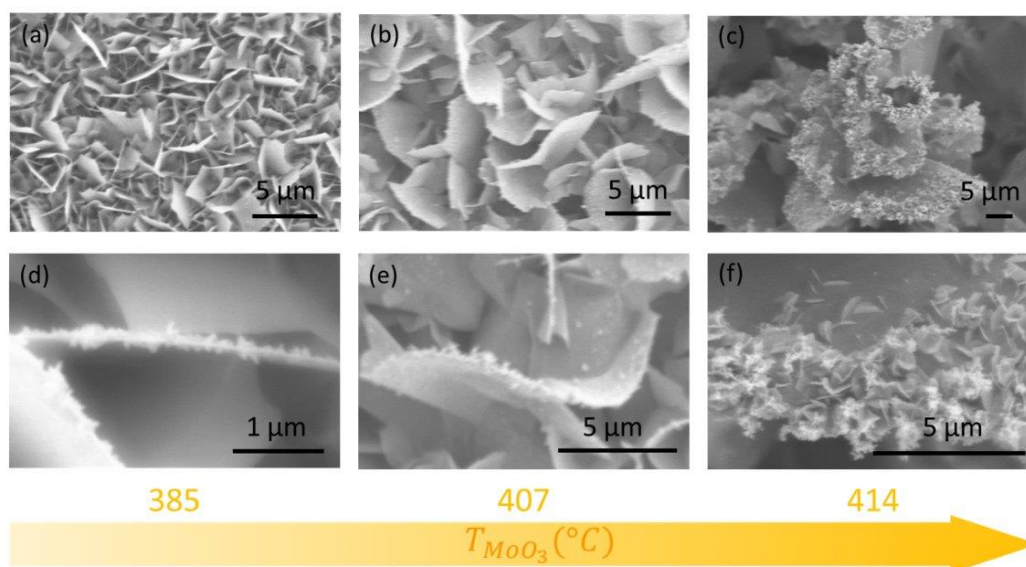


Figure 4-5. (a-c) Low magnification SEM images (accelerating voltage 3.0 kV) of the as-deposited thin films with MoO₃ positioning at 3 cm, 3.3 cm, and 3.4 cm. (d-f) High magnification SEM images (accelerating voltage 3.0 kV) , depicting the edge-enrichment features.

Samples synthesized with different growth times had variations in the average growth rate, as shown in **Figure 4-9a,b**, likely from the discrepancy of different supports. The initial nucleation occurs at the beginning of the deposition process when primary MoS₂ molecules nucleate on the bare substrate, whereas secondary nucleation occurs on the primary MoS₂ crystals themselves once they cover the substrate surface and the different surface chemistry will lead to different growth rates. Therefore, the shorter growth time, corresponding mainly to primary nucleation and crystal growth, results in slower average film growth. The longer growth time, involving secondary nucleation and growth, leads to much faster film growth. This edge enrichment mechanism also facilitates a continuous pathway for electron transfer within the film, which is beneficial for catalytic activity with lowered resistivity. The detailed growth mechanism of the vertical nanosheets by CVD was studied by Li and co-workers.⁽¹⁵⁴⁾

The morphology and film thickness change with growth time, as shown in top and tilted SEM images (**Figure 4-6**) of samples synthesized for a different time. In general, longer growth time leads to thicker as-grown films and larger top layered crystals. At an early stage - growth time of 15 min, fine nanoplatelets are crystallized on the substrate, delivering a film thickness of less than 1 μm (#), and a growth time of 60 min leads to a 3 μm thick film with the earlier-formed layer # maintained and a new layer of larger crystals (*) stacked on top. When increasing the growth time to 120 min, the film is even thicker ($\sim 7 \mu\text{m}$), with layers # and * underneath, another new top layer of even larger crystals are grown on top of the former two.

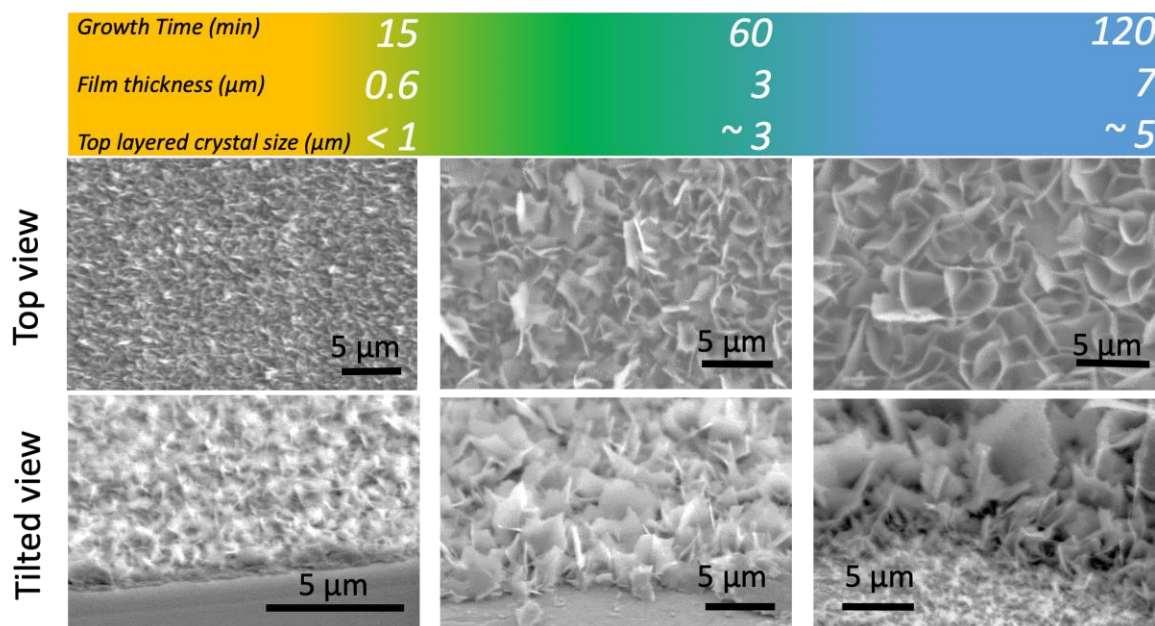


Figure 4-6. Time evolution the edge enriched MoS₂ thin film. SEM images (accelerating voltage 3.0 kV) depicting morphology (shown by zero tilt SEM images) and film thickness (shown by 60° tilt SEM images) evolution of the as-deposited nanoplatelet thin films at 866 °C with 50 s.c.c.m of Ar gas as a function of time: 15 min, 60 min, and 120 min, respectively.

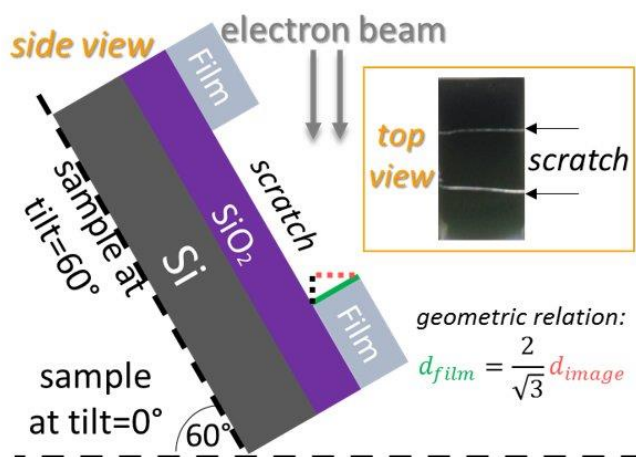


Figure 4-7. Schematic illustration of film thickness determination method by tilt SEM imaging, top right corner shows the optical image of scratches from a sample.

The film thickness is determined by SEM imaging of a tilted sample (tilt angle of 60°) and using a geometric correction, as explained schematically in **Figure 4-7**: $d_{\text{film}} = \frac{2}{\sqrt{3}} \cdot d_{\text{image}}$, where d_{film} is the actual film thickness and d_{image} is the thickness measured from tilt SEM image.

The as-grown thin films consisting of layers of nanoplatelets were further examined by aberration-corrected TEM (AC-TEM) images. TEM characterization shows that the MoS₂ sample comprises predominantly of multi-layers. **Figure 4-8a** shows a typical bundle of platelets from the top layer of the film, the size of which is consistent with that measured from low magnification SEM images (average size, 2 ~ 4 μm). Vertically standing layers with an interlayer spacing of 6.43 Å are shown in **Figure 4-8b** and vertical atomic configuration is resolved in **Figure 4-8c**. The vertically standing nanoplatelet structure can have edge dislocations present, as shown in **Figure 4-8d**, which is beneficial for HER activity. **Figure 4-8e** shows the lattice structure of few-layer MoS₂ with good crystallinity and 2H stacking order. The atomic resolved AC-TEM imaging of the edges of the MoS₂ nanoplatelets shows they have dominant zigzag termination that is relatively clean and smooth, as shown in **Figure 4-8f**. Selected area electron diffraction (SAED) patterns were recorded from the flat regions of the horizontally aligned MoS₂ and confirmed the single crystal layered structure with 2H stacking. As discussed above, the edge-rich features revealed in the AC-TEM images share consistency for all the samples in the present study (details seen in **Appendix**).

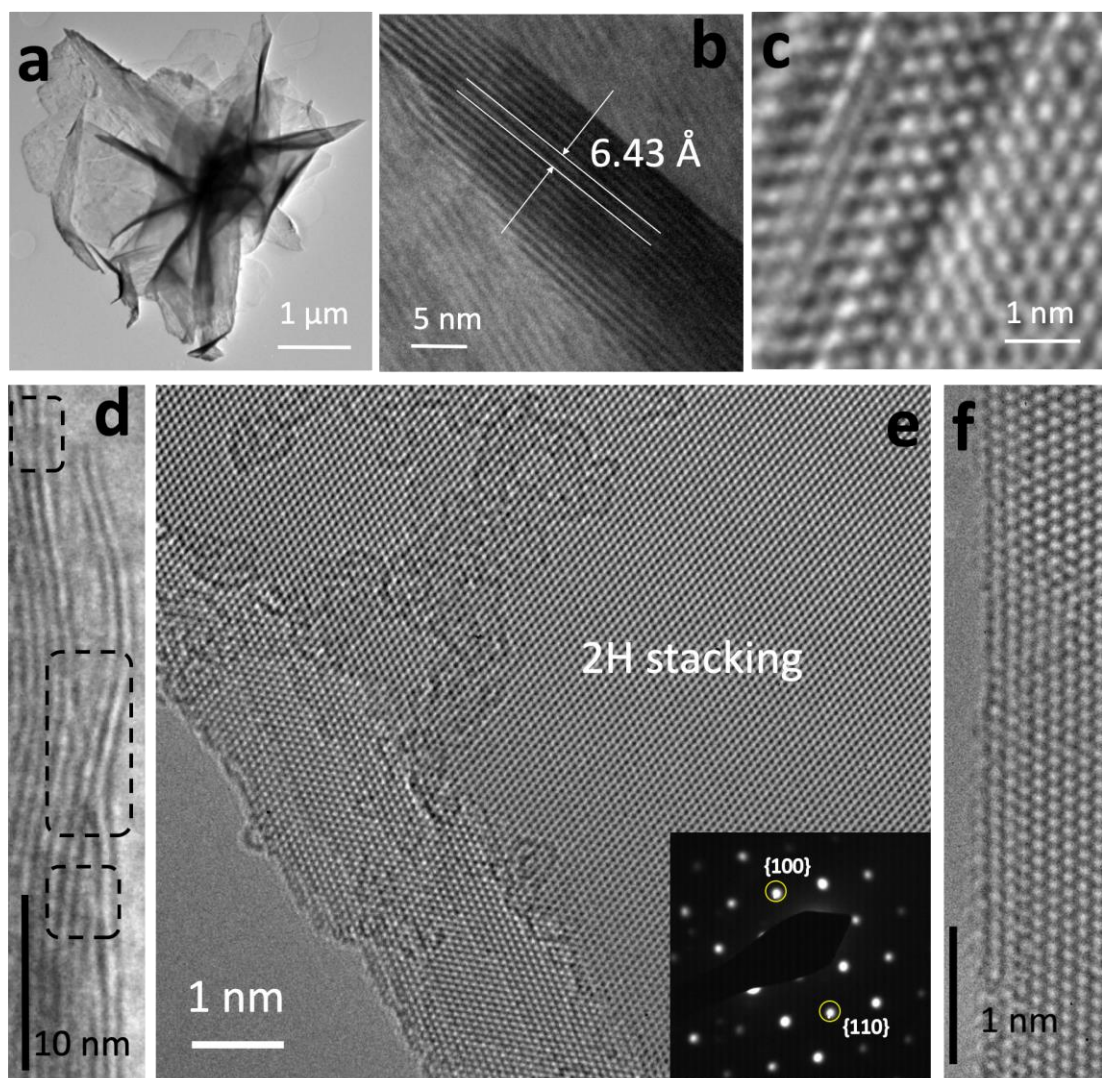


Figure 4-8. Atomic structure of the edge enriched MoS₂ thin film. TEM images (accelerating voltage 200 kV) of 120-min MoS₂ thin film: (a) nanosheet cluster from top layer; (b) perfectly vertically aligned nanosheet consisting of few layers with inter-layer spacing (d_{001}) of 6.43 Å; (c) vertically standing S-Mo-S layer; HRTEM images (accelerating voltage 80 kV) showing (d) a dislocation-rich vertical-standing nanosheet and (e) atomic structure of MoS₂ few layers with (f) smooth zigzag edge, inset: diffraction pattern.

Raman spectroscopy was used to confirm the CVD edge-exposed nanosheet thin films synthesized by aforementioned growth conditions are MoS₂. As seen in **Figure**

4-9c, two characteristic peaks are revealed, corresponding to the two vibration modes for MoS₂; in-plane vibration of molybdenum and sulfur atoms E_{2g}^1 and out-of-plane vibration of sulfur atoms A_{1g} , respectively. The result is consistent with that commonly reported in the literature for bulk MoS₂ materials.(155, 156) Here, the spectrum of a MoS₂ monolayer grown using different synthesis conditions as previously reported is presented as a reference.(157) Compared to monolayer MoS₂, all the samples studied in the present work show a decreased intensity of E_{2g}^1 and increased intensity of A_{1g} , which is due to the increased thickness (layer numbers) based on the model of van der Waals interaction and long-range coulombic interaction,(155) respectively. As depicted in the inset table of **Figure 4-9c**, the intensity ratio A_{1g}/E_{2g}^1 increases significantly from 0.79 of the terrace surface from monolayer MoS₂ to ~ 2, clearly indicating the preferential vertical orientation of the CVD thin films, matching the observations from SEM images.

The two factors to improve HER performance of a catalyst; the number of surface active sites (grain size) and reaction kinetics (charge transfer and transport within the film controlled by film thickness and catalyst-substrate contact) are coupled due to the multi-stack growth nature of this particular high-porosity network. In order to optimize the device-oriented HER activity, the two areas should be improved at the same time or one enhanced without sacrificing too much of the other, which can be tuned by growth time, precursor quantity and growth temperature.

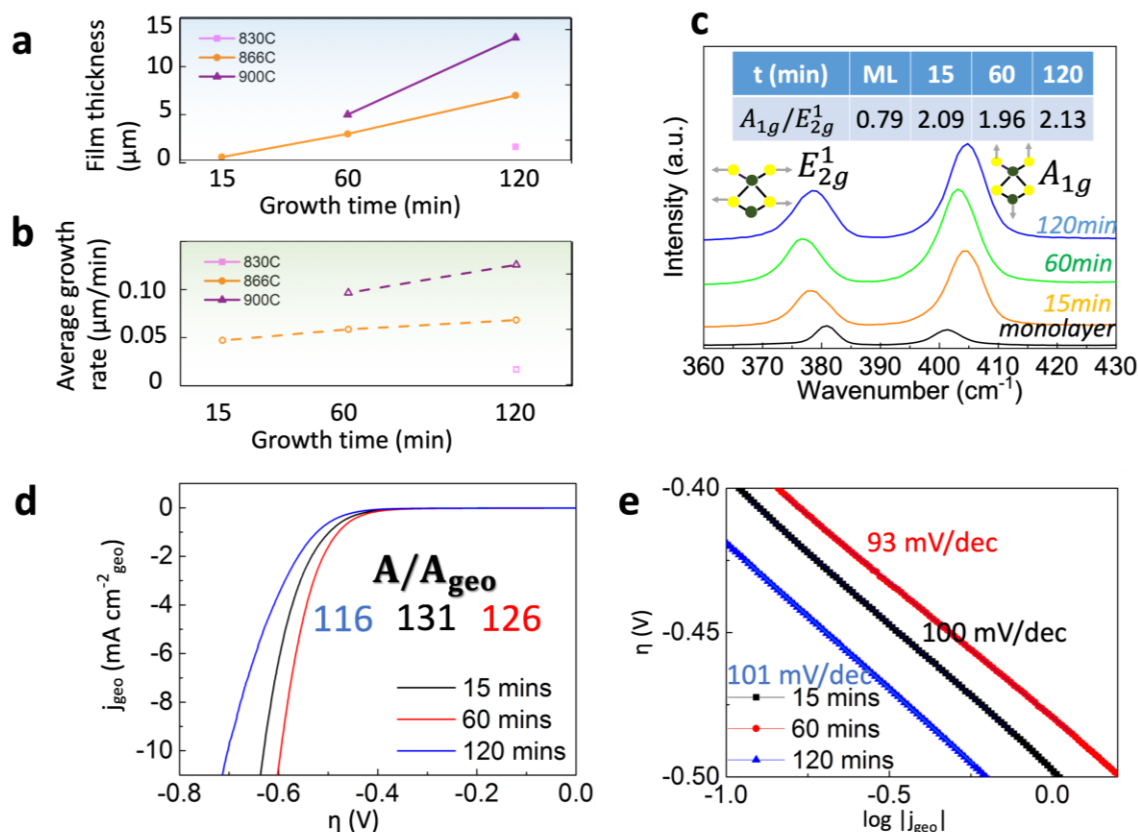


Figure 4-9. Dependence of (a) film thickness and (b) average growth rate on growth time (15 min, 60 min, and 120 min) and temperature (830 °C, 866 °C and 900 °C). (c) Raman spectra of MoS₂ samples grown for 15 min, 60 min, 120 min, respectively. The spectrum for MoS₂ monolayer is obtained from a sample grown using methods reported in reference. Inset: schematics of two characteristic Raman vibration modes in MoS₂: in-plane vibration of molybdenum and sulfur atoms E_{2g}^1 and out-of-plane vibration of sulfur atoms A_{1g} ; information on peak intensity ratio of A_{1g}/E_{2g}^1 of samples synthesized for different growth time. (d) Cathodic polarization curves (scan rate 1 mV/s, 0.5 M H₂SO₄ (aq)) with (e) corresponding Tafel plots of CVD-grown MoS₂ film on glassy carbon (values normalized by geometric area; A_{geo} : geometric area of the substrate; A: Cottrell surface area of the substrate).

HER electrocatalytic performance of a CVD-grown high-porosity network of the edge enhanced MoS₂ nanoplatelets were investigated by LSV. MoS₂ catalysts were deposited by the aforementioned CVD method directly onto GC plates, which are

used as the working electrode in a typical three-electrode electrochemical cell with 0.5 M H₂SO₄ solution. The cathodic polarization curves at a scan rate of 1 mV/s were recorded and shown in **Figure 4-9d**. Tafel plots are shown in **Figure 4-9e**. Exchange current density was determined, by fitting the linear portion of the Tafel plot at low cathodic current to the Tafel equation ($\eta = b \log|j| + a$, where j is the current density and b is the Tafel slope). EIS was performed to investigate the ohmic resistance of the thin film catalysts and shown in **Figure 4-10**. Cottrell measurement was used to measure the Cottrell surface area of MoS₂ thin films (see **section 2.4.2** and **3.6.2**). The Cottrell surface area of all the tested samples is summarized in **Table 4-1**.

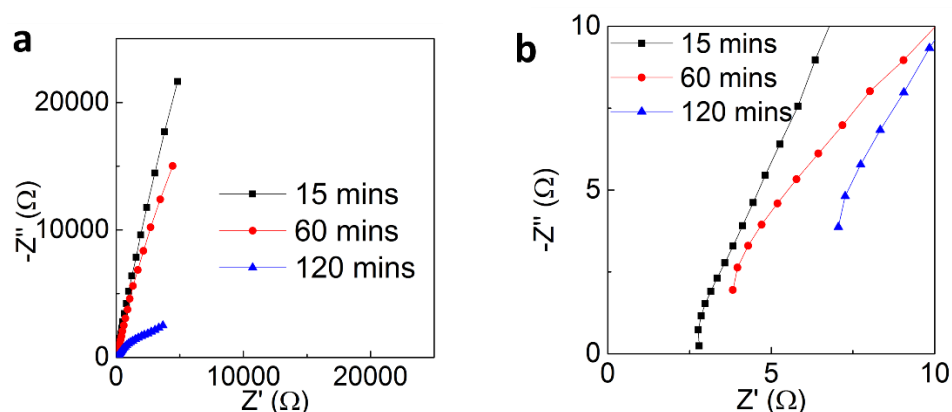


Figure 4-10. Electrochemical impedance spectroscopy (EIS) of CVD-grown MoS₂ film on GC for different growth times.

As the growth time increases, the grain size of the MoS₂ nanoplatelets also increases and measurements of the Cottrell surface area show a concomitant reduction (*i.e.* A/A_{geo} decreased from 131 to 116, see **Figure 4-9d** - inset). This is attributed to a reduced density of edges with larger platelet size. Comparison of corresponding polarization curves at 15min, 60min and 120min growth times for MoS₂ (**Figure 4-9d**) reveals three samples exhibit similar Tafel slopes of ~ 100 mV/dec (**Figure 4-9e**).

The 60 min sample performed slightly better than the other two in terms of cathodic current density.

To increase the density of catalytic active sites, more material can be deposited per geometric area (i.e area of the substrate) while preserving the edge rich structure. Increasing the mass amount of precursor is considered effective to increase the evaporation rate, which will be reflected in the concentration of precursor in the vapor phase and thus the quantity of product. As MoO₃ used for growth increased from 500 mg, 800 mg to 1000 mg, a sharp morphological change and film thickness increase have been observed as in **Figure 4-11**.

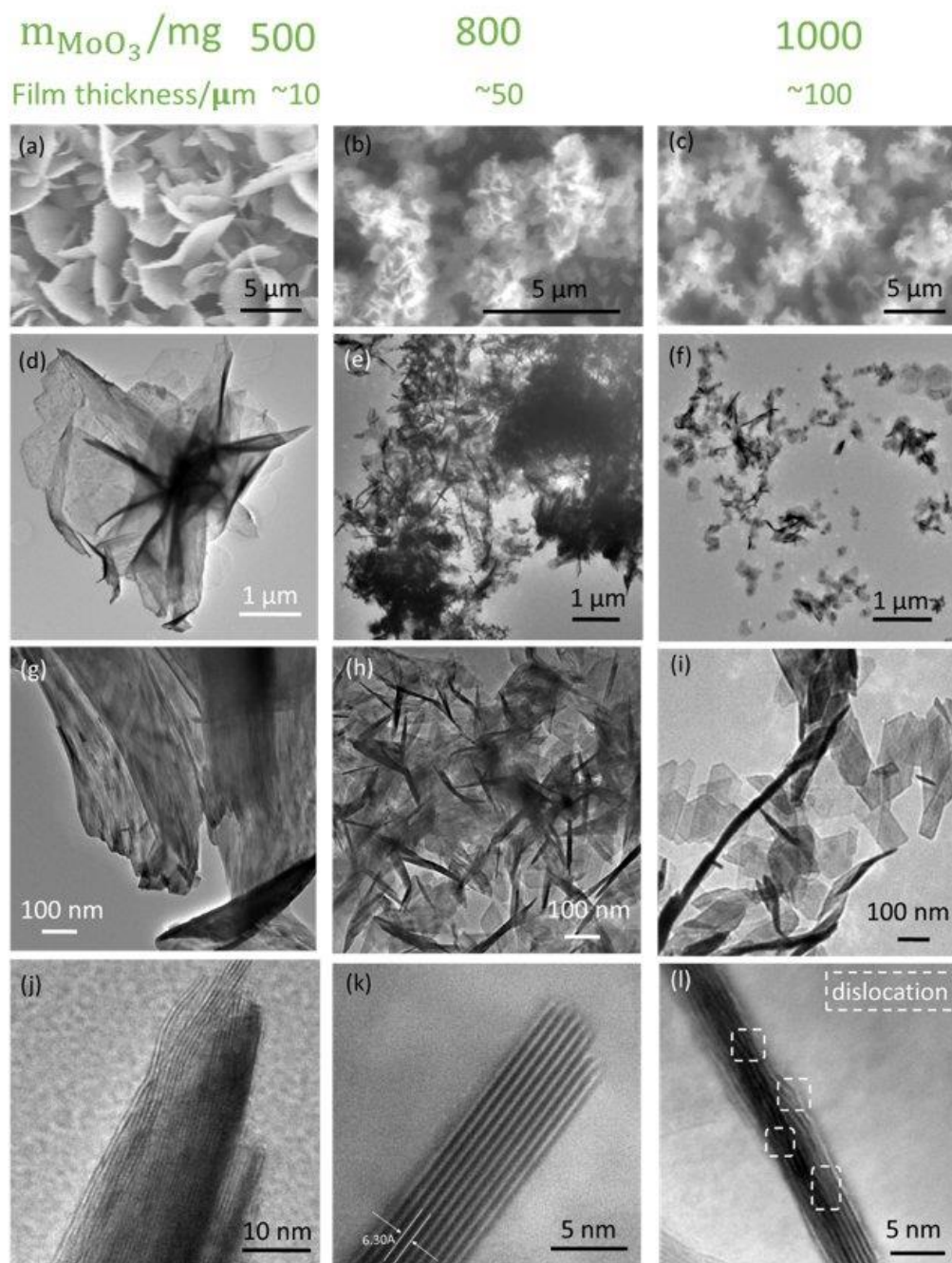


Figure 4-11. Influence of the mass amount of precursor MoO₃ on the surface morphology of the as-deposited MoS₂ thin films at 50 s.c.c.m of Ar gas for 120 min. (a, b and c) SEM images (accelerating voltage 3.0 kV) of the as-deposited thin films with the MoO₃ quantity of 500 mg, 800 mg, and 1000 mg. (d, e and f) Low magnification (g, h and i) middle magnification and (j, k, and l) high magnification TEM images (accelerating voltage 200 kV) of corresponding samples.

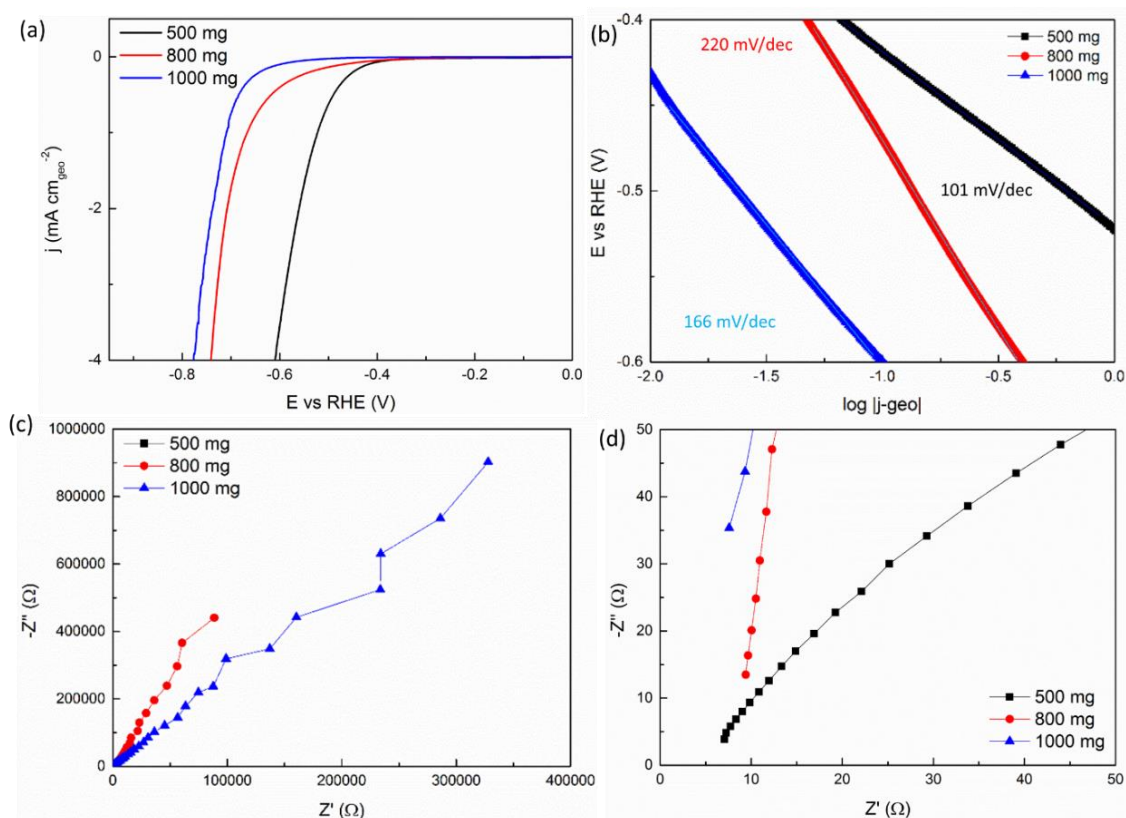


Figure 4-12. Influence of the mass amount of precursor MoO₃ on the HER electrocatalytic activities of the as-deposited MoS₂ thin films at 50 s.c.c.m of Ar gas for 120 min. (a) Cathodic polarization curves (scan rate 1 mV/s, 0.5 M H₂SO₄ (aq)); corresponding (b) Tafel plots and (c and d) EIS of CVD-grown high-porosity edge-exposed MoS₂ network on glassy carbon (values normalized by geometric area; A_{geo}: geometric area of the substrate; A: Cottrell surface area of the substrate).

Based on the SEM images shown in **Figure 4-11a-c**, with the mass amount of MoO₃ powder increasing from 500 mg to 800mg, a sharp morphological transformation is observed from the vertical aligned nanoplatelets to coral-like structure composed of fine platelets with size of ~ 1 μm on average (which can be confirmed by the low magnification TEM image in **Figure 4-11e,h**). When the mass of MoO₃ further increases to 1000 mg, coral-like morphology is maintained with extremely fine platelets of nanometer size (see the corresponding TEM image in **Figure 4-11f,i**).

From the high-resolution TEM images in **Figure 4-11j-l**, the shared feature of vertical texture and preferential growth of MoS₂ along c-axis can be confirmed with the three samples grown with different MoO₃ amounts. Moreover, the intensity ratio A_{1g}/E_{2g}^1 decreases as the mass usage of MoO₃ powder increases, suggesting the vertical texture is disturbed to some extent.

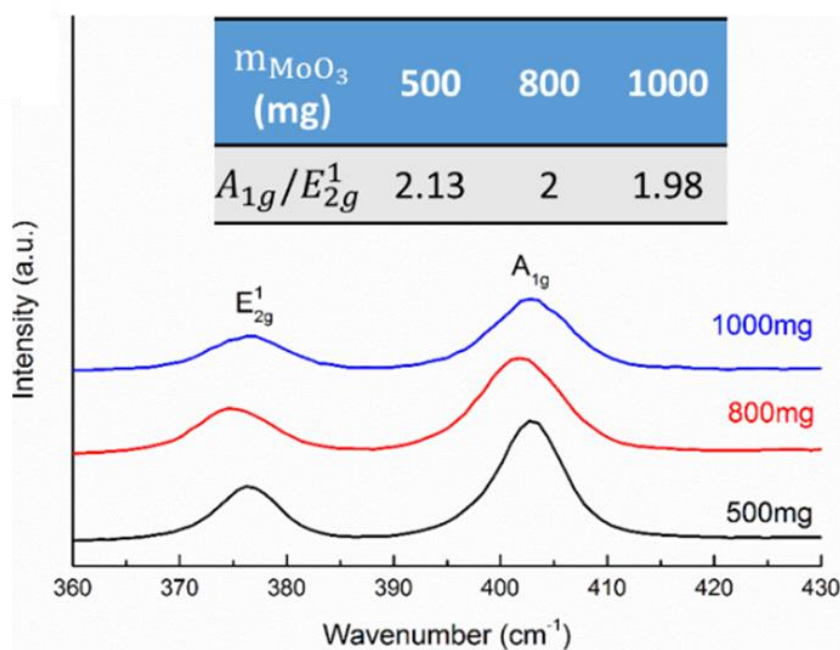


Figure 4-13. Raman spectra of MoS₂ samples synthesized with 500 mg, 800 mg and 1000 mg of MoO₃, respectively. Inset: information on the peak intensity ratio of A_{1g}/E_{2g}^1 of samples synthesized for different quantities of MoO₃.

As can be seen from **Figure 4-12a-d**, higher amount of MoO₃ (800 mg and 1000 mg) for synthesis of the catalysts leads to lower HER activity (lower cathodic current density at the same overpotential as well as higher Tafel slope), which is resulted from significantly increased charge transport impedance (Z') of thick carol-like network of very fine crystals. Z' values corresponding to 500 mg, 800 mg, and 1000

4 | Edge Enriched 3D MoS₂ Thin Films Grown by Chemical Vapor Deposition for Enhanced Catalytic Performance

mg MoO₃ are ~ 3 kΩ, ~ 88 kΩ and ~ 300 kΩ, which is in accord with the film thicknesses of ~ 10 μm, ~ 50 μm and ~ 100 μm. Other than film thickness, extremely fine grain induced rapidly increased number of grain boundaries can also contribute to the resistivity for protons to transfer. From this aspect, 500 mg of MoO₃ for CVD-growth is more favorable to deliver a higher performed catalytic water splitting device by providing improved charge transfer.

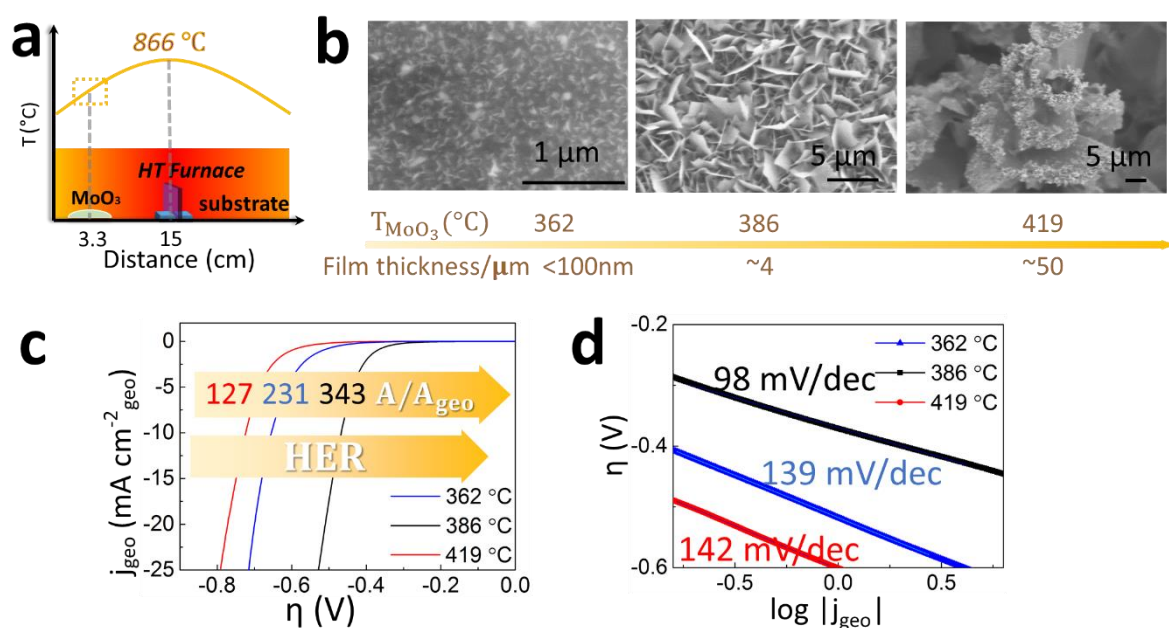


Figure 4-14. Influence of MoO₃ evaporation temperature on morphology and HER activity of MoS₂ thin films at 50 s.c.c.m of Ar gas for 120 min. (a) Schematic illustration of the temperature profile for the high-temperature furnace chamber with a set temperatures of 866 °C. (b) SEM images (accelerating voltage 3.0 kV) of the as-deposited thin films with MoO₃ positioning at 362 °C, 386 °C, and 419 °C. (c) Cathodic polarization curves (scan rate 1 mV/s, 0.5 M H₂SO₄ (aq)) with (d) corresponding Tafel plots of CVD-grown edge-rich MoS₂ film on GC (values normalized by geometric area; A_{geo}: geometric area of the substrate; A: Cottrell surface area of the substrate).

Apart from the direct adjustment of the MoO₃ amount, control of MoO₃ evaporation temperature and growth temperature also enables tunable product morphology for optimum catalytic activity towards water splitting. According to the temperature profile of the reaction chamber, as depicted in **Figure 4-14a** (actual temperature of the HT furnace at different set values can be found in **Figure 3-2**), the actual temperature of MoO₃ can be controlled by adjusting the positioning of the MoO₃ powders. A set of experiments positioning MoO₃ powder at 362 °C, 386 °C and 419 °C (distance from the left end of the HT furnace) were conducted, with the other experimental parameters remaining unchanged. The SEM images (**Figure 4-14b**) of the thin films show clearly when MoO₃ powder moves closer to the furnace center (higher evaporation temperature), the nanoplatelet morphology is retained with larger crystals (average size from <100 nm to ~4 μm and then to ~ 20 μm) and film thickness (from <100 nm to ~4 μm and then to ~ 50 μm).

Three samples with MoO₃ powder set at 362 °C, 386 °C, and 419 °C during CVD growth were tested for HER. From **Figure 4-14c**, it can be seen that 386 °C MoS₂ performs best among the three in terms of cathodic current density. In accordance with the SEM results, low precursor temperature leads to insufficient evaporation of reactant species in the vapor phase and reaction rate and thus reduced material covered on the substrate ($A/A_{\text{geo}} = 231$). When the temperature was too high, the excessive precursor flux to the sample results in increased grain size, which will, in turn, decreases the total number of accessible active edge sites participating in the HER reaction ($A/A_{\text{geo}} = 127$). On the other hand, a higher precursor temperature delivers a thicker film with higher ohmic resistance (**Figure 4-15**). So, an intermediate

temperature (386 °C) is optimal for the growth of the MoS₂ HER catalyst to maximize Cottrell surface area ($A/A_{\text{geo}} = 343$) of the film without sacrificing charge transport to the electrode.

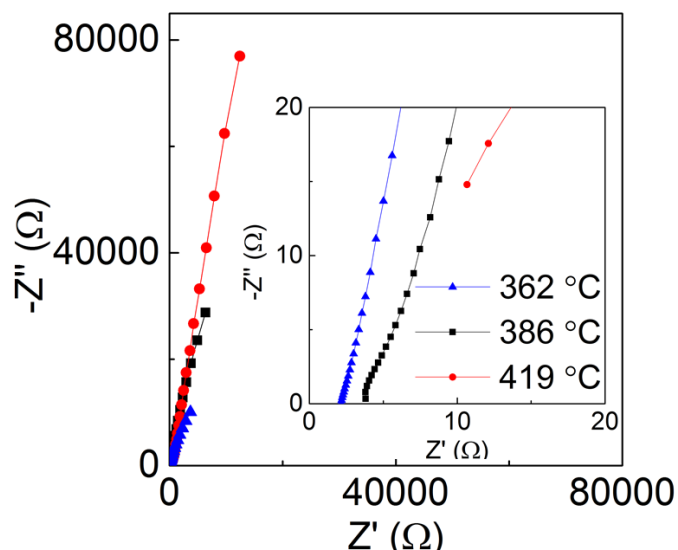


Figure 4-15. EIS of CVD-grown edge-rich MoS₂ films grown on GC at various MoO₃ evaporation temperatures.

The influence of synthesis temperature on surface morphology, film thickness, and HER activity follows a similar trend as the MoO₃ evaporation temperature (**Figure 4-16** and **Figure 4-17**).

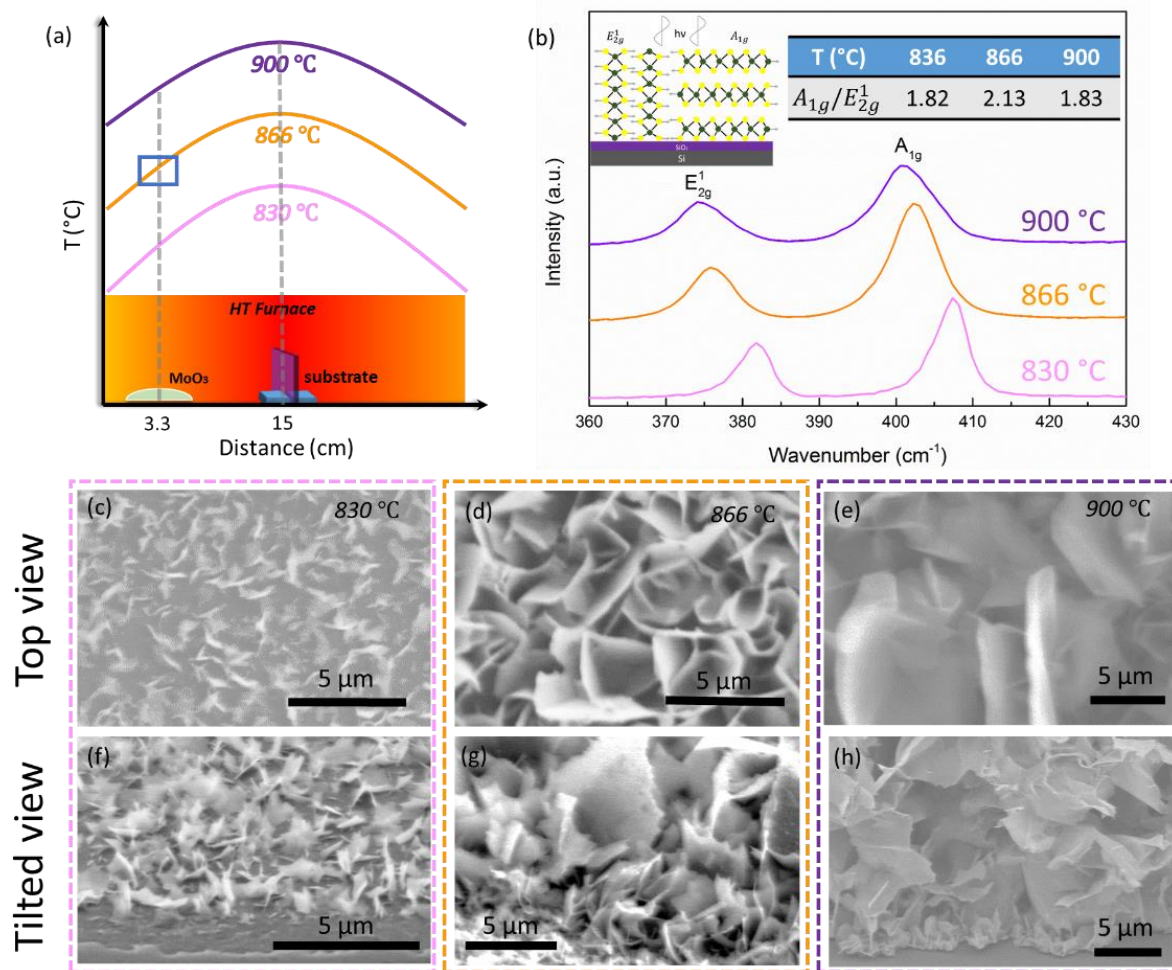


Figure 4-16. Influence of synthesis temperature on surface morphology of the as-deposited MoS₂ thin films at 50 s.c.c.m of Ar gas for 120 min. (a) Schematic illustration of the temperature profile for the high-temperature furnace chamber with set temperatures at 830 $^{\circ}\text{C}$, 866 $^{\circ}\text{C}$, and 900 $^{\circ}\text{C}$, respectively. (b) Raman spectra from MoS₂ samples CVD-synthesized at 830 $^{\circ}\text{C}$, 866 $^{\circ}\text{C}$, and 900 $^{\circ}\text{C}$, respectively. Inset: schematics of two characteristic Raman vibration modes in MoS₂: in-plane vibration of molybdenum and sulfur atoms E_{2g}^1 and out-of-plane vibration of sulfur atoms A_{1g} ; information on peak intensity ratio of A_{1g}/E_{2g}^1 of samples synthesized at different growth temperatures. (c, d, and e) Top (f, g, and h) tilted SEM images (accelerating voltage 3.0 kV) of CVD-grown samples at deposition temperatures of 830 $^{\circ}\text{C}$, 866 $^{\circ}\text{C}$ and 900 $^{\circ}\text{C}$, respectively.

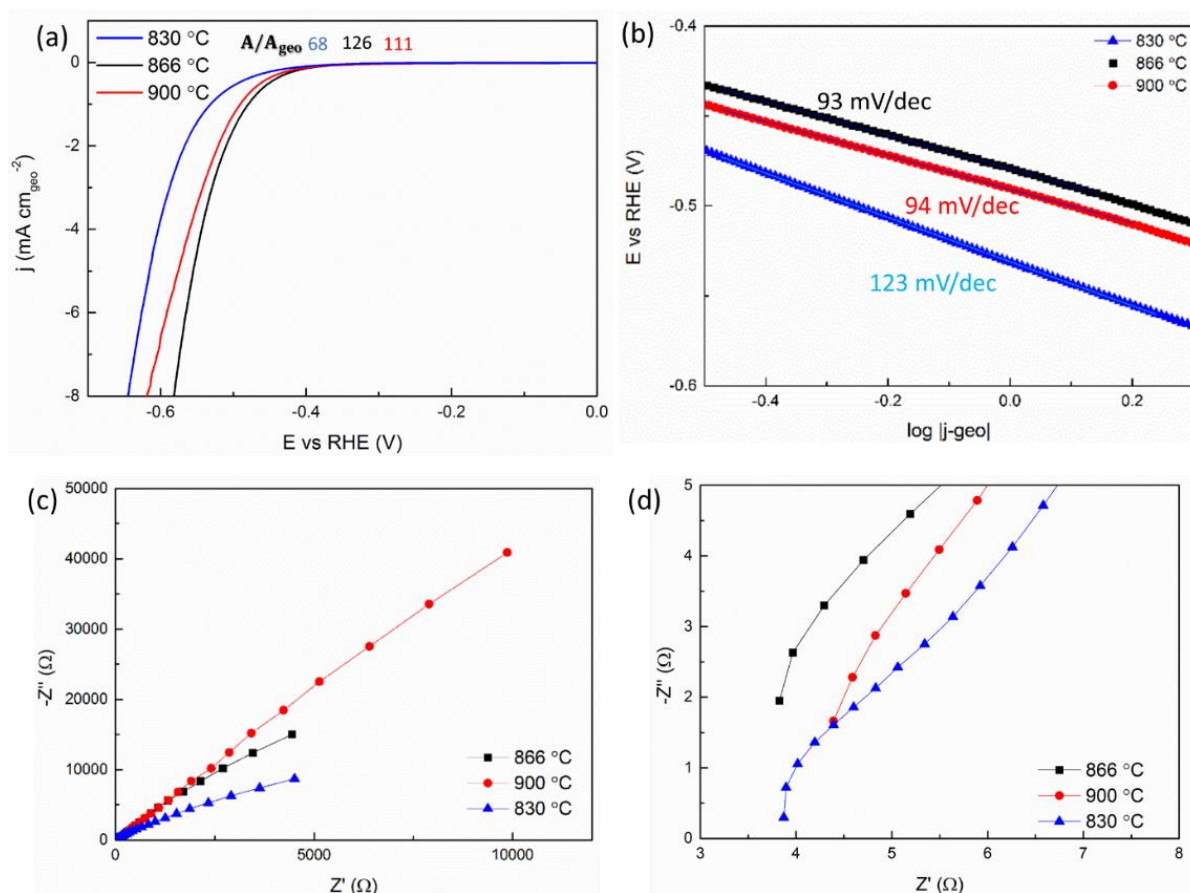


Figure 4-17. Influence of synthesis temperature on HER activity of the as-deposited MoS₂ thin films at 50 s.c.c.m of Ar gas for 120 min. (a) Cathodic polarization curves (scan rate 1 mV/s, 0.5 M H₂SO₄ (aq)); corresponding (b) Tafel plots and (c and d) EIS of CVD-grown high-porosity edge-exposed MoS₂ network on glassy carbon (values normalized by geometric area; A_{geo} : geometric area of the substrate; A : Cottrell surface area of the substrate).

As MoO₃ and substrate were both placed in the high-temperature furnace, the temperature of both changes simultaneously with each other when the set synthesis temperature changes. In this way, the control of growth temperature literally influences the substrate temperature as well as the temperature of MoO₃ powder, as demonstrated in **Figure 4-16a**. As can be seen from the SEM images in **Figure 4-16c-e**, with elevated growth temperature, the surface morphology evolves from

sparse distribution of little nanoplatelets ($< 1 \mu\text{m}$) to dense vertical-aligned thin platelets (average size, $2 \sim 4 \mu\text{m}$) and then to dense distributed large nanoplatelets with buckled edges (average size, $\sim 10 \mu\text{m}$). Also, the film thickness increased from $\sim 1 \mu\text{m}$ to $5 \sim 10 \mu\text{m}$ and then to $> 10 \mu\text{m}$ as depicted in **Figure 4-16f-h**. Raman spectra in Fig. S11b shows 866 °C delivers relatively better vertical alignment of the nanoplatelets.

From HER activity results of MoS₂ catalysts CVD-synthesized at different temperatures in **Figure 4-17a-d**, it can be seen that 866 °C-sample performs best among the three in cathodic current density.

The optimum 386 °C grown MoS₂ exhibits $60 \text{ mA/cm}_{\text{geo}}^2$ at an overpotential of 0.64 V vs. RHE. Tafel slope of 98 mV/dec lies in the lower side of the range $40 \sim 212 \text{ mV/dec}$, (5, 39, 79, 82, 90, 154, 158–161), which indicates the RDS of HER is the Volmer reaction, the conversion of protons to adsorbed atoms on the highly-porous MoS₂ surface. A j_0 of $0.19 \mu\text{A/cm}_{\text{geo}}^2$ is relatively low compared to literature ($0.25 \sim 18.2 \mu\text{A/cm}^2$) (5, 39, 79, 82, 90, 154, 158–161), which is likely due to the limited electron transport rate in semiconducting 2H-MoS₂ thin film. Summary of HER activity performances from literature and the present MoS₂ catalysts are recorded in **Table 4-2**.

The Cottrell and geometric surface areas of all samples tested for electrochemical performance towards HER are listed in **Table 4-1**. It is found that the edge-exposed nano-platelet network has a high Cottrell surface area to geometric area ratio (A/A_{geo}) up to 343.

Long-term durability testing is also an important concern for electrocatalysts, which demonstrates its thermodynamic stability. The optimum 386 °C grown MoS₂ catalyst was subjected to cycling-treatment in an acidic environment using cyclic voltammetry with a fast scan rate of 100 mV/s in order to simulate the practical working conditions of water splitting devices. The polarization curves and SEM images before and after the cycling treatment are recorded in **Figure 4-18**. Negligible change of the cathodic current and surface morphology was observed, which indicate durability of the as-grown catalyst.

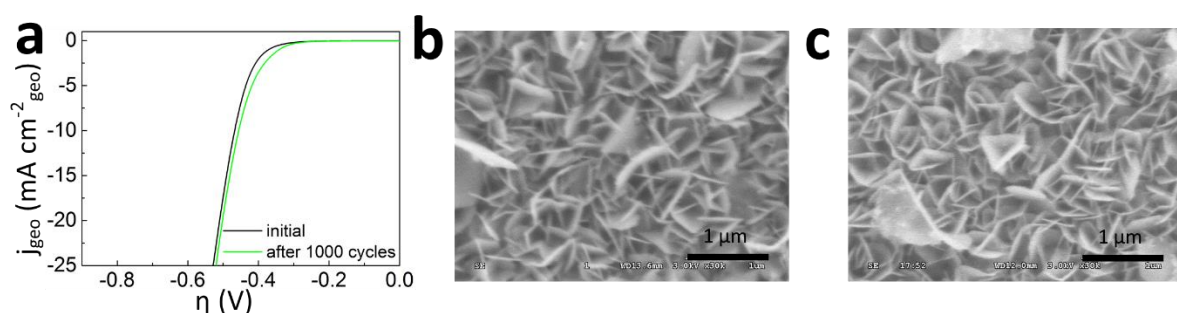


Figure 4-18. Electrochemical stability test of the optimum CVD-synthesized edge-exposed MoS₂ thin film on glassy carbon: (a) polarization curves (scan rate 1 mV/s, 0.5 M H₂SO₄ (aq)) and SEM images (accelerating voltage 3.0 kV) of the catalyst (b) before and (c) after 1,000 cycles, respectively.

Table 4-1. Summary of CVD growth condition, Cottrell surface area and electrocatalytic metrics of the samples studied in this chapter.

	Sample	1	2	3	5	6	8	12	16	18	20
CVD growth condition	<i>T/°C</i>	866	866	866	866	866	866	900	866	866	830
	<i>t/min</i>	15	60	120	120	120	60	60	60	60	60
	<i>m-MoO₃/mg</i>	500	500	500	800	1000	500	500	500	500	500
	<i>d-MoO₃/cm</i>	3.3	3.3	3.3	3.3	3.3	3.1	3.3	3.5	2	3.3
Cottrell surface area evaluation	<i>A_{ged}/cm²</i>	0.8	0.8	0.8	0.8	0.8	0.52	0.8	0.8	0.8	0.8
	<i>A/cm²</i>	104	101	93	6	6	178	89	102	185	54
	<i>A/A_{geo}</i>	131	126	116	8	7	343	111	127	231	68
HER metrics	<i>Tafel slope b (mV/dec)</i>	100	93	101	220	166	98	94	142	139	123
	<i>exchange current density j₀ (μA/cm²)</i>	0.010	0.007	0.007	0.732	0.023	0.037	0.169	0.006	0.059	0.190

Table 4-2. Summary of pure MoS₂ catalytic performances in literature.

Catalyst	Electrolyte	A _{geo}	A _{real} / A _{geo}	Onset overpotential (mV vs RHE)	b (mV/decade)	j _{0-geometric} (μA/cm ²)	j _{0-surface} (μA/cm ²)
MoS ₂ nanoparticles(5)	H ₂ SO ₄ (pH 0.24)	Not reported	<0.25	Not reported	55.2 ~ 73.8	0.13 ~ 0.31	Not reported
Defect-Rich ultrathin nanosheets(90)	0.5 M H ₂ SO ₄	3 mm diameter	Not reported	120	50	8.91	Not reported
MoS ₂ thin films(158)	0.5 M H ₂ SO ₄	0.785 cm ²	Not reported	Not reported	140 ~ 145	Not reported	0.06
vertically aligned layers(39)	0.5 M H ₂ SO ₄	Not reported	1.004	Not reported	105 ~ 120	Not reported	2.2
MoS ₂ with a double-gyroid (DG) morphology(79)	0.5 M H ₂ SO ₄	Not reported	37	150 ~ 200	50	0.69	Not reported
MoS ₂ nanosheets(159)	0.5 M H ₂ SO ₄	Not reported	56.4 m ² /g	Not reported	68	38.9	Not reported
Edge-terminated MoS ₂ with a 9.4-Å interlayer spacing(160)	0.5 M H ₂ SO ₄	Not reported	Not reported	103	49	9.62	Not reported
Vertically standing nanosheets(154)	0.5 M H ₂ SO ₄	Not reported	Not reported	Not reported	92	22.3	Not reported
“Superaerophobic” nanostructured MoS ₂ (82)	0.5 M H ₂ SO ₄	Not reported	Not reported	150	51	0.387	Not reported
Porous MoS ₂ thin film(161)	0.5 M H ₂ SO ₄	Not reported	Not reported	120	41 ~ 45	0.25	Not reported
3D-ER MoS ₂ thin film (in this thesis)	0.5 M H ₂ SO ₄	0.8 cm ²	340	200	90	0.19	0.047

4.3 Conclusion

This chapter can be concluded as below:

- I have directly engineered an edge-rich MoS₂ thin film by CVD, which has high porosity and large Cottrell surface area. This is achieved by controlling the growth conditions to promote a secondary growth stage that allows smaller MoS₂ flakes to grow perpendicular from the main preexisting flakes attached to the substrate and leads to an increase in the total number of edge sites.
- By systematically controlling the growth condition, tunable film thickness and surface morphology were achieved, enabling the optimized combination of active site quantity, inter-planar charge transport and sufficient binding with the substrate as well as fast removal of gas bubbles via a superaerophobic surface.
- The observed HER catalytic performance over a given geometric area with long-term durability is promising. The low HER activity per Cottrell surface area is compensated by the vastly enhanced high surface area porous structure.
- Further attempts could be made to improve the intrinsic catalyst activity of MoS₂ by basal surface activation, doping, intercalation or substrate interaction.

5 Activating Basal Plane Sites in 3D Edge Rich MoS₂ Thin Films for the Hydrogen Evolution Reaction

5.1 Introduction

The edge sites of layered 2H-MoS₂ are active for HER and designing effective structures has often revolved around increasing edge density. However, recent work has revealed that MoS₂ basal plane sites are also highly active when defects (cracks, holes, additional edges, SVs and O-incorporation) are introduced.(61, 83, 92, 104–110)

This holds great potential for realising fully active MoS₂ materials beyond just edge limited sites, but work has been either limited to achieving basal plane activation in monolayered flat MoS₂ crystals(92) or relying on complex and hard-to-control solution based routes(90). The basal plane activation in 3D thin films with the large surface area through controllable defect modulation offers a viable way to achieve high catalytic performance that could lead to an alternative to Pt. In addition, attention should also be paid to systematic control over defect modification and HER optimization by identifying and investigating detailed HER active structure, in order to guide the catalyst design.(92)

This chapter demonstrates how gas phase treatments can introduce defects into the basal plane of highly porous 3D MoS₂ films with massive

basal surface area (as described in **Chapter 4**). The gas phase treatments are performed post-growth and are scalable. I will present two approaches, one room temperature, O₂ plasma treatment, and the other high temperature, H₂ annealing. Treatment parameters will be carefully and systematically investigated to establish controllable morphology, structure as well as HER activity. Through such an exploration, I aim to provide structural modification guidelines for improved electrochemical property and open up a new way for noble metal-free catalyst optimization.

5.2 Results and Discussion

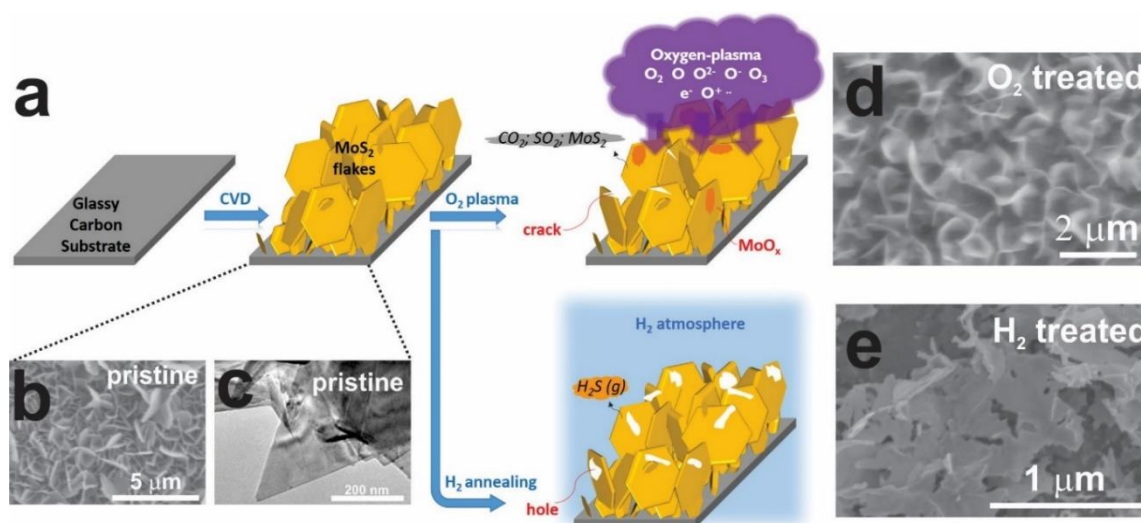


Figure 5-1. (a) Schematic of gas phase treatments of CVD grown MoS₂ thin film catalysts by O₂ plasma or H₂ etching approaches. SEM images (accelerating voltage 3.0 kV) showing the morphology of (b) pristine (TEM image (accelerating voltage 200 kV) in c showing a typical triangular domain), (d) O₂ plasma etched and (e) H₂ etched CVD MoS₂ thin film.

Figure 5-1 depicts the defect engineering route utilizing O₂ plasma and H₂ etching approaches in order to introduce additional vacancies, cracks and holes into the pristine MoS₂ catalyst system and consequently enhance the HER activity.

As described in **section 3.2.1** and **Chapter 4**, the pristine MoS₂ was synthesized by one-step CVD at growth temperature (*i.e.* temperature of substrate) of 866 °C using MoO₃ and S powder precursors for 1h, yielding a vertically standing nanoplatelet morphology, 3D porous architecture and superaerophobic surface, directly onto GC in order to be readily incorporated into the electrochemical testing setup as a working electrode to investigate the catalytic properties. An O₂ plasma was employed to create surface cracks and oxide phases via bombardment and reaction of the surface materials with an O₂ plasma, or H₂ annealing to generate irregularly shaped holes onto the basal surfaces by chemical reaction etching. O₂ plasma treatment was conducted at a pressure of 0.8~1 mPa for 0, 15 and 30 min in order to etch the materials and create defects such as pores and cracks. SEM and (in-situ) TEM were used to investigate the effect of O₂ plasma on morphological and microstructural change.

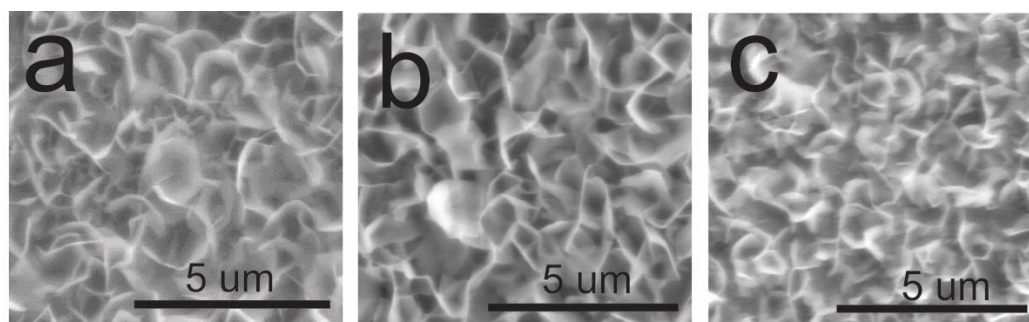


Figure 5-2. SEM images (accelerating voltage 3.0 kV) depicting the morphology of MoS₂ thin films etched by O₂ plasma for (a) 0, (b) 15 and (c) 30 min respectively.

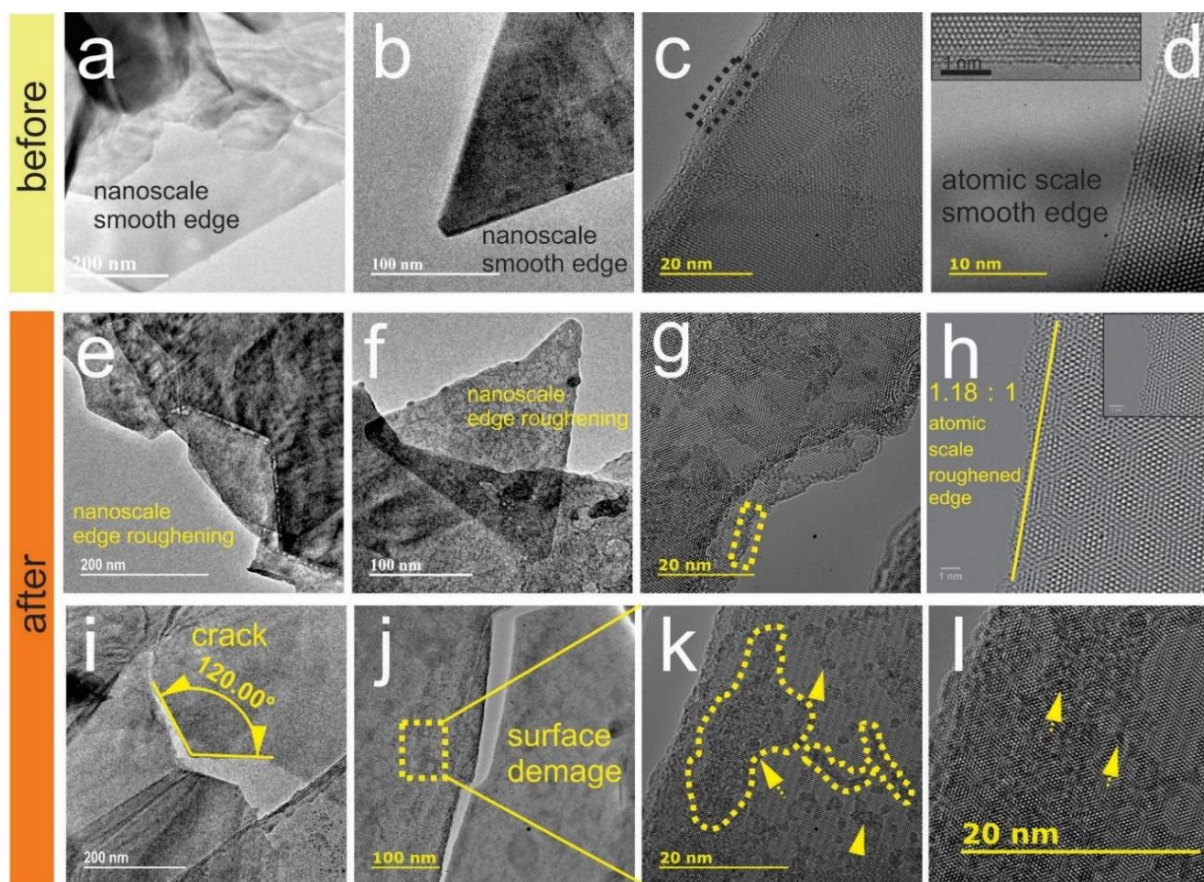


Figure 5-3. Effect of O₂ plasma treatment on the morphology and microstructure of MoS₂ nanoplatelets. TEM images of MoS₂ flakes before O₂ plasma treatment exhibiting clean and smooth edges at (a and b) nanoscale and (c and d) atomic scale. TEM images of three types of defects induced by 15 min O₂ plasma exposure: roughened edges at (e and f) nanoscale and (g and h) atomic scale; (i) microcracks and (j-l) basal surface damage at different magnifications. (TEM images a, b, e, f, i, j were taken at accelerating voltage 200 kV; HRTEM images c, d, g, h, k, l were taken at accelerating voltage 80 kV)

SEM images in **Figure 5-1d** and **Figure 5-2** demonstrate that there are no obvious microscopic changes before and after O₂ plasma treatment – the edge exposed vertical alignment of the flakes are preserved. Based on TEM analysis, the plasma process mainly introduces three types of defects to the pristine domains: 1) edge-roughening by serration/steps on the edge sites, 2) micro cracks and 3) local pits on

the basal surfaces; all accompanying material loss. MoS₂ flakes before plasma treatment depicted in **Figure 5-3a-d** possess clean and smooth edges at both nanoscale and atomic scale.

In order to understand the microstructure configuration of the O₂ plasma-induced defects in the catalyst, TEM imaging was undertaken by exposing MoS₂ on a lacey carbon grid to an O₂ plasma for 2 min to monitor any structure change of the same area before and after plasma etching. TEM characterization shows that the MoS₂ sample comprises predominantly of multi-layers. TEM images in **Figure 5-3e,f** show the nanoscale edge structure of the MoS₂ after treatment. Compared with the pre-treated sample, steps/serrations have been introduced to the edges, resulting in an increase in the number of edge sites for catalytic reaction, which will be discussed in detail later. HRTEM images in **Figure 5-3g,h** verify the edges are roughened at the atomic level. Microcracks on the basal planes of MoS₂ can be seen in **Figure 5-3i**, with 120° orientation, resulted from crystallographic symmetry of the MoS₂. **Figure 5-3j** shows the surface damage from the plasma etching process resulting in nanopores on the basal surfaces, which helps to expose more edges on the otherwise catalytic inactive basal sites. The detailed structure of basal surface damage can be observed from the yellow circle in **Figure 5-3k,l**, showing that across the basal surface of the few layered flakes there are defects that arise from the O₂ plasma etching of the MoS₂ surface. The combination of these three types of defects demonstrates that the O₂ plasma treatment is a powerful tool to create additional edge sites by etching the platelets at both nanometer and atomic level, which aligns

very well with the Cottrell surface area evaluation in **Figure 5-5** and is considered to be beneficial for HER activity with increased edge density.

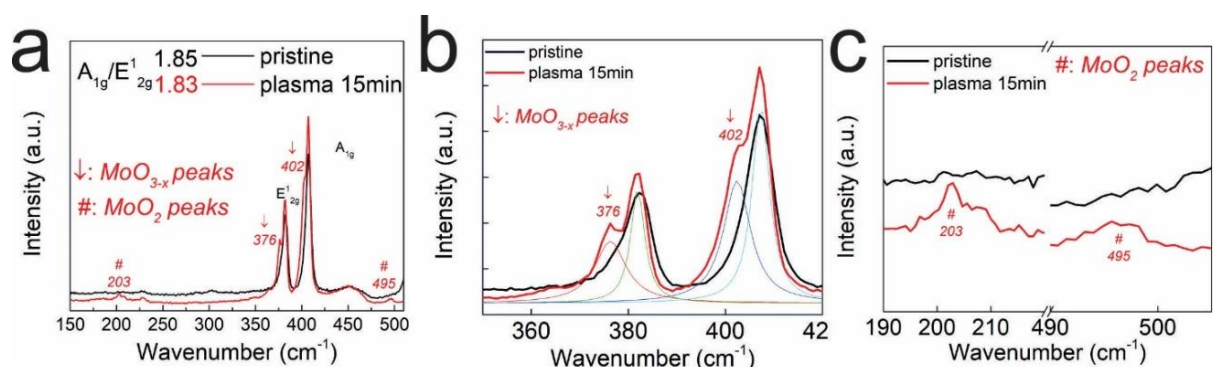


Figure 5-4. Chemical composition influenced by O₂ plasma treatment. (a) Raman spectra of CVD as prepared and 15 min O₂ plasma treated MoS₂ catalysts. Inset: two characteristic Raman vibration modes in MoS₂: in-plane vibration of molybdenum and sulfur atoms E_{2g}¹ and out-of-plane vibration of sulfur atoms A_{1g}; information on peak intensity ratio of A_{1g}/E_{2g}¹ of samples before and after O₂ plasma treatment (1.83 and 1.85, respectively); oxidation induced peaks. Characteristic peaks indicating (b) MoO_{3-x} and (c) MoO₂ phases, respectively.

Raman spectroscopy was conducted to examine the chemical composition of the O₂-etched sample. The Raman spectrum shown in **Figure 5-4a** confirms the CVD grown material is MoS₂, with the two characteristic peaks, corresponding to the two vibrational modes of MoS₂: in-plane vibration of molybdenum and sulfur atoms E_{2g}¹ and out-of-plane vibration of sulfur atoms A_{1g}, which is consistent with the literature.^(39, 82) The comparable peak intensity ratio A_{1g}/E_{2g}¹ before and after O₂ plasma confirms that the vertical alignment of the thin film has been maintained after being treated with an O₂ plasma. It is also revealed that O₂ plasma treatment does involve a small amount of oxidation of MoS₂ evidenced by the oxides peaks indicated

for MoO_{3-x} (Figure 5-4b) and MoO₂ (Figure 5-4c) phases. The effect of the oxide phase on HER activity will be discussed later on.

The Cottrell surface area evaluation and electrochemical testing were carried out to investigate the efficiency and effectiveness of O₂ plasma on the Cottrell surface area and HER activity enhancement (Figure 5-5).

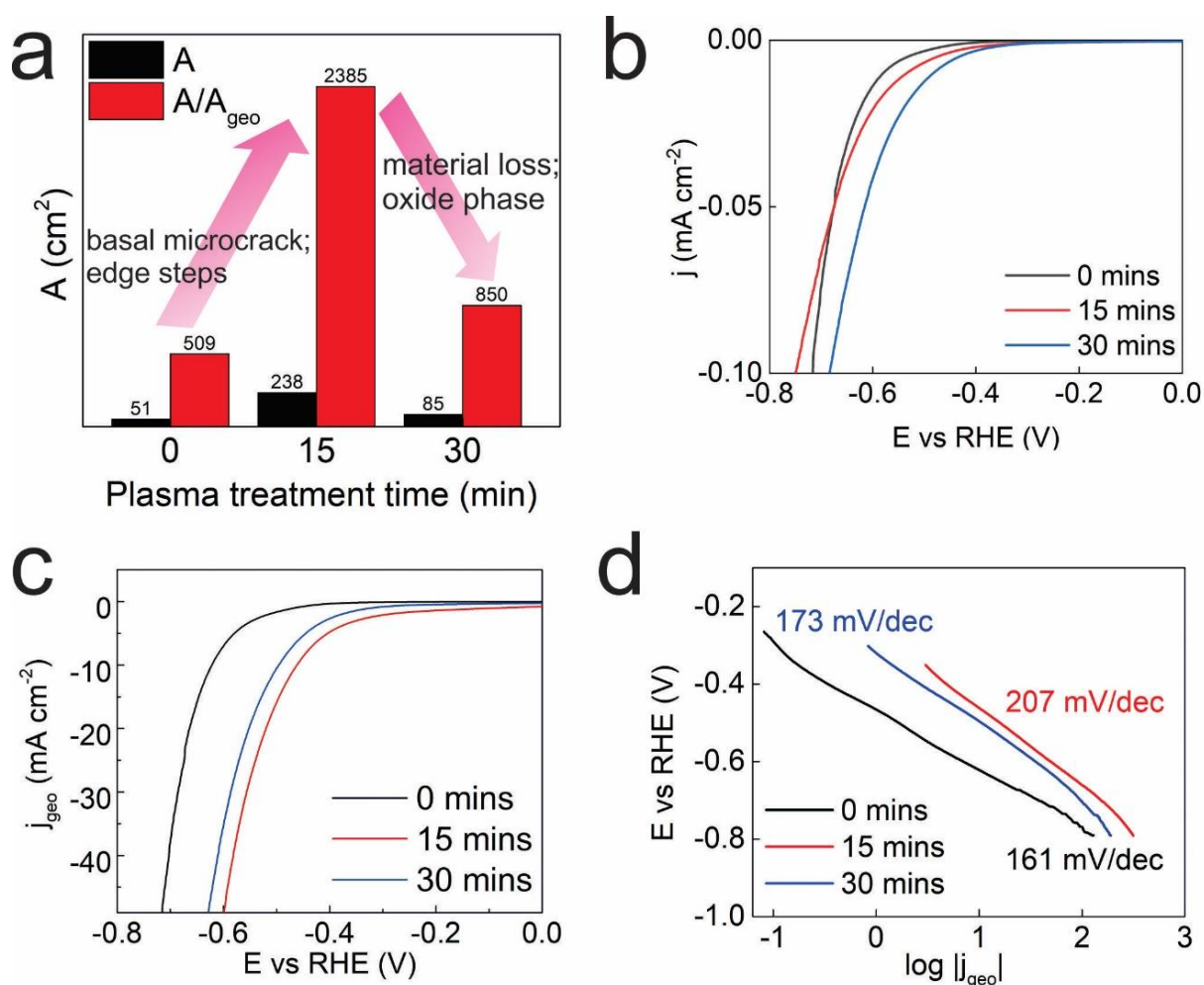


Figure 5-5. Effect of O₂ plasma etching on Cottrell surface area and electrochemical activity of 3D-ER MoS₂. (a) Cottrell surface area evaluation as a function of O₂ plasma etching time (A_{geo}: geometric area of the catalyst; A: Cottrell surface area of the catalyst). Cathodic polarization curves (scan rate 1 mV/s, 0.5 M H₂SO₄ (aq)) normalized by (b) geometric area and (c) Cottrell surface area. (d) Tafel plots of O₂ plasma treated samples under different exposure periods.

Compared to the as-grown sample, O₂ plasma etching exhibits potential in enhancing the Cottrell surface area/edge density (**Figure 5-5a**; 5-fold of the untreated sample at 15 min exposure time; 2-fold at 30 min exposure time). The lower surface area enhancement for the 30 min treatment time results from the loss of the material at prolonged plasma exposure periods.

The Cottrell surface area normalized current density j is a good indicator of the intrinsic activity (*i.e.* TOF) of the material. It can be seen from **Figure 5-5b** that the onset overpotential of plasma treated sample remains almost unchanged compared to the untreated one, indicating the type of the catalytic active sites hasn't changed – Mo edges in the MoS₂ act as catalytic sites for HER. There is a certain degree of improvement in terms of the cathodic current density when the plasma exposure time increases. This may be due to the lowered crystallographic symmetry and increased lattice distortion of MoS₂ under oxygen plasma treatment, which can boost the HER electrocatalytic activity.^(92, 162)

When it comes to the device-oriented activity (normalized by the geometric area of the electrode), there is an obvious improvement from the oxygen plasma treatment, which is consistent with the inherent activity enhancement as discussed above. It is also seen that j_{geo} reaches a maximum at 15 min exposure time and longer exposure leads to smaller improvement, following the trend of the Cottrell surface area measurement in **Figure 5-5a**, although the intrinsic activity increases linearly with extended plasma exposure time.

When discussing the aforementioned trend of overall catalytic activity, the following four factors need to be taken into consideration:

- 1) Oxygen plasma induced defects, contributing to inherent activity improvement;
- 2) Oxygen plasma increased edge density by serrated edges, microcracks and surface nanopores;
- 3) Catalyst material loss due to the destructive plasma etching process;
- 4) Chemical change of catalytically active and semiconducting sulfide to catalytically inert but conductive oxide phases (MoO₂ and MoO_{3-x}).

After 15 min of oxygen plasma, the activity per edge site is improved due to defects as discussed in **Figure 5-5b**; the number of edges is significantly increased from surface cracks, nanopores, and serrated edges, as evidenced from the Cottrell surface area measurement in **Figure 5-5a**. The two factors combined improve the overall HER activity for 15 min exposure time. When the oxygen plasma exposure time is increased to 30 min, the activity per site is still further increased as in **Figure 5-5b**, but the edge density/Cottrell surface area enhancement is limited by the loss of material. Therefore, a smaller Cottrell surface area is observed for 30 min compared to 15 min (**Figure 5-5a**). Following the trend of the Cottrell surface area measurement, the overall electrochemical activity of the 30 min treated sample also exhibits smaller improvement than 15 min, which indicates the increased activity per site cannot be compensated by the active materials loss.

The impact of the oxide phase in this materials system for HER will be discussed as following. There have been suggestions that MoO₃ is soluble in acid and will not play a role in HER in acid media.⁽⁹²⁾ However, this explanation does not necessarily apply to my system because the oxides were not necessarily formed at acid

accessible locations, given the 3D networked structure of the material. As revealed by Raman spectroscopy (**Figure 5-4**), molybdenum oxide phases were formed in the catalyst system which possesses better conductivity than MoS₂ and is beneficial to circumvent the conductivity limitation from the semiconducting nature of MoS₂. From the electrochemical impedance spectroscopy analysis in **Figure 5-6**, it's obvious that the entirety of the measured series resistance does not appear to differ significantly across samples with/without plasma exposure (range: 20 ~ 50 Ω/cm^2). This ensures that at such oxygen plasma exposure levels, the effect of as-generated oxides on decreasing the ohmic resistance in the catalytic system is negligible, or less significant than decreasing total amount of catalytic active materials (MoS₂).

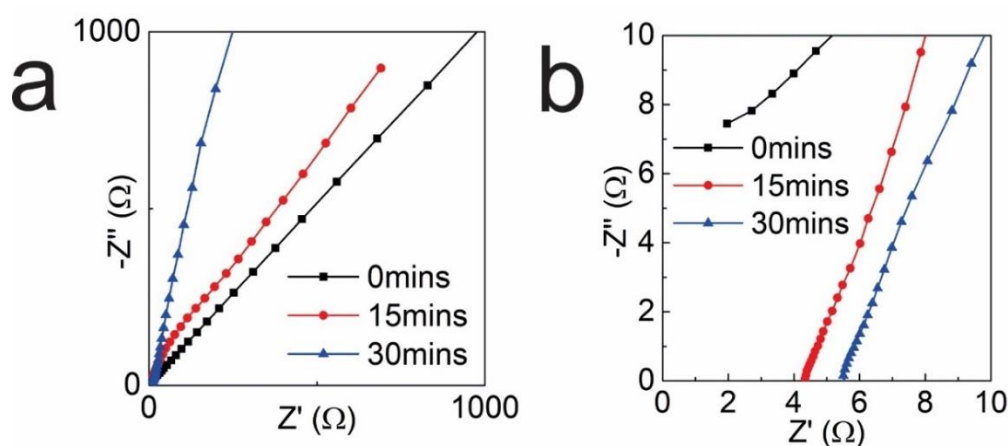


Figure 5-6. Electrochemical impedance spectroscopy (EIS) of O₂-plasma etched MoS₂ catalysts as a function of plasma exposure time.

This shows that the inherent activity and Cottrell surface area are enlarged by O₂ plasma treatment. Consequently, the total electrode activity is improved and j_0 is significantly enhanced by 18-fold (as seen in **Table 5-1**). The increased Tafel slope value of the oxygen plasma treated samples as seen in **Figure 5-5d** indicates a

higher overpotential is required in order to enhance the same amount of current density. RDS of plasma etched samples remained unchanged compared to the untreated sample and indicates a Volmer reaction. Comparison of overall HER performance under different treatment times shows that 15 min is the optimum condition in order to improve H₂ production, Cottrell surface area, and Tafel slope as well as j_0 .

An alternative gas phase etching approach is annealing in H₂ gas flow, which is likely to strip sulfur from MoS₂ and leave S vacancy defects and under high temperatures may lead to Mo removal as well. The CVD grown MoS₂ nanoplatelets were etched under Ar/H₂ gas atmosphere at 600, 700 and 800 °C. SEM measurements of samples annealed at different temperatures are summarized in **Figure 5-7b-d**.

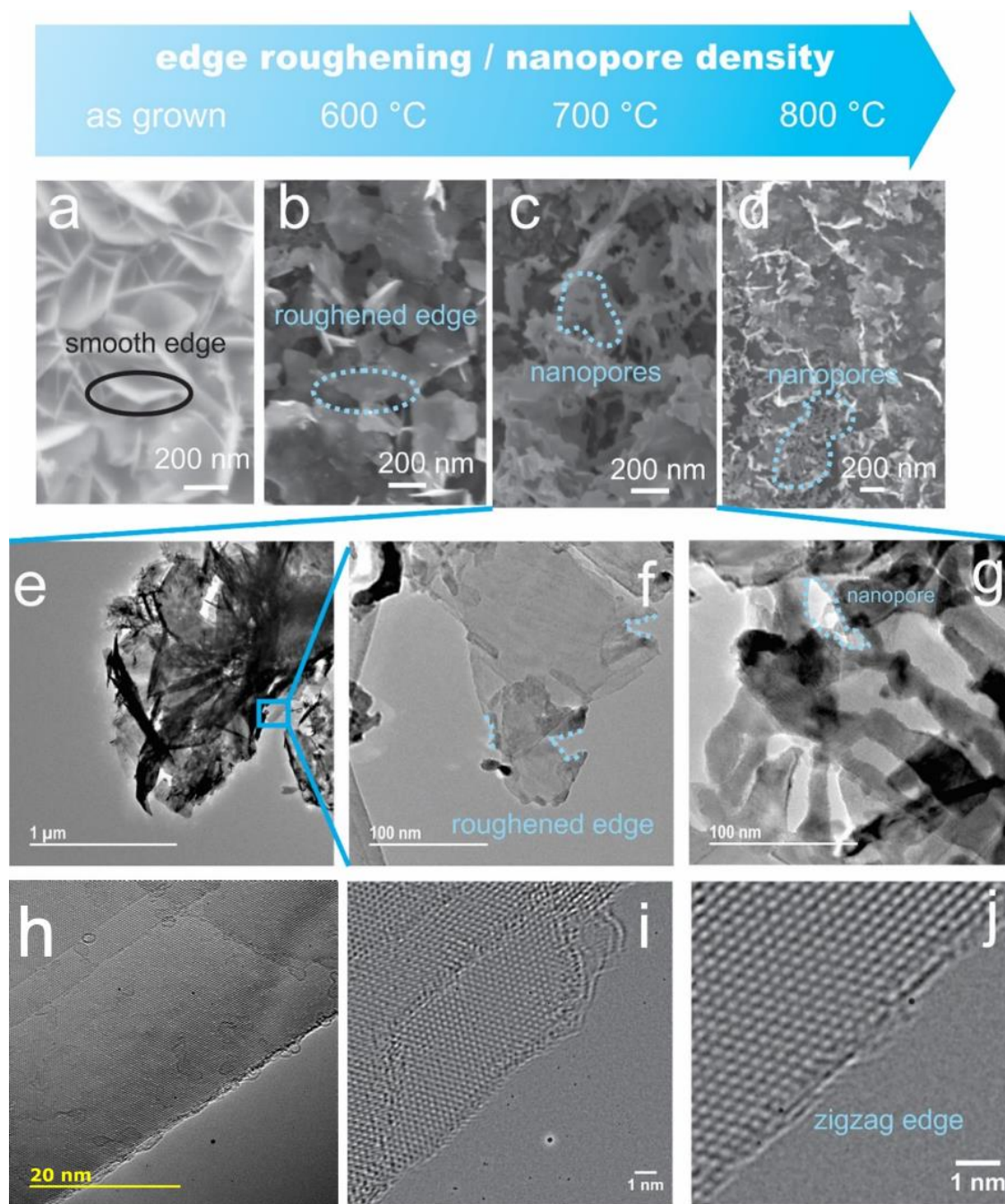


Figure 5-7. Structural investigation of the H₂ etched sample. (a-d) SEM images (accelerating voltage 3.0 kV) of the MoS₂ catalysts as-grown and etched by H₂ at 600, 700 and 800 °C, respectively. (e-g) TEM images (accelerating voltage 200 kV) of 700 °C H₂ annealed MoS₂ flakes, showing roughened edges and formation of nanopores and nanoribbons. (h-j) HRTEM images (accelerating voltage 80 kV) of 700 °C H₂ annealed MoS₂ flakes demonstrating atomic scale edge configuration.

The as-grown sample (**Figure 5-7a**) consists of perfectly smooth vertically standing nanoplatelets, but when annealed in H₂ at 600 °C, serrated features start to emerge at the edges of the nanoplatelets. With the temperature elevated to 700 °C, along with etched and serrated edges, pores are created on the basal surfaces. As the temperature is further increased to 800 °C, more material has been etched away and the whole thin film becomes significantly ragged, with some spots of the substrate being exposed. The higher the annealing temperature, the larger the density of the holes that are created on the basal surfaces, indicating loss of both S and Mo atoms. TEM imaging was used to study H₂ etching induced microstructure changes. **Figure 5-7e-g** shows that H₂ annealing promotes the formation of a large number of irregularly shaped and oriented nanopores and nanoribbons, which leads to an irregular hollow and serrated configuration across the thin film catalyst surface. HRTEM images of the same H₂ annealed sample are shown in **Figure 5-7h-j**. As opposed to O₂ plasma etching which increases the edge density by creating atomic roughened edge configuration, the edges of the H₂ annealed platelets retain their clean and smooth form as in the pristine one. The edge density enhancement mainly arises from what has been discussed – the formation of networked nanopores and nanoribbons.

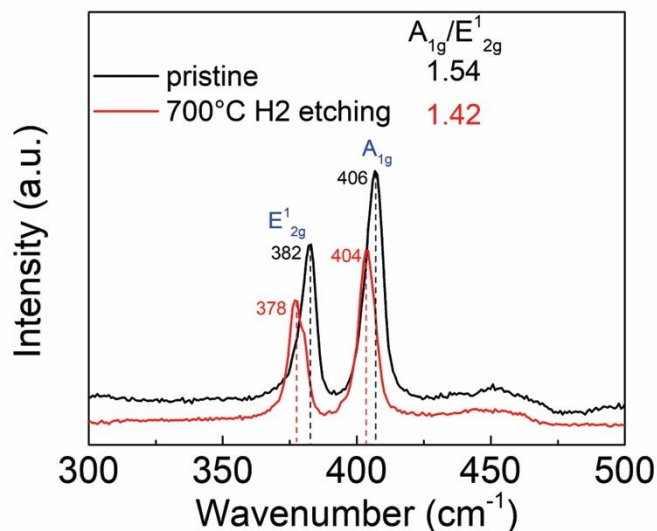


Figure 5-8. Raman spectra of pristine and 700 °C H₂ etched MoS₂ catalysts. Inset: two characteristic Raman vibration modes in MoS₂: in-plane vibration of molybdenum and sulfur atoms E_{2g}¹ and out-of-plane vibration of sulfur atoms A_{1g}; information on peak intensity ratio of A_{1g}/E_{2g}¹ of samples before and after H₂ etching.

Raman spectroscopy was used to inspect possible chemical changes introduced by H₂ annealing. As seen in **Figure 5-8**, the Raman spectrum of the H₂ etched sample at 700 °C exhibits the two characteristic peaks of MoS₂. The intensity ratio of A_{1g}/E_{2g}¹ matches the untreated sample, indicating the vertical alignment of the nanoplatelet is well maintained after high temperature reducing atmosphere H₂ etching. At the same time, the blue shift for both peaks is observed. The E_{2g}¹ vibration is studied to be mainly affected by built-in strain of the sample; while the A_{1g} vibrational mode is an indicator of the doping level.⁽¹⁶³⁾ The blue shift of the E_{2g}¹ peak can be attributed to the strain released when annealed at high temperature (700 °C) for 2h. Blue shift of A_{1g} peak is likely from the H₂ atmosphere induced doping effect.

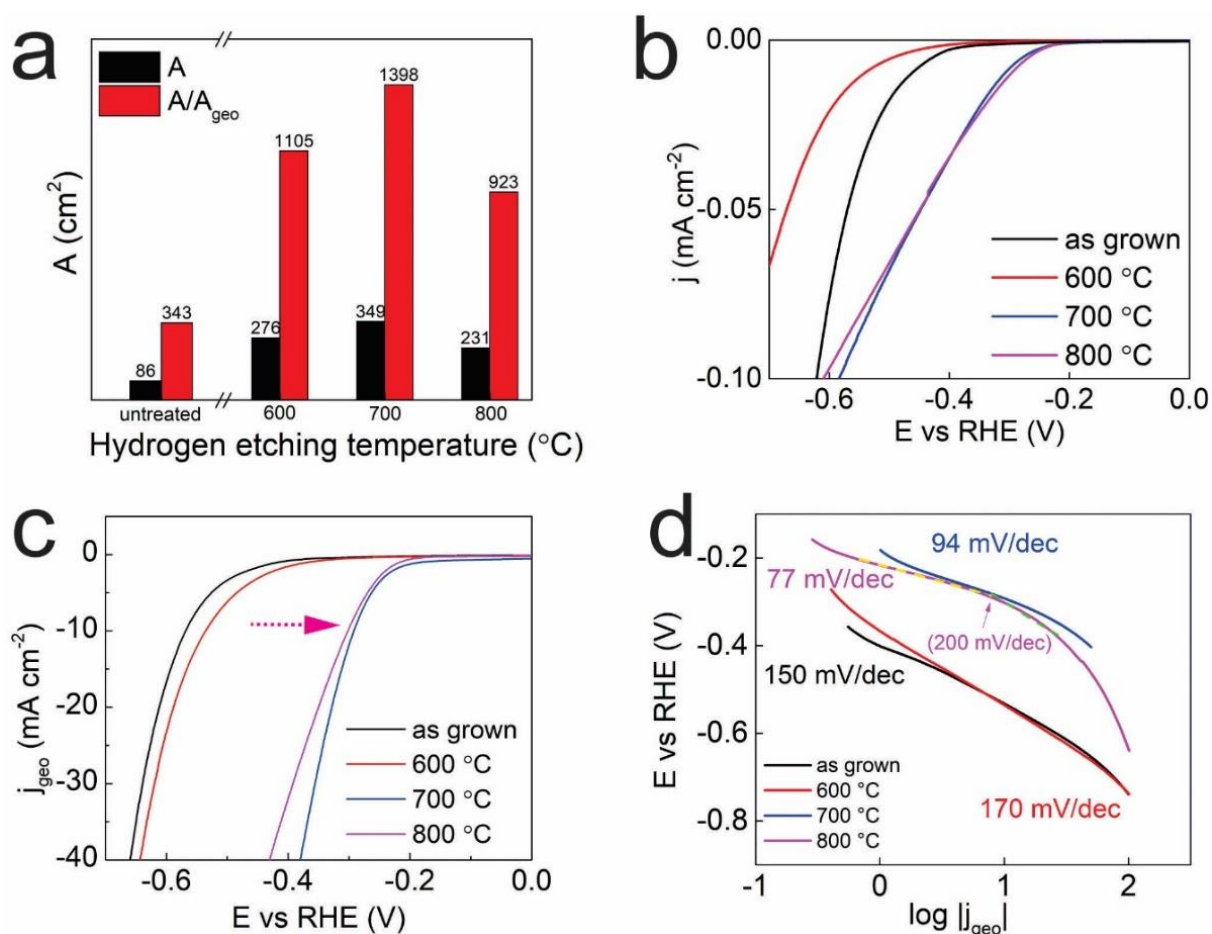


Figure 5-9. . Effect of H₂ annealing temperature on Cottrell surface area and electrochemical activity of 3D-ER MoS₂. (a) Cottrell surface area evaluation of H₂ etching process as a function of H₂ etching temperatures (A_{geo}: geometric area of the catalyst; A: Cottrell surface area of the catalyst). Cathodic polarization curves (scan rate 1 mV/s, 0.5 M H₂SO₄ (aq)) at different H₂ annealing temperatures normalized by (b) Cottrell and (c) geometric surface area. (d) Tafel plots of the H₂ etched samples under different annealing temperatures.

Surface area changes in **Figure 5-9a** reveal that H₂ annealing is effective in enhancing the surface area of the materials. As the annealing temperature increases, the surface area enhancement first increases, reaches a maximum at 700 °C (4-fold of the untreated sample, **Figure 5-9a**) and decreases at 800 °C. A temperature lower than 700 °C may not be sufficient to effectively etch MoS₂ and expose as many new

surfaces as 700 °C; whereas 800 °C is high enough that material loss and decomposition start to play dominant roles and lead to lowered surface area enhancement.

The polarization curves normalized by Cottrell surface area as in **Figure 5-9b** reveal the intrinsic activity per active site in the material. The 600 °C sample is found to start evolving hydrogen at similar overpotential as the untreated sample, indicating that at this point the type of active site hasn't changed – MoS₂ edges are the dominant active sites. The current density of 600 °C is smaller than the pristine one, due to the elimination of defects, which may contribute to the inherent catalytic activity.(26, 73, 159, 164) Samples annealed in H₂ atmosphere at 700 and 800 °C exhibit similar onset overpotentials (172 and 193 mV, respectively), which are smaller than the untreated sample (323 mV). This result implies that H₂-annealed at 700 and 800 °C, the dominant active site changes from MoS₂ edges to another type. Based on the study by Li *et.al.* on all the catalytic sites of MoS₂ for HER, in addition to the well-known catalytically active edges, sulfur vacancies serve as another type of active sites for HER.(32) The high-temperature H₂ annealing contributes to local sulfur depletion of MoS₂, which is capable of catalyzing the HER.

The total electrode activity of untreated and H₂ etched samples are summarized in **Figure 5-9c**. The 600 °C sample performs slightly better (onset overpotential 300 mV vs. 323 mV of untreated sample) than the untreated one despite lower intrinsic activity because it can be compensated by the increased number of surface area and edge density. It is not surprising that samples annealed at 700 and 800 °C demonstrate enhanced overall HER activity owing to the newly created basal plane

sulfur vacancies as active sites, as well as the increased surface area resulting a larger number of active sites. 800 °C leads to a slightly lower overall HER activity than 700 °C because of the material loss and decomposition (as evidenced by the Cottrell surface area measurement in **Figure 5-9a**) under such high temperature and reducing gas agent.

Both Cottrell surface area evaluation and electrochemical measurements demonstrate that 700 °C annealing results in the optimal Cottrell surface area enhancement and HER activity improvement (**Figure 5-9b** and **c**) with smallest Tafel slope (**Figure 5-9d**) and largest j_0 (**Table 5-1**). The optimum condition is a compromise between active site density increase and active material loss. EIS measurement in **Figure 5-10** confirms that the H₂ annealing does not change the conductivity of MoS₂ catalyst system ($\sim 20 \text{ } \Omega/\text{cm}^2$). With the 800 °C sample, a 2-regime Tafel slope is observed. This indicates that the sample undergoes a transition of RDS from the Heyrovsky to the Volmer reaction at an overpotential of $\sim 300 \text{ mV}$ vs. RHE, which may correspond to the switching of dominant catalyzing species from basal plane SVs to MoS₂ edges.

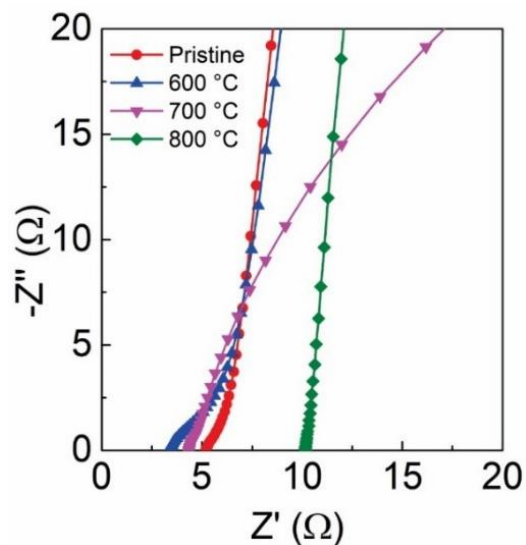


Figure 5-10. Electrochemical impedance spectroscopy (EIS) of H₂-etched MoS₂ catalysts under different H₂ annealing temperatures.

To summarize and compare the different defects introduced by two engineering methods used in this study, based on SEM and TEM analysis results as discussed in **Figure 5-3** and **Figure 5-7**, a schematic model is shown in **Figure 5-11** to illustrate the single MoS₂ domain structure as of the as-grown, H₂ etched and O₂ plasma treated samples. Compared with pristine MoS₂, irregular networks of nanoribbons and nanoholes are generated by H₂ annealing onto the basal surfaces and edges. In the case of O₂ plasma treatment, roughened edges, microcracks, quasi-ordered chained surface damage as well as second phase – MoO_x are the main defect configurations.

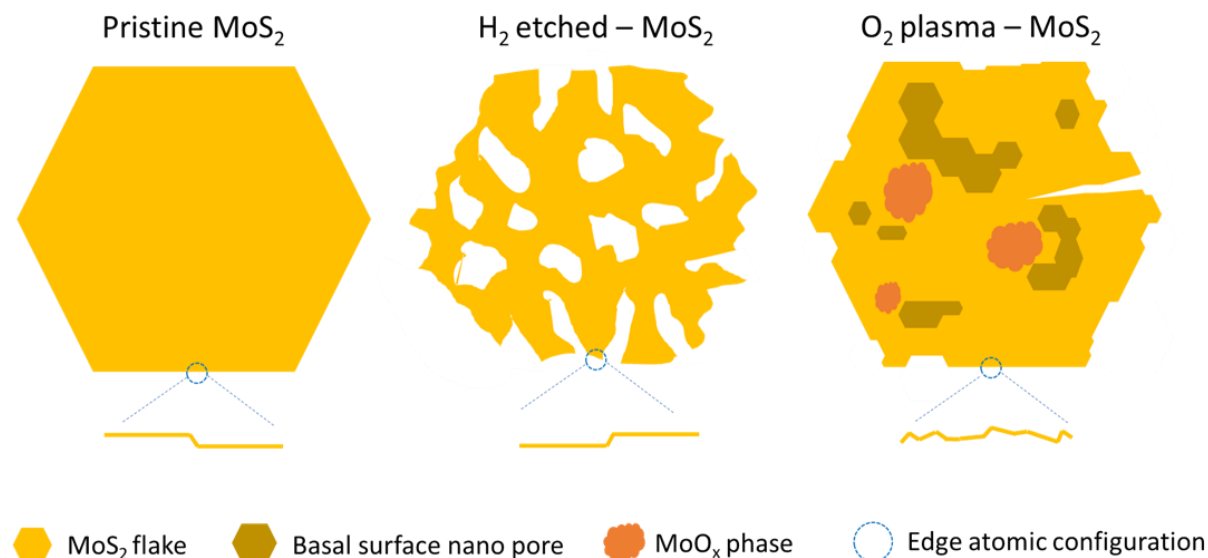


Figure 5-11. Schematic model of structural modification via defect engineering in MoS₂ nanoflakes: a comparison between O₂ plasma and H₂ etching.

The surface area enhancement is verified to be effective using both methods and can be easily controlled by tuning processing time and temperature. The above discussed structural difference leads to varied efficiency of the active sites density and HER improvement as illustrated in **Figure 5-12**. The O₂ plasma is twice as effective as H₂ annealing to increase Cottrell surface area of the catalysts (A/A_{geo} : 2385 vs. 1398). The H₂ etching is better at the enhancement of total HER activity as observed from the cathodic polarization curves (**Figure 5-12a** and **Table 5-1**) that it lowers the onset overpotential by 159 mV. The enhancement may be attributed to the creation of new type of active sites as well as the increased surface area. The overall HER activity improvement by oxygen plasma relies mainly on the increased number of catalytic active edges.

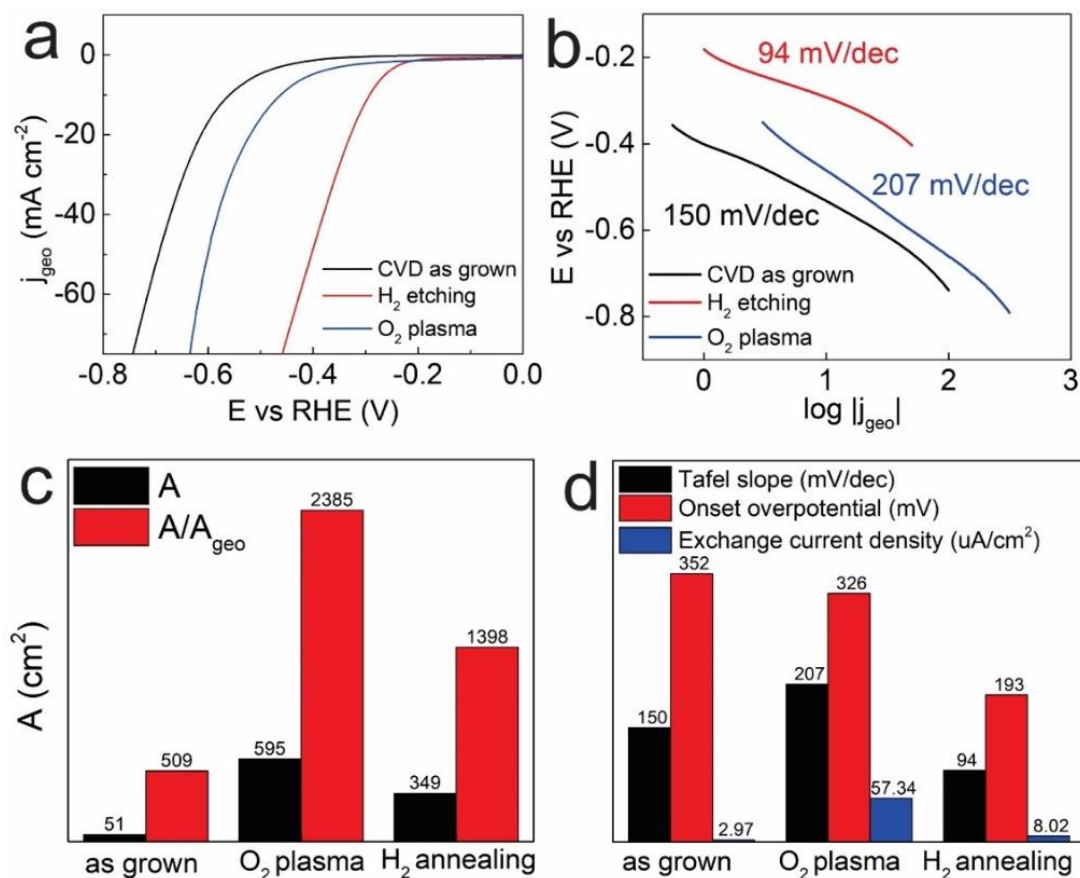


Figure 5-12. Comparison of Cottrell surface area enhancement and HER improvement for O₂ plasma treated and H₂ etched MoS₂ catalysts. (a) Cathodic polarization curves (scan rate 1 mV/s, 0.5 M H₂SO₄ (aq)), (b) Tafel plots, (c) surface area evaluation and (d) electrochemical metrics (Tafel slope, onset overpotential and exchange current density) of CVD as-grown, O₂ plasma and H₂ annealed samples.

Table 5-1. Electrocatalytic metrics for MoS₂ HER catalysts treated by O₂ plasma and H₂ annealing.

Catalysts	Onset overpotential (mV vs RHE)	Tafel slope (mV/dec)	Exchange current density ($\mu\text{A}/\text{cm}^2$)
15 min O ₂ Plasma Treated MoS ₂	326	207	57.34
30 min O ₂ Plasma Treated MoS ₂	303	173	13.18
600 °C H ₂ Etched MoS ₂	300	170	7.13
700 °C H ₂ Etched MoS ₂	193	94	8.02
800 °C H ₂ Etched MoS ₂	172	77 (200)	1.61

Table 5-2. Summary HER performances of defect-rich MoS₂-only electrocatalysts from literature.

Catalyst	Media	Onset overpotential (mV vs RHE)	Tafel slope (mV/decade)	j ₀ -geometric (μA/cm ²)
Plasma-engineered MoS ₂ thin-film(110)	0.5M H ₂ SO ₄	Not reported	105	Not reported
Sulfur vacancy rich MoS ₂ monolayer thin film(32)	0.5M H ₂ SO ₄	Not reported	65 – 85	40
Defect-rich MoS ₂ nanowall(83)	0.5M H ₂ SO ₄	95	78	450
Defect-rich MoS ₂ ultrathin nanosheets(90)	0.5M H ₂ SO ₄	120	50	8.91
Defects engineered monolayer MoS ₂ (92)	0.5M H ₂ SO ₄	300	117	Not reported
Monolayer MoS ₂ with strained sulfur vacancies(61)	Not reported	~ 0	82	~ 50
15 min O ₂ plasma treated MoS ₂ (this study)	0.5M H ₂ SO ₄	326	207	57.34
700 °C H ₂ etched MoS ₂ (in this thesis)	0.5M H ₂ SO ₄	193	94	8.02

Table 5-3. j (mA/cm²) @η=0.5 mV for defect engineered monolayer and 3D-ER MoS₂.

Approaches	Monolayer(92)	3D-ER (this study)
H ₂ etching	2.5	95
O ₂ plasma	2.5	15

The Tafel slope value indicates the RDS of the pristine, O₂ plasma treated and H₂ etched samples is Volmer and Heyrovsky reaction. H₂ etching is more desirable for practical application since it facilitates enhanced current density (H₂ generation per area) at a moderate increase of overpotential with the smallest Tafel slope in this study. The as-optimized defect-rich MoS₂ catalysts exhibit promising HER electrocatalytic potential compared to other MoS₂ only electrocatalysts from literature: 700 °C – H₂ – MoS₂ possesses Tafel slope of 94 mV/dec and an onset overpotential

of 193 mV; 15 min – O₂ – MoS₂ performs amongst the best with an excellent exchange current density of 57 $\mu\text{A}/\text{cm}^{-2}$ (normalized by geometric area).^(32, 61, 83, 90, 92, 110, 160) Detailed HER catalytic metrics comparison with literature can be found in **Table 5-2**. Especially compared with monolayer MoS₂ subject to similar process – CVD combined with O₂ plasma or H₂ etching,⁽⁹²⁾ the defect engineered 3D-ER MoS₂ in this study exhibits j_{geo} (at $\eta=0.5$ mV) of 6-fold and 38-fold, for O₂ plasma and H₂ etching approaches respectively (**Table 5-3**) benefiting from maximized usage of electrode area by the unique 3D architecture.

5.3 Conclusion

- Defect-rich vertically standing MoS₂ nanoplatelets were successfully fabricated via CVD and subsequent O₂ plasma or H₂ etching approach to be utilized as electrocatalyst towards water splitting.
- By systematically controlling the defect processing parameters; O₂ plasma exposure time or H₂ annealing temperature, tunable surface area and catalytic activity enhancement can be obtained. Insights were gained into the correlation between microstructure change and catalytic activity improvement as well as a comparison of the two defect engineering methods.
- The Cottrell surface area was significantly enlarged in both cases but via different microstructure architectures. O₂ plasma treatment introduced basal micro-cracks and local surface damage as well as promoted a saw-toothed edge configuration; H₂ etching generated irregular shaped basal surface nanopores and nanostrips.
- The electrochemical evaluation revealed that compared with H₂ etching, O₂ plasma was more effective in Cottrell surface area enhancement but less powerful

in improving HER catalytic activity, which is attributed to the catalytically less active MoO_x phase introduced by O₂ plasma treatment into the catalyst system. H₂ etching enhances the overall HER activity by creating a new type of active site as well as the increased surface area.

- Such as-designed defect-rich structures significantly enhanced edge density over the geometric area, together with the porous structure and superaerophobic surface, it enables us to construct a highly effective non-noble metal catalyst system which maximizes physical area usage of electrodes. Such defect engineering routes can be incorporated into many more Pt-free catalyst systems other than MoS₂ for improved functionality as well. This may broaden the economical application of electrocatalytic water splitting for hydrogen generation.

6 Synthesis of Surface Grown Pt Nanoparticles on Edge-enriched MoS₂ Porous Thin Films for Enhancing Electrochemical Performance

6.1 Introduction

In the pursuit of edge rich MoS₂ HER catalysts, an attractive approach is to grow vertical atomic MoS₂ layers.(39) However, this approach has difficulties to form hybrids with other materials and the total edge density per cm² of the substrate cannot be extended by 3D growth. Alternatively, in **Chapter 4** I showed that ultra-high surface area 3D MoS₂ porous thin films grown by CVD, where branched like MoS₂ platelets provide many edges for catalytic activity, may provide the solution for hybridization(165)

The lack of activity on the massive amount of surface (basal plane), however, strongly impedes the performance of MoS₂ catalysts.(61, 104) Activation of the MoS₂ basal plane will further improve activity and warrants investigation.

In light of that single heteroatom doping is capable of enhancing the activity of the surface S atoms,(145) and metal nanoclusters can facilitate electron transfer to the 2D crystals and thus modify the surface electronic structure and enhance the reactivity of MoS₂.(144, 146) One possible strategy is to produce hybrid Pt/MoS₂ composites, where small amount of Pt dopants can decorate the inactive surface

sites and make use of the full surface area of MoS₂. High dispersion of Pt dopants can be realised

simultaneously by the 3D MoS₂ scaffolding. To date, this approach has not been achieved with high surface area MoS₂ thin film catalysts. Only some research into the solution growth of Pt nanoparticles on chemically exfoliated MoS₂ monolayer flakes has been done.⁽¹⁴⁴⁾ The realisation of a hybrid Pt/MoS₂ system with high catalytic activity could potentially outperform the Pt:carbon system due to the MoS₂ acting as both substrate and catalyst. The use of high-cost Pt metals can be justified if the Pt loading is significantly lower than MoS₂.

This chapter demonstrates a facile and scalable route to prepare a Pt/MoS₂ hybrid catalyst directly on a GC electrode via the CVD-TA method to achieve controllable size, content and distribution of the nanocrystals. Comprehensive characterisation and test will be conducted to probe the morphology, microstructure and HER activity, which will help to define an effective platform to guide the design of other efficient hybrid systems.

6.2 Results and Discussion

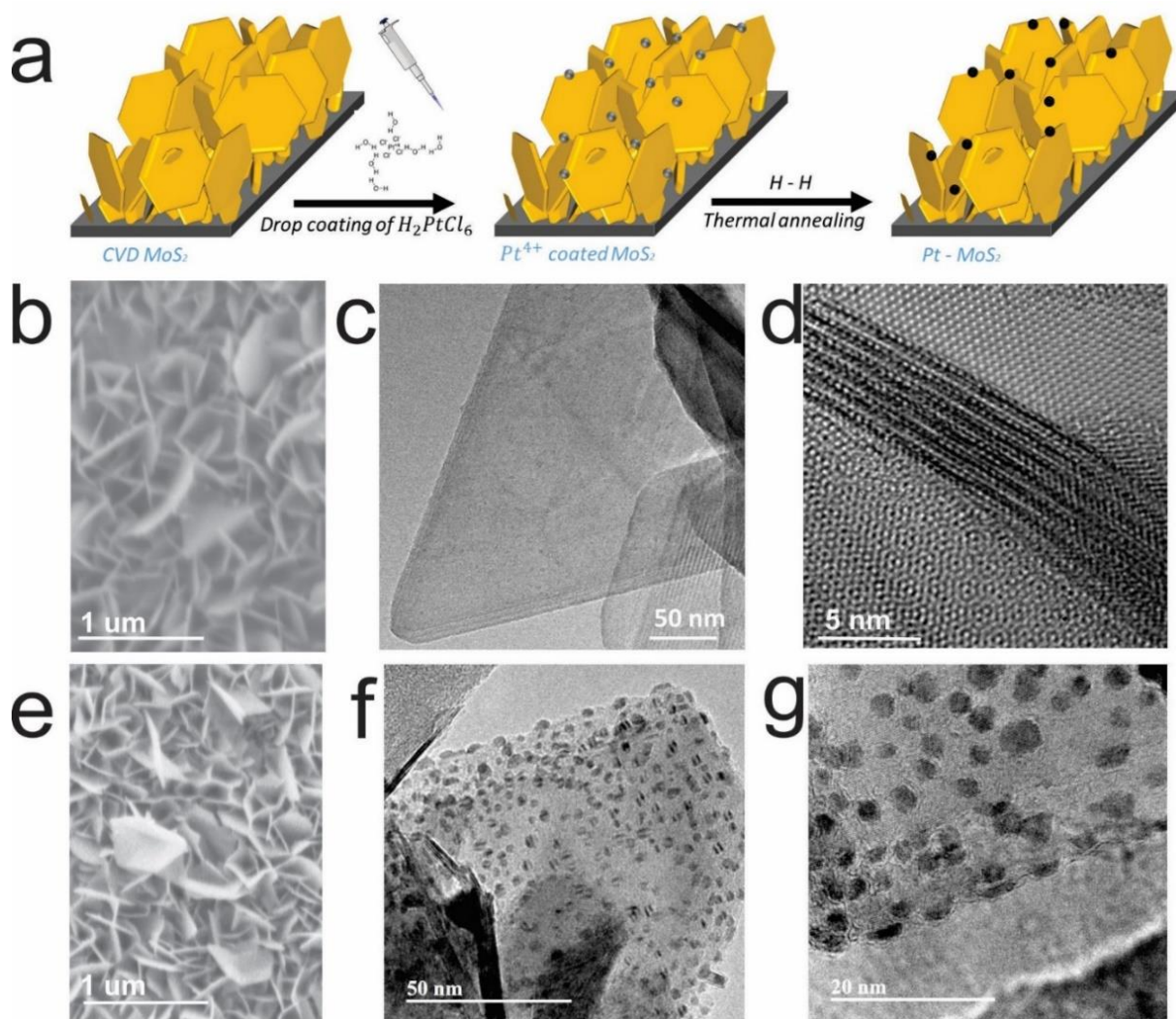


Figure 6-1. Morphological and microstructural characterisation of supported Pt nanocrystals on CVD synthesized vertically-standing MoS₂ nanoplatelets. (a) Schematic illustration of the two-stage process of drop coating – TA to prepare dispersive Pt nanoparticles growth onto 3D-ER MoS₂. SEM images (accelerating voltage 3.0 kV) showing surface morphology of (b) CVD pristine MoS₂ and (e) Pt-decorated MoS₂ (Pt/MoS₂), proving vertically alignment of nanoplatelets was preserved after the TA process. Microstructure determination using TEM imaging (accelerating voltage 200 kV) of (c and d) pristine MoS₂ and (f and g) Pt/MoS₂ hybrid catalyst.

The porous 3D thin film of Pt nanoparticles grown on edge exposed MoS₂, to be used as electrocatalyst towards hydrogen evolution, was produced via a two-step process: 1) CVD synthesis of support/host catalyst material MoS₂ (see **section 3.2.1**) and 2) formation of Pt crystals via a TA approach (see **section 3.2.3**). The TA process is illustrated in **Figure 6-1a**. The as-prepared Pt-MoS₂ was then carefully characterized by SEM, TEM, and EDX to investigate its morphology, microstructure, and elemental composition.

Figure 6-1b depicts the SEM image of CVD as-grown pristine MoS₂ consisting of vertical standing platelets with a size smaller than 1 μm . The microstructure of those MoS₂ flakes was examined by TEM images in **Figure 6-1c,d**, where the smooth and clean horizontal aligned triangular domain and vertically standing multilayers of MoS₂ can be clearly observed. From SEM image in **Figure 6-1e**, it can be found the as-received Pt-decorated MoS₂ consists of vertically-standing platelets as in its CVD as-grown counterpart. It proves that the CVD grown MoS₂ with this particular edge-terminated morphology, which is conventionally considered thermodynamically metastable, was stable and robust enough to survive the TA process in the reducing atmosphere of H₂/Ar. This ensures the resultant Pt/MoS₂ hybrid catalysts will benefit from high Cottrell surface area of active edges and superaerophobic surface structure resulting from the vertically standing MoS₂ flakes.

ADF-STEM images and its corresponding FFT of the resultant Pt nanocrystal decorated MoS₂ catalyst are shown in **Figure 6-4**, which confirms good crystallinity of the Pt/MoS₂. The black lines measuring the interlayer spacing of 0.24 nm corresponds to lattice spacing of Pt nanocrystal in the <111> direction, slightly larger

than what has been reported to be 0.23 nm.⁽¹⁴⁷⁾ FFT analysis of the entire image of **Figure 6-4a** is recorded in **Figure 6-4b,c**. {100} and {110} represent zigzag and armchair orientations of MoS₂, respectively. The crystal structure of Pt nanocrystals at different loadings and TA temperatures are summarized in **Figure 6-2** and **Figure 6-3**, with the interlayer spacing 0.23nm indicating $d_{(111)\text{Pt}}$.

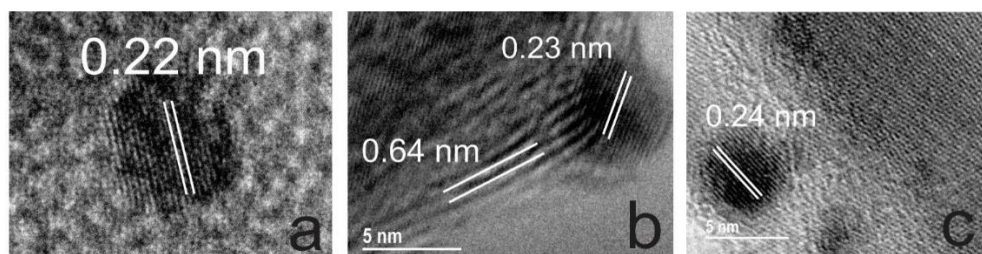


Figure 6-2. High-magnification TEM images (accelerating voltage 200 kV) of a Pt nanoparticle deposited on MoS₂ for precursor loading of (a) 11 wt%, (b) 1.1 wt% and (c) 0.11 wt%. The white lines measure interlayer spacing $d_{(001)}$ in MoS₂ of 0.64nm and $d_{(111)}$ in Pt crystal of 0.23nm, respectively.

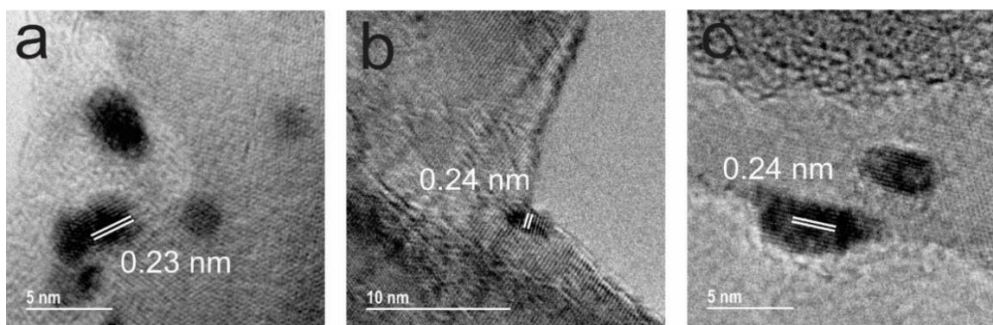


Figure 6-3. High-magnification TEM images (accelerating voltage 200 kV) of Pt nanoparticles deposited on MoS₂ for a thermal annealing temperature of (a) 400 °C, (b) 500 °C and (c) 600 °C. The white lines measure interlayer spacing $d_{(111)}$ in Pt crystal.

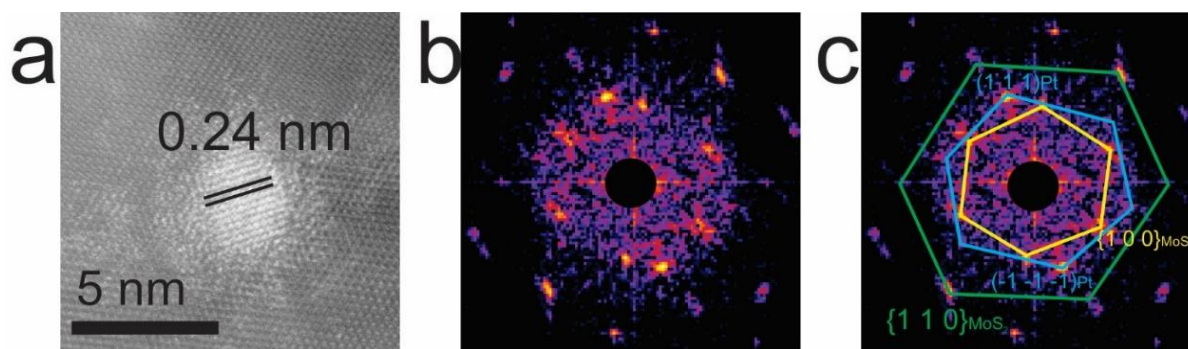


Figure 6-4. Crystallographic structure of Pt/MoS₂. (a) ADF-STEM image (accelerating voltage 60 kV) of a Pt nanocrystal attached to the MoS₂ horizontal oriented flakes, with an interlayer spacing $d_{(111)\text{Pt}}$ of 0.24 nm. (b) Power spectrum calculated from (a). (c) FFT of the entire image in (a), with reflexes from MoS₂ and Pt labeled.

In order to investigate the growth behavior and mechanisms of Pt nanocrystals on MoS₂, the TA process was carried out by tuning the Pt precursor loading, annealing temperature and time. These factors are believed to have profound influence on the number and mobility of Pt species, size distribution as well as specific surface area of as-formed Pt nanoparticles, and thus the catalytic property of the resultant hybrid catalyst.

The volume of Pt precursor drop coated onto MoS₂ before TA and geometric area of the glassy carbon electrode were kept constant at 10 μL and 1.5 cm^2 . Elemental composition of 10 mM sample was experimentally measured by EDX technique; those of 1 and 0.1 mM samples were pro-rated by the values of 10 mM sample, assuming that the Pt content in precursor remains the same as in Pt crystals formed during thermal annealing. (see **Table 6-1** and **Table 6-2**)

Table 6-1. EDX quantitative elemental analysis based composition determination of Pt-MoS₂ catalyst synthesized with 10 mM H₂PtCl₆·6H₂O:ethanol, annealed at 400 °C for 40 min.

Area	Atomic % of element Mo	Atomic % of element Pt
1	29.6	3.4
2	29.6	3.3
3	31.4	3.9
4	30.9	3.6
5	30.7	3.3
6	31.6	4.4
7	32.0	2.9
8	31.2	3.6
Average	30.9 ± 0.9	3.5 ± 0.5

Table 6-2. Elemental composition, Pt wt% and equivalent Pt loading on glassy carbon working electrode in the Pt/MoS₂ hybrid catalyst system determined by EDX at different precursor concentrations.

H ₂ PtCl ₆ ·6H ₂ O:ethanol (mM)	n _{Pt:Mo}	Pt wt%	Pt loading (µg/cm ²)
10	0.1	11 wt%	13
1	0.01	1.1 wt%	1.3
0.1	0.001	0.11 wt%	0.13

To measure the diameter of the small clusters and crystals, as illustrated in **Figure 6-5** I drew a circle which I judged to have equal area to the clusters, I then averaged the width and height of the sphere in order to get the final diameter which is displayed in the histograms. Normally 50 ~ 100 nanocrystals were measured for each average value, standard deviation and size distribution both pre- and post- electrochemical cycling. Electron microscopy images at different magnifications along with crystal size histograms are summarized for each loading to demonstrate the growth sites and

size distribution of the as-prepared Pt nanocrystals on the surface of the MoS₂ platelet.

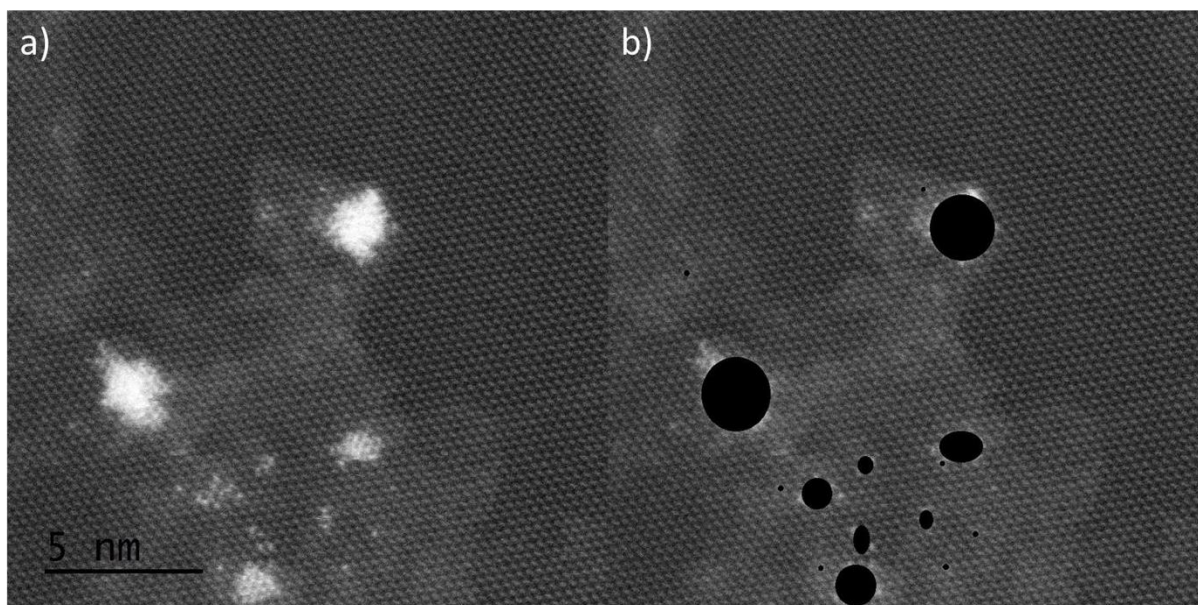


Figure 6-5. (a) Image used to measure cluster and crystal size. (b) Circles used to record the width and height of the clusters.

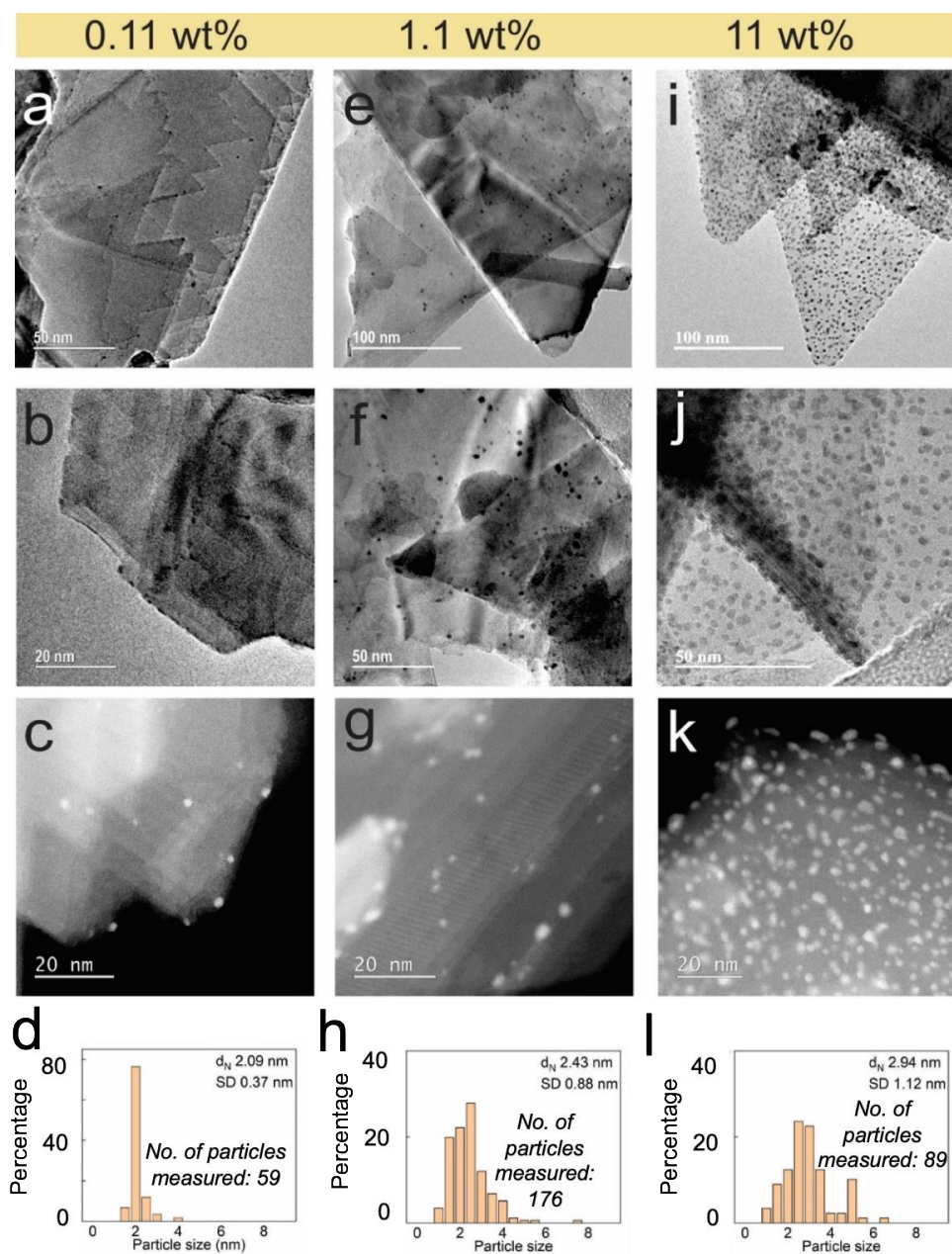


Figure 6-6. The influence of Pt metal loading on growth sites, particle density and size distribution of as-formed Pt nanocrystals on MoS₂. Low resolution TEM images (accelerating voltage 200 kV), intermediate resolution TEM images (accelerating voltage 200 kV), high resolution ADF-STEM images (accelerating voltage 60 kV) of as-prepared Pt-MoS₂ catalyst and Pt nanoparticle size histograms at Pt wt% of (a-d) 0.11 wt%, (e-h) 1.1 wt% and (i-l) 11 wt%. (Pt loading was controlled via tuning precursor concentration at 0.1 mM, 1 mM and 10 mM; the volume of drop coated precursor solution was kept constant at 10 μ L).

It can be seen from TEM and ADF-STEM images of as-prepared Pt-MoS₂ in **Figure 6-6a-k**, that when Pt wt% increases from 0.11 wt% to 11 wt%, the density of Pt nanocrystals formed on MoS₂ surface increases accordingly, due to the increased number of Pt atoms available to form crystals at elevated metal loading. Apart from a larger quantity of as-formed Pt nanocrystals, the distribution of those Pt crystals notably changed as well. At high Pt loading of 11 wt% as seen in **Figure 6-6i-k**, the Pt nanocrystals are formed uniformly across the surface of MoS₂; the distribution becomes less uniform and more randomly on the edge and basal planes in the case of 1.1 wt% (**Figure 6-6e-g**); when Pt loading reaches as low as 0.11 wt%, the nanocrystals are formed mainly at the edges of MoS₂ domains, leaving basal surfaces mostly free of Pt growth (**Figure 6-6a-c**). One possible explanation could be that the edges of CVD MoS₂ are more defective, which tend to anchor the Pt species more during their movement and thus act as the predominant nucleation sites for Pt crystals in the TA process. Another explanation can be that, before Pt crystals are formed during the TA process, drop coating and drying process of the Pt precursor are likely to form clusters and the as-formed clusters cover the MoS₂ surface unevenly and primarily on the more defective edges sites rather than basal planes. In the following TA process, under identical TA temperature/time where Pt atoms are supposed to possess the same mobility, the distribution of precursor in the drop coating process will remain in the final growth product. High-resolution ADF-STEM images in **Figure 6-6c, g and k** demonstrate that the TA synthesis method applied in this study yields only surface cluster growth of Pt atoms in the form of nanocrystals with a size of 2-3 nm and no solid evidence of atomic Pt doping. The size distributions

of the Pt nanocrystals are measured and summarized in the histograms in **Figure 6-6d, h, and l**. It is found that the higher Pt loading delivers larger average nanoparticle size. These results reveal that by tuning Pt loading, the size and growth sites of Pt nanocrystals on MoS₂ can be controlled.

In order to systematically investigate the effect of synthesis conditions on the average size and specific surface area of the Pt nanostructure. Determination of particle diameter and real surface area of the nanoparticles grown at various loadings and TA temperatures was performed based on TEM images.(166–168) Using the method discussed in **Figure 6-5**, the size (d_i) of each nanocrystal of a sample can be measured from TEM images. The number averaged (d_n) and surface averaged (d_s) particle diameters are then calculated by

$$d_n = \frac{\sum n_i d_i}{\sum n_i} \quad \text{Equation 27}$$

$$d_s = \frac{\sum n_i d_i^3}{\sum n_i d_i^2} \quad \text{Equation 28}$$

In its simplest version the specific surface area can be calculated according to the following equation:

$$A = \frac{6}{\rho d_s} \times 10^3 \quad \text{Equation 29}$$

where ρ is the density of Pt metal (21.4 g/cm³) and the resultant A is in m²/g_{Pt}. Here, d_s is better than d_n for calculation of specific surface area A . The calculated results are summarized in **Table 6-3**. The as-calculated surface area in relation to the

average particle size is in good agreement with previous studies on Pt nanoparticles synthesized on carbon supports.(142, 166–168)

Table 6-3. Number averaged (d_n) and surface averaged (d_s) particle size determined from TEM imaging analysis and specific surface area (A) calculated from d_s .

Sample	d_n (nm)	d_s (nm)	A (m ² /g _{Pt})
0.11 wt%, 400 °C	2.1 ± 0.4	2.3 ± 0.2	124
1.1 wt%, 400 °C	2.4 ± 0.9	3.2 ± 1.4	88
11 wt%, 400 °C	2.9 ± 1.1	3.8 ± 2.0	74
0.11 wt%, 500 °C	1.6 ± 0.8	2.4 ± 1.3	117
1.1 wt%, 500 °C	2.6 ± 0.8	3.2 ± 1.1	87
11 wt%, 500 °C	3.5 ± 1.7	5.2 ± 2.4	54

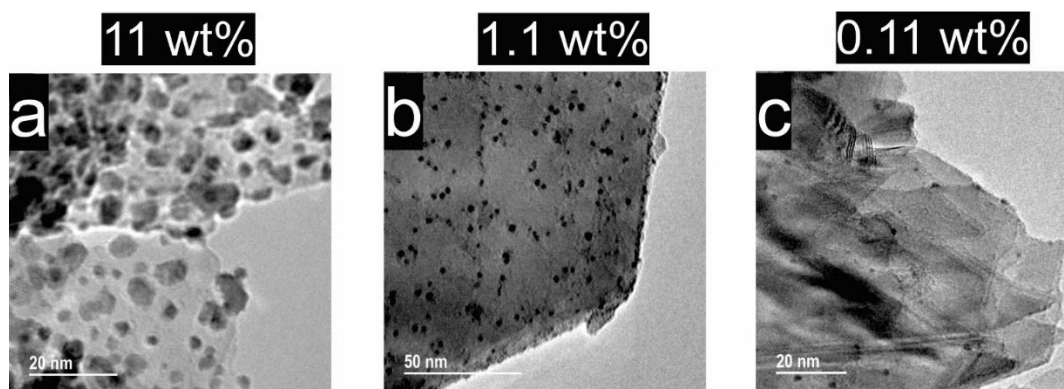


Figure 6-7. TEM images (accelerating voltage 200 kV) of Pt-MoS₂ at Pt wt% of 11 wt%, 1.1 wt% and 0.11 wt% at TA temperature of 500 °C for 40min.

The effect of Pt loading on particle size was conducted at 500 °C. The microstructure study by TEM images is shown in **Figure 6-7**. The effect of Pt loading on density and size distribution of the as-formed Pt nanoparticles at 500 °C is consistent with the 400 °C batch (**Figure 6-8b**): Pt particle size increases as Pt content increases in the hybrid materials system. Moreover, from **Figure 6-8d** it can be found that at the same

Pt loading, higher TA temperature delivers a larger average particle size. The standard deviation of d_n increases as the particle size becomes larger, which is consistent with previous studies.⁽¹⁶⁶⁾ It is worth noting that both higher loading and higher annealing temperature can increase the average particle size and subsequently decrease the specific surface area as seen in **Figure 6-8d,e**, which will influence the number of accessible active sites per mass of Pt as well as the sintering resistance during long-term operation. The TA temperature does not appear to exert a dramatic influence on Pt growth sites (comparing **Figure 6-7** with **Figure 6-6**) that 0.11 wt% Pt loading always leads to Pt nanoparticle growing at the edges of MoS₂ flakes and 11 wt% always results in the even distribution of Pt particles across the MoS₂ surface.

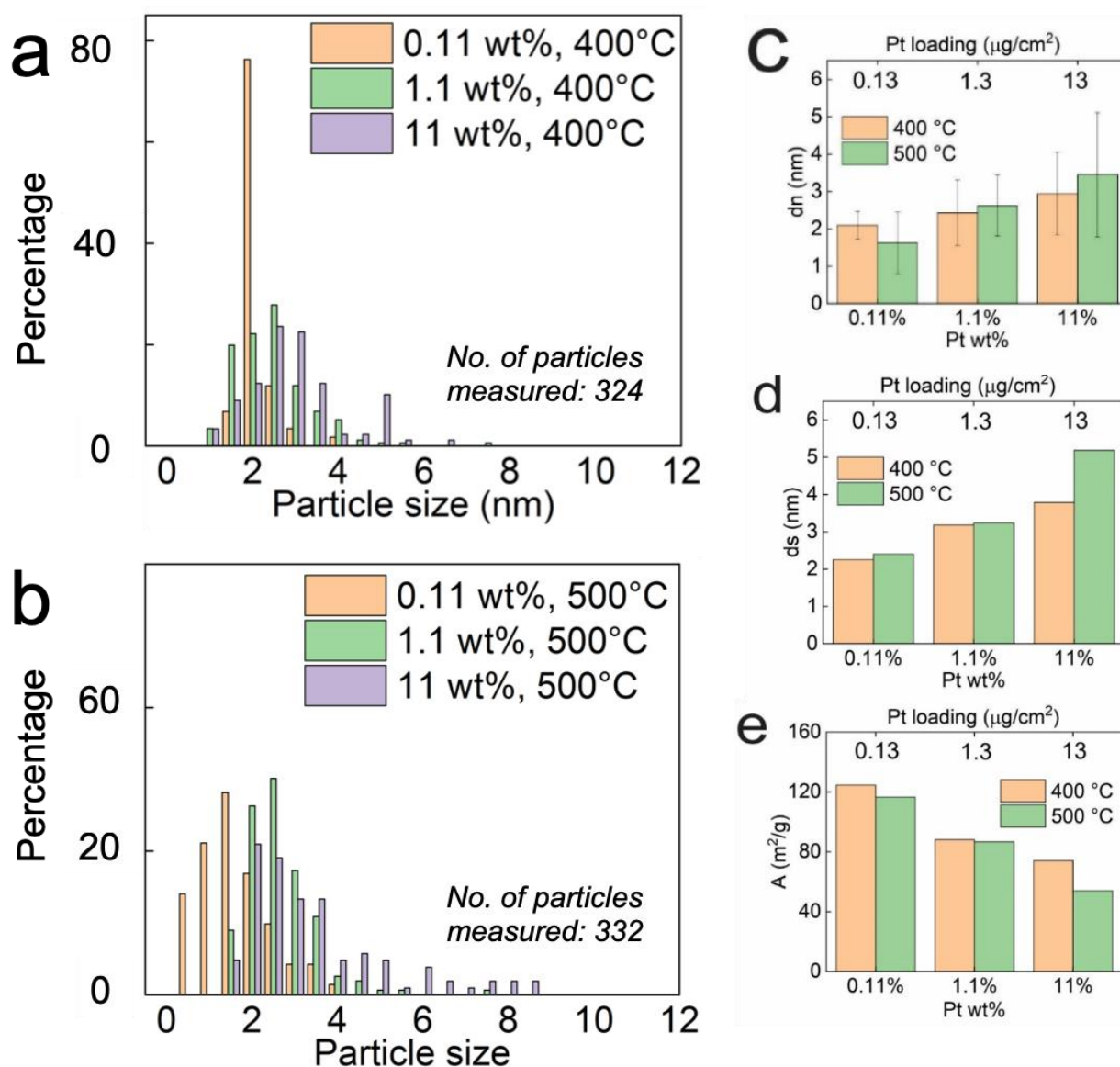


Figure 6-8. The effect of Pt loading and TA temperature on average size and specific surface area of Pt nanocrystals grown on MoS₂ nanoplatelets. (a and b) Pt nanoparticle size distribution histograms at 400 °C and 500 °C, respectively. (c) Number averaged size d_n , (d) surface averaged size d_s and (e) specific surface area A calculated from d_s of Pt nanocrystals at different loadings and TA temperatures.

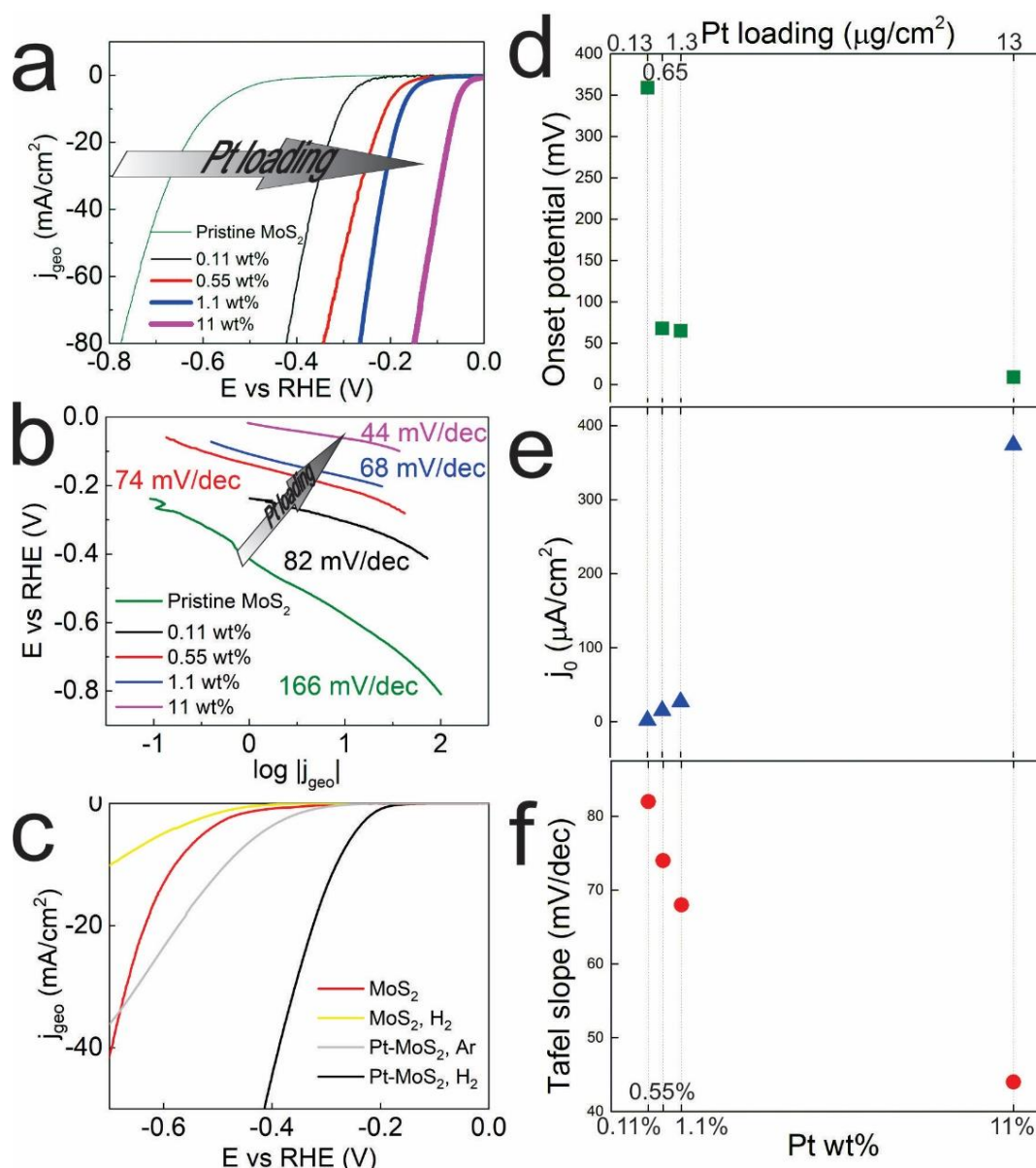


Figure 6-9. Electrocatalytic activity towards HER of the as-prepared Pt/MoS₂ catalysts as a function of Pt loading. (a) Cathodic polarization curves (scan rate 1 mV/s, 0.5 M H₂SO₄ (aq)) and (b) Tafel plots of as-received Pt/MoS₂ catalysts (values normalized by geometric area) at different Pt loadings (TA: 400 °C, 40 min) compared to pristine MoS₂. (c) Comparison of HER catalytic activities of MoS₂, H₂ annealed Pt/MoS₂ and Ar annealed Pt/MoS₂ catalysts (scan rate 1 mV/s, 0.5 M H₂SO₄ (aq)); revealing the contribution of pure Pt, MoS₂, and H₂ to the electrocatalytic activity in the present Pt-MoS₂ catalyst. (d-f) Onset overpotential, exchange current density and Tafel slope of the Pt/MoS₂ hybrid catalysts as a function of Pt wt%.

In order to understand how Pt loading and TA temperature will change structure and morphology and subsequently impact on the electrocatalytic property of the hybrid catalyst LSV and cycling treatment as described in experimental section were conducted to investigate the HER electrocatalytic performances of the as-received Pt/MoS₂ composites loaded with 0.11 wt% ~ 11 wt% Pt and annealed at 400 °C and 500 °C.

Figure 6-9 shows the influence of Pt loading on the HER activity in the hybrid Pt-MoS₂ catalyst system at the same TA temperature. First, as seen from the polarization curves in **Figure 6-9a**, the amount of deposited Pt nanoparticles on the MoS₂ platelets exerts a proportional effect on the HER activity (as indicated by the grey arrow). Although as discussed in **Figure 6-8** that higher Pt loading leads to slightly larger average particle size (2.9 nm vs. 2 nm), since Pt has extremely high HER catalytic activity, higher Pt content always leads to earlier onset of HER and larger amount of produced H₂ (corresponding current density at given overpotential). Thus, in this case, the size effect of the Pt nanoparticles on catalytic activity can be neglected and discussion will be on the bonding effect of Pt and MoS₂ with different Pt contents. The electrocatalytic metrics of the Pt/MoS₂ composites are summarized in **Figure 6-9d-f**. Detailed values can be found in **Table 6-4**. It can be seen that with Pt content increasing, the hybrid catalyst exhibits increased j_0 (**Figure 6-9e**), decreased onset overpotential (**Figure 6-9d**) and Tafel slope (**Figure 6-9f**).

Table 6-4. Summary of Pt/MoS₂ catalytic activity (onset overpotential, Tafel slope and exchange current density) for electrochemical water splitting process.

Catalyst	Onset overpotential (mV vs RHE)	Tafel slope (mV/dec)	Exchange current density ($\mu\text{A}/\text{cm}^{-2}$)
10mM Pt – 400C H ₂ 40min	9	44	373
1mM Pt – 400C H ₂ 40min	65	68	27
0.5mM Pt – 400C H ₂ 40min	68	74	15
0.1mM Pt – 400C H ₂ 40min	359	82	1.9
0.1mM Pt – 500C H ₂ 40min	130	65	0.7
1mM Pt – 500C H ₂ 40min	281	53	0.58
10mM Pt – 500C H ₂ 40min	122	31	1.54
0.1mM Pt – 600C H ₂ 40min	210	139	3.5
0.1mM Pt – 500C H ₂ 20min	103	84	1.9
0.1mM Pt – 500C H ₂ 80min	128	80	0.5

The onset overpotential represents the energy barrier for the catalyst surface to be activated to mediate HER. There is an obvious onset overpotential shift from MoS₂ to 0.11 wt% Pt/MoS₂, which implies the possible change of nature of the catalytic site. According to a previous study on Pt nanoparticles/MoS₂ nanosheets/carbon fiber hybrid system, the characteristic S2p peak shift from XPS measurements suggested the bonding effect between Pt and S and the accordingly changed electronic state density of S can enhance the catalytic activity of exposed Mo (catalytically active sites in MoS₂).⁽¹⁰⁾ It is worth noting that the onset overpotential at this point (0.11 wt%) is still much worse than Pt (~ 0 mV) and this indicates that at such loading level Pt has not yet come to play a dominant role in the catalytic process. When the Pt loading further increases from 0.11 wt% to 0.55 wt% and 1.1 wt%, the onset overpotential is observed to continue decreasing but with smaller extent (**Figure 6-9a** and **d**). This

phenomenon suggests that in the loading range of 0.11 wt% ~ 1.1 wt%, the Pt and S bonding effect enhances the activity of Mo and thus decrease the activation energy of HER. The loaded Pt particles start to contribute to the catalytic activity as well as the onset overpotential is moving towards the range of Pt/C catalyst (13 mV). Finally, when the Pt content reaches 11 wt%, the onset overpotential decreased to 9 mV, which is better than pure Pt/C (13 mV). The possible reason for the enhanced activity is the dual enhancement – highly dispersed Pt particles providing high specific surface area as well as the synergistic effect from the Pt and S bond that leads to the intrinsic improvement of Mo sites in MoS₂.

The Tafel plots of the as-received composites are shown in **Figure 6-9b** and f. The Tafel slope decreases from 166 to 44 mV/dec after loading with 11 wt% Pt. This indicates that in the Pt/MoS₂ system, hydrogen desorption is the RDS and HER proceeds through a combination of the Vomer-Heyrovsky and Volmer-Tafel mechanism; whereas hydrogen adsorption (Volmer reaction) is the RDS in pure MoS₂. It is therefore revealed that Pt contributes dominantly to the HER activity despite only 11 wt% content in the hybrid system. The increased j_0 normalized by the electrode area reflects the improved total electrode activity of Pt/MoS₂ with Pt content rising.

The comparison of HER activity of Pt/MoS₂ prepared at 400 °C and 500 °C is shown in **Figure 6-12a**. At 500 °C, the catalytic activity increases with increased Pt loading similarly to 400 °C. It should be also noticed that at the same Pt loading, the 400 °C Pt-MoS₂ always outperforms the 500 °C Pt-MoS₂ catalysts. This is due to the size effect that higher TA temperature leads to larger average Pt particle size and smaller

specific surface area (as discussed in **Figure 6-8**). Therefore, at the same Pt content, a higher annealing temperature results in fewer Pt surface active sites for HER.

In order to elucidate the role of H₂ in the TA process and HER activity of Pt/MoS₂, a control experiment was conducted by annealing the sample in Ar. It can be seen from the TEM images in **Figure 6-10** that there are barely Pt particles formed on the MoS₂ flakes under Ar (compared to H₂ annealing in **Figure 6-7** at the same precursor concentration, TA temperature and time), which reveals that H₂ ensures effective reduction of the Pt precursor and promotes Pt nanocrystal formation at the designated reaction temperature and time. The improvement of the H₂ annealed sample over the Ar annealed sample resulted mainly from thorough reducing and formation of Pt particles. H₂ induced catalytic activity improvement of MoS₂ could be excluded.

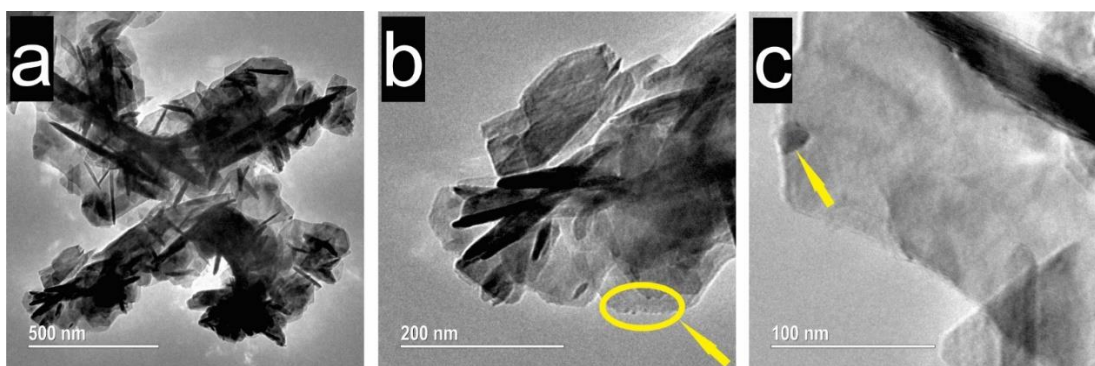


Figure 6-10. TEM images (accelerating voltage 200 kV) of Pt precursor coated MoS₂ thermal annealed in pure Ar gas (0.11 wt% Pt, 500 °C, 40min). Pt nanoparticles are formed in the circled area and indicated by the arrow.

The impact of MoS₂ as 3D scaffold is explained in **Figure 6-11**. Compared to Pt/MoS₂, the HER activity of pure Pt deposited on GC substrate is much lower, this

improvement is believed to be from the contribution of catalytic activity of MoS₂ and the nanostructured vertically standing MoS₂ layers aided the more dispersive growth of Pt nanoparticles. Despite MoS₂ is by nature semi-conductive, which brings additional ohmic loss to the electrode and in turn lowers the cathodic current density (i.e. hydrogen production), still the positive effect is more profound. Moreover, what's notable is that the polarization curve of pure Pt constantly fluctuates without MoS₂ construction platform. It is due to lack of MoS₂ high porosity network and superaerophobic surface, which allows fast removal of hydrogen gas bubbles and maintains the constant working area. This result proves that the as-designed cocatalyst Pt-MoS₂ is superior to either individual counterpart, catalytically and structurally.

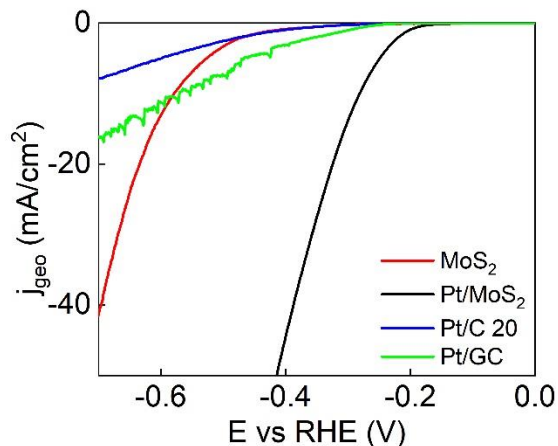


Figure 6-11. Comparison of HER activity of MoS₂, Pt/MoS₂, Pt/GC and Pt/C. Pt loading for was kept the same at 0.11 wt%. (LSV was conducted at scan rate of 1 mV/s in 0.5 M H₂SO₄ (aq))

The HER catalytic parameters of supported Pt catalysts from the literature are summarized in **Table 6-5**. It can be seen that the optimized Pt-MoS₂ (11 wt%, 400 °C) catalyst possesses an onset overpotential of 9 mV, which is amongst the best to my

best knowledge (2.7 ~ 188 mV).^(10, 11, 88, 130, 135, 169–175) The Tafel slope fits well with reported Pt-supported catalysts (27 ~ 85 mV/dec).^(10, 11, 88, 130, 135, 140, 144, 169–171, 173–176) The exchange current density of the Pt/MoS₂ is moderate compared to previous values (6.27 ~ 4420 $\mu\text{A}/\text{cm}^2$),^(11, 134, 135, 140, 169, 170, 173, 174, 176) mainly arising from the semiconducting nature of the MoS₂, which does not facilitate an good charge transfer rate.

Table 6-5. Summary of literature catalytic parameters towards HER of Pt supported catalysts. (Pt alloy systems not included)

Catalyst	Media	Pt loading ($\mu\text{g}/\text{cm}^2$)	Pt wt%	Electrochemical active surface area (m^2/g)	Onset overpotential (mV vs RHE)	Tafel slope (mV/decade)	j_0 -geometric ($\mu\text{A}/\text{cm}^2$)
Ultralow-Pt-loading bamboo-like nitrogen-doped carbon nanotubes (171)	0.5 M H ₂ SO ₄	Not reported	0.74 wt%	148.5	40	33	Not reported
Nitrogen-doped hollow porous carbon polyhedrons embedded with highly dispersed Pt nanoparticles (130)	0.1M HClO ₄	2.0	Not reported	516	2.7	27	Not reported
Ultrathin Pt Layer on Au-Nanoisland- Modified Si Photocathode (172)	0.1 M H ₂ SO ₄	Pt single layer	Not reported	Not reported	120	Not reported	Not reported
Single-Walled Carbon Nanotubes with Pseudo-Atomic-Scale Platinum (135)	0.5 M H ₂ SO ₄	0.114 - 0.570	Not reported	Not reported	27	38 - 40	1150 - 1940
Ultrafine Pt nanoparticles decorated MoS₂ nanosheets (173)	0.5 M H ₂ SO ₄	66	2.2 wt%	Not reported	31	52	256
Pt-MoOx/Mo (88)	KOH (pH14)	Not reported	Not reported	Not reported	24	58	Not reported
Pt nanocrystals on nitrogen-doped graphene (174)	Not reported	Not reported	5 wt%	1.69 cm ²	24	28	989
Multiple Carbon Nanotube Yarns and One Platinum Wire (175)	1 M KOH	Not reported	Not reported	Not reported	188	85	Not reported
Au(111)-Supported Pt Monolayer (176)	0.1M H ₂ SO ₄	Not reported	Not reported	0.0432 cm ²	Not reported	68	630

6 | Synthesis of Surface Grown Pt Nanoparticles on Edge-enriched MoS₂ Porous Thin Films for Enhancing Electrochemical Performance

Catalyst	Media	Pt loading (μg/cm ²)	Pt wt%	Electrochemical active surface area (m ² /g)	Onset overpotential (mV vs RHE)	Tafel slope (mV/decade)	j ₀ -geometric (μA/cm ²)
poly(a-terthiophene)-Pt nanoparticle hybrid material (polyTT-Pt)(169)	0.5 M H ₂ SO ₄	8550	2.9 wt%	35.7	67	37	280
Pt nanoparticles/MoS₂ nanosheets/carbon fiber(10)	0.5 M H ₂ SO ₄	Not reported	2 wt%	250.2 mF/g	5	53.6	Not reported
Pt/C with boron on the surface of support(138)	1M H ₂ SO ₄	Not reported	20 wt%	37	Not reported	Not reported	Not reported
Pt40/Vulcan XC-72(131)	1M H ₂ SO ₄	Not reported	40 wt%	40	Not reported	Not reported	Not reported
tungsten carbide-supported nano Platinum catalyst(134)	0.5 M H ₂ SO ₄	Not reported	16 wt%	Not reported	Not reported	Not reported	4420
Pt nanoparticle on Mos₂ Single layer(144)	0.5 M H ₂ SO ₄	27	36 wt%	Not reported	Not reported	40	Not reported
Films of SWCNTs and commercial platinum (Pt) blackweresequentially castonacarbon fiber electrode(CFE)(140)	0.5 M H ₂ SO ₄	1000	Not reported	30.8	Not reported	29	3290
Monolayer Platinum on Tungsten Monocarbide Substrates	0.5 M H ₂ SO ₄	Not reported	Not reported	Not reported	Not reported	Not reported	Not reported
Pt on Mo₂C(11)	0.1 M HClO ₄	Not reported	7.2 wt%	Not reported	40	38	6.27
Pt/C(170)	Not reported	Not reported	Not reported	Not reported	13	30	1220
Pt nanoparticle decorated MoS₂ vertical platelets (this work)	0.5 M H ₂ SO ₄	13	11 wt%	Not reported	9	44	373

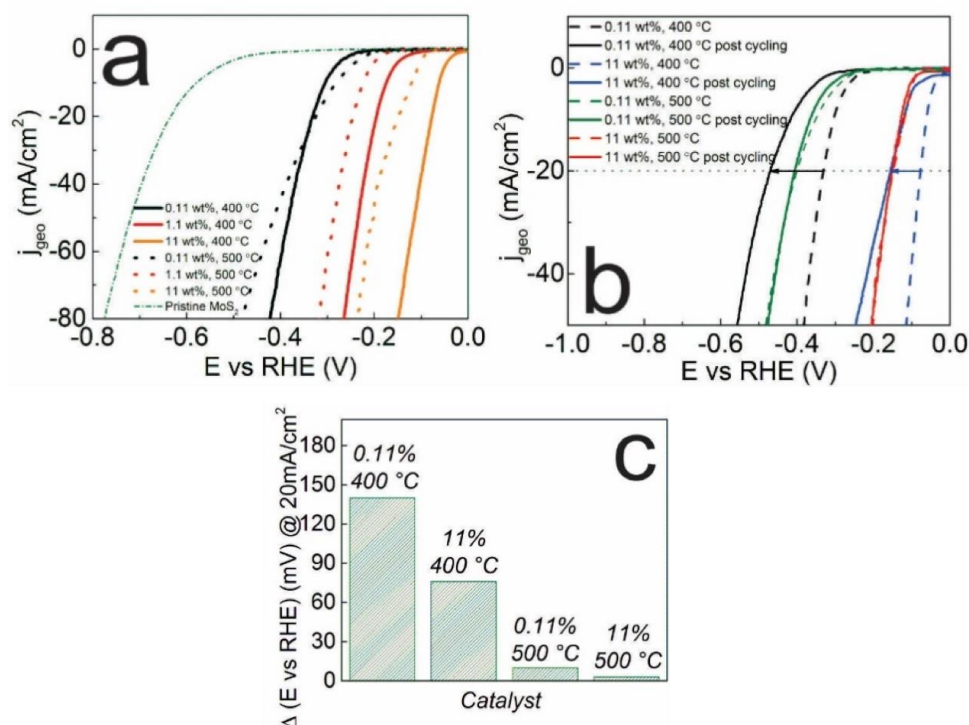


Figure 6-12. Influence of TA temperature on electrocatalytic activity and durability towards HER of the as-prepared Pt/MoS₂ catalysts. (a) Cathodic polarization curves of as-received Pt-MoS₂ catalysts on glassy carbon for different Pt wt% at 400 °C and 500 °C. (b) Influence of TA temperature on the electrocatalytic stability of Pt/MoS₂ catalysts. (c) Degradation analysis of Pt-MoS₂: overpotential increase (@ current density of 20mA/cm²) after stability test under different Pt loadings and TA temperatures. (LSV was conducted at scan rate of 1 mV/s in 0.5 M H₂SO₄ (aq))

The Pt/MoS₂ cocatalysts at high Pt loading (11 wt%) were subjected to stability treatment in acidic solution via linear sweep voltammetry with a fast scan rate of 100 mV/s for 10,000 cycles in order to simulate the working condition of practical water-splitting devices. The cathodic polarization curves and TEM images were recorded in **Figure 6-12b,c** and **Figure 6-13**, to monitor functional and microstructural changes before and after stability test. TEM images at low Pt loading (0.11 wt%) are shown in **Figure 6-14**.

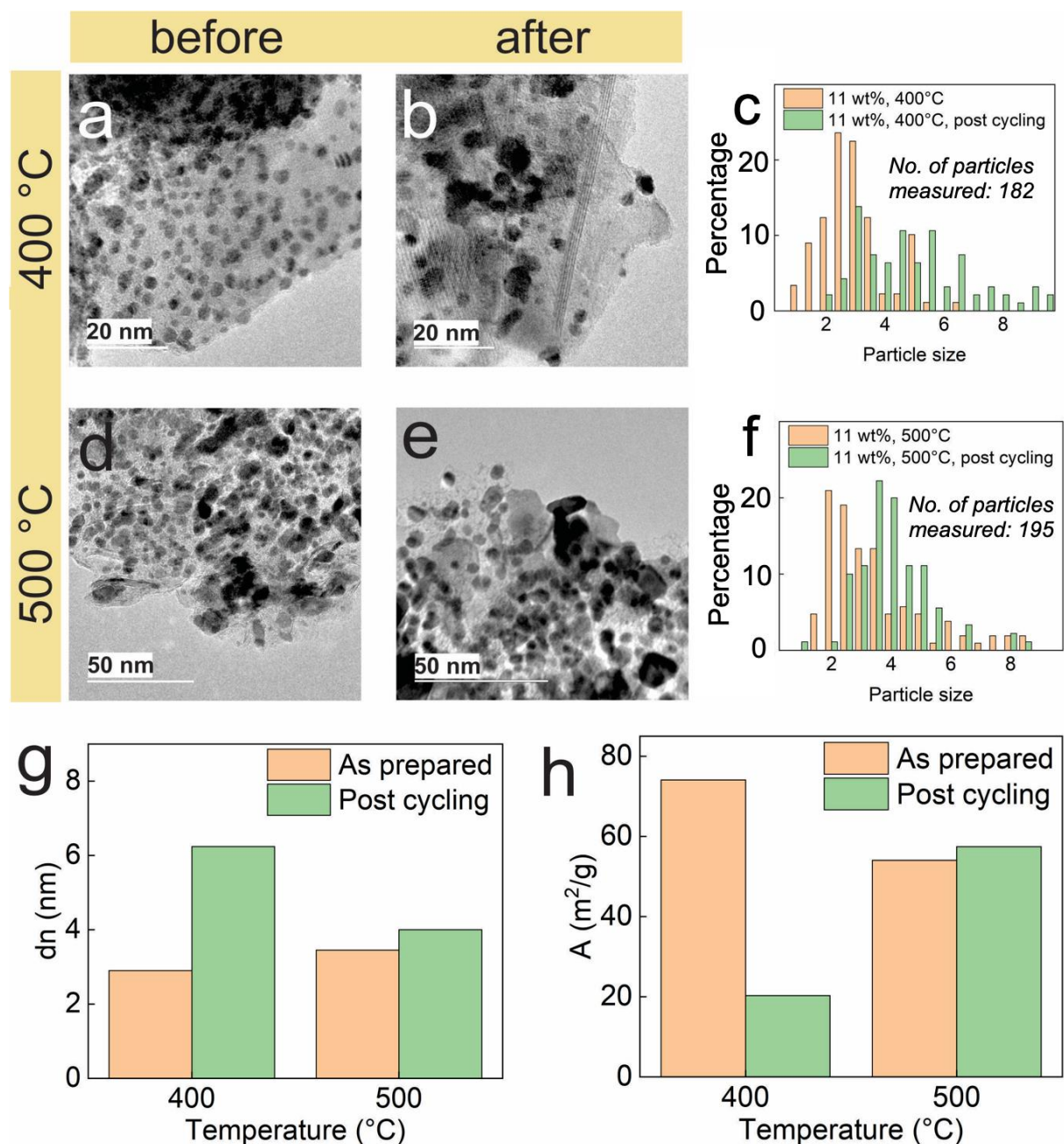


Figure 6-13. Structural degradation analysis of Pt/MoS₂ catalysts post 10,000 cycles. TEM images (accelerating voltage 200 kV) and Pt nanocrystal size histogram before and after stability test of the Pt/MoS₂ catalyst received at a TA temperature of (a-c) 400 °C and (d-f) 500 °C. (g) Number averaged particle size d_n and (h) specific surface area A degradation analysis before and after 10,000 cycles. (11 wt% Pt)

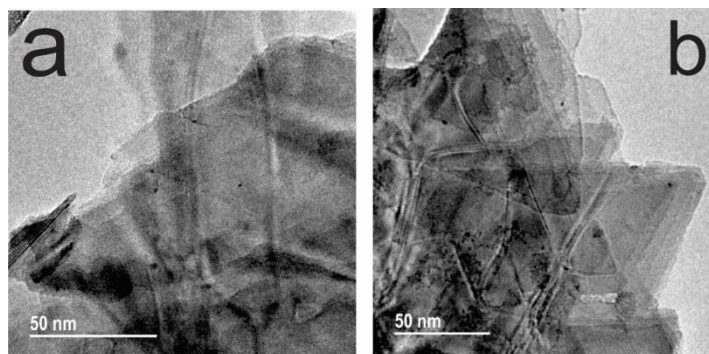


Figure 6-14. TEM images (accelerating voltage 200 kV) of the Pt-MoS₂ (a) before and (b) after 10,000 cycling treatment. (0.11 wt% Pt, TA 500 °C)

It can be seen from polarization curves of the catalysts before and after 10,000 cycles in **Figure 6-12b**, that in spite of the Pt content, 500 °C samples always exhibit better stability than 400 °C samples. In order to evaluate the degradation extent of the catalysts, the increase of overpotential required to reach current density of 20mA/cm² are extracted and summarized in **Figure 6-12c**. It demonstrates that at the same Pt loading, higher TA temperature leads to smaller degradation; at the same TA temperature, higher Pt loading leads to smaller degradation. The degradation of a nanoparticle catalyst is mainly caused by:

- 1) Nanoparticle sintering by Ostwald ripening (dissolution of metal atoms and recrystallization) or/and aggregation (thermal motion of particles);(136, 177)
- 2) Detachment of the nanoparticles from the support/electrode;
- 3) Corrosion of the support materials, in this case, MoS₂.

In order to understand the degradation determining factors and optimize further catalyst design, the microstructure of the post-cycled catalysts was studied by TEM microstructural analysis. Corresponding TEM images, Pt nanocrystal size d_n , and

specific surface area A histograms are shown in **Figure 6-13**. In good agreement with HER activity degradation, the average nanoparticle size increased from 2.9 nm to 6.2 nm and the specific surface area from 74 m²/g to 20 m²/g after cycling with the 400 °C sample. The average particle size and specific surface area of the 500 °C sample, on the other hand, stayed almost unaffected after 10,000 cycles. Firstly, as discussed before, the as-received 400 °C sample possesses a smaller average Pt particle size compared to the 500 °C sample and thus higher mobility and faster sintering. Secondly, lower TA temperature facilitates weaker bonding of Pt and Mo atoms, which will increase the migration and aggregation of Pt nanoparticles. Thirdly, lower TA temperature resulted in weaker Pt-Mo bond and tended to accelerate detachment of the Pt nanoparticles from its support/electrode. Due to the above three reasons, the 400 °C sample undergoes a faster sintering process than the 500 °C sample.

6.3 Conclusion

- In this work, I have demonstrated that an advanced hybrid catalyst of highly dispersive Pt nanocrystal grown on MoS₂ edge exposed nanoplatelet has been produced via CVD – TA method.
- The size distribution and specific surface area of Pt nanocrystals on MoS₂ were successfully controlled by tuning the Pt loading and TA parameters. It is found that when Pt wt% decreases from 11% to 0.11%, the number of Pt nanocrystals formed on the MoS₂ surface decreased accordingly. The nanoparticle distribution became less uniform on the surface of MoS₂. The average size of nanocrystals decreased and specific surface area increased. At the same Pt loading, higher TA

temperature delivers a larger average particle size and lower specific surface area.

My study demonstrated that the higher TA temperature resulted in a larger Pt particle size and a smaller initial HER activity but better long-term durability, due to the lower migration ability of larger particles and thus higher sintering resistance.

- In this hybrid catalyst system, MoS₂ contributes both functionally (*i.e.* catalytic activity benefitting from vertical alignment for enhanced high edge density) and structurally (*i.e.* porous and superaerophobic scaffold for Pt nanocrystal growth).
- The Pt/MoS₂ shows potential as a good HER catalyst for three reasons, firstly, 3D MoS₂ support promotes highly dispersive Pt nanoparticle growth; secondly, MoS₂ itself contributes to HER activity by providing active edge sites; thirdly, the Pt and S bonding effect leads to the possible enhanced activity of the active Mo sites. My work provides a new idea for optimization of microstructure and electrocatalytic functionalization in Pt/MoS₂ hybrid catalyst systems and provided a sensible route to promote the commercial viability of water electrolysis applications.

7 Conclusion and Outlook

7.1 Conclusion

As a promising energy carrier, H_2 plays a key role in a sustainable energy future by coupling to renewable energy sources. Development of cheap and efficient electrocatalysts for generation of H_2 *via* water electrolysis is one of the main challenges to widespread penetration of hydrogen energy technologies.⁽¹⁷⁸⁾ MoS_2 has been extensively utilized as an electrocatalyst for HER with edges as the primary active sites.⁽⁵⁾ Its layered structure by nature facilitates the possibility of low-dimensional nanostructure engineering,⁽⁶⁾ which could lead to enhanced active sites density and consequently advanced catalytic properties compared to its bulk counterpart.⁽¹⁷⁹⁾

- Based on the outlined strategy, the first study I have performed is the development of a reproducible and scalable synthesis method for high quality 3D-ER MoS_2 nanoplatelets utilizing a CVD method. Tailoring the CVD parameters led to an optimized MoS_2 structure for HER that consists of large MoS_2 platelets with smaller layered MoS_2 sheets growing off it in a perpendicular direction, which increases the total number of edge sites within a given geometric area. A surface area to geometric area ratio of up to ~ 340 is achieved, benefiting from the edge-exposed high porosity network. Optimized thickness of the MoS_2 film was determined for maximum

performance, revealing that increasing thickness leads to increased resistance of the MoS₂ film and reduced current density. The as-designed catalysts with edge-rich architecture and superaerophobic surface exhibit fairly good potential for HER catalysis by maximizing physical area utilization of electrodes. Furthermore, the knowledge accumulated in the precisely controllable structure and tunable catalytic properties of the 3D-ER MoS₂ provides an in-depth and transferrable strategy for the design of catalysts for different current density ranges.

- The 3D-ER-MoS₂ shows great potential as an HER catalyst. However, it has basal planes that are inactive. My research is then motivated by the pursuit of activation of basal planes by introducing defects using gas phase treatments. H₂ annealing and O₂ plasma etching of 3D-ER-MoS₂ are demonstrated to generate defects and increases active site density within the basal plane, leading to dramatic improvements in HER catalytic activity. The critical processing parameters for electrocatalytic enhancement are addressed. Both methods can increase the active sites density. The O₂ plasma treatment was more effective in increasing the number of edges by creating micro-cracks and local surface pits on the basal planes as well as structuring saw-toothed edges; H₂ etching mainly introduced irregular shaped basal surface nanopores and strips. Overall HER catalytic activity was more effectively enhanced by H₂ etching with the increased surface area as well as the generation of SVs in the basal planes, whereas O₂ plasma enhanced overall HER activity relies mainly on increased edge density. By controlling processing parameters, optimum surface area/active sites density enhancement can be achieved, together with

a robust 3D porous architecture and superaerophobic surface. The defect-rich MoS₂ catalysts exhibit excellent HER activity: 700 °C – H₂ – MoS₂ shows Tafel slope of 94 mV/dec and low onset overpotential of 193 mV; 15 min – O₂ – MoS₂ exhibits an exchange current density of 57 $\mu\text{A}/\text{cm}_{\text{geo}}^{-2}$. The defect engineered 3D-ER MoS₂ exhibits j_{geo} ($\eta=0.5$ mV) of 6-fold and 38-fold compared to monolayer MoS₂ subject to similar O₂ plasma and H₂ etching approaches, respectively. These results shall provide an effective way to realise high-performance Pt-free electrocatalysts by dual enhancement via edge enrichment and basal surface activation.

- So far, the thesis has focused solely on enhancing the HER activity of 3D-ER MoS₂. Considering high surface area 3D MoS₂ holds promise as a deposition support for highly dispersed Pt particles. A small amount of Pt grown on the MoS₂ basal surface can enhance the HER activity of MoS₂, further investigation is thus motivated into constructing a hybrid catalyst by growing Pt nanocrystals on the surface of 3D-ER MoS₂ via a CVD-TA approach. The hybrid material shows promising results as an electrocatalyst for HER. By varying the Pt synthesis condition - precursor loading and TA temperature - the deposition sites, size and morphology of Pt nanostructures can be controlled. The size effect of the Pt nanoparticles on catalytic activity and sintering resistance is discussed. Results show that higher Pt loading yields better HER performance despite smaller specific surface area. Higher TA temperature delivers a larger average particle size of Pt crystals and lowers HER activity. Larger average size leads to fast sintering and thus poor durability of the

catalyst. The optimized Pt-MoS₂ catalyst (400 °C, 11 wt%) reported in this study possesses a superior overpotential of 9 mV (close to zero), Tafel slope of 44mV/dec and moderate exchange current density of 373 $\mu\text{A}/\text{cm}^2$; it also exhibits activity degradation of 140 mV @ 20mA/cm² after 10,000 cycles. The outstanding HER activity is attributed to highly-dispersed Pt nanoparticles grown on MoS₂ basal surfaces, large MoS₂ edge density and Pt – S bonding effect induced activity improvement of MoS₂, as well as 3D porous network assisted superaerophobic surface. Benefitting from the correlation between HER performance and growth behaviors of Pt on MoS₂ surfaces, the optimal route for a highly active and stable co-catalyst can be established.

In conclusion, the novel research in this thesis has been presented with regard to three major areas. Each was given a dedicated focus for one chapter. **Chapter 4** established a versatile CVD method to produce 3D-ER MoS₂ thin films for enhanced HER catalytic activity. **Chapter 5** developed gas phase defect treatments to controllably activate the basal surfaces in 3D-ER MoS₂ to further improve the HER performance. **Chapter 6** synthesized Pt nanoparticles on 3D-ER MoS₂ thin films and constructed highly effective composites with minimized Pt loading. The bespoke CVD and post-growth approaches open up the reliable and scalable way for MoS₂ thin film based catalyst design. The resultant unique 3D-ER porous architectures extend the promise to a cross-referable material platform to expand the applications of TMD materials towards new areas.

7.2 Outlook

This thesis work devoted to nanostructured MoS₂ thin film based HER electrocatalysts can be developed further along the following directions:

In this thesis, the CVD method was exploited as an effective approach to design and produce materials of desired morphology and structure. Success has been gained in reproducible synthesis of 3D-ER structure with similar flake size and film thickness. Yet such as-prepared thin films of similar morphology and structure did not yield completely consistent HER activity. Further attempts should be put into improving the HER activity consistency of the CVD synthesized products.

Regarding the catalytic activity evaluation, current emphasis has been put on cathodic polarization measurement as well as Tafel slope and exchange current density evaluation. In future, H₂ gas production should be measured, in order to gain a full idea of the water splitting efficiency.

Although, the research projects reported in this thesis, focusing on synthesizing novel HER active structures, provide well-defined models to bridge realistic catalytic system and previous theoretical predictions, deepened insights should be gained into the fundamental electrochemical mechanisms behind the catalytic reaction, identifying the detailed active structure and intrinsic activity per site. For this purpose, *in situ* characterisations and calculations should be conducted.

As to the pristine 3D-ER MoS₂ porous thin film, in spite of high real surface area and fairly good total electrode activity, the Tafel slope and exchange current density are not among the best in the literature. The limiting factor lies in the semiconducting

nature of 2H-MoS₂. The active site density and conductivity is contradictory. Nanostructure can increase the edge density but may further decrease conductivity due to slow interparticle and interdomain electron transport. Approaches to improve the conductivity are speculated to boost the HER activity. Post-growth intercalation could potentially be an option, by which the 2H → 1T transformation will be triggered. This will enable us to construct a highly active electrode by a combination of fully active materials as well as maximized usage of the physical area of the electrode.

In addition, defect engineering of 3D-ER MoS₂ needs to be further extended by using H₂ plasma treatment. This could possibly enable dual enhancements because a plasma is more effective to increase edges at the atomic level and H₂ treatment can generate SVs as a new type of active sites.

Lastly, regarding Pt/MoS₂ composite catalysts, the work has been conducted on Pt nanoparticles grown on MoS₂. Further work should involve preparation of atomic level Pt doping on 3D-ER MoS₂. In this way, the activation of 2H-MoS₂ basal planes will rely on an ultra-low amount of Pt. Consequently, a fully active MoS₂ catalyst system can be realised in a much more economical way.

Appendix

Supporting Information on Chapter 4

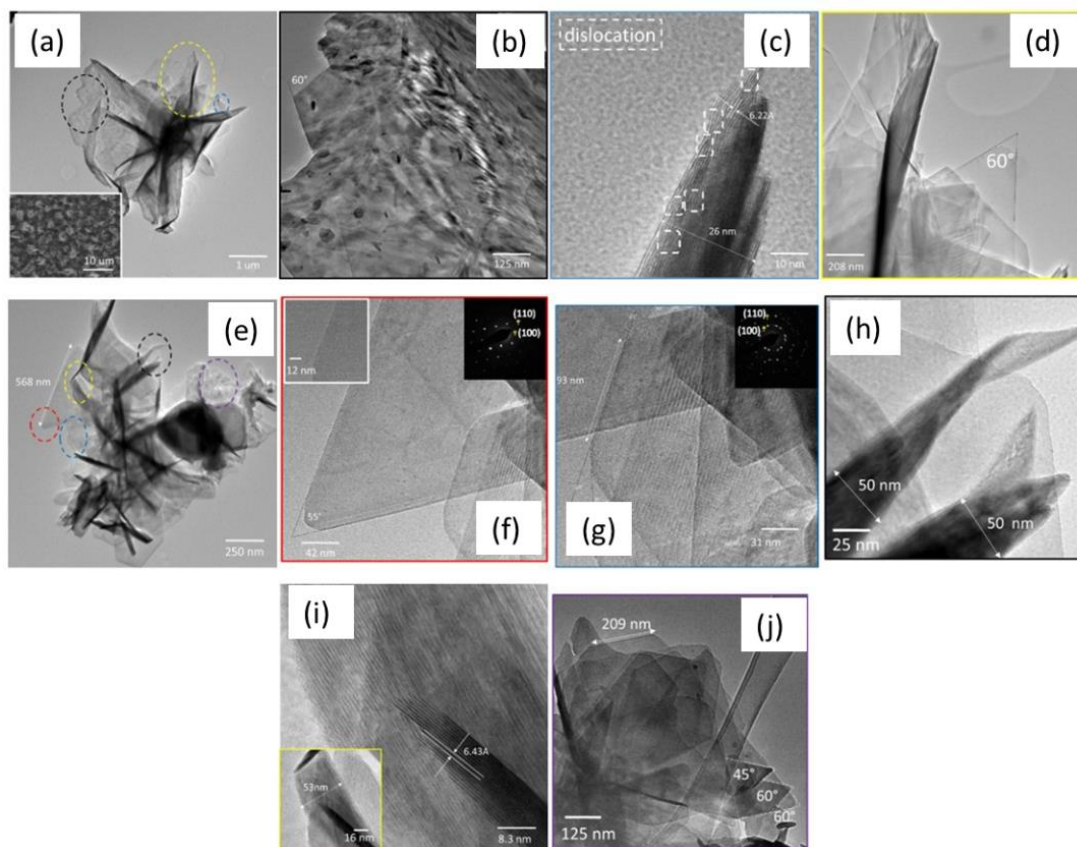


Figure A1. (a-j) TEM images of as-deposited samples at growth temperature of 866 °C. Inset in (a): SEM image of the thin film; insets in (f) left: zoomed in area of the edge and right: diffraction pattern of the imaged area; inset in (g): diffraction pattern of the imaged area; inset in (i): low magnification TEM image of the corresponding area.

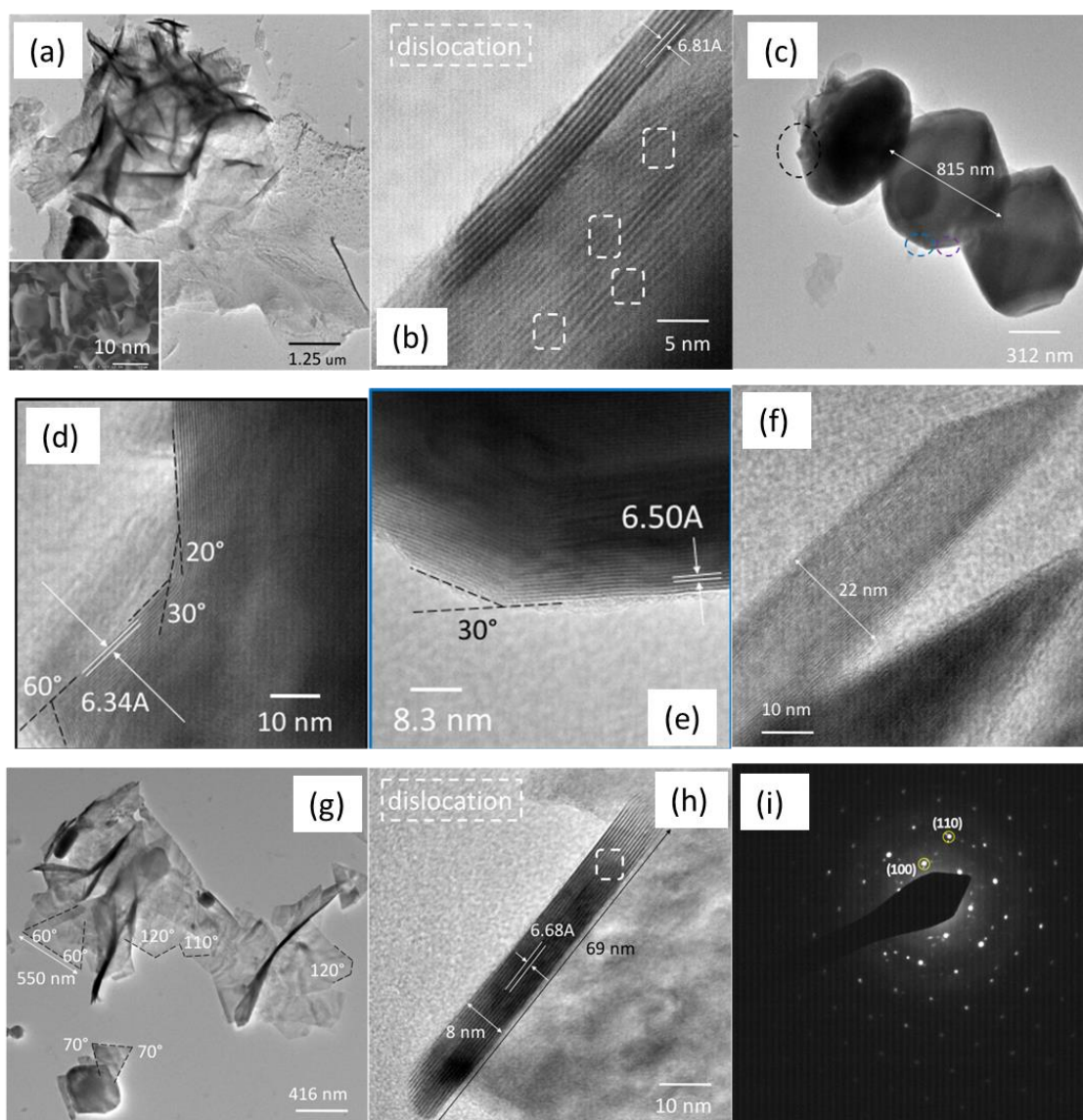


Figure A2. (a-h) TEM images of as-deposited samples at growth temperature of 900 °C. Inset in (a): SEM image of the sample. (i) The electron diffraction pattern of the multi-layered area of the sample.

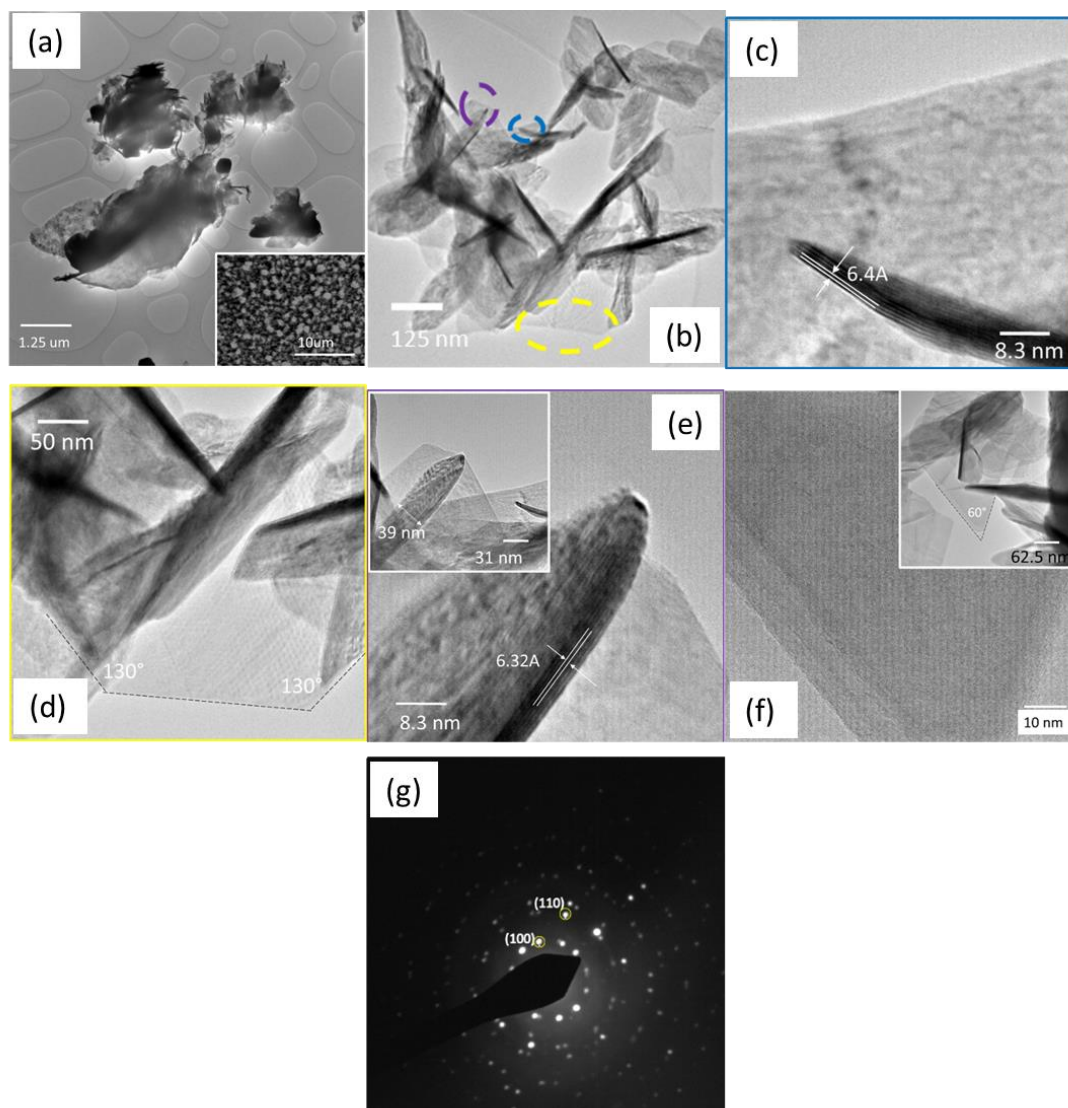


Figure A3. (a-f) TEM images of as-deposited samples under 60 min/866 °C. Inset in (a): SEM image of the sample; insets in (e and f): low magnification images of the corresponding areas. (g) The electron diffraction pattern of the sample in the multi-layered area.

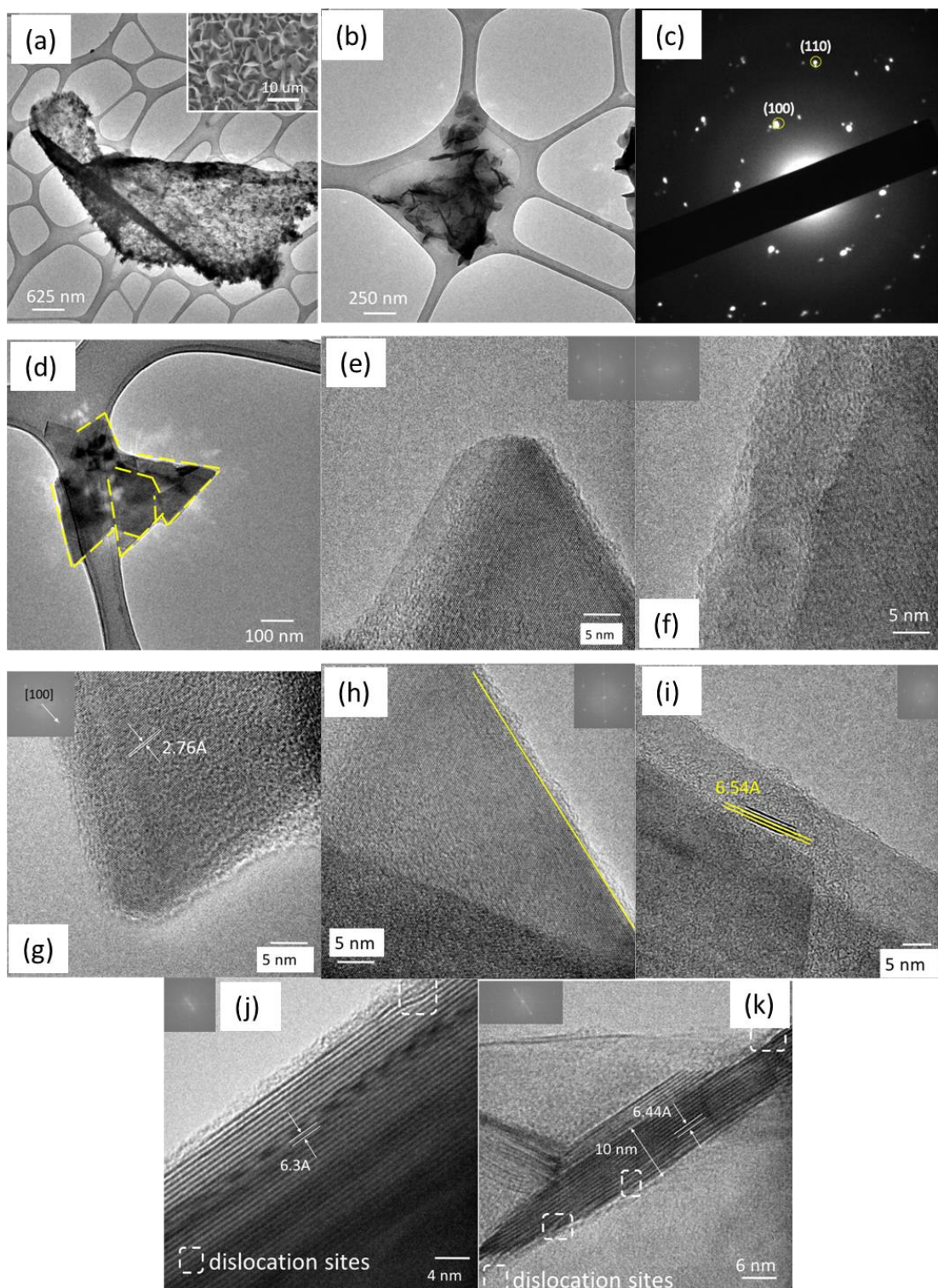


Figure A4. (a, b and d-k) TEM images of as-deposited samples under 100 min/866 °C. Inset in (a): SEM image of the sample; insets in (e-k) fast Fourier transform (FFT) of the corresponding TEM images. (c) The electron diffraction pattern of the multi-layered area of the sample.

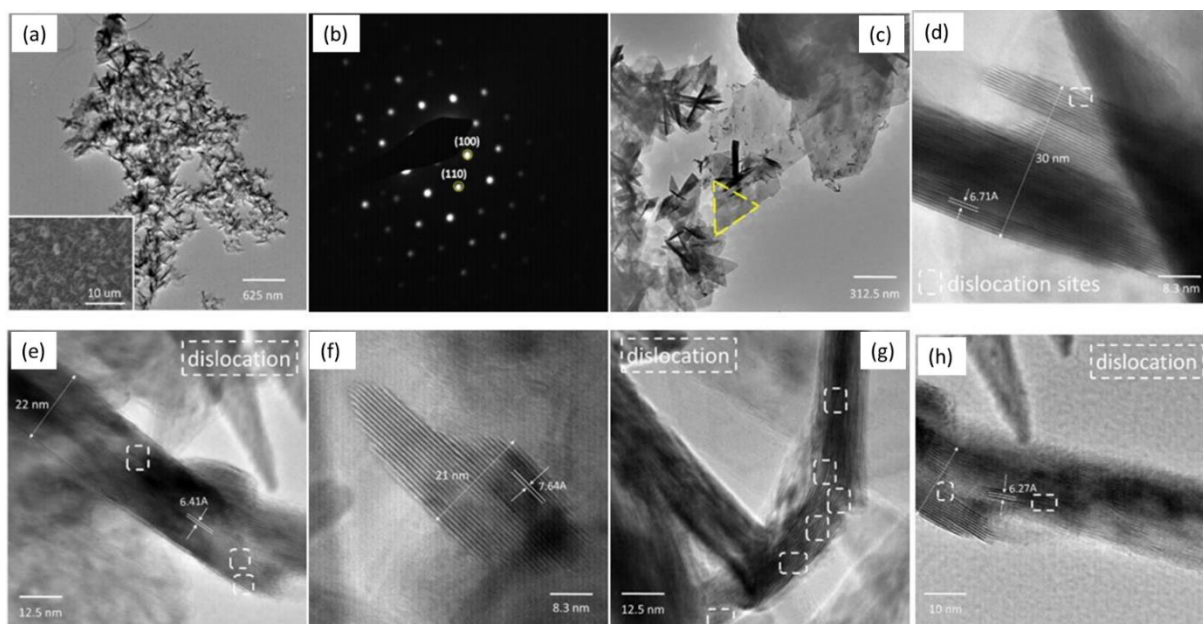


Figure A5. (a and c-h) TEM images of as-deposited samples under 60 min/900 °C. Inset in (a): SEM image of the sample. (b) The electron diffraction pattern of monolayer area of the sample.

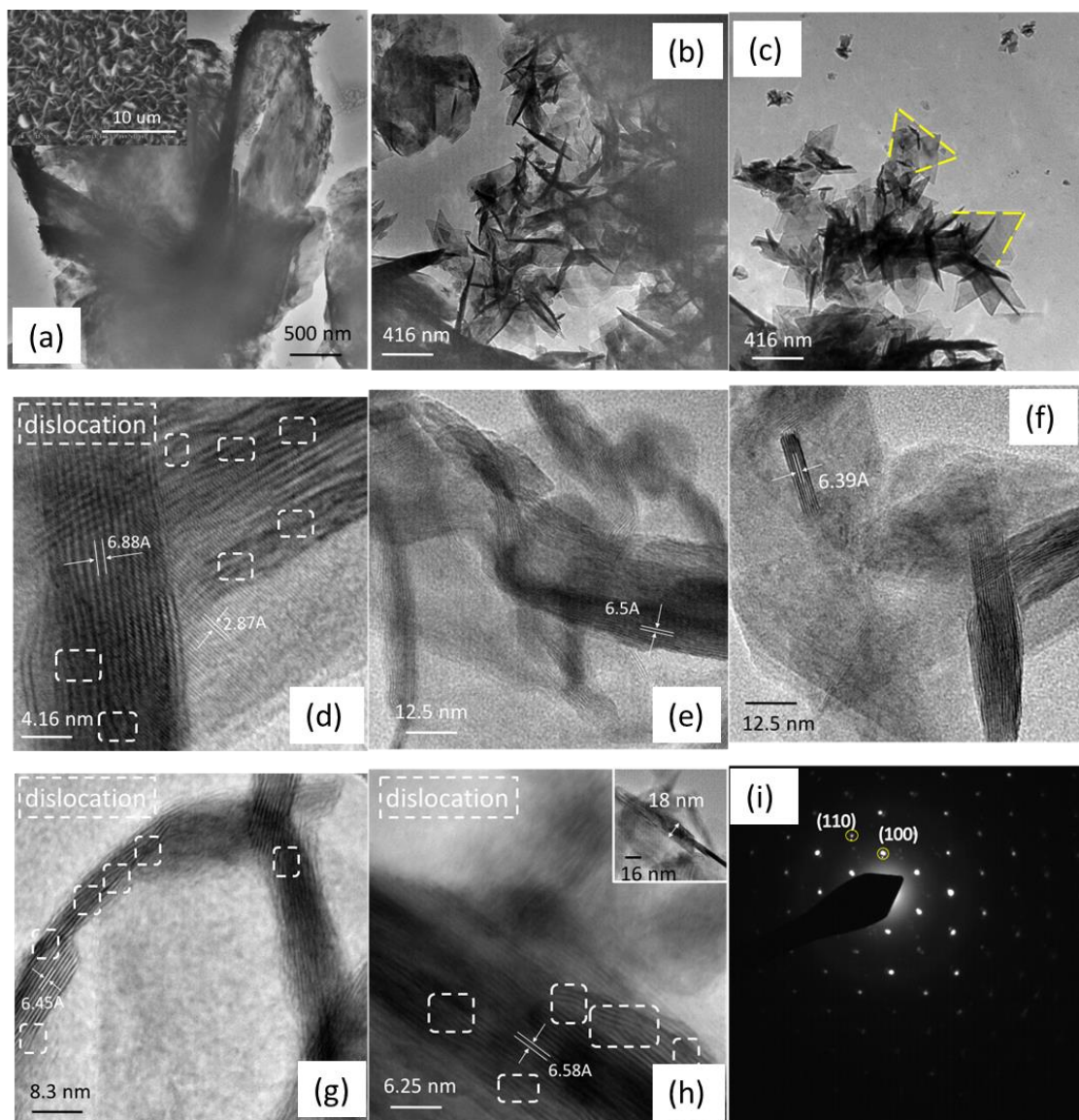


Figure A6. (a-h) TEM images of as-deposited samples with 600 mg MoO₃. Inset in (a): SEM image of the sample; inset in (h) low magnification image of the corresponding area. (i) The electron diffraction pattern of monolayer area of the sample.

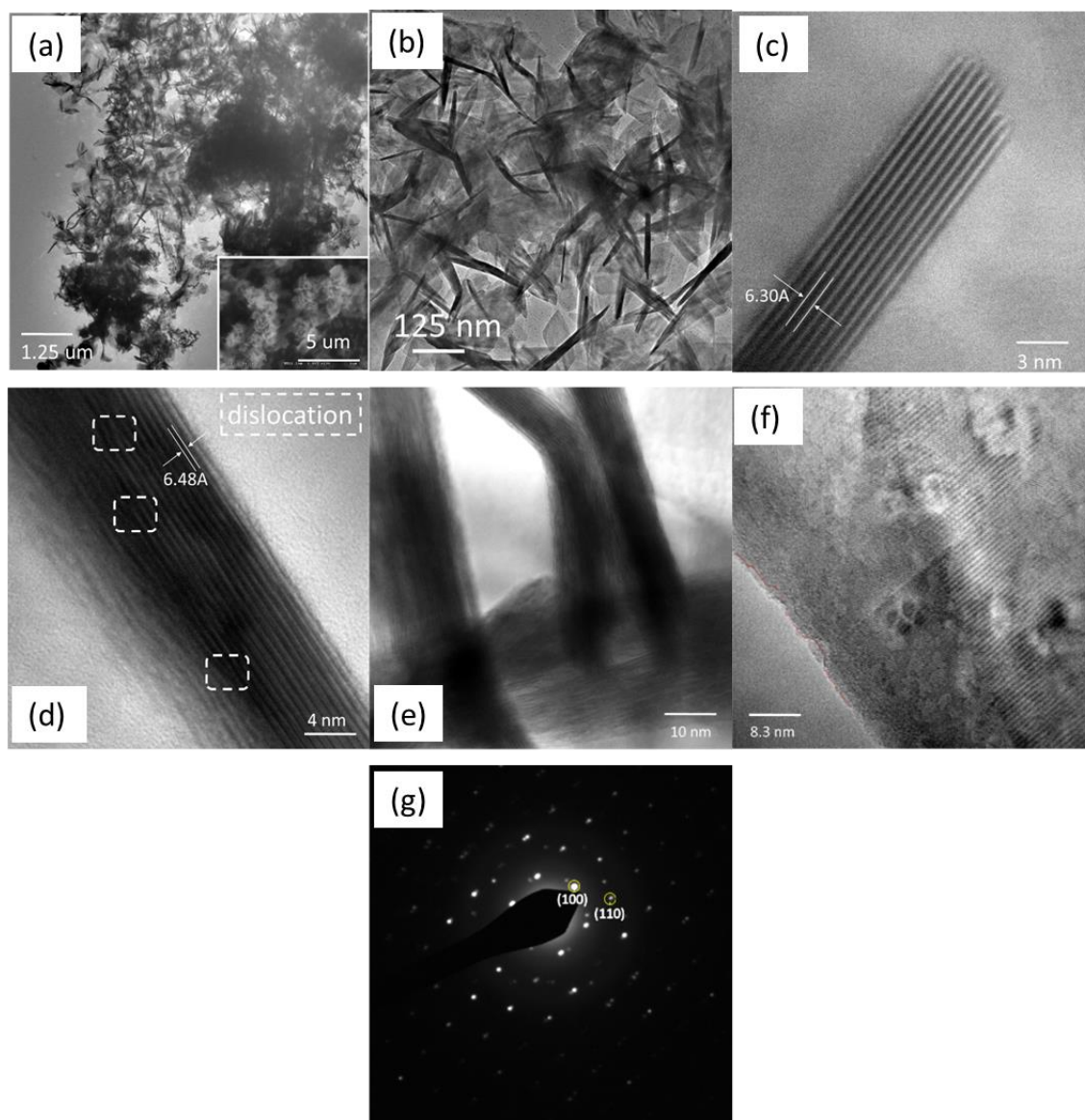


Figure A7. (a-f) TEM images of as-deposited samples with 800 mg MoO₃. Inset in (a): SEM image of the sample. (g) The electron diffraction pattern of the sample in the multi-layered area.

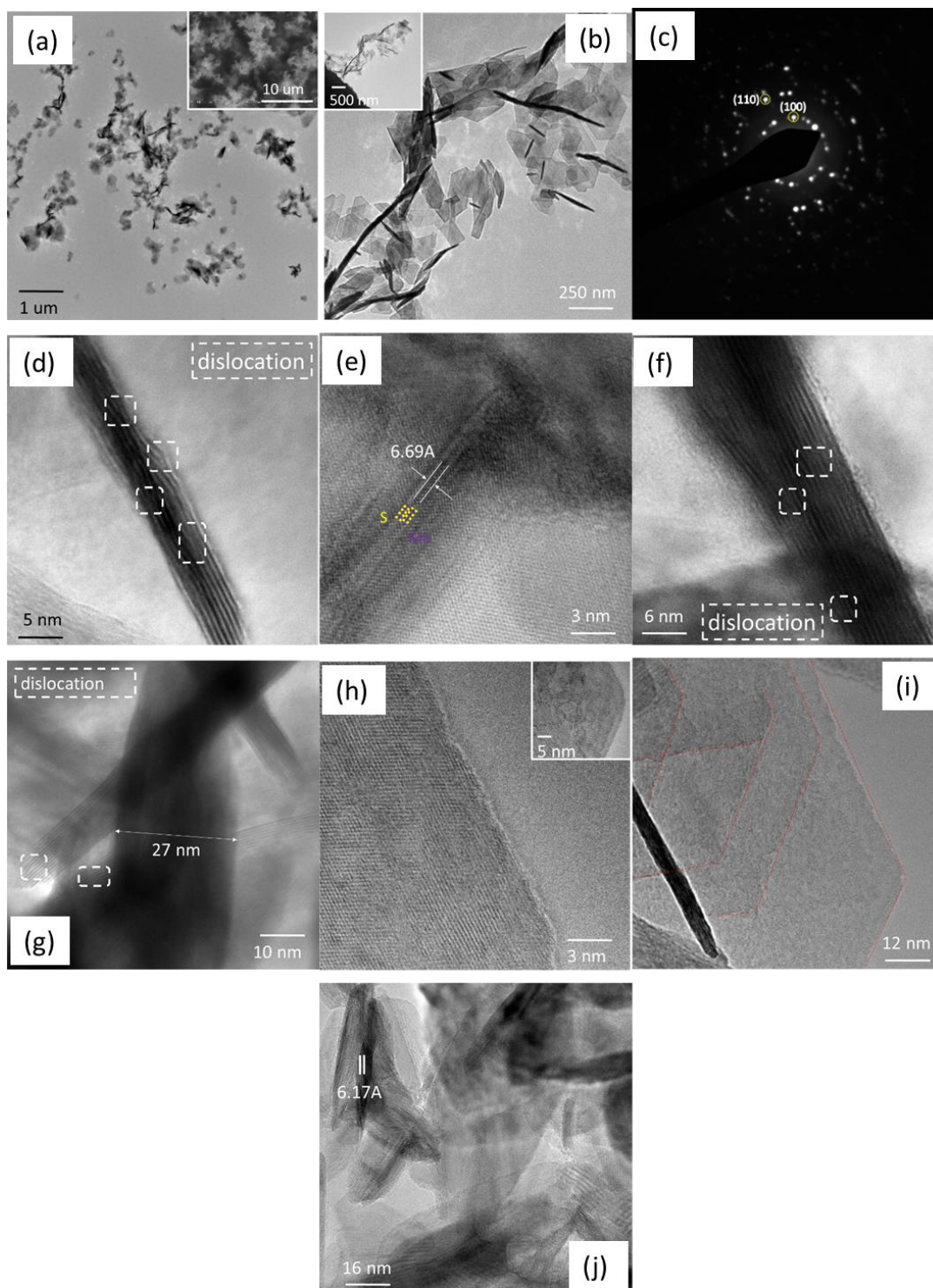


Figure A8. (a-b and d-j) TEM images of as-deposited samples with 1000 mg MoO₃. Inset in (a): SEM image of the sample; insets in (b and h): low magnification images of the corresponding areas. (c) The electron diffraction pattern of the sample in the multi-layered area.

Supporting Information on Chapter 5

Table B1. Plasma treatment recipes for MoS₂ materials from literature.

Material	Power/W	Pressure			Time/s	Gas
		mbar	Pa	Torr		
Thin film(110)	100	0.4	40	0.3	0-720	Oxygen/Argon
Monolayer(121)	100	0.4	40	0.25-0.35	0-6	Oxygen 30%, argon 80%
Monolayer(114)	100	0.33	33	0.25	0-6	Oxygen 30%, argon 80%
Monolayer(180)	25	0.26	26	0.2	5	Argon
Monolayer(92)	300	13.33	1333	10	0-30	Oxygen
Few layer (20 nm)(49)	30-50	0.007	0.7	-	300	Nitrogen

Supporting Information on Chapter 6

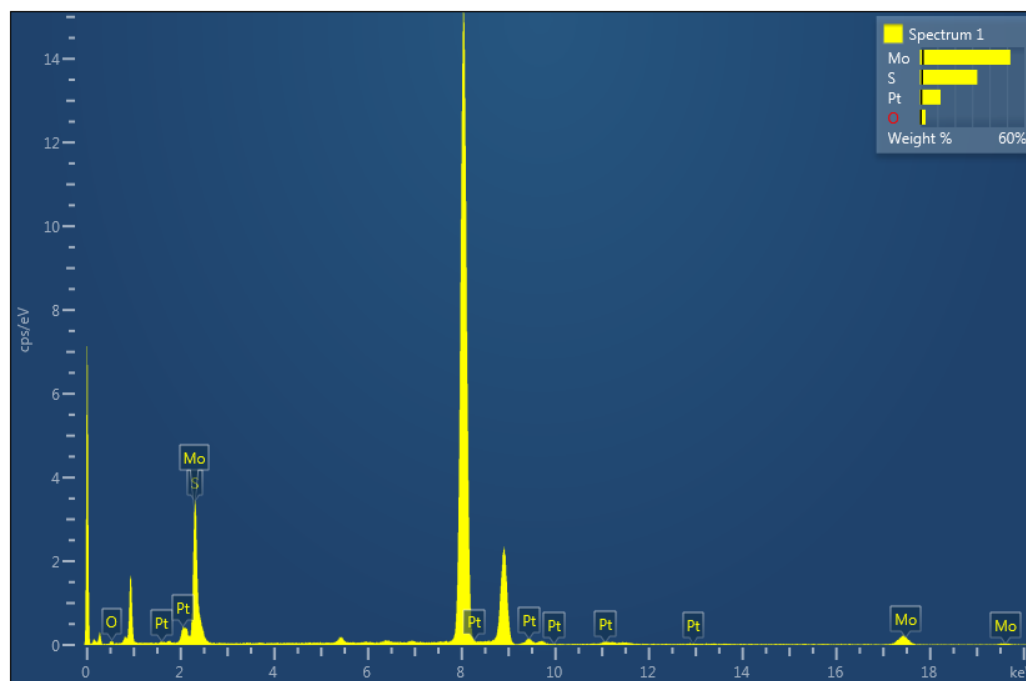


Figure C1. EDX spectrum of Pt-MoS₂ catalyst synthesized with 10 mM H₂PtCl₆·6H₂O:ethanol, annealed at 400 °C for 40 min.

References

1. J. Ohi, Hydrogen energy cycle: An overview. *J. Mater. Res.* **20**, 3180–3187 (2005).
2. W. Won *et al.*, Design and operation of renewable energy sources based hydrogen supply system: Technology integration and optimization. *Renew. Energy*. **103**, 226–238 (2017).
3. R. J. Toh *et al.*, Catalytic properties of group 4 transition metal dichalcogenides (MX_2 ; M = Ti, Zr, Hf; X = S, Se, Te). *J. Mater. Chem. A*. **4**, 18322–18334 (2016).
4. J. K. Nørskov *et al.*, Trends in the exchange current for hydrogen evolution. *J. Electrochem. Soc.* **152**, J23 (2005).
5. T. F. Jaramillo *et al.*, Identification of active edge sites for electrochemical H_2 evolution from MoS_2 nanocatalysts. *Science*. **317**, 100–102 (2007).
6. Z. W. She *et al.*, Combining theory and experiment in electrocatalysis: Insights into materials design. *Science*. **355**, 146 (2017).
7. N. Abas *et al.*, Review of fossil fuels and future energy technologies. *Futures*. **69**, 31–49 (2015).
8. H. Vrubel *et al.*, Revealing and accelerating slow electron transport in amorphous molybdenum sulphide particles for hydrogen evolution reaction. *Chem. Commun.* **49**, 8985 (2013).

9. A. B. Laursen *et al.*, A high-porosity carbon molybdenum sulphide composite with enhanced electrochemical hydrogen evolution and stability. *Chem. Commun.* **49**, 4965–7 (2013).
10. D. Hou *et al.*, Pt nanoparticles/MoS₂ nanosheets/carbon fibers as efficient catalyst for the hydrogen evolution reaction. *Electrochim. Acta.* **166**, 26–31 (2015).
11. Y. N. Regmi *et al.*, Carbides of group IVA, VA and VIA transition metals as alternative HER and ORR catalysts and support materials. *J. Mater. Chem. A.* **3**, 10085–10091 (2015).
12. F. M. Sapountzi *et al.*, Electrocatalysts for the generation of hydrogen, oxygen and synthesis gas. *Prog. Energy Combust. Sci.* **58**, 1–35 (2017).
13. S. Anantharaj *et al.*, Recent trends and perspectives in electrochemical water splitting with an emphasis on sulfide, selenide, and phosphide catalysts of Fe, Co, and Ni: A Review. *ACS Catal.* **6**, 8069–8097 (2016).
14. I. Roger *et al.*, Earth-abundant catalysts for electrochemical and photoelectrochemical water splitting. *Nat. Rev. Chem.* **1**, 0003 (2017).
15. C. Jiang *et al.*, Photoelectrochemical devices for solar water splitting-materials and challenges. *Chem. Soc. Rev.* **46**, 4645–4660 (2017).
16. P. Atkins *et al.*, *Physical chemistry* (Oxford University Press, 2006).
17. A. J. Bard *et al.*, *Electrochemical methods fundamentals and applications* (John Wiley & Sons, 1944).

18. C. G. Morales-Guio *et al.*, Nanostructured hydrotreating catalysts for electrochemical hydrogen evolution. *Chem. Soc. Rev.* **43**, 6555 (2014).
19. J. Su *et al.*, Synthesis and application of transition metal phosphides as electrocatalyst for water splitting. *Sci. Bull.* **62**, 633–644 (2017).
20. Y. P. Zhu *et al.*, Ultrafine Metal Phosphide Nanocrystals in Situ Decorated on Highly Porous Heteroatom-Doped Carbons for Active Electrocatalytic Hydrogen Evolution. *ACS Appl. Mater. Interfaces.* **7**, 28369–28376 (2015).
21. H. Li *et al.*, Atomic structure and dynamics of single platinum atom interactions with monolayer MoS₂. *ACS Nano.* **11**, 3392–3403 (2017).
22. S. S. Chou *et al.*, Understanding catalysis in a multiphasic two-dimensional transition metal dichalcogenide. *Nat. Commun.* **6**, 1–8 (2015).
23. Y. Zheng *et al.*, Hydrogen evolution by a metal-free electrocatalyst. *Nat. Commun.* **5**, 1–8 (2014).
24. R. Parsons, The rate of electrolytic hydrogen evolution and the heat of adsorption of hydrogen. *Trans. Faraday Soc.* **54**, 1053–1063 (1958).
25. J. D. Benck *et al.*, Catalyzing the hydrogen evolution reaction (HER) with molybdenum sulfide nanomaterials. *ACS Catal.* **4**, 3957–3971 (2014).
26. Y. Yan *et al.*, Recent development of molybdenum sulfides as advanced electrocatalysts for hydrogen evolution reaction. *ACS Catal.* **4**, 1693–1705 (2014).
27. D. M. F. Santos *et al.*, Hydrogen production by alkaline water electrolysis. *Quim.*

Nova. **36**, 1176–1193 (2013).

28. A. Maljusch *et al.*, Revealing onset potentials using electrochemical microscopy to assess the catalytic activity of gas-evolving electrodes. *Electrochem. commun.* **38**, 142–145 (2014).
29. X. Zou *et al.*, Noble metal-free hydrogen evolution catalysts for water splitting. *Chem. Soc. Rev.* **44**, 5148–5180 (2015).
30. Z. Jin *et al.*, Three-dimensional amorphous tungsten-doped nickel phosphide microsphere as an efficient electrocatalyst for hydrogen evolution. *J. Mater. Chem. A.* **2**, 18593–18599 (2014).
31. J. Juodkazytė *et al.*, Solar water splitting: Efficiency discussion. *Int. J. Hydrogen Energy.* **41**, 11941–11948 (2016).
32. G. Li *et al.*, All the catalytic active sites of MoS₂ for hydrogen evolution. *J. Am. Chem. Soc.* **138**, 16632–16638 (2016).
33. A. Imre *et al.*, Electrochemical determination of the fractal dimension of fractured surfaces. *Acta Metall.* **40**, 1819–1826 (1992).
34. J. C. Myland *et al.*, Cottrell's equation revisited: An intuitive, but unreliable, novel approach to the tracking of electrochemical diffusion. *Electrochem. commun.* **6**, 344–350 (2004).
35. M. Chhowalla *et al.*, The chemistry of two-dimensional layered transition metal dichalcogenide nanosheets. *Nat. Chem.* **5**, 263–275 (2013).
36. B. Radisavljevic *et al.*, Single-layer MoS₂ transistors. *Nat. Nanotechnol.* **6**, 147–

50 (2011).

37. I. Song *et al.*, Synthesis and properties of molybdenum disulphide: from bulk to atomic layers. *RSC Adv.* **5**, 7495–7514 (2015).
38. D. Kong *et al.*, Synthesis of MoS₂ and MoSe₂ films with vertically aligned layers. *Nano Lett.* **13**, 1341–1347 (2013).
39. S. Wang *et al.*, Atomic structure of defects and dopants in 2D layered transition metal dichalcogenides. *Chem. Soc. Rev.* **47**, 6764-6794 (2018),.
40. H. Wang *et al.*, High electrochemical selectivity of edge versus terrace sites in two-dimensional layered MoS₂ materials. *Nano Lett.* **14**, 7138–7144 (2014).
41. M. Asadi *et al.*, Robust carbon dioxide reduction on molybdenum disulphide edges. *Nat. Com.* **5**, 4470 (2014).
42. F. Wypych *et al.*, 1T-MoS₂, a new metallic modification of molybdenum disulfide. *J. Chem. Soc. Chem. Commun.* **1884343**, 1386–1388 (1992).
43. H. Wang *et al.*, Physical and chemical tuning of two-dimensional transition metal dichalcogenides. *Chem. Soc. Rev.* **44**, 2664–80 (2015).
44. X. Chia *et al.*, Layered transition metal dichalcogenide electrochemistry: journey across the periodic table. *Chem. Soc. Rev.* **47**, 5602-5613 (2018),.
45. T. Takeno *et al.*, Deposition and structural analyses of molybdenum-disulfide (MoS₂)-amorphous hydrogenated carbon (a-C:H) composite coatings. *Diam. Relat. Mater.* **19**, 548–552 (2010).
46. D. Bhaduri *et al.*, On tribological behaviour and application of TiN and MoS₂-Ti

composite coating for enhancing performance of monolayer cBN grinding wheel. *Wear.* **268**, 1053–1065 (2010).

47. X. Z. Ding *et al.*, Tribological properties of Cr- and Ti-doped MoS₂ composite coatings under different humidity atmosphere. *Surf. Coatings Technol.* **205**, 224–231 (2010).
48. R. Gadow *et al.*, Composite coatings with dry lubrication ability on light metal substrates. *Surf. Coatings Technol.* **151–152**, 471–477 (2002).
49. T.-H. Su *et al.*, Effects of nitrogen plasma treatment on the electrical property and band structure of few-layer MoS₂. *Appl. Phys. Lett.* **108**, 033103 (2016).
50. J. Guo *et al.*, Synthesis of graphene-like MoS₂ nanowall/graphene nanosheet hybrid materials with high lithium storage performance. *Catal. Today.* **246**, 165–171 (2015).
51. L. Chen *et al.*, MoS₂/graphene nanocomposite with enlarged interlayer distance as a high performance anode material for lithium-ion battery. *J. Mater. Res.* **31**, 3151–3160 (2016).
52. T. Stephenson *et al.*, Lithium ion battery applications of molybdenum disulfide (MoS₂) nanocomposites. *Energy Environ. Sci.* **7**, 209–231 (2014).
53. Y. Teng *et al.*, MoS₂ nanosheets vertically grown on graphene sheets for lithium-ion battery anodes. *ACS Nano.* **10**, 8526–8535 (2016).
54. J. Z. Wang *et al.*, Development of MoS₂-CNT composite thin film from layered MoS₂ for lithium batteries. *Adv. Energy Mater.* **3**, 798–805 (2013).

55. C. Zhai *et al.*, Two dimensional MoS₂/graphene composites as promising supports for Pt electrocatalysts towards methanol oxidation. *J. Power Sources*. **275**, 483–488 (2015).
56. D. Lin *et al.*, Fast preparation of MoS₂ nanoflowers decorated with platinum nanoparticles for electrochemical detection of hydrogen peroxide. *RSC Adv.* **6**, 52739–52745 (2016).
57. L. Yuwen *et al.*, General synthesis of noble metal (Au, Ag, Pd, Pt) nanocrystal modified MoS₂ nanosheets and the enhanced catalytic activity of Pd–MoS₂ for methanol oxidation. *Nanoscale*. **6**, 5762–5769 (2014).
58. H. Tributsch *et al.*, Electrochemistry and photochemistry of MoS₂ layer crystals. I. *J. Electroanal. Chem.* **81**, 97–111 (1977).
59. X. L. Fan *et al.*, Site-specific catalytic activity in exfoliated MoS₂ single-layer polytypes for hydrogen evolution: Basal plane and edges. *J. Mater. Chem. A*. **2**, 20545–20551 (2014).
60. C. Tsai *et al.*, Theoretical insights into the hydrogen evolution activity of layered transition metal dichalcogenides. *Surf. Sci.* **640**, 133–140 (2015).
61. P. Raybaud *et al.*, Ab Initio study of the H₂-H₂S/MoS₂ gas-solid interface: The nature of the catalytically active sites. *J. Catal.* **189**, 129 (2000).
62. H. Topsøe *et al.*, Future challenges of hydrotreating catalyst technology. *ACS Div. Fuel Chem. Prepr.* **49**, 568–569 (2004).
63. H. Li *et al.*, Activating and optimizing MoS₂ basal planes for hydrogen evolution

- through the formation of strained sulphur vacancies. *Nat. Mater.* **15**, 48–53 (2016).
64. C. Tsai *et al.*, Electrochemical generation of sulfur vacancies in the basal plane of MoS₂ for hydrogen evolution. *Nat. Commun.* **8**, 1–8 (2017).
 65. Q. Tang, D. Jiang, Mechanisms of hydrogen evolution reaction on 1T-MoS₂ from first principles. *ACS Catal.* **6**, 4953–4961 (2016).
 66. B. Hinnemann *et al.*, Biomimetic hydrogen evolution: MoS₂ nanoparticles as catalyst for hydrogen evolution. *J. Am. Chem. Soc.* **127**, 5308–5309 (2005).
 67. T. F. Jaramillo *et al.*, Identification of active edge sites for electrochemical H₂ evolution from MoS₂ nanocatalysts. *Science*. **317**, 100–102 (2007).
 68. D. B. Putungan *et al.*, A first-principles examination of conducting monolayer 1T'-MX₂ (M = Mo, W; X = S, Se, Te): promising catalysts for hydrogen evolution reaction and its enhancement by strain. *Phys. Chem. Chem. Phys.* **17**, 21702–21708 (2015).
 69. H. Wang *et al.*, Electrochemical tuning of MoS₂ nanoparticles on three-dimensional substrate for efficient hydrogen evolution. *ACS Nano*. **8**, 4940–4947 (2014).
 70. U. Maitra *et al.*, Highly effective visible-light-induced H₂ generation by single-layer 1T-MoS₂ and a nanocomposite of few-layer 2H-MoS₂ with heavily nitrogenated graphene. *Angew. Chemie - Int. Ed.* **52**, 13057–13061 (2013).
 71. H. Wang *et al.*, Electrochemical tuning of vertically aligned MoS₂ nanofilms and

- its application in improving hydrogen evolution reaction. *Proc. Natl. Acad. Sci. U. S. A.* **110**, 19701–19706 (2013).
72. M. A. Lukowski *et al.*, Enhanced hydrogen evolution catalysis from chemically exfoliated metallic MoS₂ nanosheets. *J. Am. Chem. Soc.* **135**, 10274–10277 (2013).
 73. H. Vrubel *et al.*, Hydrogen evolution catalyzed by MoS₃ and MoS₂ particles. *Energy Environ. Sci.* **5**, 6136 (2012).
 74. C. G. Morales-Guio *et al.*, Hydrogen evolution from a copper(I) oxide photocathode coated with an amorphous molybdenum sulphide catalyst. *Nat. Commun.* **5**, 3059 (2014).
 75. W. Chen *et al.*, Tuning the electronic and chemical properties of monolayer MoS₂ adsorbed on transition metal substrates. *Nano Lett.* **13**, 509–514 (2013).
 76. D. Voiry *et al.*, Enhanced catalytic activity in strained chemically exfoliated WS₂ nanosheets for hydrogen evolution. *Nat. Mater.* **12**, 850–855 (2013).
 77. Y. Yan *et al.*, Vertically oriented MoS₂ and WS₂ nanosheets directly grown on carbon cloth as efficient and stable 3-dimensional hydrogen-evolving cathodes. *J. Mater. Chem. A* **3**, 131–135 (2015).
 78. Z. Chen *et al.*, Core-shell MoO₃-MoS₂ nanowires for hydrogen evolution: A functional design for electrocatalytic materials. *Nano Lett.* **11**, 4168–4175 (2011).
 79. J. Kibsgaard *et al.*, Engineering the surface structure of MoS₂ to preferentially

- expose active edge sites for electrocatalysis. *Nat. Mater.* **11**, 963–969 (2012).
80. Y. Li *et al.*, MoS₂ nanoparticles grown on graphene: An advanced catalyst for the hydrogen evolution reaction. *J. Am. Chem. Soc.* **133**, 7296–7299 (2011).
81. D. Kong *et al.*, Synthesis of MoS₂ and MoSe₂ films with vertically aligned layers. *Nano Lett.* **13**, 1341–1347 (2013).
82. Z. Lu *et al.*, Ultrahigh hydrogen evolution performance of under-water “superaerophobic” MoS₂ nanostructured electrodes. *Adv. Mater.* **26**, 2683–2687 (2014).
83. J. Xie *et al.*, Defect-rich MoS₂ nanowall catalyst for efficient hydrogen evolution reaction. *Nano Res.* **10**, 1178–1188 (2017).
84. X. Zhang *et al.*, Direct synthesis of large-scale hierarchical MoS₂ films nanostructured with orthogonally oriented vertically and horizontally aligned layers. *Nanoscale*. **8**, 431–439 (2016).
85. W. Xu *et al.*, Large dendritic monolayer MoS₂ grown by atmospheric pressure chemical vapor deposition for electrocatalysis. *ACS Appl. Mater. Interfaces* **10**, 4630–4639 (2018).
86. A. Behranginia *et al.*, highly efficient hydrogen evolution reaction using crystalline layered three-dimensional molybdenum disulfides grown on graphene film. *Chem. Mater.* **28**, 549–555 (2016).
87. D. Merki *et al.*, Amorphous molybdenum sulfide films as catalysts for electrochemical hydrogen production in water. *Chem. Sci.* **2**, 1262–1267 (2011).

88. C. Jian *et al.*, Enhanced hydrogen evolution reaction of MoO_x/Mo cathode by loading small amount of Pt nanoparticles in alkaline solution. *Int. J. Hydrogen Energy*. **42**, 17030–17037 (2017).
89. W. Xu *et al.*, Growing and etching MoS₂ on carbon nanotube film for enhanced electrochemical performance. *Molecules*. **21**, 1–10 (2016).
90. J. Xie *et al.*, Defect-rich MoS₂ ultrathin nanosheets with additional active edge sites for enhanced electrocatalytic hydrogen evolution. *Adv. Mater.* **25**, 5807–5813 (2013).
91. J. Xie *et al.*, Controllable disorder engineering in oxygen-incorporated MoS₂ ultrathin nanosheets for efficient hydrogen evolution. *J. Am. Chem. Soc.* **135**, 17881–17888 (2013).
92. G. Ye *et al.*, defects engineered monolayer MoS₂ for improved hydrogen evolution reaction. *Nano Lett.* **16**, 1097–1103 (2016).
93. Y. Yang *et al.*, Edge-oriented MoS₂ nanoporous films as flexible electrodes for hydrogen evolution reactions and supercapacitor devices. *Adv. Mater.* **26**, 8163–8168 (2014).
94. Y. Jung *et al.*, Metal seed layer thickness-induced transition from vertical to horizontal growth of MoS₂ and WS₂. *Nano Lett.* **14**, 6842–6849 (2014).
95. H. Wang *et al.*, MoSe₂ and WSe₂ nano films with vertically aligned molecular layers on curved and rough surfaces. *Nano Lett.* **13**, 3426–3433 (2013).
96. A. P. S. Gaur *et al.*, Optical and vibrational studies of partially edge-terminated

- vertically aligned nanocrystalline MoS₂ thin films. *J. Phys. Chem. C.* **117**, 26262–26268 (2013).
97. V. G. Pol *et al.*, Micro to nano conversion: A one-step, environmentally friendly, solid state, bulk fabrication of WS₂ and MoS₂ nanoplates. *Cryst. Growth Des.* **8**, 1126-1132 (2008).
98. P. G. Li *et al.*, Thermal conversion of tungsten oxide nanorods to tungsten disulfide nanoflakes. *J. Alloys Compd.* **474**, 463–467 (2009).
99. M. A. Lukowski *et al.*, Enhanced hydrogen evolution catalysis from chemically exfoliated metallic MoS₂ nanosheets. *J. Am. Chem. Soc.* **135**, 10274-10277 (2013).
100. G. Zhou *et al.*, Vertically aligned MoS₂/MoO_x heterojunction nanosheets for enhanced visible-light photocatalytic activity and photostability. *CrystEngComm.* **16**, 9025–9032 (2014).
101. H. Zhu *et al.*, The design and construction of 3D rose-petal-shaped MoS₂ hierarchical nanostructures with structure-sensitive properties. *J. Mater. Chem. A.* **2**, 7680–7685 (2014).
102. A. Prabakaran *et al.*, WS₂ 2D nanosheets in 3D nanoflowers. *Chem. Commun.* **50**, 12360–12362 (2014).
103. J. W. Seo *et al.*, Two-dimensional nanosheet crystals. *Angew. Chemie - Int. Ed.* **46**, 8828–8831 (2007).
104. X. Hai *et al.*, Rational design of freestanding MoS₂ monolayers for hydrogen

- evolution reaction. *Nano Energy*. **39**, 409–417 (2017).
105. X. H. Zhang *et al.*, Defect-rich O-incorporated 1T-MoS₂ nanosheets for remarkably enhanced visible-light photocatalytic H₂ evolution over CdS: The impact of enriched defects. *Appl. Catal. B Environ.* **229**, 227–236 (2018).
 106. A. V. Krivosheeva *et al.*, Theoretical study of defect impact on two-dimensional MoS₂. *J. Semicond.* **36**, 122002 (2015).
 107. J. A. Spirko *et al.*, Electronic structure and reactivity of defect MoS₂: I. Relative stabilities of clusters and edges, and electronic surface states. *Surf. Sci.* **542**, 192–204 (2003).
 108. W. Zhou *et al.*, Intrinsic structural defects in monolayer molybdenum disulfide. *Nano Lett.* **13**, 2615–2622 (2013).
 109. L. Yang *et al.*, Hierarchical spheres constructed by defect-rich MoS₂/carbon nanosheets for efficient electrocatalytic hydrogen evolution. *Nano Energy*. **22**, 490–498 (2016).
 110. L. Tao *et al.*, Plasma-engineered MoS₂ thin-film as an efficient electrocatalyst for hydrogen evolution reaction. *Chem. Commun. (Camb)*. **51**, 7470–3 (2015).
 111. G. Ye *et al.*, defects engineered monolayer MoS₂ for improved hydrogen evolution reaction. *Nano Lett.* **16**, 1097–1103 (2016).
 112. R. Ionescu *et al.*, Oxygen etching of thick MoS₂ films. *Chem. Commun.* **50**, 11226 (2014).
 113. S. Xiao *et al.*, Atomic-layer soft plasma etching of MoS₂. *Sci. Rep.* **6**, 19945

(2016).

114. N. Kang *et al.*, Photoluminescence quenching in single-layer MoS₂ via oxygen plasma treatment. *J. Phys. Chem. C*, 140828114311002 (2014).
115. H. Zhou *et al.*, Thickness-dependent patterning of MoS₂ sheets with well-oriented triangular pits by heating in air. *Nano Res.* **6**, 703–711 (2013).
116. M. Yamamoto *et al.*, anisotropic etching of atomically thin MoS₂. *J. Phys. Chem. C.* **117**, 25643–25649 (2013).
117. D. Geng *et al.*, Fractal etching of graphene. *J. Am. Chem. Soc.* **135**, 6431–6434 (2013).
118. Y. Zhang *et al.*, Anisotropic hydrogen etching of chemical vapor deposited graphene. *ACS Nano.* **6**, 126–132 (2012).
119. J. Jadwiszczak *et al.*, Oxide-mediated recovery of field effect mobility in plasma-treated MoS₂. *Sci Adv.* **4**, 5031 (2018).
120. M. R. Islam *et al.*, Electrical property tuning via defect engineering of single layer MoS₂ by oxygen plasma. *Nanoscale.* **6**, 10033-10039 (2014).
121. X. Wei *et al.*, Mo-O bond doping and related-defect assisted enhancement of photoluminescence in monolayer MoS₂. *AIP Adv.* **4**, 123004 (2014).
122. J. Xie *et al.*, Vertically aligned oxygen-doped molybdenum disulfide nanosheets grown on carbon cloth realizing robust hydrogen evolution reaction. *Inorg. Chem. Front.* **3**, 1160–1166 (2016).
123. H. P. Komsa *et al.*, Two-dimensional transition metal dichalcogenides under

- electron irradiation: Defect production and doping. *Phys. Rev. Lett.* **109**, 1–5 (2012).
124. H. Zhang, R. Lv, Defect engineering of two-dimensional materials for efficient electrocatalysis. *J. Mater.* **4**, 95–107 (2018).
125. B. H. Kim *et al.*, Effect of sulphur vacancy on geometric and electronic structure of MoS₂ induced by molecular hydrogen treatment at room temperature. *RSC Adv.* **3**, 18424 (2013).
126. W. S. Leong *et al.*, Tuning the threshold voltage of MoS₂ field-effect transistors via surface treatment. *Nanoscale.* **7**, 10823–10831 (2015).
127. D. V. Esposito *et al.*, Low-cost hydrogen-evolution catalysts based on monolayer platinum on tungsten monocarbide substrates. *Angew. Chemie - Int. Ed.* **49**, 9859–9862 (2010).
128. Y.-P. Xiao *et al.*, Hanging Pt hollow nanocrystal assemblies on graphene resulting in an enhanced electrocatalyst. *Chem. Commun.* **48**, 10331 (2012).
129. R. Ma *et al.*, Efficient electrocatalysis of hydrogen evolution by ultralow-Pt-loading bamboo-like nitrogen-doped carbon nanotubes. *Mater. Today Energy.* **6**, 173–180 (2017).
130. J. Ying *et al.*, Nitrogen-doped hollow porous carbon polyhedrons embedded with highly dispersed Pt nanoparticles as a highly efficient and stable hydrogen evolution electrocatalyst. *Nano Energy.* **40**, 88–94 (2017).
131. S. A. Grigoriev *et al.*, Evaluation of carbon-supported Pt and Pd nanoparticles

- for the hydrogen evolution reaction in PEM water electrolyzers. *J. Power Sources*. **177**, 281–285 (2008).
132. H. A. Gasteiger *et al.*, Activity benchmarks and requirements for Pt, Pt-alloy, and non-Pt oxygen reduction catalysts for PEMFCs. *Appl. Catal. B Environ.* **56**, 9–35 (2005).
 133. E. Kemppainen *et al.*, Scalability and feasibility of photoelectrochemical H₂ evolution: the ultimate limit of Pt nanoparticle as an HER catalyst. *Energy Environ. Sci.* **8**, 2991–2999 (2015).
 134. J. F. Sheng *et al.*, Preparation of tungsten carbide-supported nano platinum catalyst and its electrocatalytic activity for hydrogen evolution. *Wuli Huaxue Xuebao/ Acta Phys. - Chim. Sin.* **23**, 181–186 (2007).
 135. M. Tavakkoli *et al.*, Electrochemical activation of single-walled carbon nanotubes with pseudo-atomic-scale platinum for the hydrogen evolution reaction. *ACS Catal.* **7**, 3121–3130 (2017).
 136. P. Paciok *et al.*, On the mobility of carbon-supported platinum nanoparticles towards unveiling cathode degradation in water electrolysis. *J. Power Sources*. **365**, 53–60 (2017).
 137. L. Zhao *et al.*, A newly-designed sandwich-structured graphene–Pt–graphene catalyst with improved electrocatalytic performance for fuel cells. *J. Mater. Chem. A*. **3**, 5313–5320 (2015).
 138. H. C. Ma *et al.*, Effect of borohydride as reducing agent on the structures and

- electrochemical properties of Pt/C catalyst. *Appl. Surf. Sci.* **252**, 8593–8597 (2006).
139. C. H. Choi *et al.*, Tuning selectivity of electrochemical reactions by atomically dispersed platinum catalyst. *Nat. Commun.* **7**, 1–9 (2016).
140. G. Girishkumar *et al.*, Single-wall carbon nanotube-based proton exchange membrane assembly for hydrogen fuel cells. *Langmuir*. **21**, 8487–8494 (2005).
141. C. Huang, C. Li, G. Shi, Graphene based catalysts. *Energy Environ. Sci.* **5**, 8848 (2012).
142. T. O. M. Samuels *et al.*, Three dimensional hybrid multi-layered graphene–CNT catalyst supports via rapid thermal annealing of nickel acetate. *J. Mater. Chem. A*. **00**, 1–13 (2017).
143. B. G. Rao *et al.*, Hydrodesulfurization of thiophene over few-layer MoS₂ covered with cobalt and nickel nanoparticles. *Chempluschem*. **78**, 419–422 (2013).
144. X. Huang *et al.*, Solution-phase epitaxial growth of noble metal nanostructures on dispersible single-layer molybdenum disulfide nanosheets. *Mol. Ther.* **4**, 1444 (2013).
145. J. Deng *et al.*, Triggering the electrocatalytic hydrogen evolution activity of the inert two-dimensional MoS₂ surface via single-atom metal doping. *Energy Environ. Sci.* **8**, 1594–1601 (2015).
146. D. Deng *et al.*, Catalysis with two-dimensional materials and their

- heterostructures. *Nat. Nanotechnol.* **11**, 218–230 (2016).
147. S. Wang *et al.*, In situ atomic-scale studies of the formation of epitaxial Pt nanocrystals on monolayer molybdenum disulfide. *ACS Nano.* **11**, 9057–9067 (2017).
148. B. Govinda Rao *et al.*, Decoration of few-layer graphene-like MoS₂ and MoSe₂ by noble metal nanoparticles. *J. Clust. Sci.* **23**, 929–937 (2012).
149. F. Şen, G. Gökağaç, Different sized platinum nanoparticles supported on carbon: AnXPS study on these methanol oxidation catalysts. *J. Phys. Chem. C.* **111**, 5715–5720 (2007).
150. N. Yang *et al.*, Two-dimensional graphene bridges enhanced photoinduced charge transport in dye-sensitized solar cells. *ACS Nano.* **4**, 887 (2010).
151. J. Kim *et al.*, Enhanced electrocatalytic properties of transition metal dichalcogenides sheets by spontaneous gold nanoparticle decoration. *J. Phys. Chem. Lett.* **4**, 1227–1232 (2013).
152. N. Zhang *et al.*, Growth Control of MoS₂ nanosheets on carbon cloth for maximum active edges exposed: an excellent hydrogen evolution 3D cathode. *ACS Appl. Mater. Interfaces.* **7**, 12193–12202 (2015).
153. Y. Yan *et al.*, Ultrathin MoS₂ nanoplates with rich active sites as highly efficient catalyst for hydrogen evolution. *ACS Appl. Mater. Interfaces.* **5**, 12794–12798 (2013).
154. H. Li *et al.*, Synthesis and characterization of vertically standing MoS₂

- nanosheets. *Sci. Rep.* **6**, 21171 (2016).
155. X. Zhang *et al.*, Phonon and Raman scattering of two-dimensional transition metal dichalcogenides from monolayer, multilayer to bulk material. *Chem. Soc. Rev.* **44**, 2757–2785 (2015).
156. H. Li *et al.*, From bulk to monolayer MoS₂: Evolution of Raman scattering. *Adv. Funct. Mater.* **22**, 1385–1390 (2012).
157. S. S. Wang *et al.*, Shape evolution of monolayer MoS₂ crystals grown by chemical vapor deposition. *Chem. Mater.* **26**, 6371–6379 (2014).
158. Y. Yu *et al.*, Layer-dependent electrocatalysis of MoS₂ for hydrogen evolution. *Nano Lett.* **14**, 553–558 (2014).
159. Z. Wu *et al.*, MoS₂ nanosheets: A designed structure with high active site density for the hydrogen evolution reaction. *ACS Catal.* **3**, 2101–2107 (2013).
160. M.-R. Gao *et al.*, Edge-terminated molybdenum disulfide with a 9.4-Å interlayer spacing for electrochemical hydrogen production. *Nat. Commun.* **6**, 7493 (2015).
161. Z. Lu *et al.*, In situ fabrication of porous MoS₂ thin-films as high-performance catalysts for electrochemical hydrogen evolution. *Chem. Commun. (Camb)*. **49**, 7516–8 (2013).
162. S. Mouri *et al.*, Tunable photoluminescence of monolayer MoS₂ via chemical doping. *Nano Lett.* **13**, 5944–5948 (2013).
163. S. Wang *et al.*, All chemical vapor deposition growth of MoS₂: h-BN vertical van

- der Waals heterostructures. *ACS Nano*. **9**, 5246–5254 (2015).
164. Y. H. Chang *et al.*, Highly efficient electrocatalytic hydrogen production by MoS_x grown on graphene-protected 3D Ni foams. *Adv. Mater.* **25**, 756–760 (2013).
165. S. Li *et al.*, Edge enriched 2D MoS₂ thin films grown by chemical vapor deposition for enhanced catalytic performance. *ACS Catal.* **7**, 877–886 (2016).
166. J. Zheng *et al.*, Size-dependent hydrogen oxidation and evolution activities on supported palladium nanoparticles in acid and base. *J. Electrochem. Soc.* **163**, 499–506 (2016).
167. J. Perez *et al.*, Particle size effect for ethanol electro-oxidation on Pt/C catalysts in half-cell and in a single direct ethanol fuel cell. *J. Electroanal. Chem.* **654**, 108–115 (2011).
168. S. Trasatti, O. A. Petrii, Real surface area measurements in electrochemistry. *J. Electroanal. Chem.* **327**, 353–376 (1992).
169. S. Chakrabartty *et al.*, Polymer-based hybrid catalyst of low Pt content for electrochemical hydrogen evolution. *Int. J. Hydrogen Energy*. **42**, 22821–22829 (2017).
170. M. Jahan *et al.*, A graphene oxide and copper-centered metal organic framework composite as a tri-functional catalyst for HER, OER, and ORR. *Adv. Funct. Mater.* **23**, 5363–5372 (2013).
171. K. T. Park *et al.*, Surface structure of single-crystal MoS₂ (0002) and Cs/MoS₂ (0002) by X-ray Photoelectron Diffraction. *J. Phys. Chem.* **100**, 10739–10745

(1996).

172. C. Das *et al.*, Selective deposition of an ultrathin Pt layer on a Au-nanoisland-modified Si photocathode for hydrogen generation. *ACS Omega*. **2**, 1360–1366 (2017).
173. W. Ren *et al.*, Ultrafine Pt nanoparticles decorated MoS₂ nanosheets with significantly improved hydrogen evolution activity. *Electrochim. Acta*. **241**, 316–322 (2017).
174. B. Jiang *et al.*, Pt nanocrystals on nitrogen-doped graphene for the hydrogen evolution reaction using Si nanowires as a sacrificial template. *Nanoscale*. **9**, 10138–10144 (2017).
175. Y. Wu *et al.*, Fiber-shaped supercapacitor and electrocatalyst containing of multiple carbon nanotube yarns and one platinum Wire. *Electrochim. Acta*. **245**, 69–78 (2017).
176. W. Liao, S. Yau, Au(111)-supported Pt monolayer as the most active electrocatalyst toward hydrogen oxidation and evolution reactions in sulfuric acid. *J. Phys. Chem. C*, **121**, 19218-19225 (2017).
177. A. V. Virkar, Y. Zhou, Mechanism of catalyst degradation in proton exchange membrane fuel cells. *J. Electrochem. Soc.* **154**, 540 (2007).
178. M. T. M. Koper, Hydrogen electrocatalysis: A basic solution. *Nat. Chem.* **5**, 255–6 (2013).
179. X. Chia *et al.*, M. Pumera, Electrochemistry of nanostructured layered

transition-metal dichalcogenides. *Chem. Rev.* **115**, 11941–11966 (2015).

180. P. K. Chow *et al.*, Defect-induced photoluminescence in monolayer semiconducting transition metal dichalcogenides. *ACS Nano*. **9**, 1520–1527 (2015).