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Strain Engineering of Monolayer MoS₂ for Electrocatalysis Enhancement and Band Structure Modulation

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Abstract

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In this dissertation, strain engineering is utilized to modulate the band structure of monolayer MoS₂ and enhance its catalytic performances. A general electron-beam lithography fabrication process is developed to fabricate a flexible electrochemical nanodevice, which is further combined with a biaxial beam bending method to apply biaxial tensile strain on the monolayer MoS₂ samples. After introducing the tensile strain, the electrochemical capacitance and hydrogen evolution reaction behavior of the monolayer MoS₂ are characterized using two types of experiments.

In the first experiment, the newly developed nanodevice is applied to measure the Density of States (DOS) of the MoS₂. Measuring the intrinsic DOS and defect states of atomically thin layered materials are of profound importance for understanding their exotic physical properties and real life applications. Typically, the measurements of defect states require either ultra-high vacuum or low temperature. Here, we measured the defect states of two-dimensional (2D) materials in an ambient environment rooting on the electrochemical capacitance. The highest energy resolution of the electrochemical capacitance spectrum approaches 116 meV, close to the theoretical limit of thermal broadening at room temperature ($3.5 k_B T = 91 \text{ meV}$). Meanwhile, the absolute energy positions of the DOS can be obtained by integrating a reference electrode in our electrochemical system. With this approach, the DOS and defect states in monolayer MoS₂ are mapped out by measuring its electrochemical capacitance. We can also monitor the DOS evolution during the electrochemical reactions. Our result on the mercury ions adsorption shows that the Mo defects in monolayer MoS₂ dominate the chemical adsorption procedure. This work paves the way towards a new platform for measuring the intrinsic DOS and defect states of 2D materials under an ambient environment.

Following the electrochemical capacitance measurements, the hydrogen evolution reaction property was determined using the monolayer MoS₂ as the catalyst. The catalytic property is highly dependent on the number of active sites and the turnover frequency (TOF) of a catalyst. While increasing the number of active sites eventually approaches a saturation point, theoretically raising the TOF can improve the catalysis performance in a linear manner. On the other side, the TOF has a strong correlation with the DOS of the material. Thus, it is critical to develop a strategy for establishing a relationship between the electronic structure and TOF. The purpose of this endeavor was to use strain engineering to uncover this missing puzzle piece. Tensile strain contributes to spin-orbital coupling in monolayer MoS₂, resulting in an increased electronic state near the conduction band edge. As demonstrated experimentally, this unusual electronic structure in strained monolayer MoS₂ leads to an unanticipated three-zone catalysis process and an ultrahigh TOF of 27.75 s⁻¹ in the hydrogen evolution reaction, which is superior to platinum. This study shed important light on the interrelationship between the strain condition, electronic states, and catalytic property.

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Dedication

To my family

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1 INTRODUCTION

1.1 BACKGROUND AND MOTIVATION

The exponentially growing global-scale energy cost has raised increasing concerns in recent years. The global energy demand, which mainly relies on fossil resources, including coal, oil, and gas, was around 18 TW in 2013 [1]. However, it is projected to increase to 40 TW in 2040 due to the tremendous population explosion and industry expansion [1]. This increasing demand will cause a shortage of energy supply, especially as fossil resources are exhausted. Moreover, the climate change induced by the heavy use of fossil fuels has also resulted in worldwide concerns. Therefore, there are strong incentives to diversify our energy sources and reduce our dependency on fossil fuels by utilizing renewable energy sources such as solar, wind, and hydroelectric power.

Among the different kinds of energy resources, the electricity sector accounts for approximately 12% of the global energy demand [2]. At the same time, the demand for electricity undergoes an explosive increase, especially with the popularization of electric vehicles. The global sales amount of electric vehicles was over 3 million in 2020, although affected by the pandemic [3], but may reach up to five million in 2021 after the pandemic [4]. Meanwhile, the European Union (EU) recently announced to limit the greenhouse gas emissions to 45% by 2030 and reach the overall goals of carbon neutrality by 2050 in the “2050 long-term strategy” [5]. To achieve this goal, the transportation emission should be reduced at least 50% to 95 g/km in 2020~2021 [5]. Under this situation, the electric cars will replace more traditional vehicles in the coming decades and further increase the electricity demand. The tremendously increasing demand for electricity is also happening in the semiconductor industry. Although the evolution of fabrication processes has led

to the lower and lower energy cost of chips, the blowing-out requirement of productions still leads to the increasing electricity demand in future decades.

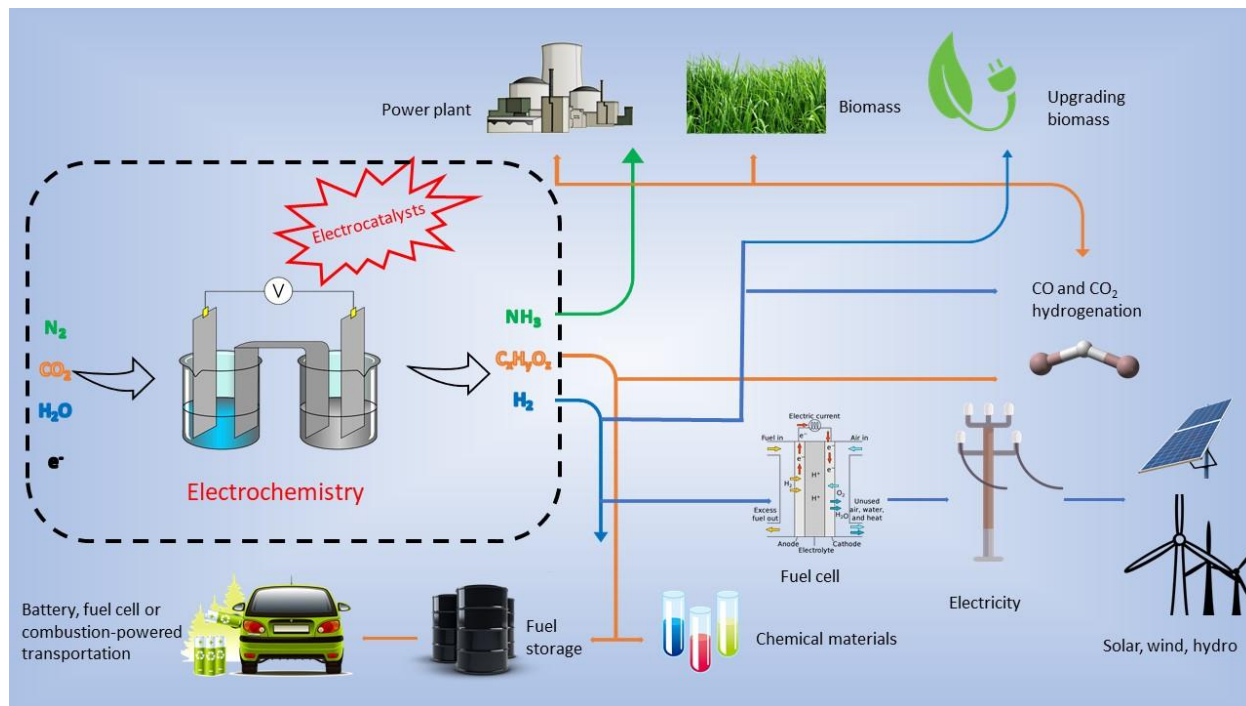


Figure 1-1. Schematic of a sustainable energy landscape based on electrocatalysis

Apart from the promising electricity, other critical energy sectors, such as the chemical industry, also require the development of sustainable energy. In 2010, the energy demand for the production of industrial chemicals was 8% (1.5 TW) of global energy, which was almost entirely from fossil fuels [6]. To meet the worldwide requirement for commercial products, such as plastics and fertilizers, energy use in the chemical industry is expected to nearly double between 2010 and 2040 [6]. Finding a sustainable, fossil fuel-free method to produce industrial chemicals, such as hydrogen peroxide (2.2 Mt year^{-1}), methanol (40 Mt year^{-1}), hydrogen (50 Mt year^{-1}), propylene

(73 Mt year⁻¹), ethylene (115 Mt year⁻¹), and ammonia (175 Mt year⁻¹) is an urgent problem to be solved [7]. This new method could become a substantial step in reducing carbon dioxide emissions, while providing the chemicals needed to make the products used globally daily [8, 9]. Error! Reference source not found. illustrates the potentially sustainable pathways for the productions of critical fuels and chemicals, such as hydrogen, hydrocarbons, oxygenates, and ammonia, either in place of or in conjunction with conventional energy productions [7].

The earth's atmosphere provides a universal source of water, carbon dioxide, and nitrogen, which can be converted into future products via electrochemical processes combined with renewable energy if suitable electrocatalysts are developed. For example, the water-splitting reaction, which consists of the hydrogen and oxygen evolution half-reactions, has gathered considerable attention as a potential source of sustainable hydrogen [10, 11]. Hydrogen is a desirable energy carrier that can be used to develop clean electricity in fuel cells, where chemical energy is converted to electrical energy via hydrogen oxidation and oxygen reduction reactions (ORR) [12]. Hydrogen peroxide, a critical chemical in the pulp- and paper-bleaching and water treatment industries, can also be potentially produced via the oxygen reduction reaction [13]. Through preliminary electroreduction, carbon dioxide captured from the atmosphere or directly from point sources could be used as a feedstock for fuels, commodity chemicals, fine chemicals, and precursors to polymers and plastics [14]. Similarly, the electroreduction of nitrogen to ammonia would enable the synthesis of fertilizers sustainably and locally at the place of applications and the required concentration, avoiding distribution costs from the inflexibly large-scale, centralized Haber-Bosch process [15].

The previous literature demonstrates that the water-splitting process can provide a sufficient clean-energy source, H_2 . However, even at the desirable thermodynamic energy level, an extra kinetic energy is required to push the reaction forward. This kinetic energy is a variable depending on different catalysts. Thus, developing the optimum catalyst for chemical reactions always attracts tons of attention. The development of improved electrocatalysts with the required efficiency and selectivity for the chemical transformations is critical to realizing this vision. There are generally two strategies to improve an electrocatalyst system's activity (or reaction rate). The first method is increasing the number of active sites on a given electrode (e.g., through adjusted catalyst structuring or increased catalyst's loading to expose more active sites). The second method is improving the intrinsic activity of each active site of a catalyst [11]. These strategies (Error! Reference source not found.) are not mutually exclusive and should be pursued concurrently to achieve the most remarkable improvement in activity. Of course, there is a physical limitation of the number of active sites that can be loaded onto an electrode without impairing critical processes such as the charge and mass transport [11]. Error! Reference source not found. depicts a plateau effect that has been observed in practice with high catalyst loadings [7]. On the other hand, increasing intrinsic activity results in a direct increase in electrode activity, which alleviates transport issues associated with high catalyst loadings. Additionally, catalyst activity is quantified in terms of orders of magnitude; the intrinsic activity difference between a good and a bad catalyst can be more than ten orders of magnitude, while there are only one to three orders of magnitude differences between a high-loading and a low-loading catalyst [11]. As evidenced by the rapidly growing number of publications on the subject, electrocatalysis has advanced significantly in recent years.

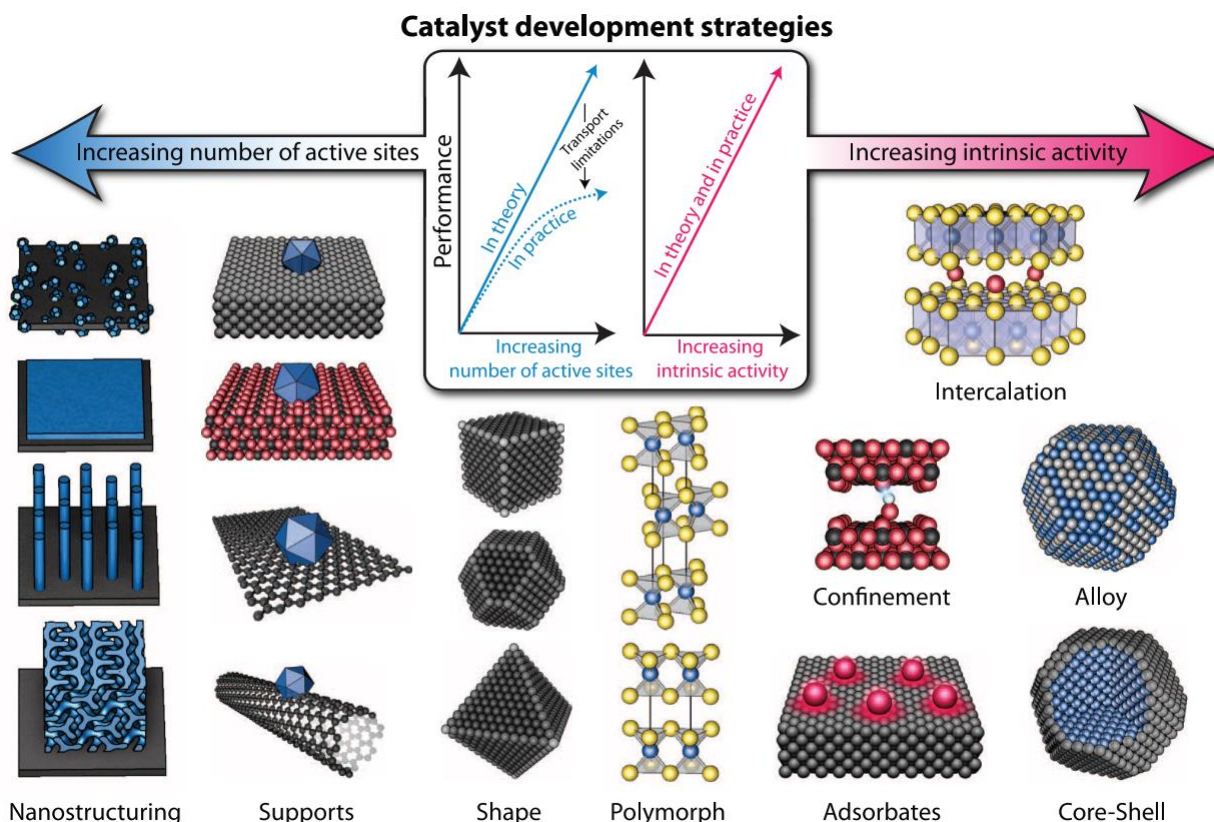


Figure 1-2. Schematic of two different catalyst development strategies: one aims to increase the number of active sites, the other increases the intrinsic activity of each active site [11]

In this dissertation, a framework is proposed to identify a few crucial features of a catalyst's surface area that are required but may not be sufficient for high activity. This work will present theoretical results focusing on understanding the HER process, the physical properties and specific points of potential catalysts, the mechanism of the strain adjusting process, and the quantum electrochemical capacitance of two-dimensional (2D) material. The next step would be to extend the intrinsic properties, including the catalyst's electronic property and band structure. Developing modeling approaches that use minimal resources to predict reaction mechanisms and rate data rapidly and

accurately across a broad range of catalyst materials under different strain conditions can provide important guidance for future work. Also, in this work, a new advanced experimental method is developed for applying controlled strain on the flexible electronic device, including the monolayer material. We demonstrate how this relatively quick, basic, and straightforward approach can be effectively used to produce improved catalysts. In addition, a novel approach to measure the quantum capacitance of 2D materials is established for revealing the electronic structure change under different strain conditions. In this work, we can describe current theoretical approaches for advancing these types of findings (for example, on reaction rates and mechanisms under strain conditions) through more detailed calculations utilizing kinetic models. The combination of a descriptor-based approach covering a large number of systems with a comprehensive research of individual systems has been beneficial. Future advances in theory and experiments will provide a more complete picture of catalysis on surfaces.

1.2 HYDROGEN EVOLUTION REACTIONS

The water-splitting strategies can be classified into two major categories: water electrolysis and water photolysis. Water electrolysis requires the external input of electricity to trigger the water-splitting process [16-18]. Photolysis such as photoelectrochemical (PEC) and photocatalytic water splitting devices rely on semiconductor materials, which can generate excited charge carriers and split water without an external electricity input by absorbing solar energy [19, 20]. Regardless of the device configuration, the overall water splitting reaction remains the same: e.g., $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$ (in the acid condition). This reaction requires an energy input of $\Delta G = 237.1\text{ kJ/mol}$ at standard conditions, corresponding to a thermodynamic voltage requirement of 1.23 V [19, 21, 22].

Not only the thermodynamic requirement, but extra kinetic energy is also always needed to trigger this reaction. This extra energy difference from different catalysts will lead to a different overpotential in the HER process. Thus, appropriate active catalysts are required to minimize the overpotential necessary to drive the HER [19, 23]. The HER is a most used example of a two-electron transfer reaction with one catalytic intermediate, H^* (where $*$ denotes an active site on the catalyst's surface). It may occur through either the Volmer-Heyrovsky or the Volmer-Tafel mechanism [19, 23]. The HER separates into two half-reactions into Volmer step and Heyrovsky step. In the Volmer step, the HER reaction is $H^+ + e^- + * \rightarrow H^*$; while the HER in the Heyrovsky step is $H^* + H^+ + e^- \rightarrow H_2 + *$. The Tafel step is a single step HER, which is: $2 H^* \rightarrow H_2 + 2 *$. If the electrode can provide sufficient active sites, the HER will take the Volmer–Tafel step. Otherwise, it will go through the Volmer–Heyrovsky step. However, in both cases, the reaction proceeds through hydrogen atoms adsorbed at the catalyst's (electrode's) active surface site. Thus, the overall reaction rate is influenced by the free energy of hydrogen adsorption energy, ΔG_H , as initially described by Parsons [24]. If the bond between hydrogen to the surface is too weak, the hydrogen ions are very difficult to bond to the active site on the electrode surface. The adsorption step will limit the overall reaction rate. If the hydrogen to surface bond is too strong, the already bonded hydrogens are difficult to be desorpted for generating the H_2 . Thus, the reaction–desorption step will limit the overall reaction rate. Optimal HER catalysts have hydrogen adsorption energies close to $\Delta G_H = 0$, binding hydrogen neither too weakly nor too strongly. This means a suitable catalyst with the smallest over potential can make the HER very smooth. An active catalyst requires to combine reaction intermediate(s) neither too strongly nor too weakly. Understanding how to control the binding energies of reactive intermediates on a surface is critical for developing high-performance materials. As a result, a volcano relationship emerges in order to plot

experimentally measured current exchange densities for different kinds of catalyst materials against ΔG_H at the appropriate coverage calculated from density functional theory (DFT). This quantitative illustration is also called the Sabatier principle (Error! Reference source not found.) [16, 17, 25]. The volcano plot can give a depiction of different electrochemical reaction and serves as a framework for examining catalysts in a variety of chemical reactions.

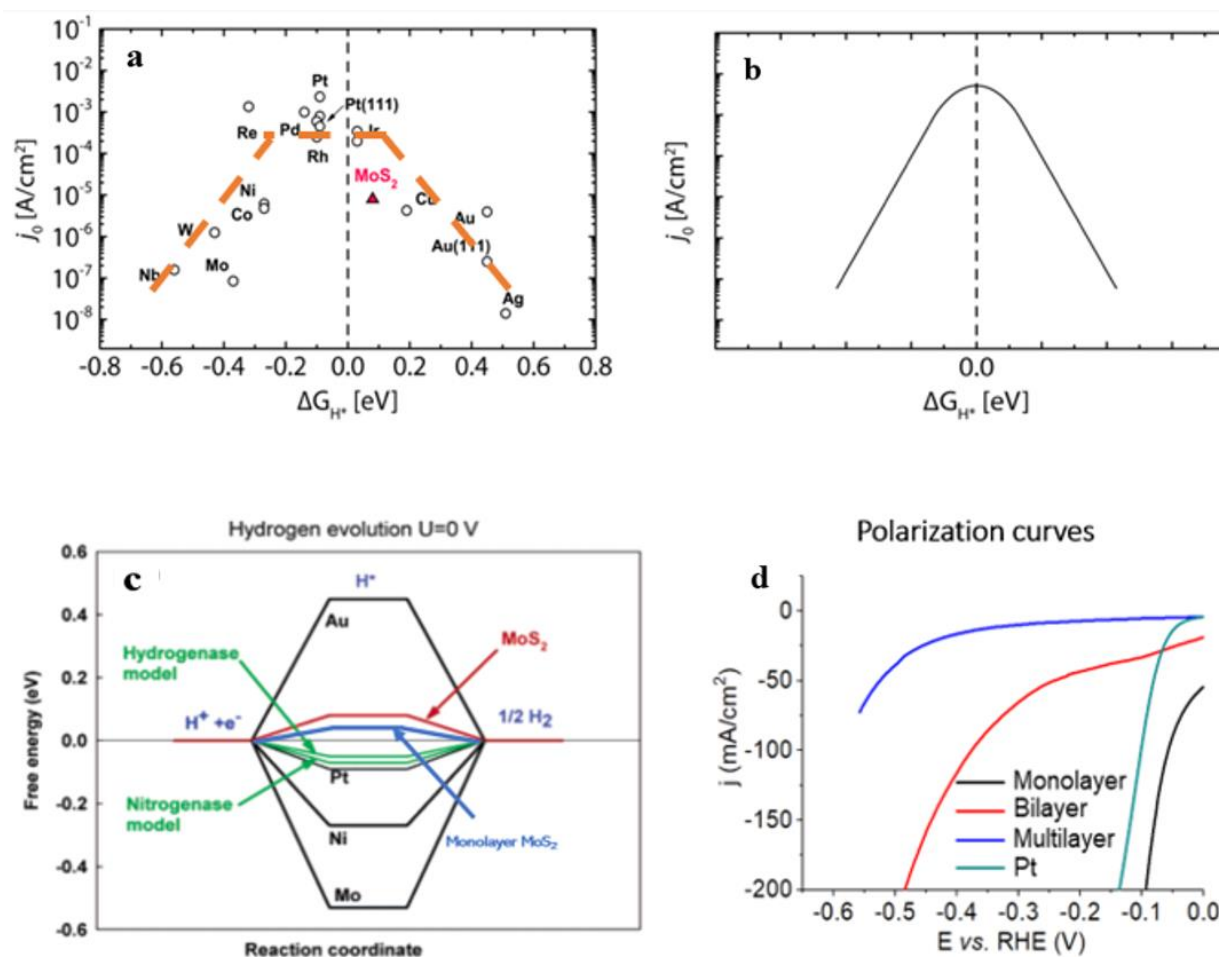


Figure 1-3. Volcano plots and HER polarization curves: (a) experimental results of HER catalysis property of different materials [24], (b) calculation result of a volcano plot [24], (c) experimental and theoretical HER volcano map of monolayer MoS₂ vs. other materials, (d) polarization curve of MoS₂ and Pt

Exchange current density is described as a function of hydrogen adsorption free energy for various HER catalysts in the reaction. In this experimental volcano plot, the rare metal material platinum (Pt) with slightly negative hydrogen absorption energy has the highest HER activity. Also, the theoretical HER volcano predicts catalysts with zero hydrogen binding energy will have the highest activity. This is due to no extra energy needed in the reaction process.

Although these volcano plots provide insight into the optimum catalyst for a given class of catalyst materials, additional factors excluded in the simple descriptor-based model are needed to quantitatively determine the absolute reaction rates. For instance, there are variations in the size of kinetic barriers from one class of materials to the next in the HER process. Therefore, unlike the theoretical results, many transition-metal dichalcogenides (TMD) materials (e.g., MoS₂, WSe₂, MoSe₂) are observed to have lower exchange current densities than the precious metals shown in Error! Reference source not found.c, even though noble metals usually have a ΔG_H value near the optimum. As shown in Error! Reference source not found.c, in the volcano plot, the monolayer MoS₂ shows an extremely low overpotential close to 0 eV [26]. My previous work collaborated with Dr. Yan (Error! Reference source not found.d) has confirmed the monolayer MoS₂ is an excellent HER catalyst, even better than Pt. The monolayer MoS₂ catalyst can reach a current density of 100 mA/cm² at 0.05 V vs. RHE in this research. This means the monolayer MoS₂ has an extremely low kinetic barrier in the HER process. For a given potential versus the reversible hydrogen electrode (RHE), kinetic barriers can also change as a function of pH, resulting in an observed pH dependence of current density [18]. Regardless of the variations that may be involved in the processes (e.g., pH or kinetic barriers), the activity volcano does not shift left or right, but rather only up and down, indicating that the descriptor is still useful for identifying the binding

characteristics of optimal HER catalysts [20]. However, to gain a complete quantitative understanding of these effects, more detailed and efficient methods for calculating electrochemical barriers for proton transfer reactions involving hydroxide and hydronium ions are required as an important goal of future modeling [17, 21, 22, 24, 27-29].

Based on the superior catalytic performance of these TMD materials in the HER process, we will discuss the transition-metal dichalcogenide materials in the next section.

1.3 TRANSITION-METAL DICHALCOGENIDES (TMDs)

Ever since the isolation of graphene in 2004, 2D layered materials have become a fast-growing research field that has achieved many exciting findings. Unlike traditional thin films, 2D materials only have several atomic layers with a thickness of ~ 0.3 nm to ~ 5 nm. With weak van der Waals interactions between the layers, these materials can be easily thinned to a single or few layers via mechanical and chemical exfoliation from the bulk. With the unusual structure, the 2D materials exhibit novel properties such as semiconductor-metal transition, localization of electrons and/or Cooper pairs, and photoluminescence shift as the thickness reduces. Transition-metal dichalcogenide (TMD) monolayers MX_2 as a type of well-known 2D materials are atomically thin semiconductors. In the MX_2 , M represents the transition-metal atoms (Mo, W, etc.), and X represents the chalcogen atoms (S, Se, or Te). They are alternately stacked together (Error! Reference source not found.). Compared to first-row transition-metal dichalcogenides, the distinguishing feature of these TMD materials is the interaction of large atoms in the two-dimensional structure. Also, these 2D TMD materials have some specific properties. For example, the monolayer MoS_2 shows a particular direct bandgap, while other layer numbers show an indirect bandgap. Due to these specific features, these TMDs are potentially suitable catalysts in HER

reaction [30-34]. From previous research, the overall activity of the 2H-phase TMD catalyst mainly originates from the active edge sites rather than the inert basal plane [26, 35]. Therefore, efforts have been made either to maximally expose edge sites using various nanostructures such as mesoporous films, nanoparticles, defect rich films, and vertical nanoflakes [36-38], or to improve the intrinsic catalytic activity of edge sites using chemical doping, enhanced defect density, and enhanced coupling between substrates and monolayers [30, 31, 39, 40]. However, the overall catalytic performance of TMD-based catalysts is limited by the relatively small fraction of edge sites compared to that of basal plane bulk sites. The critical challenge is activating the TMD basal plane by increasing basal plane sites' number and catalytic activity.

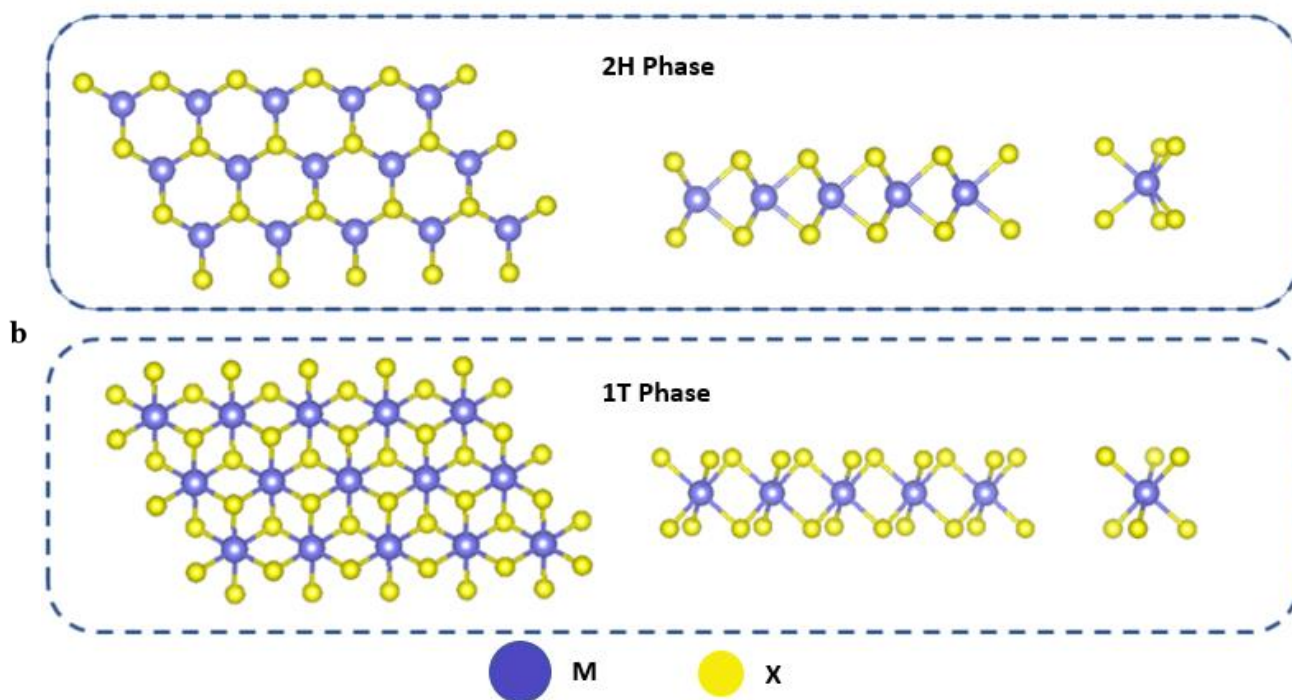


Figure 1-4. Schematic lattice structure of MX₂: (a) top view and side view of a 2H phase of an MX₂ molecular unit, (b) top view and side view of a 1T phase of an MX₂ molecular unit

Recently, strategies to synthesize a new family of so-called “Janus TMDs” have been reported by two independent groups [41, 42]. Unlike the traditional TMD materials, by changing one layer of chalcogen atoms to a different one, the highly asymmetric Janus MXY is constructed. This substitutional method for constructing the Janus structure is consistent with the mechanism described in recently published experimental methods [41]. Currently, only one representative Janus TMD, $MoSSe$, has been reported. However, other Janus systems may be synthesized using similar techniques. In general, the lattice parameter value in Janus TMD structures (XY) lies between the ones of its parent structures, namely, MX_2 and MY_2 . For example, the half-thickness of $MoSSe$ is 3.251 Å [43]. The length of the MX/MY bond, as well as the thickness of the Janus monolayer, increases with heavier metal elements entering Janus TMDs. However, the lattice constant of Janus monolayers containing the same chalcogen elements is nearly identical regardless of the metal element, indicating that chalcogen atoms are critical in determining the structural properties. By comparing the difference between lattice constants of the Janus TMD and its parent structures, we see that effective compressive and tensile strains co-occur on the lighter and the heavier chalcogen sides, respectively.

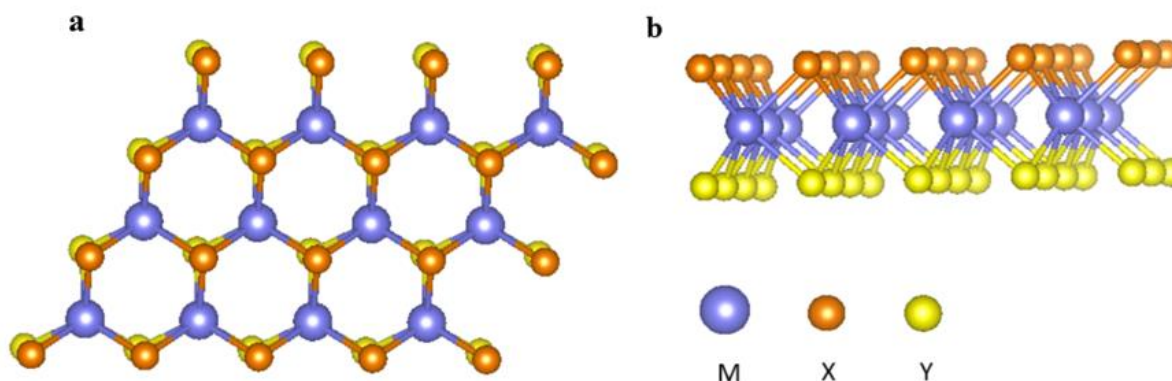


Figure 1-5. Schematic lattice structure of Janus TMD materials: (a) top view of the lattice structure of a Janus TMD material, (b) side view of the lattice structure of a Janus TMD material

This bonding length asymmetry directly leads to an uneven bonding force between electrons and the atomic core at the top and bottom layers. This difference further leads these Janus TMD materials to have unique electronic properties. The electronic structure calculations are performed to gain deeper insight into H adsorption on various surfaces. These Janus TMDs have a different computed total density of states (TDOS) and projected density of states (PDOS) of pristine and defective [44]. This is caused by the change in the electronic structure during H adsorption in the vicinity of defects.

Thus, for improving the basal plane's catalysis ability, Janus TMD material is proposed. This category of TMD material has asymmetry bonding length on M atom's etch sides, enabling them to have unusual ΔG_H in the HER process. For example, MoSSe has been synthesized via two different synthetic pathways. Lu et al. reported a method using a modified CVD-grown MoS₂

monolayer whose top-layer sulfur atoms are stripped off and replaced by H atoms and then followed by a thermal selenization, forming a structurally stable Janus MoSSe monolayer in which the Mo atoms are covalently bonded to underlying S and top layer Se atoms [41]. Another approach starts from the CVD as-grown MoSe₂ monolayers on a SiO₂/Si substrate, followed by a sulfurization of the top layer Se in a controlled substitutional reaction with vaporized sulfur [42]. Unlike the randomly alloyed MoSSe, both methods result in highly asymmetric Janus monolayers and provide a structure with an intrinsic strain and electric field within the monolayer, enabling an alternative way to tune the HER activity in TMD catalysts [45]. This enlightened us that applying strain to catalyst may even improve the HER process.

The polarization curve (current-voltage plot) is frequently used in the HER test to evaluate HER catalytic activity and compare HER catalysts. Once the current density reaches 10 mA/cm², the potential value (E_0) has been adopted to quantify the HER activity. After comparing different HER catalysts, Pt (1.5×10^{15} sites/cm²) shows the highest current density for HER activity. In this electrocatalytic window, nonreactive Au shows almost zero HER activity. In the relaxed defective Janus TMDs, there is no noticeable structural disruption observed for the range of vacancy concentrations. Notably, the introduction of defects results in a decrease in ΔG_H . In between lies the pristine 2H-phase MoS₂ and Janus WSSe monolayers, where the order of HER activities of these TMDs are WSSe with Se-vacancy (−158 meV) > WSSe with S vacancy (−174 meV) > pristine WSSe (−264 meV) > pristine WS₂/WSe₂ from the theoretical calculation [7]. This trend holds true for all Janus TMDs, indicating that the presence of single S-, Se-, or Te-vacancies significantly enhances the binding between H and Janus TMD monolayers, thereby converting the inert basal plane into a catalytically active site for HER. However, most of the TMD/Janus TMD

materials are not stable in the air condition. So, most of the researches are focused on the MoS₂ which can be obtained easily and is stable in air condition.

1.4 MOLYBDENUM DISULFIDE (MoS₂)

Molybdenum disulfide (MoS₂) is one of the most focused TMD materials in recent years due to its simple structure and specific electronic properties, which allow it to be exploited as a lubricant, 2D transistor, hydrodesulfurization catalyst, and so on (Error! Reference source not found.). Bulk MoS₂ crystals have a layered structure. The monolayer MoS₂ is arranged with the sulfur atoms and molybdenum atoms as a sandwich structure by the strong covalent bonds. Bulk MoS₂ is composed of the stacking monolayer layers bonded by the weak van der Waals force. There are two bulk crystal structures depending on the stacking methods: semiconducting 2H phase (trigonal prismatic) and metallic 1T (octahedral prismatic) phase [46].

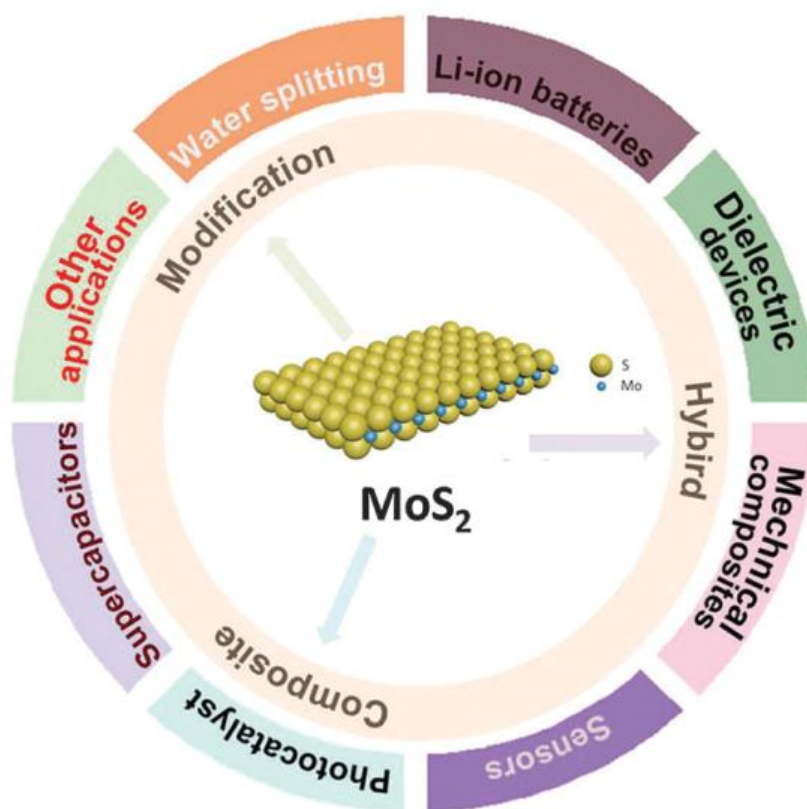


Figure 1-6. Wide applications of MoS₂ [46]

In previous electrochemistry works on bulk MoS₂ crystals, it was pointed out that bulk MoS₂ is not an active HER catalyst since it has a hexagonally packed layered structure with a 6.5 Å van der Waals gap separating each sheet, as shown in Error! Reference source not found. [11, 47-49]. This gap between layers does not provide any free electrons or holes. In this situation, the demand for MoS₂ with a variety of specific surface sites was raised. In the bulk crystal, the electron and hole carrier mobilities along the basal plane is approximately 2200 times faster than along the perpendicular direction between sheets [50]. Due to the lack of defects, the basal plane is always considered as the inert material due to its thermodynamically stable property [51-53].

In contrast, the edges of the MoS₂ layers have a higher activity for the HER due to the dangling bonds [26]. Profiting from the large edge-surface ratio in the nanoscale MoS₂ than the bulk MoS₂, MoS₂ can significantly improve HER activity when the material's scale reduces to nanometer [26, 35].

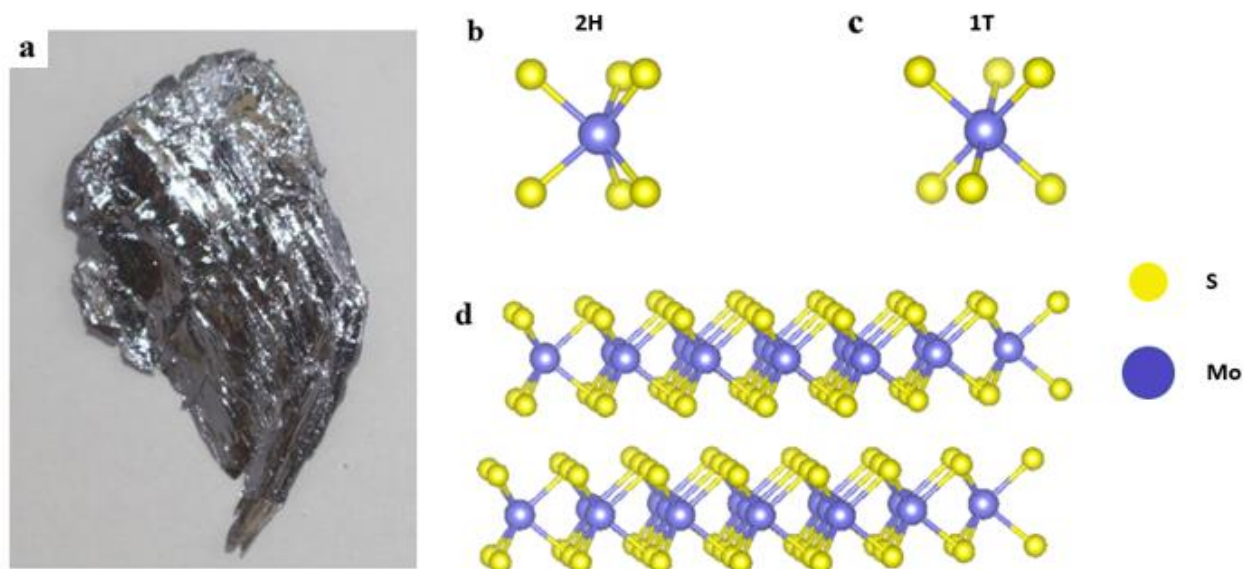


Figure 1-7. Photo and lattice structure of MoS₂: (a) photo of a bulk MoS₂, (b) 2H phase structure of MoS₂, (c) 1T phase structure of MoS₂, (d) side view of atomic layers structure of MoS₂

Thus, the monolayer MoS₂ has attracted wide attention due to its potential electrochemical applications, such as energy conversion and energy storage. The hydrogen evolution reaction (HER) is a critical step in electrochemical water splitting and demands an efficient and low-cost catalyst [54, 55]. An efficient catalyst must be able to accelerate proton reduction with a minimal overpotential and have fast kinetics [56, 57]. In the HER system, platinum (Pt) is a promising catalyst with an almost thermo-neutral ΔG_{H} . Pt locates very near the top of the hydrogen volcano

and requires negligible overpotentials to achieve high reaction rates in acidic solutions. However, the scarcity and high cost of Pt limit its widespread technological use. This has triggered the development of MoS₂-based HER catalysts, which served as an excellent example of theory-guided discovery and design of new electrocatalysts. Benefiting from its metallic edge, 2H-MoS₂ is considered a potential low-cost succedaneum of Pt [58-60]. Thus, numerous studies have attempted to enhance the 2H-MoS₂ catalytic activity by promoting its conductivity, e.g., composite MoS₂ with high conductivity materials [61] and converting semiconductive 2H-MoS₂ to metallic 1T-MoS₂ [62].

In the previous works, MoS₂ used in HER was inspired by hydrogen-producing enzymes such as hydrogenases and nitrogenases in nature. Hinnemann and co-workers calculated with density functional theory (DFT) that the Mo ($\bar{1}010$) edge of MoS₂ possesses a hydrogen binding energy of approximately 0.08 eV (near the optimal value 0 eV) at 50% hydrogen coverage. This binding energy is very close to the most active precious metal catalysts, such as Pt. On the other hand, the basal plane exhibits a ΔG_H of 1.92 eV, which explains the insufficient activity of bulk MoS₂ crystals [63]. Led by the MoS₂ theoretical prediction, scientists synthesized MoS₂ on a carbon black support to expose as many edge sites as possible. They reported a geometric area-normalized current density of 10 mA cm⁻²_{geo} at ~175 mV overpotential with a membrane electrode assembly setup. This is the most active non-precious metal HER catalyst reported in acid at that time [26]. In 2007, it was experimentally confirmed that the MoS₂ edges are active catalysts for the HER by depositing single monolayer MoS₂ nanoparticles on Au (111) synthesized by physical vapor deposition of Mo in an H₂S environment [35]. After quantifying the nanoparticle area and edge length by scanning tunneling microscopy (STM), they confirmed that the measured HER activity and reaction rate is scaled with perimeter length rather than area. The per-site activity (turnover

frequency) of MoS₂ edges was very high, yet still 50–100 times lower than that of Pt [64]. The insights gained by means of theory and fundamental experimental studies consequently sparked significant efforts aimed at developing MoS₂ catalysts with improved activity approaching that observed for platinum surfaces.

Also, the electronic property of MoS₂ is exceptional. The band structure changes from indirect bandgap to direct bandgap after the layers are reduced from multi- to mono- layer in MoS₂ (Error! Reference source not found.**a**) [46]. In particular, one observes a progressive change in the indirect energy gap from the bulk to about 2 eV for monolayer MoS₂. In contrast, the difference in the direct gap is not significant, with a shift of only 0.1 eV from the bulk to the monolayer (Error! Reference source not found.**b**) [65]. As a result, the energy crossover of indirect and direct gaps is reached at the limit of the monolayer MoS₂, with the bilayer having a tiny energy difference between direct and indirect energy gaps. However, due to not requiring extra phonon involvement, the excitation of electrons from the valence band to conduction band is still easier in monolayer MoS₂ than multilayer MoS₂. This difference leads to a difference in HER performance between mono- and multi- layer MoS₂ samples. In the previous collaboration work led by Dr. Yan from Prof. Yang's group, we report an interesting phenomenon. Although monolayer MoS₂ has a larger band-gap and inferior conductivity than multilayer MoS₂, the monolayer MoS₂ shows a much superior HER performance (the MoS₂ nanosheets used in the experiment are 2H-phase). Our results demonstrate that the excellent HER activity in monolayer MoS₂ benefits from the better alignment between the conduction band bottom and hydrogen evolution potential.

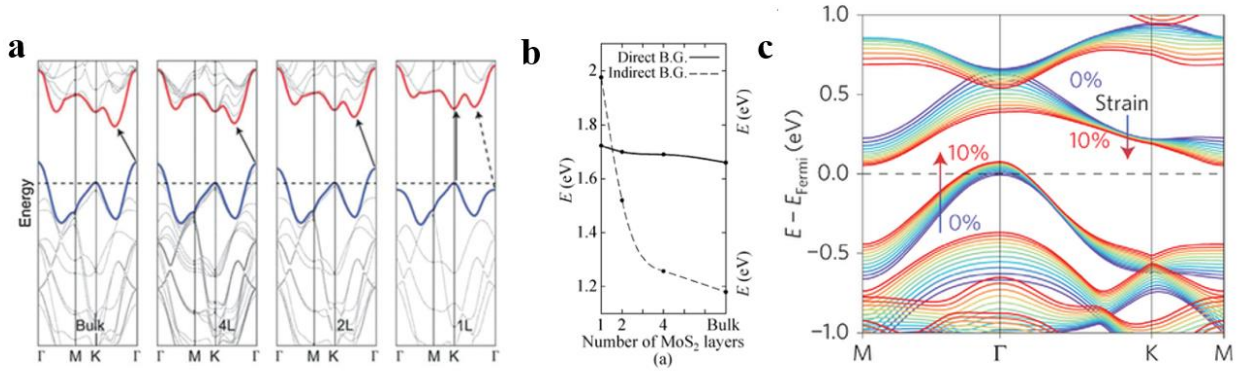


Figure 1-8. Band structure of MoS₂: (a) the band structure of MoS₂ with different layers [46], (b) the direct and indirect bandgap crossover in MoS₂ [65], (c) the band structure changing of MoS₂ under strain [66].

In addition to achieving superior performance by reducing the layer numbers, it has also been found that the strain can affect the property of 2D materials, especially the electronic structures. After applying the strain, the electronic property, the crystal structure, and the ferromagnetic transformation of 2D materials will be affected [32, 67-70]. After applying biaxial strain to MoS₂, the electronic properties of two-dimensional honeycomb structures of MoS₂ have been studied using first-principles calculations based on density functional theory (Error! Reference source not found.c) [66]. A change from semiconductor to metal has been predicted after applying compressive or tensile biaxial strain on bilayer and monolayer MoS₂. These changes present exciting possibilities for engineering the electronic properties of two-dimensional structures of MoS₂. Based on the calculation, Scalise et al. predicted that the semiconductor-to-metal transition would happen in monolayer MoS₂ under a tensile strain of about 10% or a compressive strain of

about 15% [69]. In monolayer MoS₂, a transition from the direct-to-indirect gap is also observed upon applying a much lower strain (~2%).

Additionally, defects and applied strain influence the HER activity of TMD monolayers. Previous research has established that the HER process necessitates certain alterations to the TMD basal plane, which can be accomplished by applying a large amount of tensile strain to 1T-phase WS₂ [31] or by creating and S-vacancies in strained 2H-phase MoS₂ [32]. The formation of chalcogen vacancies becomes less energetically favorable due to the screening effect between vacancies when the defect concentration is increasing [32]. This is in good agreement with previously reported trends in 2H-MoS₂, where the introduction of stable vacancies reduces ΔG_H from 2 to 0.18 eV [32]. For example, in 2H-phase MoS₂, a condition of 3.12 percent S-vacancy and 8% strain, or equivalently 12.5 percent S-vacancy and 1% strain, is required to reach $\Delta G_H \approx 0$ eV [32]. Such large strain and defect concentrations are indispensable in activating the basal plane of 2H-phase MoS₂ because either mechanism alone is insufficient to modify the system's total energy adequately. However, experimentally achieving such high strain and defect concentrations is challenging.

1.5 DEVELOPMENT OF 2D MATERIAL TESTING DEVICE

Electrochemical conversion is a critical step in the conversion of renewable energy, and electrocatalysts are critical because they may increase the speed and efficiency of chemical reactions. Thus, the ongoing interest in electrocatalysis is motivated by both mechanism discovery and performance optimization. However, traditional electrochemical approaches such as in situ dynamic monitoring, external field modulation, and single entity electrocatalytic detection remain unexplored. Notably, inspired by the recent success of nano electronic semiconductor devices, the

emerging field of on-chip electrocatalytic microdevices has shown as a powerful alternative platform to traditional techniques. These microdevices are focusing on the electrochemical behaviors at individual nanowire/nanosheet as the working electrode. This kind of device system enables several advantages, including in situ electronic/electrochemical measurements and fine-tuning the microstructure of individual catalysts. With this setup, we can constantly expand to test electrochemical processes directly and obtain previously unobtainable information. In recent years, there is a large development of these test devices and platforms. With these well-designed devices, the efforts to better understand electrochemical processes using this sort of microdevice are specifically studied and described, including dynamic monitoring, external field regulation, active site identification, and single structural factor regulation. For example, the addition of additional fields (electric, light, and magnetic) that can tune the catalyst's intrinsic energy band structure or cooperatively alter the molecule/ion distribution at the solid–electrolyte interface may provide a new direction and opportunities for performance optimization. However, precisely applying an additional field via typical electrochemical methods is exceedingly hard, and hence has received little attention.

Additionally, in situ investigation of electrocatalytic interfaces is very instructive but exceedingly hard. These interfaces are typically buried between the electrode surface and liquid electrolytes, making them impossible to reach using standard spectroscopic methods. Thus, it is critical to creating innovative electrochemical testing platforms to get a better understanding of electrocatalytic processes and their application to the design of high-performance catalysts (**Error! Reference source not found.**).

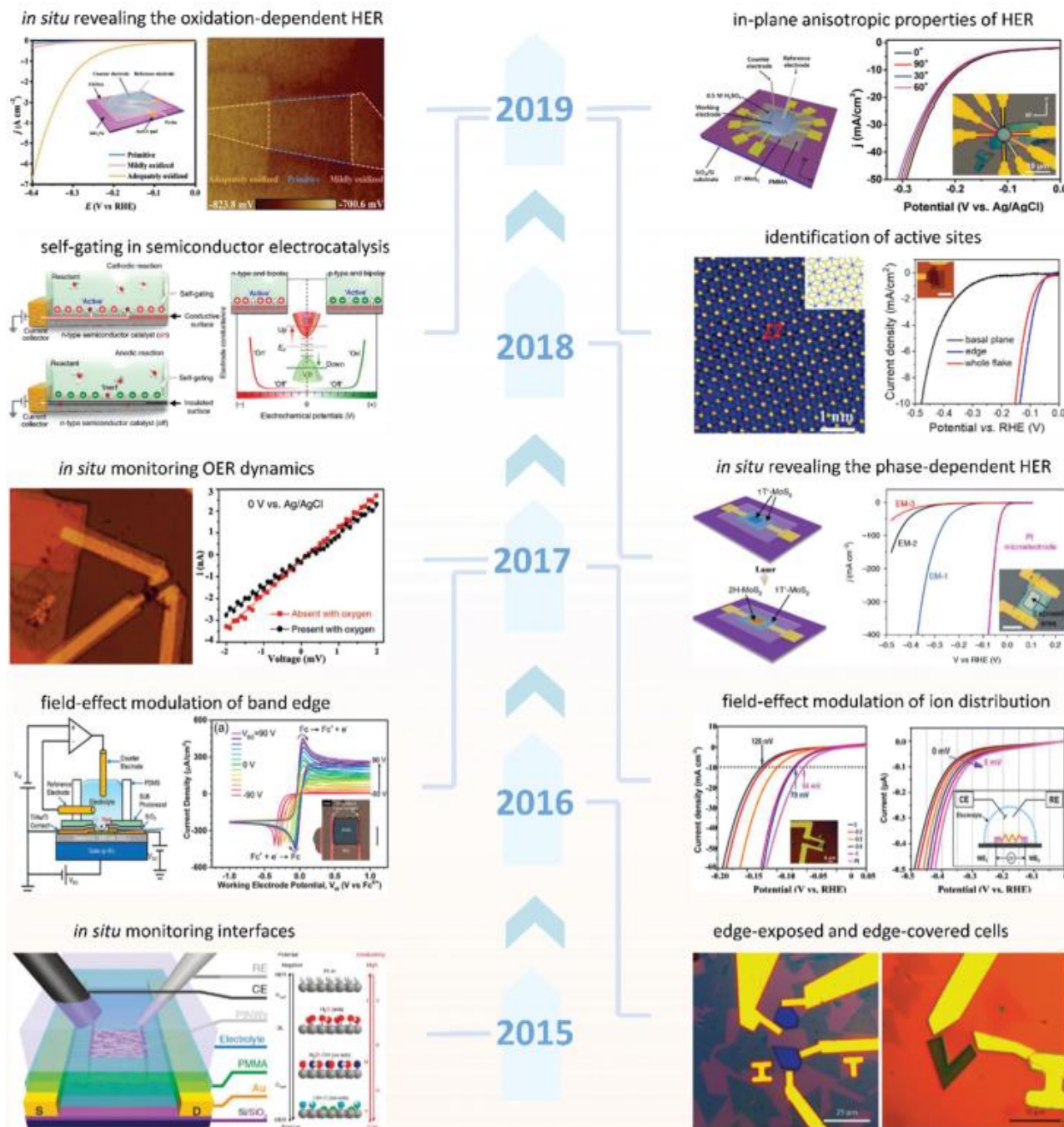


Figure 1-9. The development of the on-chip device for 2D materials from 2015 – 2019 [31, 71-80]

In 2015, for in situ monitoring the electrochemical surface conditions of metal nanocatalysts, Duan and co-workers first proposed a novel on-chip electrocatalytic microdevice [71]. This on-chip micro-scale device has evolved into a platform technology, demonstrating unique benefits in the direct probing of a wide variety of electrocatalytic processes in order to collect previously unobtainable information. This kind of novel microdevice has many advantages in the electrochemical field. First of all, in this kind of platform, a single nanowire or nanosheet is frequently employed as a micro working electrode, eliminating the need for binders and conductive carbon additives that are frequently used in conventional electrochemical techniques. Secondly, the shape and structure of the catalyst within the microdevice may be accurately created and controlled, which is necessary for removing experimental uncertainties and enabling quantitative or semi-quantitative basic investigations. Thirdly, it is far easier to monitor changes in the physical characteristics of individual nanowires/nanosheets (for example, conductivity) within a nanodevice. As a result, the structural benefits of this microdevice model were continually enlarged and enhanced as a strong instrument for discovering novel phenomena and clarifying electrochemical basics at the nanoscale during future research procedures. Also, with this novel platform, it is possible to modulate the external electric field with controllable intensity and direction by applying a back gate voltage through the dielectric on the substrate. In 2016, Manish Chhowalla et al. conducted a thorough study of the distribution of catalysis active sites in MoS_2 . Their study confirmed that the high defective edge of MoS_2 has the highest catalysis ability [31]. In 2017, Yan et al. demonstrated that, during the HER process, by applying an external electric field through the back gate could effectively adjust the H^+ distribution and enhance the adsorption process of H^+ on the catalyst surface [73]. In 2019, He et al. elucidated a self-gating phenomenon in semiconductor electrocatalysis. In the same work, they unraveled the interfacial carrier

concentration of semiconductors is modulated during electrocatalytic processes [76]. They discovered that the applied electrochemical voltage substantially modulated the surface carrier concentration of a semiconductor catalyst during electrocatalytic processes, comparable to the gate modulation of field-effect transistors. This self-gating effect creates a charge transport channel on the semiconductor surface with super-high conductivity, enables carrier transfer at the semiconductor-electrolyte interface [76].

Based on the previous content, since 2015, the first show up of this on-chip test platform, many interesting works have been done with these microdevices. However, there is still a lack of 2D material electrochemical testing platform that allows applying strain to the nanosheet directly. In our work, learning from the previous 2D device fabrication, a new flexible 2D material test platform is established. With this microdevice, we are able to apply 2% tensile strain, either uniaxial or biaxial, to the monolayer material directly. Also, we can measure the in-situ quantum/electrochemical capacitance change during different potentials. The in situ HER property under different strain conditions can also be discovered by using this microdevice. The details will be covered in the following content.

1.6 STRAIN ENGINEERING IN 2D MATERIALS

Strain can exist in both planar and buckled 2D nanomaterials (2DNMs). For example, buckled structures or out-of-plane deformation are generated in 2DNMs to relieve some of the strain. Compared to a planar film with evenly or regionally distributed single strain (tensile or compressive), corrugations in 2DNMs include spatially dispersed tensile and compressive strain concurrently (e.g., tensile strain at the ridge and compressive strain at the valley of wrinkles). Also, because of their extraordinary thinness and fragility, strain in 2DNMs is mainly produced by their

contact with substrates experimentally. Thus, contacts between 2DNMs and substrates are critical for strain engineering. Additionally, additional techniques for inducing strain in suspended 2DNMs include pressured blisters and tip indentation.

As illustrated in **Figure 1-10a**, thermal fluctuating ripples were also anticipated in the stanene monolayer at ambient temperature [81]. Due to the stanene's low Young's modulus, these thermally generated ripples in stanene are bigger than those in silicene and graphene. Interestingly, ripples and wrinkles only occur in the zigzag direction but not in the armchair direction for some 2DNMs (e.g., phosphorene) under tension. Mechanical exfoliation occurs when the interfacial adhesion force between samples and substrates draws the MoS₂ sheets into intimate contact with the substrate surface, resulting in the separation of 2D nanomaterials from bulk materials. The tape's adherence to the 2DNMs on the substrate surface during a release may result in thin layers of 2DNMs partly delaminating from the substrate surface. In certain situations, reaching mechanical equilibrium requires contracting the 2DNM to produce the wrinkle seen in **Figure 1-10b** [82]. The interaction of the 2DNMs flakes' bending energy and interfacial adhesion energy leads to wrinkles and, consequently, uniaxial strain in the 2DNMs flakes.

Applying strain to the substrate of 2DNMs is another method for introducing strain. 2DNMs have been transferred to bendable electronics substrates (PMMA, PDMS, PET, and Polycarbonate). By applying tensile tension or compressing on both sides of the substrates (**Figure 1-10c**), 2DNMs undergo the same strain as the substrate, assuming no relative slip [83]. For instance, in one study, thin films of MoS₂ were mechanically exfoliated and placed over a layer of cross-linked SU-8 photoresist-coated polycarbonate. Following that, titanium clamps were evaporated to prevent

MoS₂ from sliding across the substrate. MoS₂ was subjected to uniaxial strain by controlled bending of the polycarbonate substrate in a four-point bending device.

Additionally, similar to graphene wrinkle engineering, a thin coating of 2DNMs was applied on pre-stretched substrates. The elastomeric substrate's uniaxial tension was released, allowing the development of well-aligned one-dimensional periodic wrinkles in the 2DNMs. This technique creates reproducibly large-scale wrinkles (micrometers in height, spaced by tens of micrometers) in thick MoS₂ flakes (more than 10–15 layers), whereas thin MoS₂ layers (3–5 layers) display wrinkles between 50 and 350 nm in height and with a wavelength of a few micrometers (**Figure 1-10i** and **Figure 1-10j**) [84]. The same approach was used to investigate the strain effect in black phosphorus, with tests and characterizations done in a short period to avoid black phosphorus degeneration, as seen in **Figure 1-10f** and **Figure 1-10g** [85].

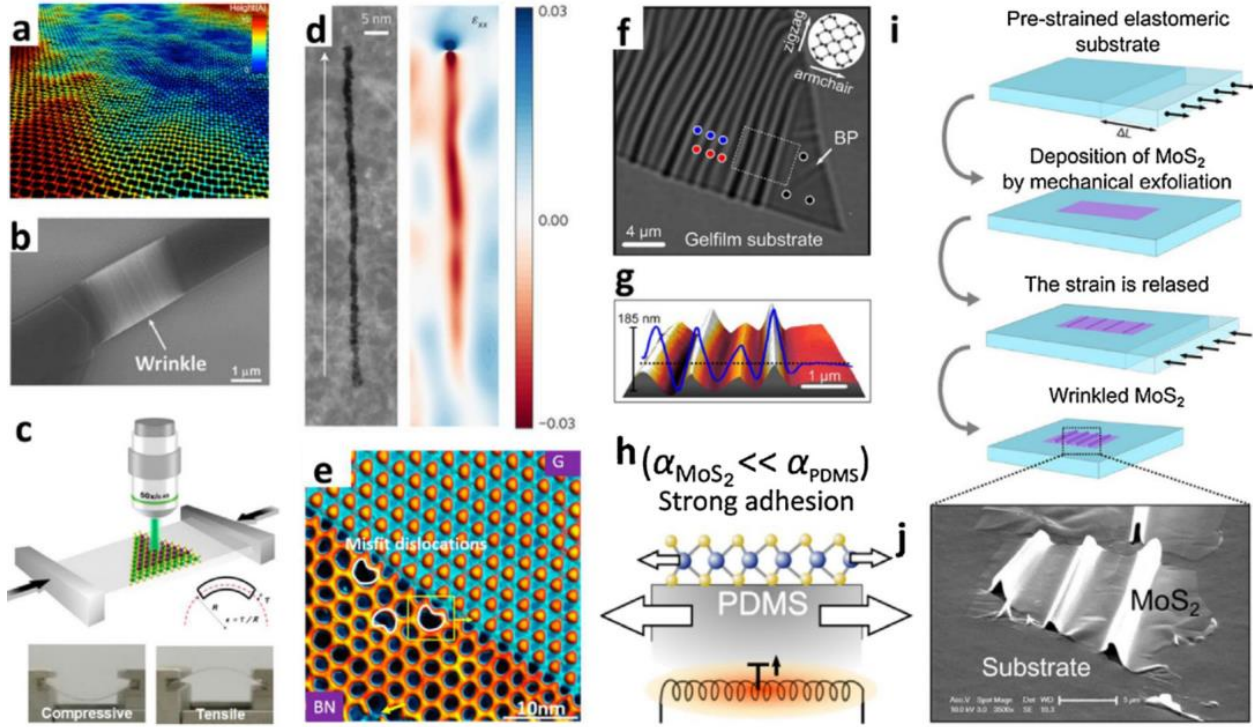


Figure 1-10. Strain engineering in 2DNMs: (a) thermal expansion introduced strain in monolayer sample; (b) SEM image of introduced wrinkles on mechanical exfoliated method MoS₂; (c) schematic of compressive and tensile strain in WS₂/MoS₂ vertical heterostructure substrate by bending; (d) STEM image (left) and its strain map (right) of a MoS₂ 1D channel formed from an intrinsic 5|7 dislocation in WSe₂; (e) magnified STM image of lattice disorder at graphene/BN heterostructure boundary; (f) transmission-mode optical image of a ripples 10 nm thick black phosphorus flake; (g) atomic force microscopy topography image for the dashed line rectangular region in (f); (h) schematic of the thermal expansion experiments with MoS₂ on SiO₂ (f) and PDMS substrates (g); (i) schematic of prestretched substrate compressive strain introducing method, and (j) SEM of wrinkled MoS₂ on substrate [81, 82, 84-89].

On the other hand, due to the fact that substrates and 2DNMs have different thermal expansion coefficients and lattice constants, it is predicted that non-uniform and localized strain (lateral) will accumulate on the 2DNMs throughout the CVD process. Strain is applied to heteroepitaxy-grown thin films up to a crucial layer thickness (on the order of a few nanometers) [90, 91]. In both

vertical and lateral heterostructures, the critical thickness is dependent on the lattice constant mismatch at the interface, with a larger critical thickness anticipated for a greater lattice constant mismatch. Unlike their three-dimensional counterparts, the two-dimensional thin film, on the other hand, may undergo out-of-plane deformations to relieve interfacial strain without introducing dislocations. In certain situations, as seen in **Figure 1-10e**, the interfacial strain relaxes at the one-dimensional interface due to the development of misfit dislocations. Interfacial strain and relaxation layer thickness also depend on other interfacial characteristics, such as interface defect and inter-weak layer [86]. The interlayer's high defect density and significant relaxing ability are predicted to minimize the interfacial strain and critical thickness caused by mismatched lattices. In another method, MoS₂ on a heated PDMS substrate produces thermal expansion of the MoS₂; nevertheless, due to the PDMS substrate's higher thermal expansion coefficient, the PDMS substrate can generate an extra biaxial strain in the MoS₂, as seen in **Figure 1-10h**. In comparison, the reference samples with MoS₂ on SiO₂ generate less strain, which is owing to SiO₂'s lower thermal expansion coefficient and a smaller thermal expansion mismatch between MoS₂ and SiO₂. Additionally, the laser beam may be used as a heat source to produce localized heating and strain control in the MoS₂; however, the highest strain achieved by this approach is negligible (0.2 percent) [92].

Also, phase engineering by strain has enabled enhanced electrocatalytic activity via a switch from the semiconducting 2H-phase to the metallic 1T-phase [30, 37]. Without the introduction of a metastable 1T phase, Li et al. reported the first viable experimental method to activate the basal plane of the 2H-phase MoS₂ by creating S-vacancies and applying tensile strains [32]. In their work, MoS₂ was deposited on a substrate with Au nanocones by chemical vapor deposition (CVD). Later, capillarity-force induced strains were used to tune the hydrogen adsorption free energy

(ΔG_H) to the optimum value in the 2H-phase MoS_2 samples with S vacancies ranging from 9 to 19%. The strained 2H-phase MoS_2 monolayers with S vacancies achieved a similar catalytic activity ($\Delta G_H = 0.08$ eV) to that of MoS_2 2H-phase edge sites ($\Delta G_H = 0.06$ eV). However, this technique requires precise control of both the strain and S vacancy concentration, which remains a significant experimental challenge [32]. There is still lacking a method to study the strain-catalysis property by applying strain directly. Thus, in our research, we developed a new experimental method to control the tensile strain in 2D materials. Also, to fully realize the potential of TMD catalysts, a new method that can efficiently and effectively tune the catalytic properties is needed. This part will be discussed in later content. Also, a new test method is established for characterizing the electronic property change under different strain conditions. In this electrochemical test, the density of states (DOS) and the shape of the band structure will be plotted. With this new testing system, the in-situ change on material's quantum capacitance can be unraveled.

Since the bandgap can affect the HER activity and strain engineering can potentially adjust the bandgap, we proposed to reveal the relationship between the HER activity and strain on monolayer MoS_2 . Our goal is to design a method to apply strain to these monolayer materials. In this project, due to the predicted shrinkage of the bandgap after applying tensile strain, a better HER catalysis activity is expected to happen in monolayer MoS_2 .

2 EXPERIMENTAL TECHNIQUES

This chapter describes some of the key equipment and methods used for the work in this dissertation.

2.1 OPTICAL MICROSCOPY

A Nikon Eclipse ME600 microscope (Error! Reference source not found.) is used to find a monolayer sample on the substrate. The magnification of this microscope is adjustable from 100 $\times$ to 10000 $\times$. Under optical microscopy, the MoS₂ will show different colors with different layer numbers. Based on this difference, we can recognize the monolayer MoS₂ during the optical-searching process. After this step, Raman spectroscopy will be used to examine the exact layer number of samples.

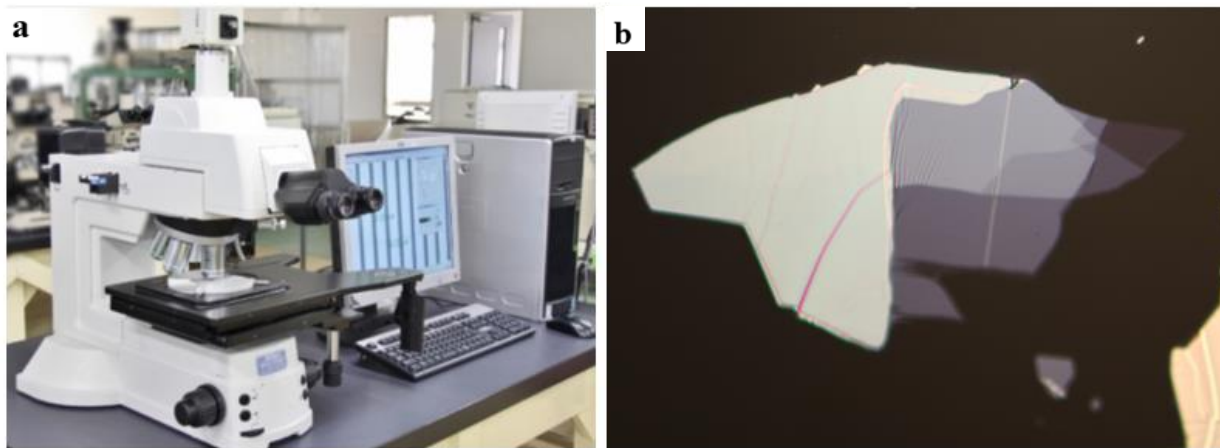


Figure 2-1. Optical microscope and image of MoS₂: (a) the Nikon Eclipse ME 600 microscope, (b) a MoS₂ sample with different layer numbers under optical microscopy

2.2 MAGNETRON SPUTTERING COATING

The magnetron sputtering coating system in Prof. Junlan Wang's lab (**Error! Reference source not found.a**) is used to deposit a Cr film to create a conductive layer for the later e-beam photolithograph process. The model name of this magnetron sputtering system is AJA-Orion. There are three different target guns set in the main chamber, one RF and two DC guns. The base vacuum of the main chamber is 10^{-8} mTorr, and the maximum running power is 500 W. The coating layer material Cr is placed in one of the DC guns. The coating time and power are 10 s and 100 w for getting a 20 nm thickness conductive layer.

Also, another PVD method is used to deposit the electrode connecting to the MoS_2 . The Ti and Au film electrodes were deposited by the thermal evaporator from the shared facility center in the UW (**Error! Reference source not found.b**). There are four thermal sources that can allow co-evaporation of up to two materials with the scalable output voltage of up to 10 V. 100×100 mm substrate hold can be programmed to heat up to 600°C and rotates between 0 - 60 rpm. The base vacuum is 1×10^{-7} mbar. At a certain deposition rate, the system controls the power automatically. The temperature is controlled below 45°C to prevent the bending of the PET substrate. The Ti layer is designed as a bonding layer between PET and gold.

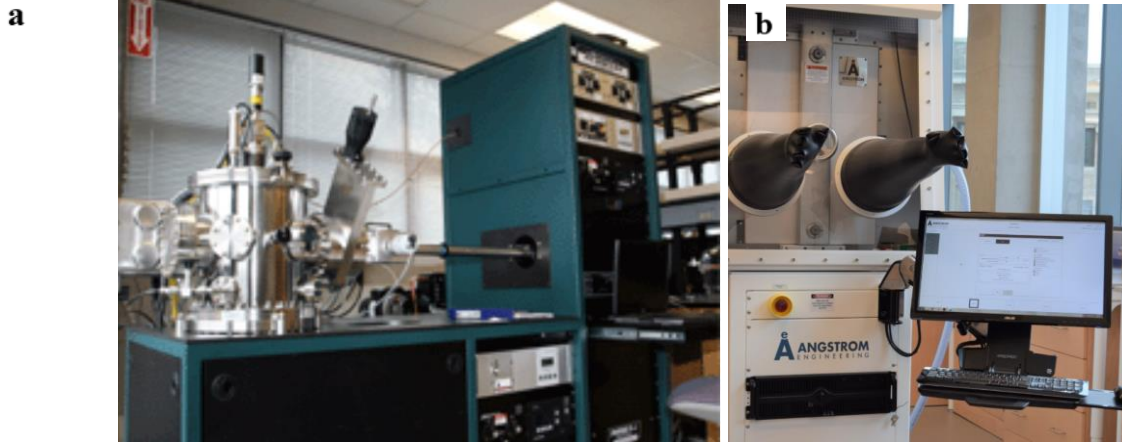


Figure 2-2. Deposition tool for the device fabrication: (a) the AJA-Orion magnetron sputtering system, (b) the Angstrom Engineering Nexdep thermal evaporator

2.3 SPIN COATING

A Laurell WS-400BZ model spin coater (Error! Reference source not found.**a**) is used for getting the photo resistance coating layer for the future electron-beam photolithography process. The layer material is PMMA-495 A4 and PMMA-950 A4. The relationship between layer thickness and spin speed is shown in Error! Reference source not found.**b & c** [93]. For obtaining the appropriate thickness ($\sim 1.5 \mu\text{m}$), the coating speed is 4000 rpm for 1 min. Otherwise, a too thick photo resistance coating layer will cause inaccurate lithography to the material. A too-thin coating layer will lead the later lift-off process unsmooth.

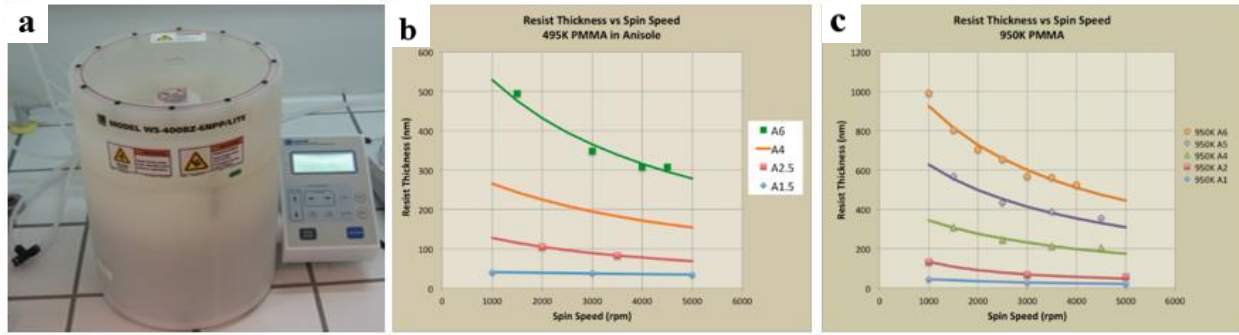


Figure 2-3. Spin coating tool and PMMA spin-coating thickness: (a) the Laurell WS-400BZ model spin coater, (b) coating thickness vs. spin speed for PMMA 495 class, (c) coating thickness curve vs. spin speed for PMMA 950 class [93]

2.4 RAMAN SPECTROSCOPY

The Raman spectroscopy was used to determine the sample's layer number. Raman spectroscopy is a technique that can detect the vibration mode of the bond between atoms. Due to the vibration difference between different atoms, the monolayer or bilayer MoS_2 shows different peak positions from multilayer samples. As shown in Error! Reference source not found. **b**, when the layer number of material is reduced to one, the E^{1}_{2g} and A_{1g} peaks shift to each other [94]. This phenomenon can be used to confirm the layer number of a monolayer TMD material.

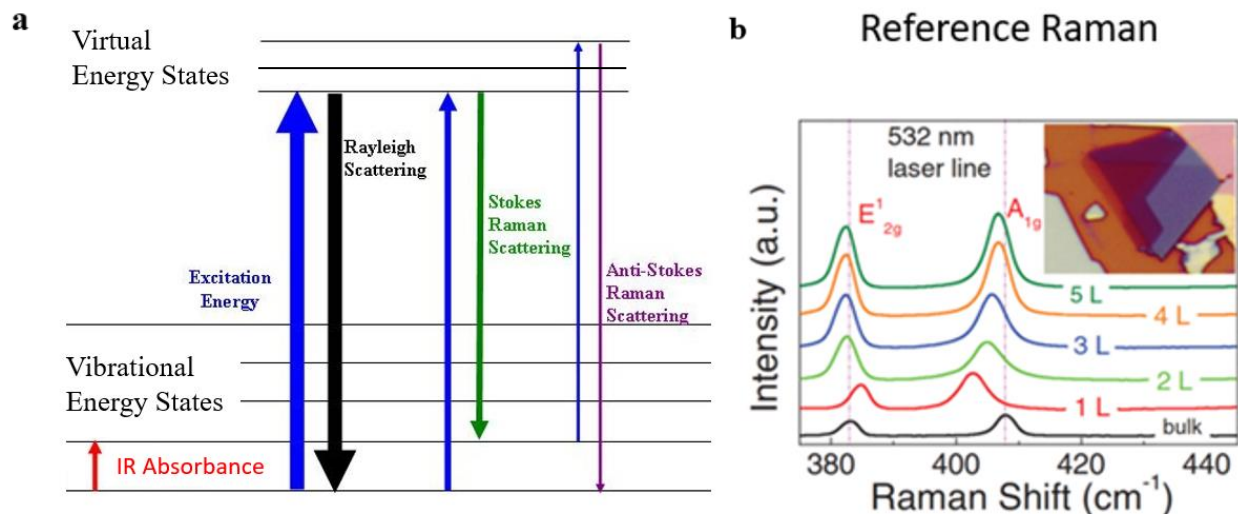


Figure 2-4. Schematic of Raman Spectra and Raman results of MoS₂: (a) principles of Raman spectroscopy, (b) reference Raman spectra result for MoS₂ from the literature [94]

The principle of Raman spectroscopy is based on the fact that the bonding mode of atoms can be influenced by the jumping or vibration of electrons (Error! Reference source not found.a). The Raman effect's magnitude is proportional to the polarizability of the electrons in a molecule. It is a type of inelastic light scattering in which the sample is excited by a photon. This excitation briefly places the molecule in a virtual energy state prior to the photon's release. Inelastic scattering occurs when the released photon has a different energy than the incident photon (either lower or higher). After the scattering event, the sample is in a different rotational or vibrational state. Once the molecule changes its rotational-vibrational-electronic state, the dispersed photon must shift to different energy and thus frequency to maintain the system's total energy constant. This energy difference is equivalent to the difference in energy between the molecule's initial and final rovibronic states. If the last state has higher energy than the initial state, the scattered photon will drop to a lower frequency (lower energy) in order to keep the same total energy. This is referred

to as a Stokes shift or downshift. If the final state has lower energy, the scattered photon will undergo an anti-Stokes shift or upshift. Also, in order to exhibit a Raman effect, a molecule must demonstrate a change in its dipole-electric polarizability with respect to the vibrational coordinate corresponding to the rovibronic state. The Raman scattering intensity is proportional to this change in polarizability. As a result, the Raman spectrum (scattering strength as a function of frequency shifts) is dependent on the molecule's rovibronic states.

With these specifications, the Raman Spectra is the desired method to examine the atomic layer numbers of a 2D material by examining its E_{2g}^1 and A_{1g} peaks. E_{2g}^1 peak reflects the opposite vibration of two S atoms with respect to the Mo atom, while the A_{1g} peak reflects the out-of-plane vibration of only S atoms. When the layer number of MoS_2 shrinks to two layers or one layer, the vibration mode of S atoms will be affected and further leads a Raman peak shifting.

2.5 SECOND-HARMONIC GENERATION SPECTROSCOPY

Second-harmonic generation (SHG) spectroscopy was used to test the edge direction of MoS_2 for adding uniaxial strain. SHG, also called frequency doubling, is a nonlinear optical process in which photons interacting with a nonlinear material are effectively ‘correlated’ to form new photons having twice the frequency of initial photons. SHG was firstly demonstrated by Franken and his colleagues in 196 [95].

The laser source used in the SHG test is completed with the help of Dr. Xi Wang in Prof. Xiaodong Xu’s group. The light source used in the test is an 810 nm femtosecond laser. The power used in the test is 300-microwatts. A hexagonal flower shape polar plot will be obtained from the test as a function of the crystal’s azimuthal angle θ . Based on the fitting of the dots of the SHG test, the

direction of the MoS₂ lattice direction can be decided. There are two different directions in MoS₂, as shown in Error! Reference source not found.; one direction is zigzag, another is armchair. The terminated atoms are different on these two edges. At the zigzag edge, the terminated atom usually is Mo. At the armchair edge, the edge usually ends with a pair of Mo and S atoms. This difference between the two edges will lead to electrochemical and electronic properties' difference.

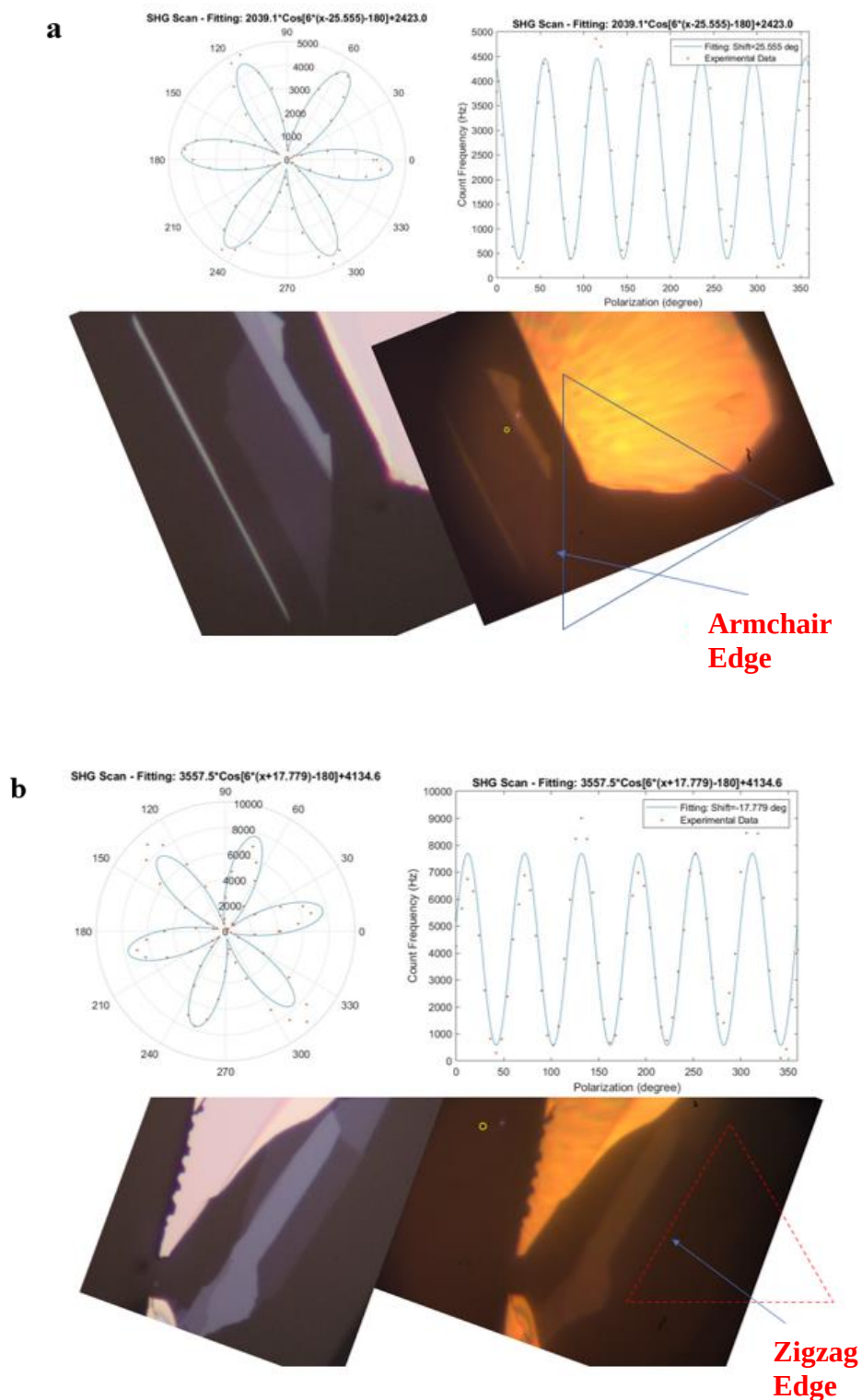


Figure 2-5. SHG results of monolayer MoS₂: (a) SHG plot for an armchair direction monolayer MoS₂ sample, (b) SHG plot for a zigzag direction monolayer MoS₂ sample

2.6 ELECTROCHEMICAL PROBE STAGE AND ELECTROCHEMICAL WORKSTATION

Electrochemical measurements were carried out by combining an electrochemical workstation (BioLogic SP-300) and a probe station in Prof. Yang's lab. The electrochemical test system consists of a 3-electrode experimental setup (**Error! Reference source not found.a**). The reference electrode is saturated calomel, the counter electrode is carbon, and the working electrode is gold. These two probes are set on an electrochemical testing stage that connects to the working electrode (**Error! Reference source not found.b & c**). The reference electrode can provide the reference potential reading. The counter electrode can provide the other information in the test. All the electrodes will connect to an electrochemical workstation (**Error! Reference source not found.d**).

With the BioLogic SP-300 electrochemical Workstation, the current vs. voltage, impedance, and capacitance results can be obtained\ during the test. The SP-300 is a state-of-the-art research grade potentiostat featuring a range of 50 nA to 20 A, built-in Electrochemical Impedance Spectroscopy (EIS), and high-end specifications such as 7 MHz max frequency, floating mode, analog filtering, built-in calibration board, and stability bandwidths. The SP-300 potentiostat's modular chassis can integrate an optional high current/high voltage option board (up to 20 A & up to 48 V) or a second potentiostat board (either standard or EIS). The instrument can also be used as a multiple-user system as two different researchers can use each channel board independently.

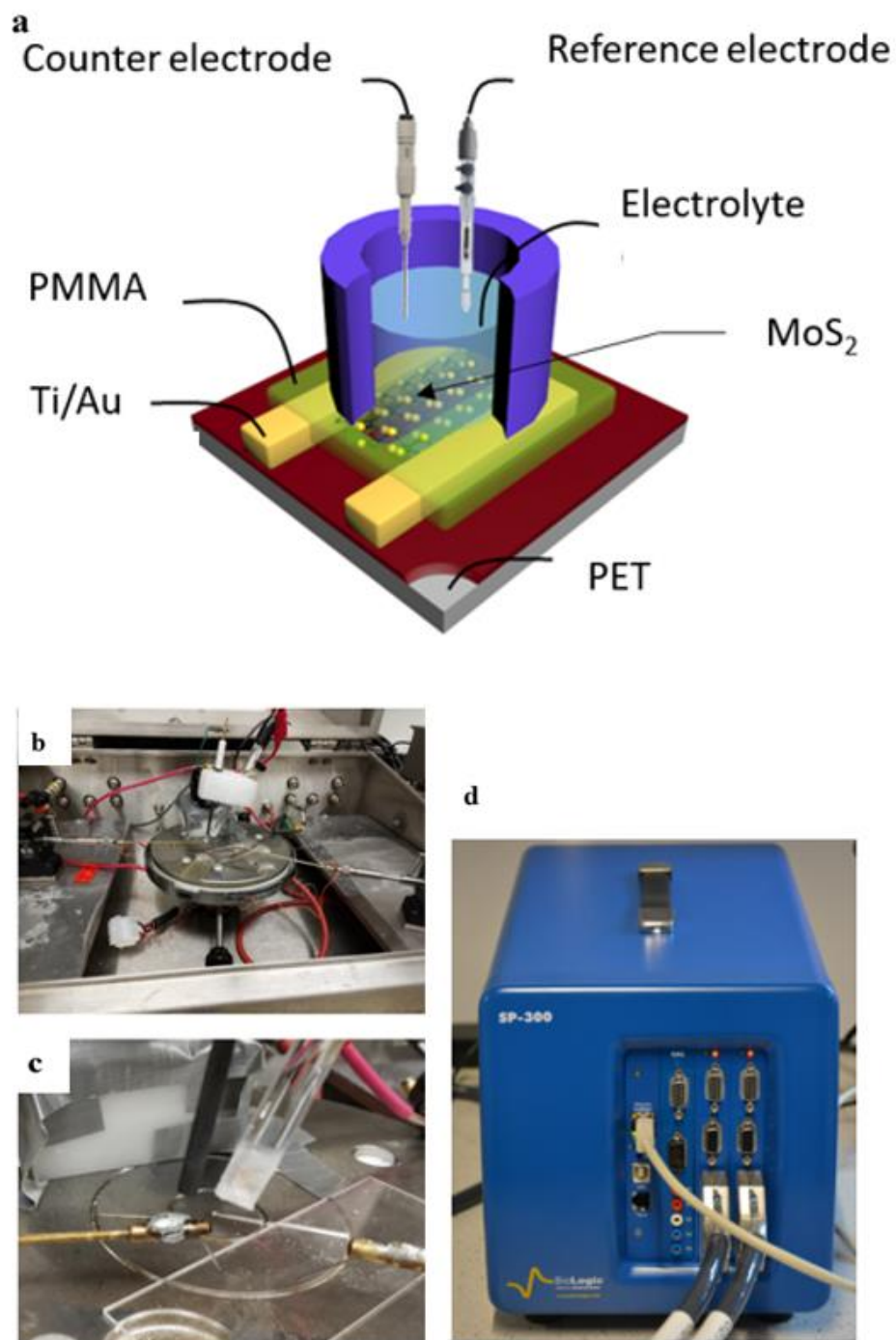


Figure 2-6. The electrochemical test setup: (a) schematic of the electrochemical test set up, (b) & (c) real photos of the electrochemical test stage with four probes, (d) BioLogic SP-300 potentiostat

2.7 TESCAN XYZ SCANNING ELECTRON MICROSCOPE/ELECTRON BEAM LITHOGRAPHY MACHINE

The TESCAN VEGA3 (Prof. Xu's lab, Physics-Astronomy-Building, UW) is a tungsten thermionic emission SEM system suitable for high- and low-vacuum operations (Error! Reference source not found.). A high spatial resolution with secondary electron and backscatter detector allows the observation with fine surface details. This is a vital feature for the comprehensive characterization of material research. Also, this SEM is equipped with the electron beam lithography tool. Under the electron beam lithography mode, the SEM is equipped with an electrostatic blanker and DrawBeam software to write features on photoresist with dimensions of a few tens of nanometers. The following is its working condition:

- Wafer Size: up to 20×20 mm
- Source: Schottky Field Emission Gun
- Acceleration voltage: 0.2 - 30 kV
- Minimum electron beam spot size: ~ 2.5 nm
- Minimum Electron beam current: ~ 10 pA



Figure 2-7. The TESCAN VEGA3 XYZ scanning electron microscope/electron beam lithography machine

3 DESIGN AND FABRICATION OF THE 2D FLEXIBLE TEST PLATFORM

Based on previous theoretical predictions, MoS₂ should undergo anisotropic nonlinear elastic deformation up to an extra-large ultimate strain of 0.24, 0.37, and 0.26 for armchair, zigzag, and biaxial deformation, respectively. Experimental observations predicted an ultimate strain without fracture of MoS₂ is 11% [70, 96]. Thus, with an appropriate method, we should be able to successfully apply tensile strain to the monolayer MoS₂ sample. Also, based on the theoretical prediction, the MoS₂'s band structure and catalysis property will be changed after applying strain. This motivated us to measure the electronic structure and HER catalysis difference between unstrained and strained MoS₂.

Thus, this project requires the design and fabrication of a flexible test device to subject the monolayer MoS₂ to different strain conditions. The project's objective is to apply strain engineering to adjust the bandgap in monolayer MoS₂ and validate the bandgap change by testing the HER activity. For the measurement of the catalysis activity, an electrochemical test terminal will be used in the experiments.

3.1 DEVELOPMENT OF DEVICE FABRICATION PROCEDURE

3.1.1 Flexible Substrate Selection

As discussed in section **Error! Reference source not found.**, there are many works about the fabrication of an in-chip microdevice. However, none of the existing works has examined the strain applying electrochemical microdevice. In order to realize the experimental design - applying the

strain, a flexible test device needs to be developed. Inspired by the research of Rogers et al. [97, 98], a new method to fabricate flexible circuit devices is proposed in the current project. The first step is selecting an appropriate substrate for the device. Usually, the substrate for the 2D materials is the Si wafer. However, to facilitate the application of strain, a flexible substrate needs to be selected. Several different polymer materials were considered as the potential substrate in the device design process, including PDMS, PC, PET, etc.

Polydimethylsiloxane (PDMS), also known as dimethylpolysiloxane or dimethicone, is a member of the group of polymeric organosilicon compounds known as silicones. Due to its versatility and properties, PDMS is the most widely used silicon-based organic polymer. It is best known for its extraordinary rheological (or flow) properties. PDMS is an optically clear material that is inert, non-toxic, and non-flammable in general. It is one of a number of different types of silicone oil (polymerized siloxane). It is used in a variety of commercial products, including contact lenses, medical devices, and elastomers; it is also found in shampoos (as an antifoaming agent), food (as an antifoaming agent), caulking, lubricants, and heat-resistant tiles [99]. PDMS is also used for making a dome which is desired for transferring 2D materials. In our experimental test, we tried to exfoliate MoS_2 onto the PDMS substrate. However, the adhesion force between MoS_2 and PDMS is not stable. And the PDMS cannot survive in acetone during the lift-off process.

The next polymer we tested was polycarbonates. Polycarbonates (PCs) are a class of thermoplastic polymers with chemical structures that contain carbonate groups. Polycarbonates are strong, resistant materials that are optically transparent in certain grades. They are widely used in engineering fields and quite easy to work with by molding and thermoforming. Polycarbonates have a wide variety of uses due to these qualities. Polycarbonates lack a specific resin identification

number (RIC) and are therefore classified as "Other," the seventh RIC on the list. The precursor monomer bisphenol A may be present in polycarbonate products (BPA) [99]. In the 2D materials' experimental field, PC is used as a sealing film or adhesive layer between the PDMS dome and substrate. The reason for abandoning the PC is also because it cannot survive acetone.

PET, or polyethylene terephthalate, is the most widely used thermoplastic polyester resin. PET is commonly utilized in textile fibers, containers for beverages and foods, thermoforming, and technical resins in conjunction with glass fiber. PET is a polymer composed of repeating ($C_{10}H_8O_4$) units of the monomer ethylene terephthalate. PET is often recycled and carries the resin identification symbol "1". (RIC). PET can exist as an amorphous (transparent) or semi-crystalline polymer, depending on its processing and thermal history. Depending on the crystal structure and particle size of the semicrystalline substance, it may appear transparent (particle size less than 500 nm), grey, or white (particle size up to a few micrometers) [99]. PET was identified to be the best substrate for attaching the monolayer MoS_2 samples and further applying the tensile strain using the biaxial beam bending method. Also, PET can survive in both the acetone and the IPA environment. These specific properties make it a suitable substrate in the following experiment.

3.1.2 Conductive Layer Development

After the selection of the appropriate substrate material, the next important step is to fabricate an electric test device on the selected PET substrate. For achieving the nanoscale circuits, the electron beam photolithography method is widely using in the traditional Si-based MEMS fabrication process, but it is rarely used on flexible (polymer-based) substrates. Thus, how to develop electrodes on a polymer substrate is a major challenge in this project. Not only the smoothness of the polymer substrate is far below that of a silicon substrate, but also the polymer is nearly

insulated. This makes the photolithography process on a polymer substrate much more complicated than on a Si substrate. For overcoming these challenges, the first step is to select an appropriate material as the conductive layer for the electron beam process.

The poly(3,4-ethylene dioxythiophene) polystyrene sulfonate (PEDOT: PSS) was first selected as the conductive layer. This is a rare conductive polymer. One component in this mixture is sulfonated polystyrene which is made up of sodium polystyrene sulfonate. Some members in the sulfonyl groups are deprotonated and carry a negative charge. The other component, poly (3,4-ethylene dioxythiophene) (PEDOT), is a conjugated polymer and has positive charges, and is based on polythiophene. This polymer can stick to the charged macromolecules and form a macromolecular salt [99]. The PEDOT: PSS was coated on the PET substrate by the spin coating method. However, because of the mechanical exfoliating process, some glue tends to remain on the surface of PET. And these glue-covered places will cause a cluster of PEDOT on them. Then these clusters will generate a nonuniformly conductive area on the surface, which will affect the Ebeam photolithography process.

During the second try, an Al layer was deposited on the substrate as the conductive layer using magnetron sputtering deposition. The Al target was placed into the DC gun. Then a 100 W power was applied to the target under 4 mTorr Ar environment. A 50 nm thickness conductive layer was obtained after 18 mins deposition. However, an aluminum oxide layer will form on top of the Al layer after exposure to air. This oxide layer will lead to poor conductivity and affect the E-beam lithography process.

In the third try, inspired by the SEM coating method, a 20 nm carbon layer was coated through the PVD method. This carbon layer can provide the conductive layer to the polymer substrate and has good smoothness. However, we did not find an appropriate way to remove this carbon thin film after the lithography step.

At last, a Cr layer was deposited by the magnetron sputtering method and was found to be the best conductive layer. During the magnetron sputtering, the Cr source was placed in the RF gun. The deposition condition is 90 W and 5 mTorr in the Ar environment. The deposition time is 720 s. After the deposition, the Cr-covered PET was tested in the electron beam lithography process. Several L-shaped signs were tested under different current densities to determine the best Ebeam condition.

After the E-beam process, this Cr layer can be removed by a Cr etchant. Then, the developer (IPA: water 7:3) was used to develop the sign. After testing, 20 s is the best time for the development. A 10s development time will cause the PMMA to remain on the substrate, while a 30 s development time will cause the edge of the sign not to be sharp. Also, the layer thickness of PMMA is well designed for a better lift-off process.

3.1.3 Photoresist Development

The development of making a good photoresist coating took a long time. At the beginning of this project, due to the lack of experience of coating on PET substrate, we used the PMMA coating parameters of a similar device for Si substrate. However, due to the surface roughness difference between PET and Si, the coating parameter of PMMA on Si does not work for PET. After several trials, we found that double the thickness of the photoresist on Si works best for the PET substrate.

Also, the thickness and layer numbers of PMMA can directly affect the later lift-off process. In this study, two different PMMAs are involved. One is PMMA 495 A4; another is PMMA 950 A4. These two PMMAs have different viscosities. First, one layer of PMMA 495 and one layer of PMMA 950 were spin-coated on the PET surface at 4000 rpm. These two PMMA layers were found not thick enough for exposing and lift-off processes. Under this configuration, the lift-off process always peels off the Au electrode and leads to failure. So, three layers of PMMA were designed in the fabrication process for a better lift-off result. This three-layer PMMA design can effectively enlarge the deposition angle of Au and creates a gap between the deposited electrode and nearby PMMA. As shown in Error! Reference source not found.**b**, the gap generated between the bottom of the PMMA 495 and the deposited gold electrode can smooth the lift-off process, which is important in the fabrication process.

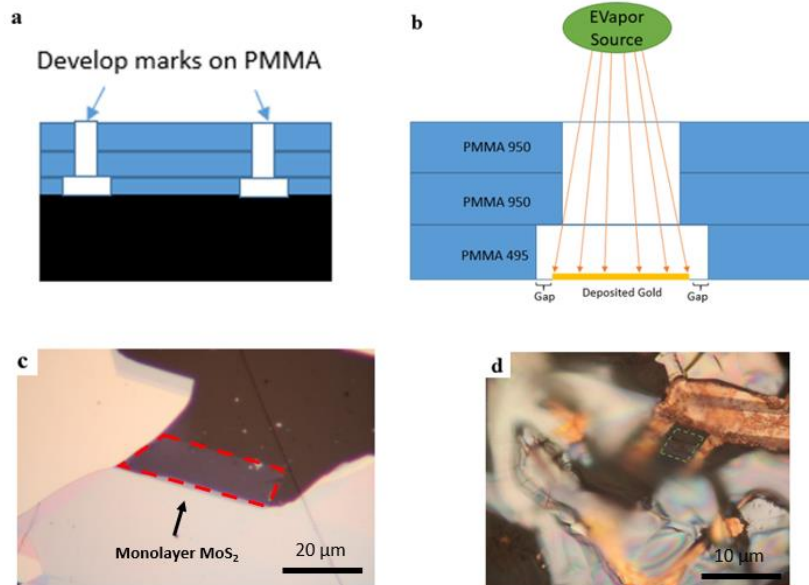


Figure 3-1. PMMA development of MoS₂ device: (a) schematic of three-layer PMMA with marks, (b) schematic of Au electrode deposition, (c) a monolayer MoS₂ sample (d) Au electrode on (c) with opened test window

After depositing the gold electrode, the sample will then be soaked in acetone for 48 hrs on a hot plate at 55°C. The temperature and soaking time were determined by multiple tests for yielding the best electrode.

After obtaining the Au electrodes, another two layers of PMMA 495 and PMMA 950 were spin-coated on the sample for opening a test window (Error! Reference source not found.d). In the process, the conductive metal layer needs to be deposited to the PMMA's top surface again for the E-beam process. And after locating the sample position, the cross-shaped marks are be E-beamed around the sample. At last, an appropriate size window will be opened by developing and removing the photoresistance in the selected region.

3.2 FABRICATION FLOW

After the determination of the materials for the substrate, photoresist, conducting layer, and electrode, the experimental procedure was finalized. In the experiment, mono-layer, bilayer, and multilayer MoS₂ nanosheets were mechanically exfoliated from one bulk single-crystal MoS₂, ensuring the samples' consistency. The MoS₂ nanosheets used in the experiment were confirmed to have the 2H-phase. The layer numbers were estimated based on the contrast under the optical microscope and then confirmed by the Raman Spectroscopy.

In this project, the substrate for MoS₂ is selected to be polyethylene terephthalate (PET), which can be used to apply strain easily. Then, MoS₂ samples are transferred from 3M tape to the PET substrate after mechanical exfoliating a bulk MoS₂ several times. Thus, some MoS₂ thin pieces will stay on the PET substrate. After that, an optical microscope is used for identifying monolayer

MoS₂ samples from the thin samples based on the special color of the monolayer MoS₂ on the PET, which is placed on a 380 nm SiO₂ wafer.

After identifying monolayer MoS₂, a two-step E-beam lithography process will be used to develop the electrode on the selected MoS₂ to facilitate later electrochemical testing microdevice. One-layer polymethyl methacrylate (PMMA) 495 and two-layer PMMA 950 will be spin-coated onto the PET substrate and dried by 50 °C for 15 mins. The usage of different PMMAs is for getting different reaction areas because PMMA 495 and PMMA 950 have different photon sensitivity within the E-beam lithography process. By using a magnetron sputtering system, a 10 nm thick Cr layer is deposited onto the PMMA layer as a conductive layer on the PMMA. After finishing all these preparations, the E-beam photolithography method is used to make electrodes and a test window for later HER catalysis tests on the monolayer MoS₂ samples.

After exposing the electrode area, 5 nm Ti and 80 nm Au will be deposited over the entire PET substrate by thermal evaporation. Then, the entire substrate is immersed in acetone solution for 72 hours to lift Au and Ti except for the electrode area. After lifting off, the sample will be washed with isopropanol and dried with the N₂ three times. Afterward, a new layer of 950 PMMA A4 was spin-coated on the sample as the passivation layer at 800 rpm for 10 s and then 4000 rpm for 40 s. The photoresist 950 PMMA A4 was dried at 60 °C on a hot plate for 5 min. A 495 PMMA A4 was then spun on the 950 PMMA A4 layer with the same spin and baking procedure. The bilayer PMMA well was etched using the electron-beam lithography and the 3:7 water/IPA aqueous developer to expose the reaction area of the monolayer MoS₂ flake. Finally, a plastic electrolyte container (10 – 15 mL) was constructed on the bilayer PMMA to ensure a stable electrochemical

environment during the electrochemical measurements. The process flow is shown in Error! Reference source not found. **a - f**.

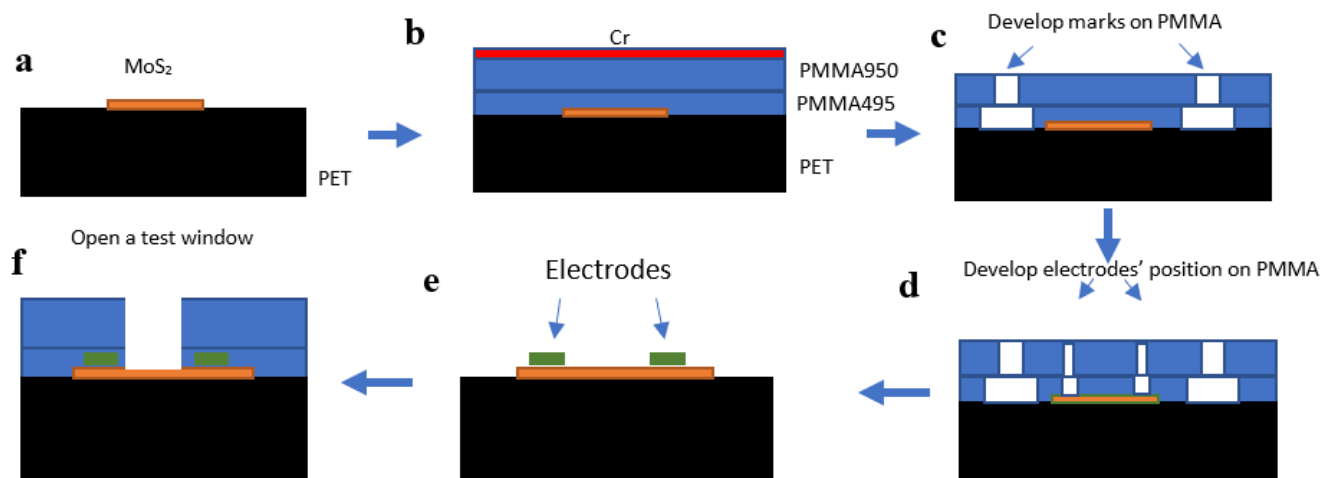


Figure 3-2. Fabrication process of the flexible HER catalysis test device: (a) monolayer MoS_2 sample on PET substrate, (b) two-layer PMMA with Cr conductive layer on monolayer MoS_2 , (c) developed PMMA with E-beam lithography markers, (d) electrode window opening on the MoS_2 , (e) deposited electrodes on the monolayer MoS_2 sample, (f) electrochemical test window on the monolayer MoS_2

The project aims to apply strain engineering to reduce the bandgap in monolayer MoS_2 and validate the bandgap change by testing the HER activity. This project requires the design and fabrication of flexible test devices to subject the monolayer MoS_2 to different strain conditions. For measuring the catalysis activity, an electrochemical test terminal is used in the experiments. The MoS_2 nanosheets, a graphite electrode, and a saturated calomel electrode (SCE) serve as the working, counter, and reference electrodes, respectively. The Ti/Au (5/80 nm) contact electrodes were protected by covering them with a polymethyl methacrylate (PMMA) layer to avoid electrolyte

corrosion. A window exposing the sample was created with electron beam lithography. Subsequently, a plastic electrolyte container was attached to the PMMA to ensure an approximately constant electrolyte concentration for the measurements' duration. The plastic electrolyte container can hold ~ 20 ml electrolyte and exhibits much better cycling stability than the droplet configuration.

3.3 TENSILE STRAIN APPLICATION SETUP

Based on the theoretical predictions, the MoS₂ should undergo anisotropic nonlinear elastic deformation up to an extra-large ultimate strain: 0.24, 0.37, and 0.26 for armchair, zigzag, and biaxial deformation, respectively. Experimental observations predicted a maximum strain of MoS₂ is 11% [70, 96].

After fabricating the MoS₂ electrochemical test device, the strain applying device in this project will be facilitated (Error! Reference source not found.a). The principle is based on biaxial plate bending. The previous PET substrate with MoS₂ and electrode is attached to another PET cross by superglue in this process. And a dome-shaped glass dish is selected as a holding substrate for bending PET cross to the desired shape. By measuring the total thickness of the PET cross and PET substrate, the neutral axis of the substrate can be defined. And the single direction strain can be calculated by the equation: $\varepsilon = \frac{t/2}{(\frac{t}{2}+R)}$. Where R is the radius of the dome and t is the total thickness of the two PET substrates (the thickness of the MoS₂ monolayer sample is ignored). Domes with different radius R are used to apply different amounts of strain.

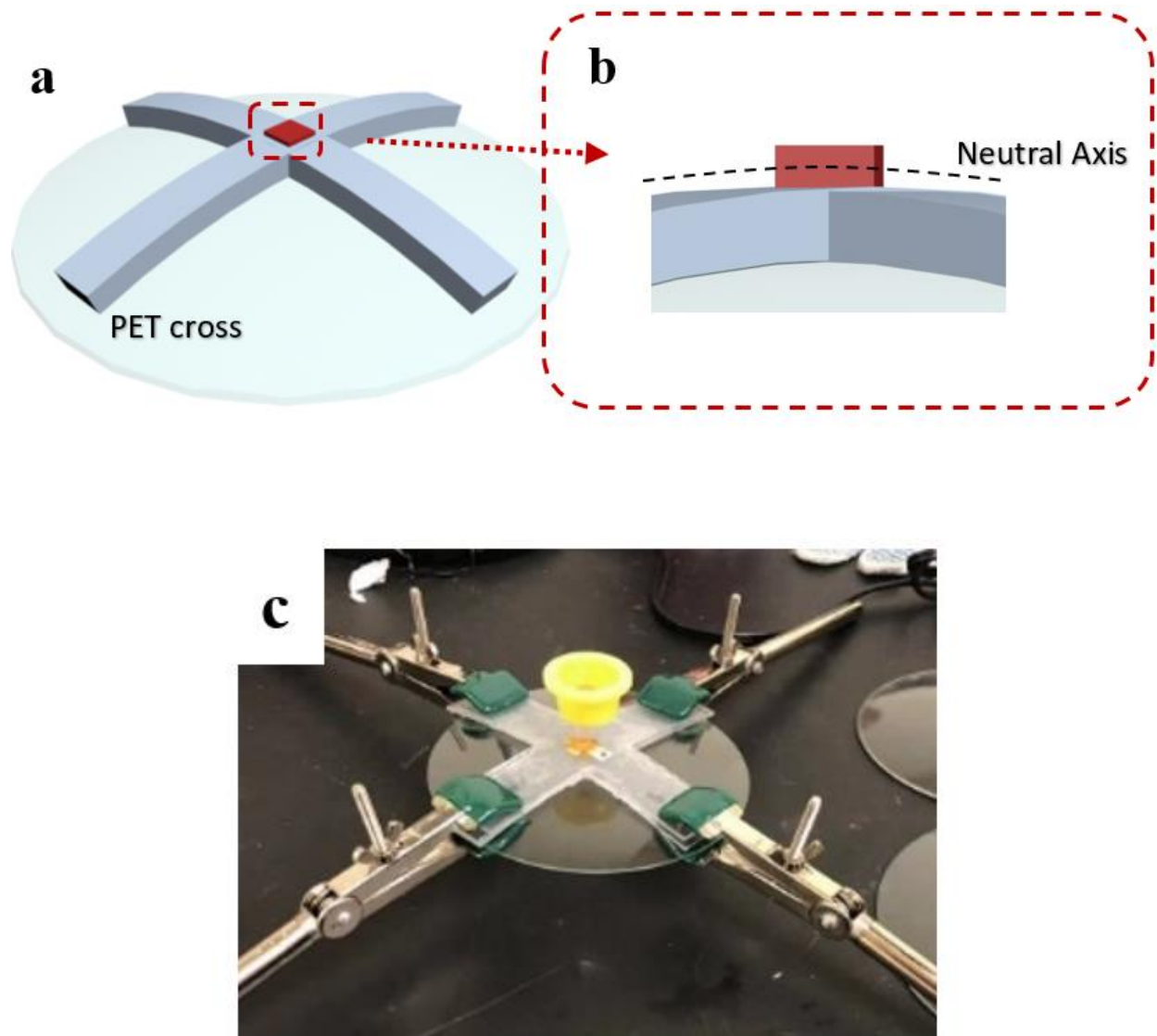


Figure 3-3. Applying strain using biaxial beam bending: (a & b) the schematic of biaxial strain application method, (c) photo of applying strain using the flexible device

3.4 ELECTROCHEMICAL TEST SETUPS AND CONDITIONS

There are two major electrochemical tests in the experiment. First, the electronic property and electrochemical quantum capacitance of monolayer MoS₂ will be tested. Second, the HER test with monolayer MoS₂ as the catalyst will run under different strain conditions. The electronic property and electrochemical capacitance can be used to understand the intricacies of the HER catalysis performance change. The electrochemical test setups for electrochemical/quantum capacitance and HER tests are different.

In the electrochemical capacitance test, for getting accurate capacitance results, different ionic liquids have been tested, including [BMIM] [PF₆], [BMIM] [BF₄], and [EMIM] [DCA]. The capacitance test of different ionic electrolytes was conducted with a 2-electrode setup with one electrode as carbon and the other as Pt. The reason of choosing Carbon and Pt as electrodes are Carbon is a good conductive electrode while Pt is stable and inert in most of conditions. For studying the testing frequency effect on the electrolyte, all ionic electrolytes were tested from 5 Hz to 100 Hz. We demonstrated that the [EMIM] [DCA] has the highest C_{ion} of over 120 $\mu\text{F}/\text{cm}^2$ at 5 Hz (Error! Reference source not found.**a**) but has a smaller electrochemical stability window than that of [BMIM] [BF₄] and [BMIM] [PF₆] (Error! Reference source not found.**b**). The [BMIM] [BF₄] can achieve near 120 $\mu\text{F}/\text{cm}^2$ at 5 Hz and -1.9 V to 1.9 V working range. This can cover most TMD materials. For [BMIM] [PF₆], it has a capacitance of around 20 $\mu\text{F}/\text{cm}^2$ at 5 Hz but the most extensive working range (-2.05 V to 2.3 V). This electrolyte can be used in the test when the capacitance testing range exceeds other ionic electrolytes. The electrochemical degradation potentials of the ionic liquids are further converted to the absolute energy (eV vs. vacuum), as

shown in Error! Reference source not found.**b**. Since [BMIM] [BF₄] covers the entire operating range of the monolayer MoS₂, it was chosen as the ideal ionic liquid for the electrolyte.

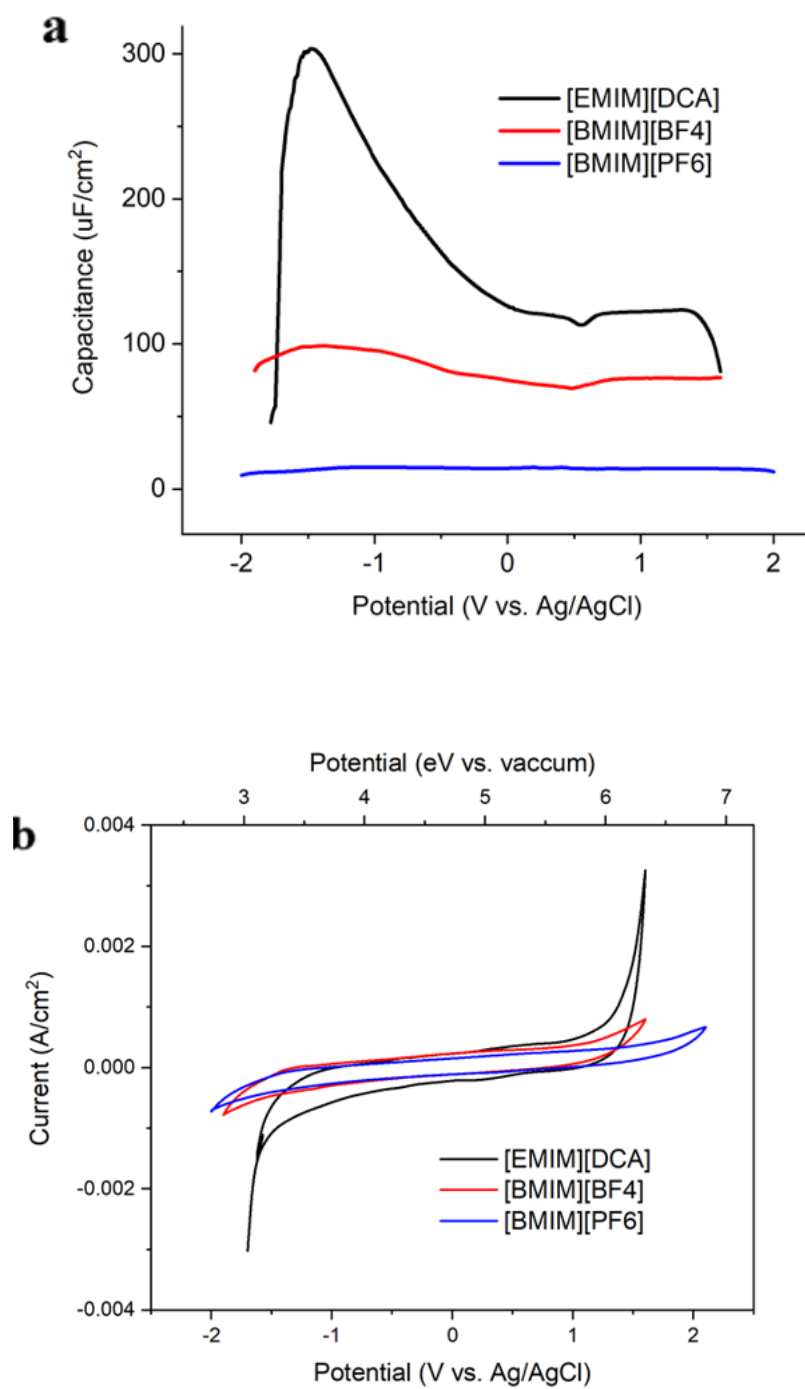


Figure 3-4. Band alignment of the ionic electrolytes [EMIM] [DCA], [BMIM] [BF₄], and [BMIM] [PF₆]: (a) the potential dependent areal capacitances at 5 Hz, (b) polarization curves at 10 mV/s

After the electrochemical capacitance test, the HER catalysis activity is measured by the same probe stage and potentiostat. The whole system includes one saturated calomel electrode as the reference electrode, one carbon electrode as the counter electrode. In the experiment, 0.5 mol/L sulfuric acids is chosen as the electrolyte. The electrolyte is in a rubber container which is attached to the opened test window on the top PMMA layer. Tests were run under different test potentials to get different currents, reflecting the HER reaction speed in MoS₂. By drawing the current vs. potential plot, the overpotential of reaction can be found. Also, the HER activities on the same sample under different strain conditions can be compared. The Tafel slope is also extracted for revealing the electrochemical reaction mechanism of HER for MoS₂ under different strain conditions. Further, the impedance will be tested for measuring the interface resistance between the electrode and electrolyte by electrochemical impedance spectroscopy (EIS).

4 ELECTROCHEMICAL CAPACITANCE AND DEFECT ENERGY STATES

4.1 BACKGROUND OF ELECTROCHEMICAL/QUANTUM CAPACITANCE OF 2D MATERIALS

In any chemical reaction process, the reaction prefers to happen at a certain potential. With this potential, the systems will keep the lowest energy level during the reaction. For understanding the intrinsic process in the reaction, especially around the reaction energy level, determination of the electronic state is important. In a catalyst triggering a reaction, the reaction potential relates to the catalyst's certain energy level with the lowest kinetic energy. In the HER test, the reaction energy level is around 4.44 eV which is close to the conduction band position of monolayer MoS₂. So, the characterization of the MoS₂'s band structure is investigated for analyzing the intrinsic change in the MoS₂ catalyzing HER test. There are two major methods to characterize the band structure. One is by scanning tunneling spectroscopy/scanning tunneling microscopy (STS/STM), and the other is through angle-resolved photoemission spectroscopy (ARPES).

STS is an experimental technique that uses a scanning tunneling microscope (STM) to investigate the local density of electronic states (LDOS) and bandgap of surfaces and materials on surfaces at the atomic scale [100]. Error! Reference source not found. **a & b** show the working mechanism of STS. STS is often defined as the observation of changes in constant-current topography with tip-sample bias, the local measurement of the tunneling current versus tip-sample bias (I-V) curve, or the measurement of the tunneling conductance, dI/dV . Due to the fact that the tunneling current in a scanning tunneling microscope flows only in a zone with a diameter of 5 Å, STS is unique in comparison to other surface spectroscopy techniques that average over a greater surface region.

STS has its origins in some of Gerd Binnig and Heinrich Rohrer's first STM work, in which they observed variations in the appearance of certain atoms in the (8×8) unit cell of the Si (111) – (8×8) surface as a function of tip-sample bias [101]. STS enables the investigation of the local electronic structure of metals, semiconductors, and thin insulators on a scale that is not possible with other spectroscopic techniques. Additionally, simultaneous recording of topographic and spectroscopic data is possible.

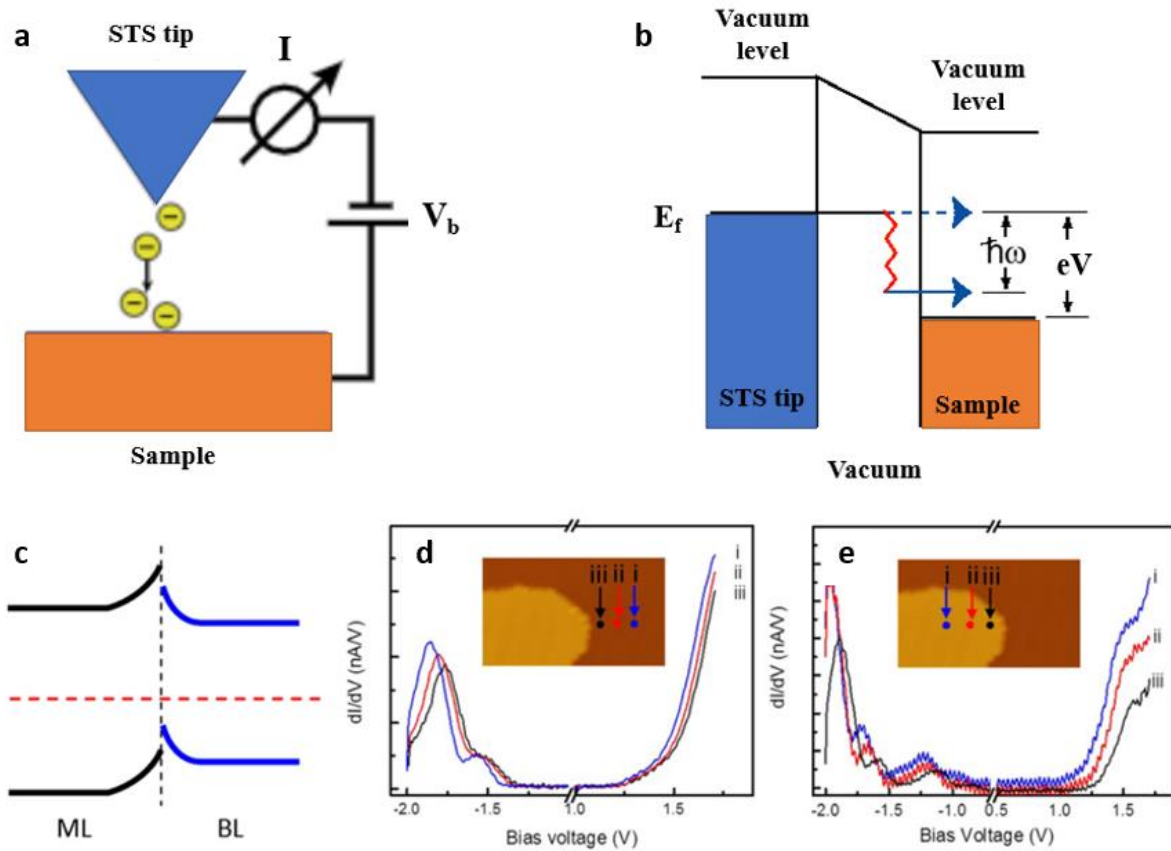


Figure 4-1. Schematic and results of STS/STM device and results of WSe₂: (a) schematic of STS/STM device, (b) schematic of the mechanism of STS/STM, (c) schematic diagram of electronic bands at the boundary between monolayer (ML) and bilayer (BL) WSe₂, showing the band-bending and band-edge shifting effect (relative to the Fermi level) due to different electron

affinity of the two films, (d) and (e) STS differential conductance spectra of ML (d) and BL (e) WSe₂ at varying distances from the step edge (see insets), revealing the band-bending effect [102]

In Error! Reference source not found. **c, d, e**, Liu et al. used STS to show the band structure of mono- and bi-layer WSe₂. While STS is capable of providing spectroscopic data with incredible spatial resolution, it does have significant limits. Chemical sensitivity is absent in the STM and STS. Due to the tunneling experiments have a bias range of a/b , where a is the apparent barrier height, STM and STS sample only available at valence electron states. STM and STS studies are often incapable of extracting element-specific information, as chemical bond formation significantly perturbs the valence states. Also, with STS, it is hard to get absolute energy vs. E_f . On the other hand, due to requiring the current transaction in the substrate, the STS cannot work on an insulating substrate, e.g., a 300 nm SiO₂ substrate. All these disadvantages limit the application of STS/STM.

ARPES is a technique used in condensed matter physics to determine the electrons' allowable energies and momenta in a solid crystalline material. It is based on the photoelectric phenomenon, in which a sufficiently energetic photon ejects an electron from a material's surface. The technique maps the electronic band structure and Fermi surfaces directly by measuring the emitted photoelectrons' kinetic energy and emission angle distributions. ARPES is ideally suited for one- or two-dimensional material analysis. It has been used by physicists to study superconductors operating at high temperatures, graphene, topological materials, quantum well states, and materials showing charge density waves.

ARPES devices include a monochromatic light source that generates a narrow beam of photons, a sample holder attached to a manipulator that positions the material sample, and an electron spectrometer (Error! Reference source not found.**a**). The equipment is housed in an ultra-high vacuum (UHV) environment, which protects the sample and prevents the released electrons from dispersing. After being dispersed in two perpendicular directions in terms of kinetic energy and emission angle, the electrons are steered to a detector and counted to produce ARPES spectra—slices of the band structure in a single momentum direction. Specific ARPES instruments can extract a part of the electrons alongside the detector in order to determine their spin polarization.

Electrons in crystalline solids can occupy only particular energies and momenta, as quantum physics prohibits them from occupying other states. They combine to generate a continuum of states known as the solid's band structure. The band structure of a material dictates whether it is an insulator, a semiconductor, or a metal, as well as how well it conducts electricity and in which directions it conducts best. It also determines how a material behaves in a magnetic field. Error! Reference source not found.**b-e** show the relationship between contours of photoemission intensity as a function to the binding energy for a momentum line going through the K point in Graphite and LiC_6 [103].

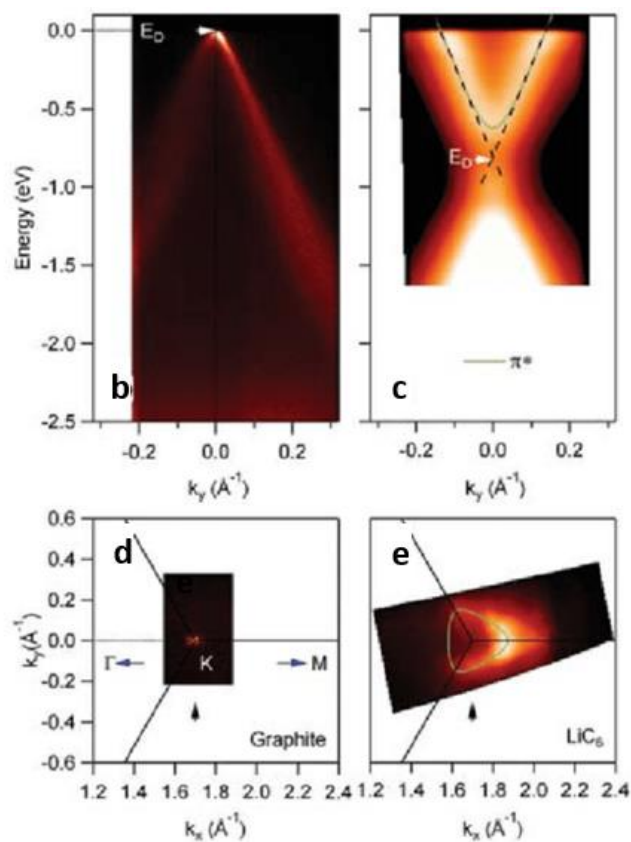
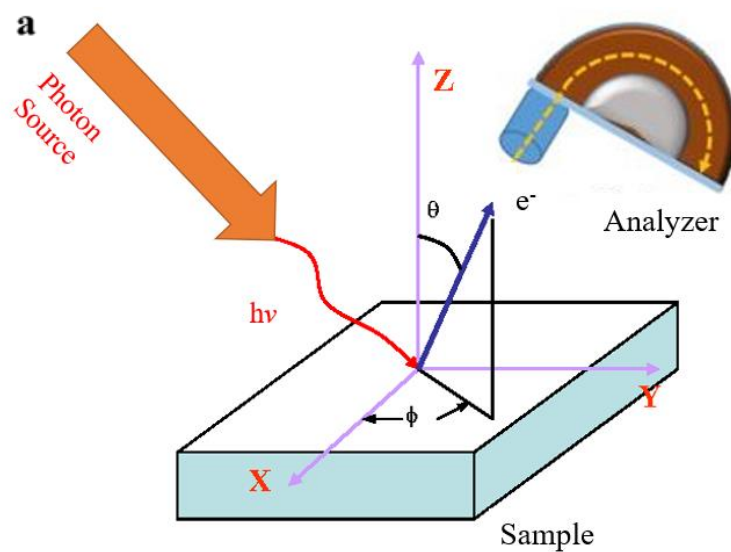


Figure 4-2. Schematic and plot of APRES: (a) schematic of an APRES system, (b-c) the relationship between contours of photoemission intensity as a function to the binding energy for a

momentum line going through the K point in Graphite and LiC_6 [103], (d)-(e) intensity from a narrow interval (± 10 meV) around the Fermi level of Graphite and LiC_6 [103]

The kinetic energy of the released electron can be used to compute its velocity and absolute momentum. ARPES can also determine the two in-plane momentum components that are conserved during the photoemission process by measuring the emission angle relative to the surface normal. In many circumstances, if necessary, the third component can also be rebuilt. ARPES has been used to plot the occupied band structure of a wide variety of metals and semiconductors, states appearing in their projected band gaps. These quantum-well states arise in systems with reduced dimension, one-atom-thin materials such as graphene transition metal dichalcogenides, and a variety of topological materials. Additionally, it has been used to map the underlying band structure, gaps, and quasiparticle dynamics in highly correlated materials such as high-temperature superconductors and charge density wave materials.

However, there are still disadvantages of ARPES. This technique can only work under high vacuum conditions ($< 10^{-8}$ Pa). Also, the detection range is confined by the position of the Fermi energy surface. If the sample's E_f is in the Valence Band (VB), APRES only can get the band structure plot of VB. If the E_f is in the material's conduction band, APRES can get the information of the VB lower than E_f . So, the application of APRES is limited.

On the other hand, defects are commonly found in two-dimensional solids and often introduce unique properties absent in pristine materials [104-106]. For example, in the case of two-dimensional (2D) MoS_2 , the quantum yield increases sharply from 0.6% to over 95% by tuning the defect states, making it a prospective material for the next-generation light-emitting diodes

[107]. Controlling the defect states in MoS₂ can also significantly improve its hydrogen generation performance [108, 109]. The density of states (DOS) and corresponding defect states are typically characterized by scanning tunneling spectroscopy (STS) [110, 111] and photoemission spectroscopy (PES) [112, 113]. Combining STS and PES measurements to obtain high-quality data for the electronic properties of 2D materials is often challenged by the stringent requirements of high-quality samples. Usually, STS requires a clean and atomically flat substrate with adequate conductivity, while the PES needs large single-crystalline domains with high uniformity. Meanwhile, both measurements above require either ultra-high vacuum or low temperature for gathering high-quality data. Thus, characterization of the DOS by the electrochemical method is a potential way to understand the material's intrinsic property. An electrochemical capacitance test was proposed to understand further the electronic properties of a 2D material at room temperature.

4.2 ELECTROCHEMICAL CAPACITANCE TEST

Measuring the intrinsic Density of States (DOS) and defect states of atomically thin layered materials are of profound importance for understanding their exotic physical properties and their applications in real life. Typically, the measurements of defect states require either ultra-high vacuum or low temperature. We measured the defect states of two-dimensional (2D) materials in an ambient environment rooting on electrochemical capacitance. The highest energy resolution of the electrochemical capacitance spectrum approaches 116 meV, close to the theoretical limit of thermal broadening at room temperature ($3.5 k_B T = 91 \text{ meV}$). Meanwhile, the absolute energy positions of the DOS can be given by integrating a reference electrode in the electrochemical system. With the approaches above, the DOS and defect states in monolayer MoS₂ are mapped out by measuring the electrochemical capacitance. We can also monitor the DOS evolution during

chemical reactions. Our preliminary result on the mercury ions adsorption shows the Mo defects in monolayer MoS₂ dominate the chemical adsorption procedure. This work paves the way towards a new platform for measuring the intrinsic DOS and defect states of 2D materials under an ambient environment.

Based on the previous content, it's necessary to develop a method to characterize the electronic property of 2D materials, which can be used widely. In the electrochemical test, one of the most fundamental properties of the catalyst is the capacitance of the surface between the matter and electrolyte. This catalyst-electrolyte interface determines the ability to carry the charge and further governs the current flowing through that interface. Based on this theory, in the electrode-electrolyte testing experiment (Error! Reference source not found.), the model shows a three-capacitance system that includes C_{quantum} , C_{Hemholtz} , and $C_{\text{counter electrode}}$.

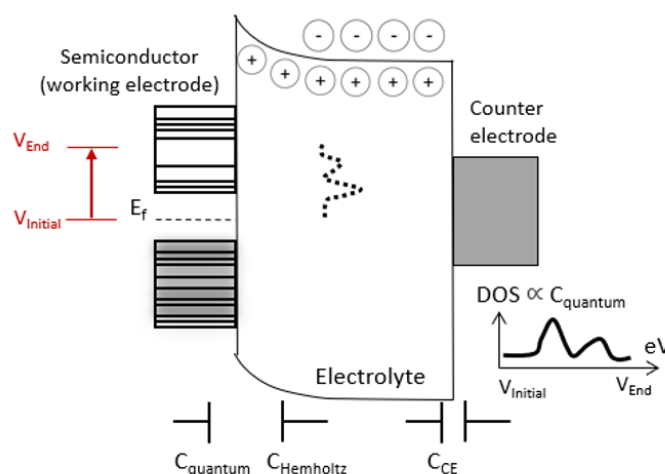


Figure 4-3. Schematic of the interface between semiconductor electrode and electrolyte.

The Helmholtz layer is also called the electrical double layer. The electrolyte side of the double layer is believed to be composed of two layers (**Error! Reference source not found.**). The inner layer, which is closest to the electrode, contains solvent molecules and occasionally other species (ions or molecules) that have been reported to be selectively adsorbed. Additionally, this inner layer is referred to as the compact, Helmholtz, or Stern layer. The inner Helmholtz plane (IHP) is the location of the electrical centers of the particularly adsorbed ions. It is located at a distance of x_1 . The overall charge density in this inner layer due to specifically deposited ions is σ^i ($\mu\text{C}/\text{cm}^2$). Solvated ions can approach the electrode only at a distance of x_2 ; the outer Helmholtz plane (OHP) is the locus of the centers of these nearest solvated ions. Because the solvated ions interact with the charged electrode via long-range electrostatic forces, their interaction is virtually independent of the ions' chemical characteristics. These ions are said to be adsorbed nonspecifically. As a result of the solution's thermal agitation, the nonspecifically adsorbed ions are spread in a three-dimensional region called the diffuse layer, which extends from the OHP into the bulk of the solution [114]. With this model, several previous works studied the quantum capacitance for different 2D materials.

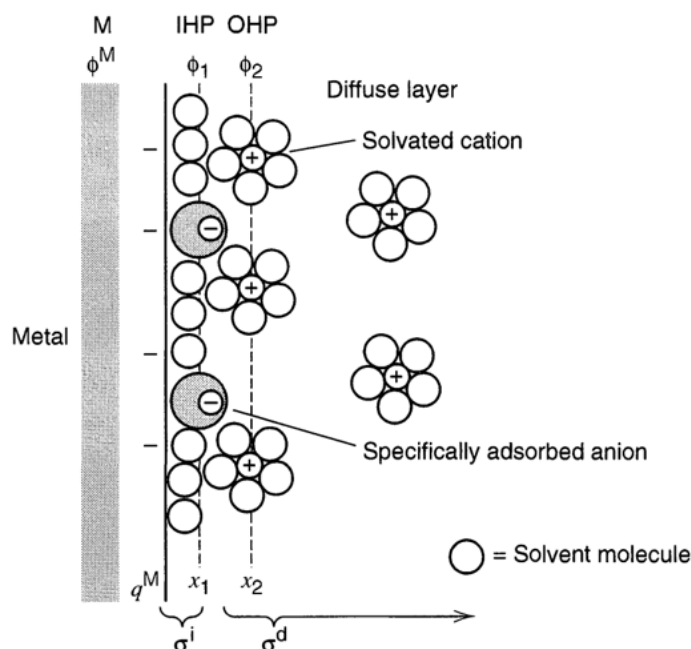


Figure 4-4. Schematic of a double region layer model [114]

In Xia et al.'s work, the quantum capacitance of monolayer graphene is measured [115]. The graphene interfacial capacitance was determined using a typical three-electrode electrochemical cell equipped with a potentiostat that regulates the potential of graphene in relation to a reference electrode (a platinum electrode). In their study, the usage of an electrochemical gate and an ionic liquid reduces the Debye ionic screening length to a few angstroms, so making quantum capacitance a significant component of the observed capacitance. The ionic liquid is chemically inert and stable, but more crucially, its Debye ionic screening length is nearly zero, implying that quantum capacitance is the major source of capacitance measured. Additionally, they present a simple hypothesis with a single parameter (impurity concentration) that quantitatively explains the quantum capacitance measurement. In this hypothesis, the measured capacitance only includes

two contributions: one is the capacitance which is raised from the double-layer (Helmholtz layer), the other is the intrinsic quantum capacitance of graphene. The capacitance of the Helmholtz layer is due to the accumulation of ions in the charged electrode. This can be calculated by modeling the $C_{\text{Helmholtz}}$ to a parallel capacitance. In the BMIM-PF6 ion liquid condition, the $C_{\text{Helmholtz}}$ is around $21 \mu\text{F}/\text{cm}^2$. After this, the quantum capacitance of monolayer graphene can be isolated from the total capacitance (Error! Reference source not found.a) [116].

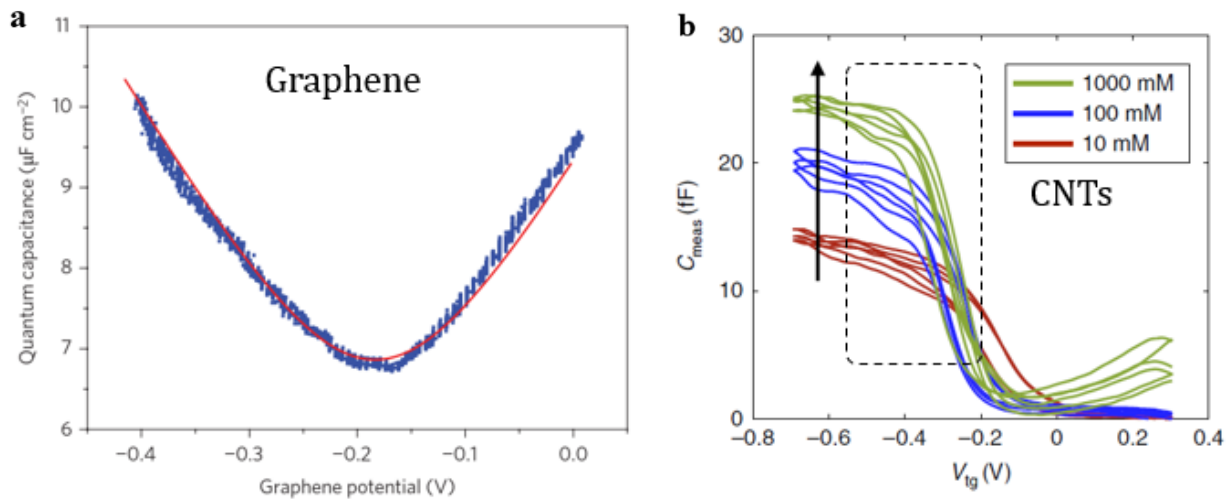


Figure 4-5. Quantum capacitance of small dimension materials: (a) quantum capacitance of single-layer graphene [115], (b) quantum capacitance of carbon nanotubes at three different ionic concentrations (10 mM, 100 mM, 1 M) [117]

In Li and Burke's work, the combined quantum and electrochemical capacitance of carbon nanotube were measured [117]. In 1D material, because of the size shrinkage, the dimension of the device is comparable to the electron wavelength. Under this small size, the wave function of an electron around the atom may return to its original value. However, it's difficult to resolve the small capacitance (small dimension material) above the background stray capacitance (over 100

pF). In this work, the author developed an on-chip shield. With this shield, the combined quantum and electrochemical capacitance were measured. In Error! Reference source not found.**b**, the quantum capacitance of carbon nanotubes is measured under different densities of ionic liquid. This approach, which has been demonstrated in principle for carbon nanotubes, is applicable to a broad class of reduced dimensional devices made of any material, including nanowires, nanoribbons, and quantum dots. As such, this is a significant measurement of the quantum effects on capacitance in reduced dimensional systems in contact with liquid electrolytes, a critical and growing theme at the interface of nanotechnology, energy, and life.

There is still a lacking of relative work about the measurement of quantum capacitance and electrochemical capacitance on the flexible substrate under different strain conditions. Studying the electrochemical capacitance can help understand the strain effect on the monolayer MoS₂'s electronic states, and how this change after applying strain will further affect the performance of this material, such as its catalysis property in HRE. For obtaining accurate results of the strain effect on HER in 2D materials, the electronic properties of MoS₂ were studied under different strain conditions in the study, including the Density of States and Electrochemical Capacitance.

4.3 EXPERIMENT RESULTS

4.3.1 Experiment Mechanism and Setup

In this work, a device with an ionic electrolyte potential gate was established. Error! Reference source not found. is a schematic of the ionic gate adjusting effect on a 2D material. In the established system, the V_{initial} is the original balance energy level which is at the bandgap (Error! Reference source not found.**a**). After applying a potential to the ionic electrolyte, the balanced energy level

will be moved either up into the conduction band or down into the valance band (Error! Reference source not found.**b**). In the model, the balanced energy level equals the Fermi level. When the Fermi level is moved into the conduction band, the system will have the extra position for electrons at the valley of the conduction band. These newly filled electrons will bring the whole system extra capacitance. This change can be recorded and describe the density state of this material.

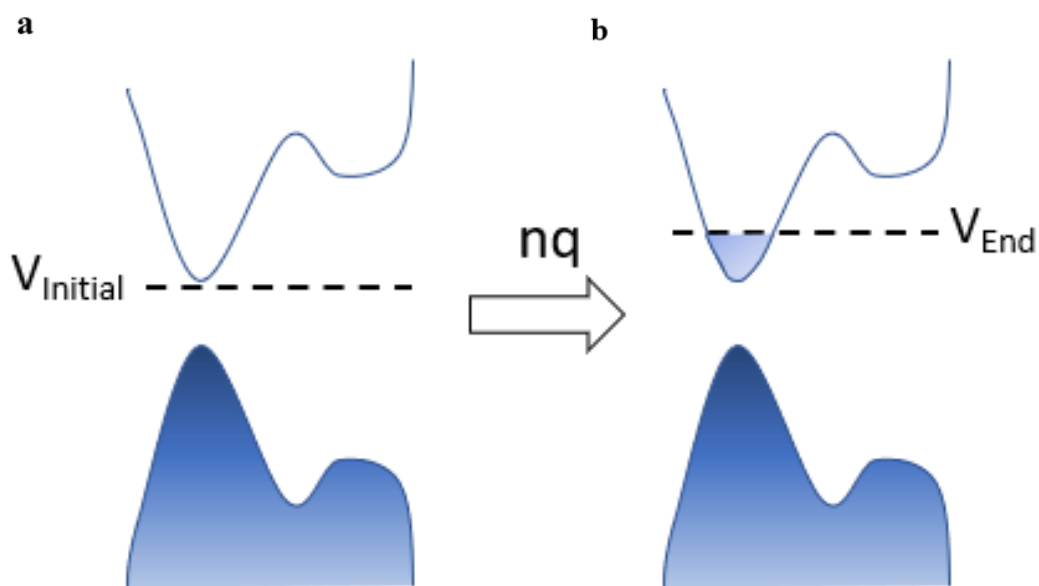


Figure 4-6. Schematic of the ionic electrolyte gate adjusting effect on the band structure: (a) the original Fermi level position of a material before adding potential, (b) Fermi level position after the electrolyte gate adjustment

For examining the accuracy of this method, the testing method and electrochemical/quantum capacitance data of the MoS₂ basal plane is presented in the following content. Electrochemical capacitance (C_{total}), measurable at the ambient environment, can be considered the sum of two

series-connected contributors [117-119]. One is the double-layer capacitance originated from the polarized electrolyte ions (C_{ion}). The other is the solid electrode capacitance (C_e). If the solid electrode is made of a 2D material, the solid electrode capacitance is proportional to its DOS [120, 121]. Since there is a relation:

$$1/C_{total} = 1/C_{ion} + 1/C_e \quad (1)$$

The $C_{total} \approx C_e$ when the $C_{ion} \gg C_e$, the measurable C_{total} can be proportional to the DOS of 2D materials. The critical steps in implementing the concept are identifying the electrolytes with (i) high areal capacitance that much larger than the C_e and (ii) broad electrochemical stability window that can cover the conduction band minimum (CBM) and valence band maximum (VBM) of 2D materials.

Thus, for determining the most suitable electrolyte for the electrochemical/ quantum capacitance test, three different commercially available ionic liquids are investigated. In the electrochemical test, the capacitance and electrochemical window of ionic liquids were measured in a three-electrode electrochemical cell, in which the Pt-wire acts as the counter electrode, the glassy carbon electrode serves as the working electrode, and the Ag/AgCl/BMIMCl works as the reference electrode. The electrochemical impedance spectroscopy (EIS) is applied to measure the ionic liquid capacitances within the frequency range of 10^6 to 0.1 Hz. Ten points were recorded per frequency decade at a sinus amplitude of 10 mV. The electrochemical window of ionic liquids is determined using cyclic voltammetry at a scan rate of 10 mV/s.

There are two critical parameters in selecting the suitable electrolyte for the electrochemical capacitance measurement. One is high capacitance, and the other is the appropriate electrolyte

stability window. We demonstrated that the [EMIM] [DCA] has the highest C_{ion} of over 120 $\mu\text{F}/\text{cm}^2$ at 5 Hz (**Error! Reference source not found.a**) but has a smaller electrochemical stability window than that of [BMIM] [BF₄] (**Error! Reference source not found.b**). The electrochemical degradation potentials of the ionic liquids are further converted to the absolute energy (eV vs. vacuum), as shown in **Error! Reference source not found.b**. Afterward, we compared the calculated band edges of a series of 2D materials [122, 123] to the electrochemical window of [BMIM] [BF₄] and [EMIM] [DCA] (**Error! Reference source not found.**). It suggests that the [BMIM] [BF₄] can be used to measure the DOS and defect states for all of the six 2D semiconductors listed in **Error! Reference source not found.**. The [EMIM] [DCA] can serve as a candidate in measuring the 2D materials with high C_e .

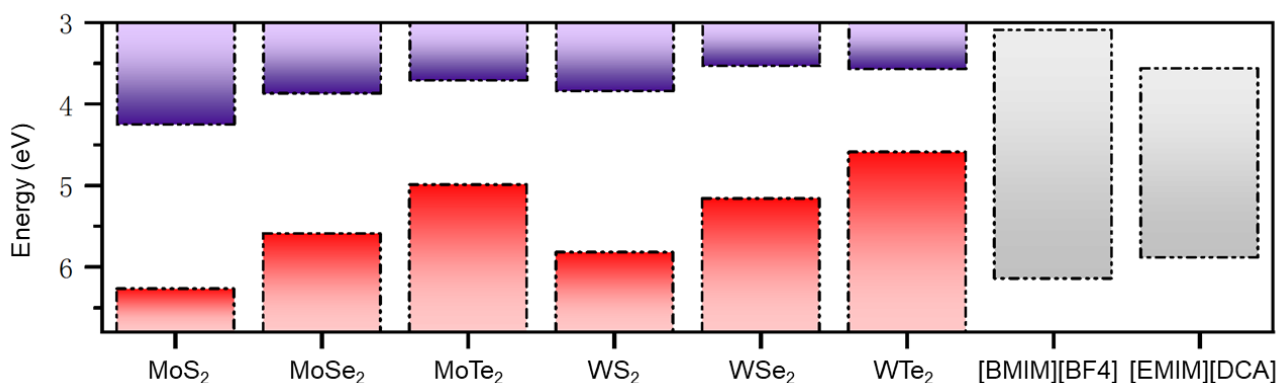


Figure 4-7. Band alignment of 2D materials and the ionic electrolyte: the real capacitance at 5 Hz. The band alignment of the monolayer MoS₂, MoSe₂, MoTe₂, WS₂, WSe₂, and WTe₂ to the measured electrochemical stability windows of [BMIM] [BF₄] and [EMIM] [DCA]. The 2D material band edges are obtained from calculation results [122, 123].

Thus, the ionic liquid [BMIM] [BF₄] is selected to meet the requirement above. It has a high capacitance and a wide electrochemical window of ~3.5 V [124, 125].

We verified this test method by using the basal plane of monolayer MoS₂. This system is of interest because it has been intensely investigated in experiments and simulations; thus, we can cross-compare the electrochemical capacitance spectrum with the DOS obtained in the literature. In this electrochemical test, a Pt-wire counter electrode and an Ag/AgCl reference electrode were integrated into the previously fabricated nanodevice to form a three-electrode electrochemical system, in which the monolayer MoS₂ flake act as the working electrode (**Error! Reference source not found.**). For the Ag/AgCl reference electrode, the 1-Butyl-3-methylimidazolium chloride was dissolved in [BMIM] [BF₄] with a final concentration of 0.1 M, serving as the electrolyte in the reference electrode to stabilize the silver chloride concentration. During the electrochemical measurements, the ionic liquid, [BMIM] [BF₄], was applied as the electrolyte. Electrochemical measurements were carried out by combining an electrochemical workstation (BioLogic SP-300) and a probe station. Staircase potentiometric electrochemical impedance spectroscopy (SPEIS) was applied to measure the capacitance (C_{total}) at the MoS₂-electrolyte interface and the tunneling current (I) transported from MoS₂ to the electrolyte at different electrochemical potentials. An electrochemical capacitance spectrum and electrochemical tunneling spectrum can be plotted using C_{total} vs. potential and I vs. potential, respectively.

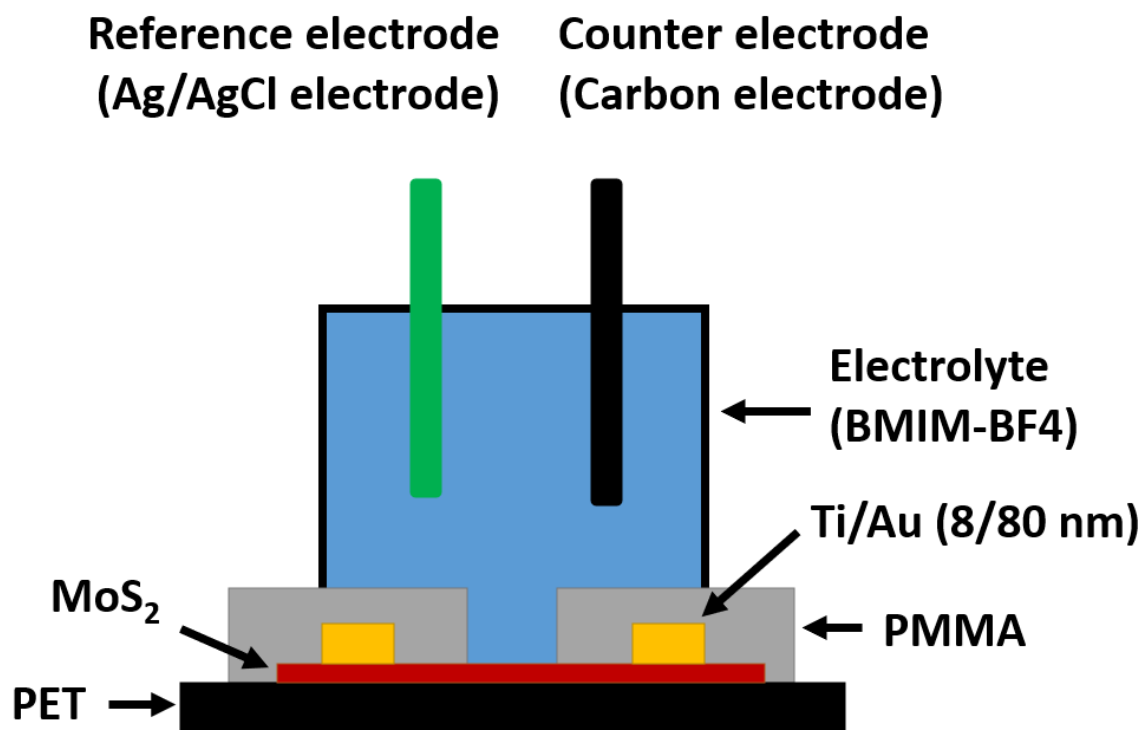


Figure 4-8. Schematic of electrochemical/quantum capacitance test system

In a typical experiment, we scanned the working electrode potential using SPEIS from its open circuit potential to -1.5 V vs. Ag/AgCl with a step potential of 5 mV. -1.0 V vs. Ag/AgCl corresponds to 3.23 eV vs. vacuum, which is ~ 0.5 eV higher than the MoS₂ conduction band minimum (CBM) as predicted by the calculation [123, 126]. Thus, the electrons had been filled into the MoS₂ CBM during this procedure. For each potential step, a one-second waiting time is set to decrease the influence of electrochemical kinetics. The impedance is excited under a single sine mode at 5 Hz with a sinus amplitude of 50 mV. Each capacitance was averaged with five measurements. When the working electrode potential approaches -1.5 vs. Ag/AgCl, we directly scan it back to 2.5 V vs. Ag/AgCl with the same frequency, amplitude, step potential, and step waiting time. During the scanning, the C_{total} and I were recorded at each electrochemical potential.

Two scan frequencies, 5 and 100 Hz, are selected to investigate the DOS of the MoS₂ basal plane. Under the former frequency, the [BMIM] [BF₄] provides a capacitance of 61.7 uF/cm² (Error! Reference source not found.**a**), much higher than the C_e (~4 uF/cm²) at the pristine basal plane of monolayer MoS₂ CBM [127]. Increasing the frequency from 5 to 100 Hz, the C_{ion} decreases sharply to 0.8 uF/cm², lower than the C_e at monolayer MoS₂ CBM (Error! Reference source not found.**a**). Clear VBM and CBM are captured in the electrochemical capacitance measurement with a bandgap of 1.8 eV (Error! Reference source not found.**b**) of the MoS₂ basal plane. In addition to the apparent CBM position at 0.1 V vs. Ag/AgCl (4.83 eV vs. vacuum), another threshold occurs around -0.3 V vs. Ag/AgCl, which matches very well with the STS results at low temperatures [128-130]. Thus, no apparent threshold is observed in the electrochemical capacitance spectrum (the black line in Error! Reference source not found.**b**). More details and different performances on the chemical capacitance property of various ionic electrolytes will be discussed in the later content.

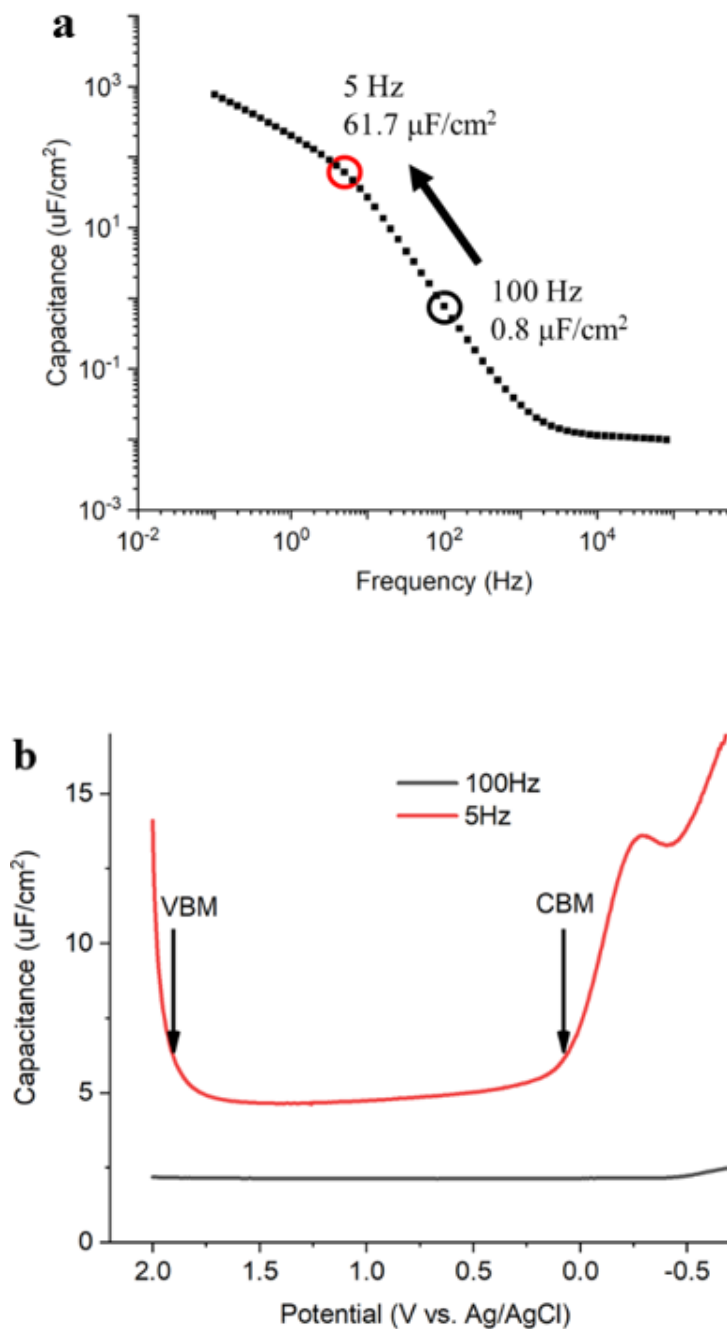


Figure 4-9. Electrolyte capacitances and MoS₂ QCSs at various frequencies: (a) the frequency-dependent capacitance of BMIM-BF₄ at the open circuit potential. The capacitance of the [BMIM] [BF₄] at 100 and 5 Hz are 0.8 and 61.7 $\mu\text{F}/\text{cm}^2$, respectively. (b) The QCSs of a pristine monolayer MoS₂ basal plane at 100 Hz (black line) and 5 Hz (red line). The indicated bandgap of the monolayer MoS₂ basal plane is 1.8 eV.

After the electrochemical test, the STS/STM is also introduced into this work to verify the electrochemical capacitance results. The electrochemical tunneling spectrum (current vs. potential) and corresponding dI/dV -V spectrum are shown in Error! Reference source not found.. They further verified the CBM and VBM positions of monolayer MoS_2 are 0.1 V and 1.9 V vs. Ag/AgCl, respectively. This comparison confirmed that testing the band structure by using the electrochemical/quantum capacitance method is reliable. We will use this method in the later electrochemical/quantum capacitance of strained MoS_2 .

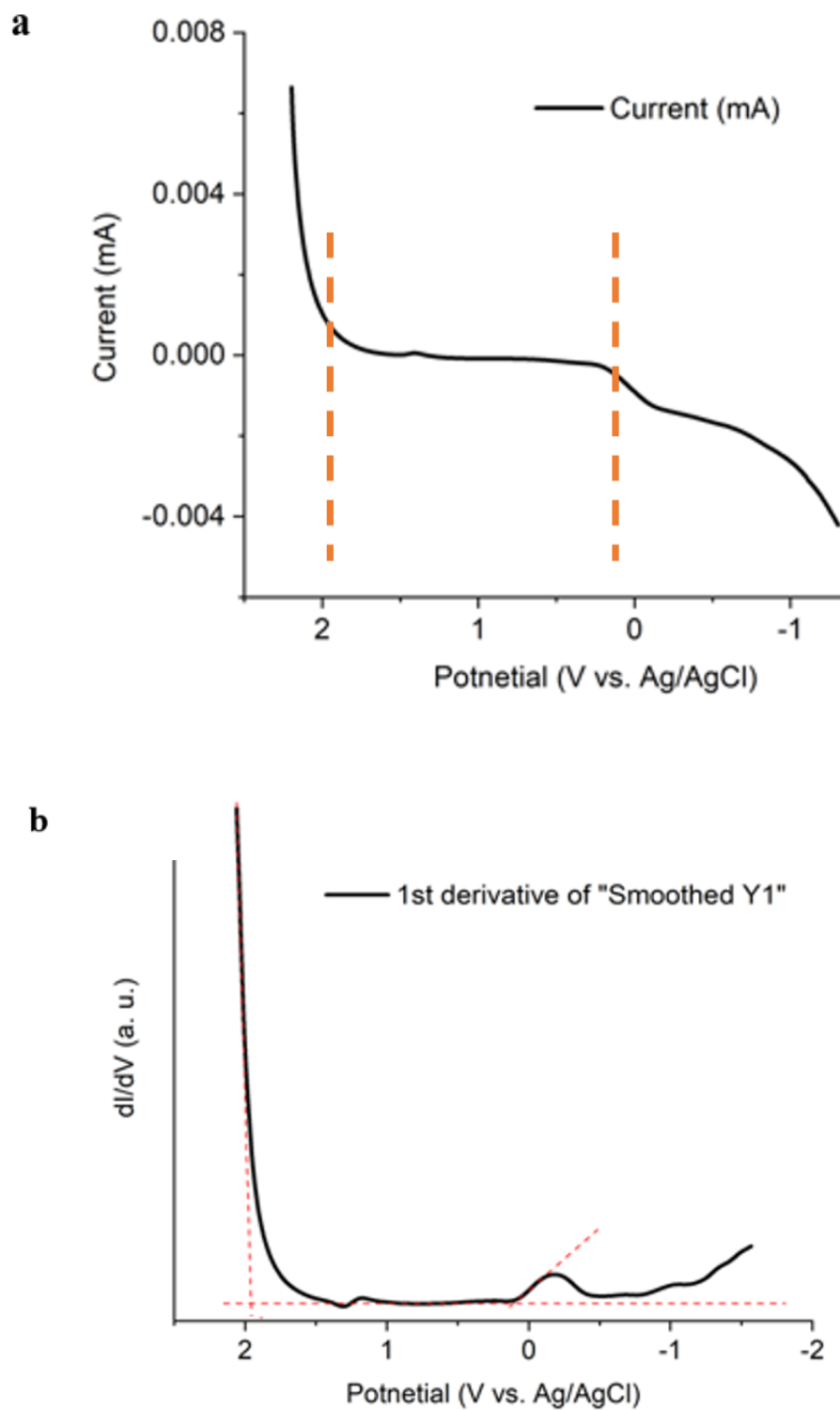


Figure 4-10. Results of electrochemical capacitance tests: (a) the electrochemical tunneling current as a function of the applied potential, (b) the dI/dV -V spectrum.

4.3.2 Electrochemical/Quantum Capacitance of Monolayer MoS₂ Edge

As discussed in previous sections, the most active position of MoS₂ in the HER process is the edge. Therefore, in this work, the electrochemical capacitance study will be focused on the edge of monolayer MoS₂, which is never revealed before. There are two edge orientations in a 2H-phase MoS₂: the zigzag and the armchair. These two edges have different exposed atoms and may have different electrochemical/quantum capacitance. As shown in Error! Reference source not found. **a&b**, a secondary-harmonic generation test platform is used to determine the lattice structure of the edge. And a special micro test device is built on the labeled edge (Error! Reference source not found. **c, d**).

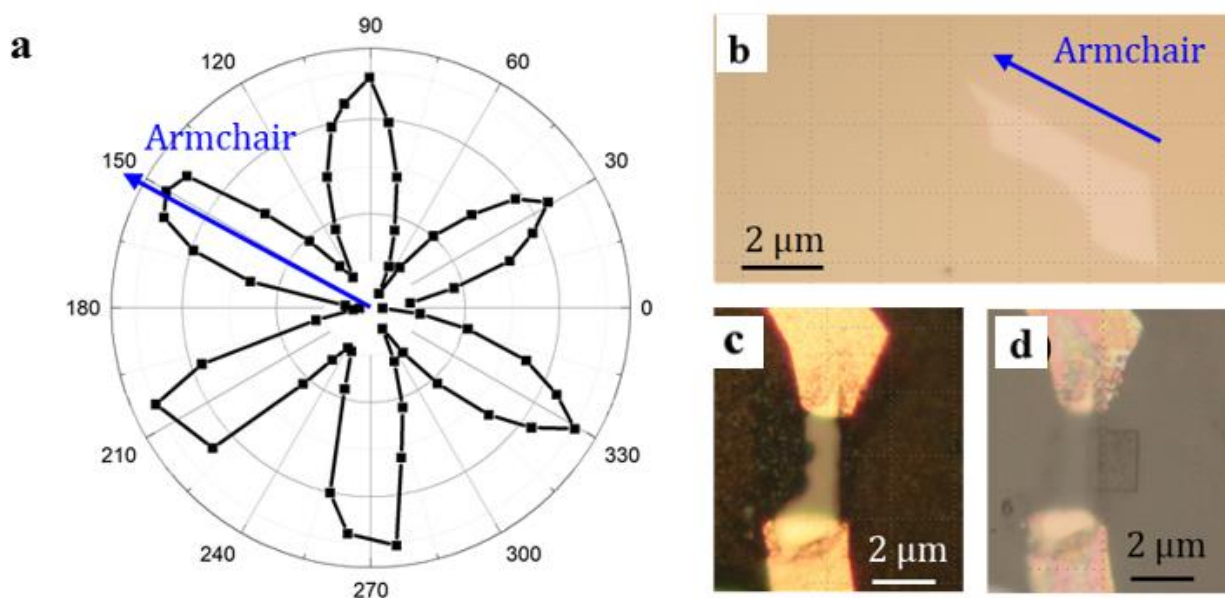


Figure 4-11. SHG result and testing device of armchair direction monolayer MoS₂: (a) the resonant SHG intensity is parallel to the incident laser polarization as a function of the MoS₂ crystal orientation, (b) microscope image of the monolayer MoS₂ with the armchair (blue arrow) edge of the monolayer sample determined by the SHG, (c) the Ti/Au electrodes deposited on the MoS₂,

(d) a PMMA950/PMMA495 bilayer coated on the Ti/Au contacts and MoS₂, with a window (the dark brown area) opened to expose the armchair edge

Two experiments are further applied to investigate the defect states in monolayer MoS₂ using electrochemical capacitance. In the first experiment, the defect states at the MoS₂ zigzag edge and armchair edge are measured separately. The edge categories of MoS₂ are determined through the second-harmonic generation (SHG) spectroscopy (Error! Reference source not found.**a, b**) [131]. For investigating the defect state at the MoS₂ zigzag edge, the sample is covered by a PMMA insulating layer with the zigzag edge exposed in the ionic liquid (Error! Reference source not found.**c, d**). The PMMA layer contributes ignorable capacitance comparing to MoS₂. Hence the capacitance is mainly provided from the MoS₂ zigzag edge. The measured electrochemical capacitance spectrum is shown in Error! Reference source not found.**e & f**. Compared with the MoS₂ basal plane, there are two significant differences in the electrochemical capacitance spectrum. The first one is that four new peaks appearing in the bandgap of MoS₂, which can be attributed to the rich defect states at the MoS₂ edge. The main peak at 1.6 eV vs. Ag/AgCl can be identified as the signal of Mo-vacancies after comparing with the calculated results [132]. A more significant amount of Mo defects appears at the zigzag edge, indicating that the MoS₂ is terminated with the Mo atoms, as shown in the schematic crystal structure (Error! Reference source not found.**e**). This matches well with the theoretical calculation results that the Mo-edge is the energetically favored termination compared with the S-edge [133, 134]. The second difference is that the formed defect states shift the CBM more negative and VBM more positive. It suggests that the amount of defect can modulate the semiconductor material CBM, VBM, and the bandgap, highlighting new opportunities to optimize material performance through defect engineering. The defect states tuned band edge positions and bandgap is also observed in the MoS₂ with its armchair edge exposed

(Error! Reference source not found.f). We can find the peak representing S-vacancies (0.7 V vs. Ag/AgCl) is more significant than that of Mo-vacancies at the MoS₂ armchair edge, which is attributed to the lower formation energy of S-vacancy than Mo-vacancy [132].

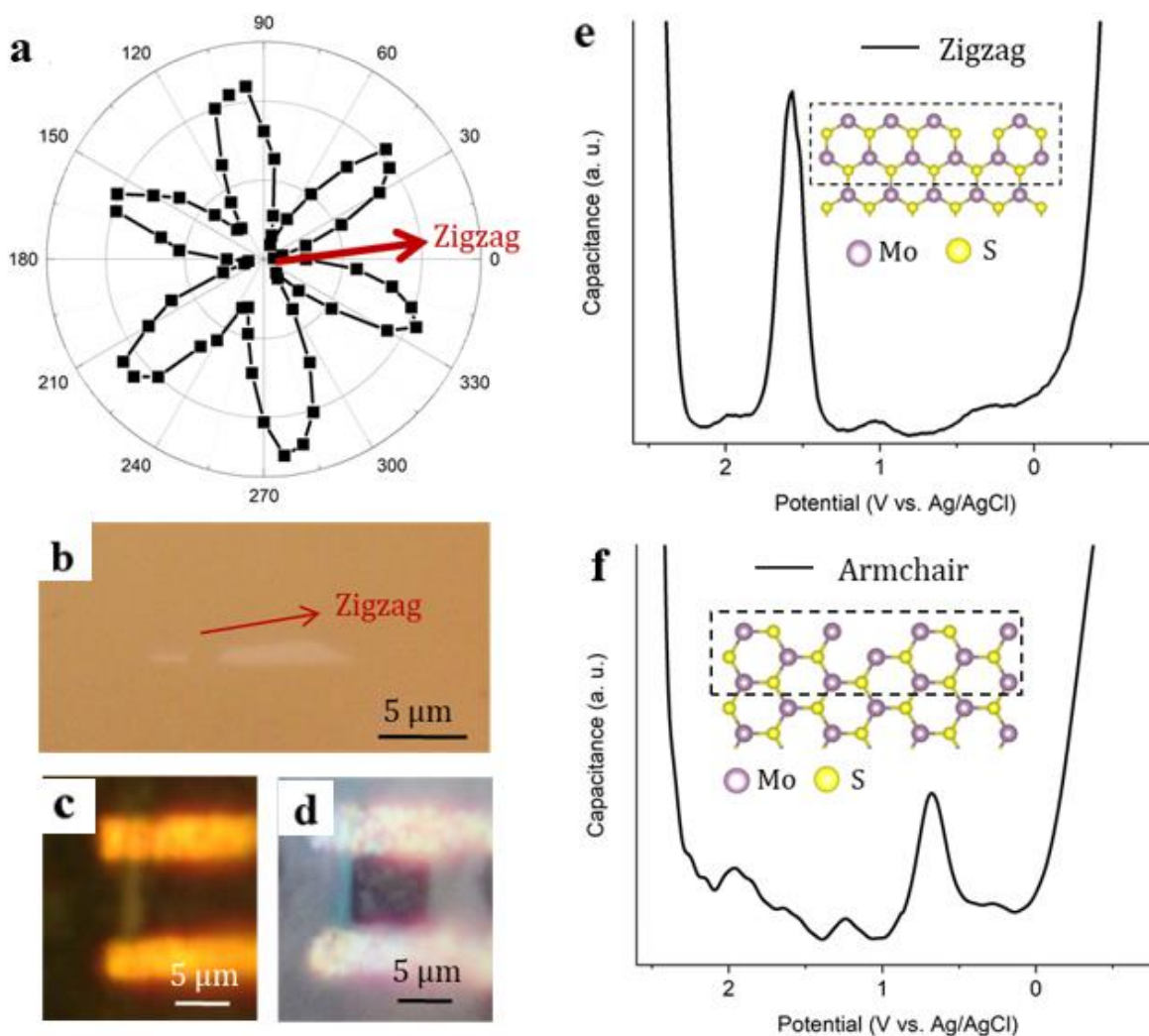


Figure 4-12. Edge-dependent defect energy levels in monolayer MoS₂: (a) the resonant SHG intensity parallel to the incident laser polarization as a function of the crystal orientation, (b) the microscope image of the monolayer MoS₂. The zigzag (red arrow) edge of the monolayer sample is determined by the SHG shown in **a**. (c, d) The Ti/Au electrodes are deposited on the MoS₂: (c) a PMMA950/PMMA495 bilayer is coated on the Ti/Au contacts and MoS₂, and (d) a window (the

dark brown area) is opened to expose the zigzag edge. (e) The QCS of the MoS₂ zigzag edge. The most prominent peak locates at 1.6 V vs. Ag/AgCl is attributed to the Mo defects. The inset figure is the proposed crystal structure at the zigzag edge, showing that Mo atoms terminate the MoS₂-zigzag edge. (f) The QCS of the MoS₂ armchair edge. The S defects become the dominant defects in the bandgap of MoS₂. The inset figure shows the proposed crystal structure at the armchair edge.

4.3.3 Adsorption Peak on Vacancy Sites on MoS₂

In the second experiment, we applied electrochemical capacitance spectroscopy to monitor the MoS₂ DOS variation in solvent-related reactions. Both the MoS₂ basal plane and edges are exposed in the electrolyte; hence we can find the peaks representing S- and Mo-vacancies in the electrochemical capacitance spectroscopy (Error! Reference source not found.a). Afterward, the monolayer MoS₂ is soaked in a 100 ppm HgCl₂ aqueous solution for 5 mins. The Hg⁺ adsorption is of interest because it is one of the most poisonous and widespread environmental pollutants, causing several deadly diseases even at low concentrations [135]. After the HgCl₂ solvent treatment, the peak area ratio of Mo-vacancies to S-vacancies increased from 0.17 to over 0.85, indicating the available charge at the Mo-vacancies has increased fourfold (Error! Reference source not found.b). This can be attributed to that the negatively charged Mo-vacancies prefer to adsorb the Hg²⁺ ions while the S-vacancies do not (Error! Reference source not found.c).

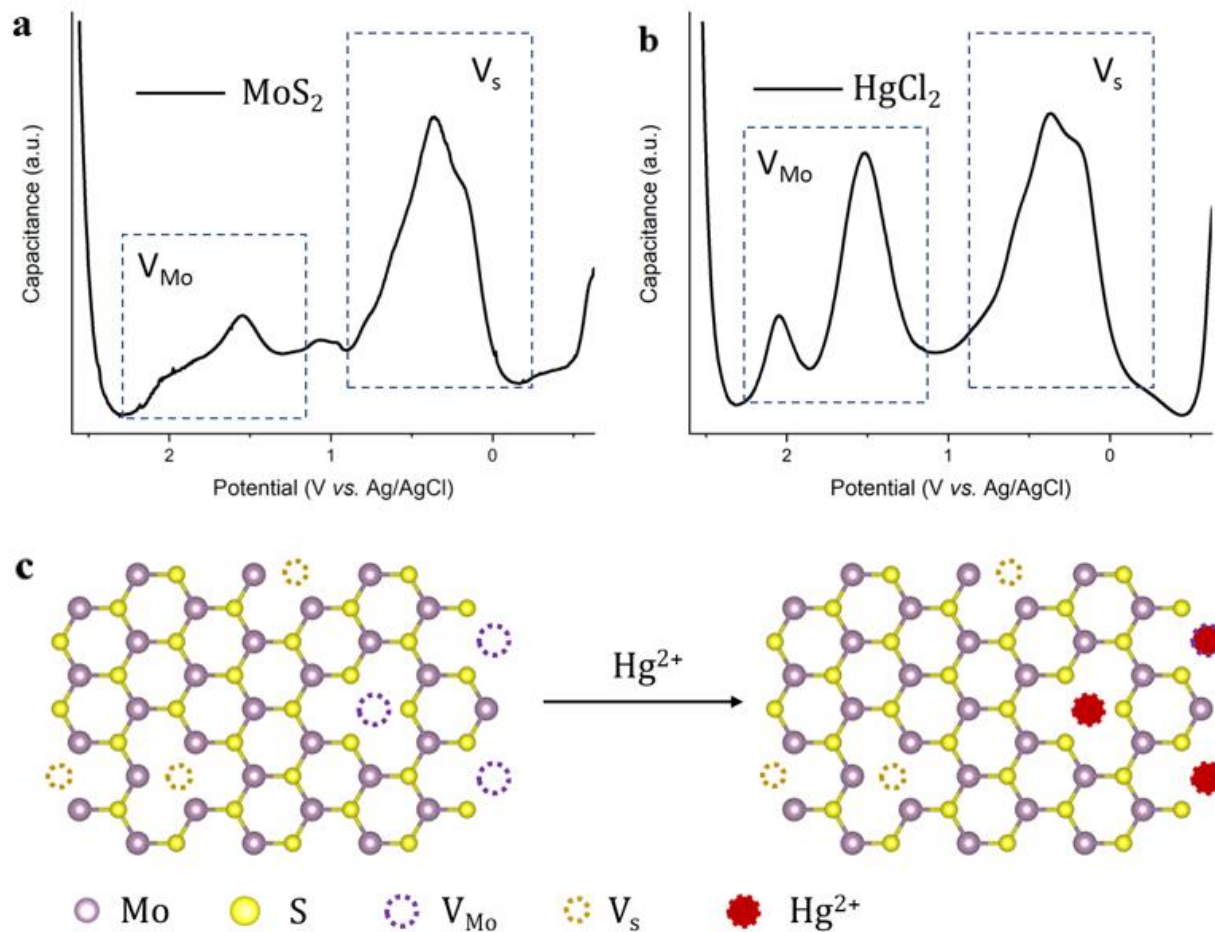


Figure 4-13. Mercury ion adsorption enhanced defect energy levels: (a, b) the QCS of monolayer MoS₂ before (a) and after (b) soaking in 100 ppm HgCl₂ aqueous solution for 5 mins, (c) the schematic of MoS₂ crystal structure change during the 100 ppm HgCl₂ aqueous solution treatment.

Based on the five electrochemical capacitance spectra obtained in the above experiments, we summarized the full width at half maximum (FWHM) of the 25 peaks in the 5 electrochemical capacitance spectra to estimate the energy resolution at room temperature. The highest energy resolution approaches 116 meV, close to the thermal Fermi function broadening at room

temperature ($3.5k_B T = 91$ meV) [136]. This indicates that this test has a higher energy resolution compared to other test methods.

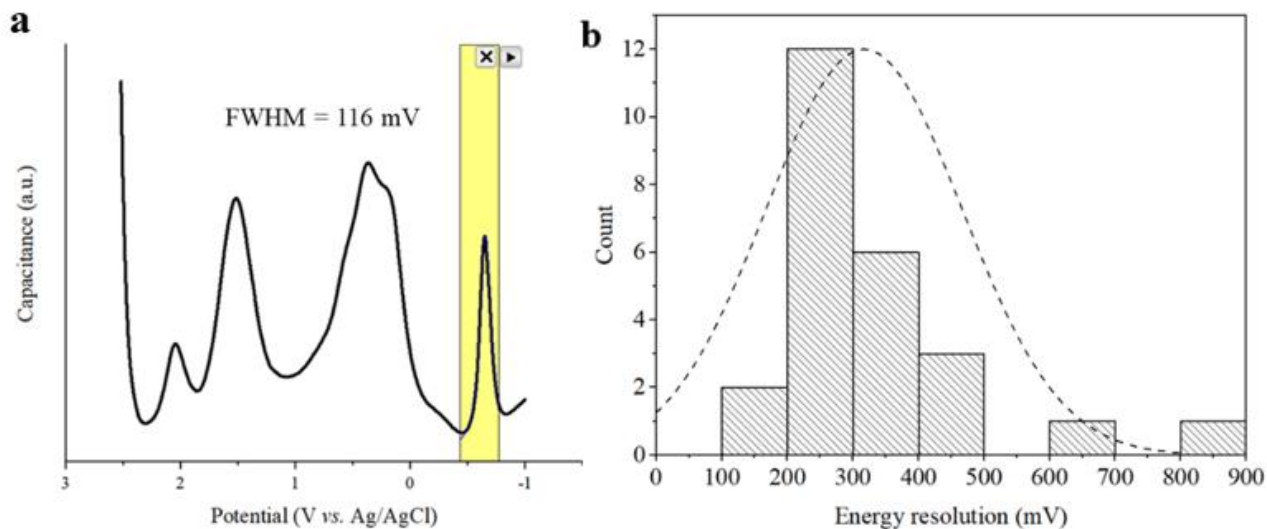


Figure 4-14. Electrochemical capacitance result of MoS_2 : (a) one of the peaks in the MoS_2 electrochemical capacitance spectrum (the yellow area) has an FWHM of 116 mV, (b) the FWHMs of 25 peaks in the 5 electrochemical capacitance spectra are measured and summarized. The mean energy resolution is 317 mV, with the highest one of 116 mV.

4.3.4 Strain Effect on Electrochemical/Quantum Capacitance of Monolayer MoS_2

Also, the capacitance of strained monolayer MoS_2 is measured. Firstly, the SHG test was run on the monolayer MoS_2 samples for adding the correct uniaxial strain. This method can determine the zigzag and armchair edge of the selected sample. The test involves placing the monolayer MoS_2 sample on the SHG stage, setting the power to 10 mW, keeping the signal collector spinning while shining the laser on the sample. As shown in Error! Reference source not found.a, with different atomic lattice directions, the system will show different peak directions.

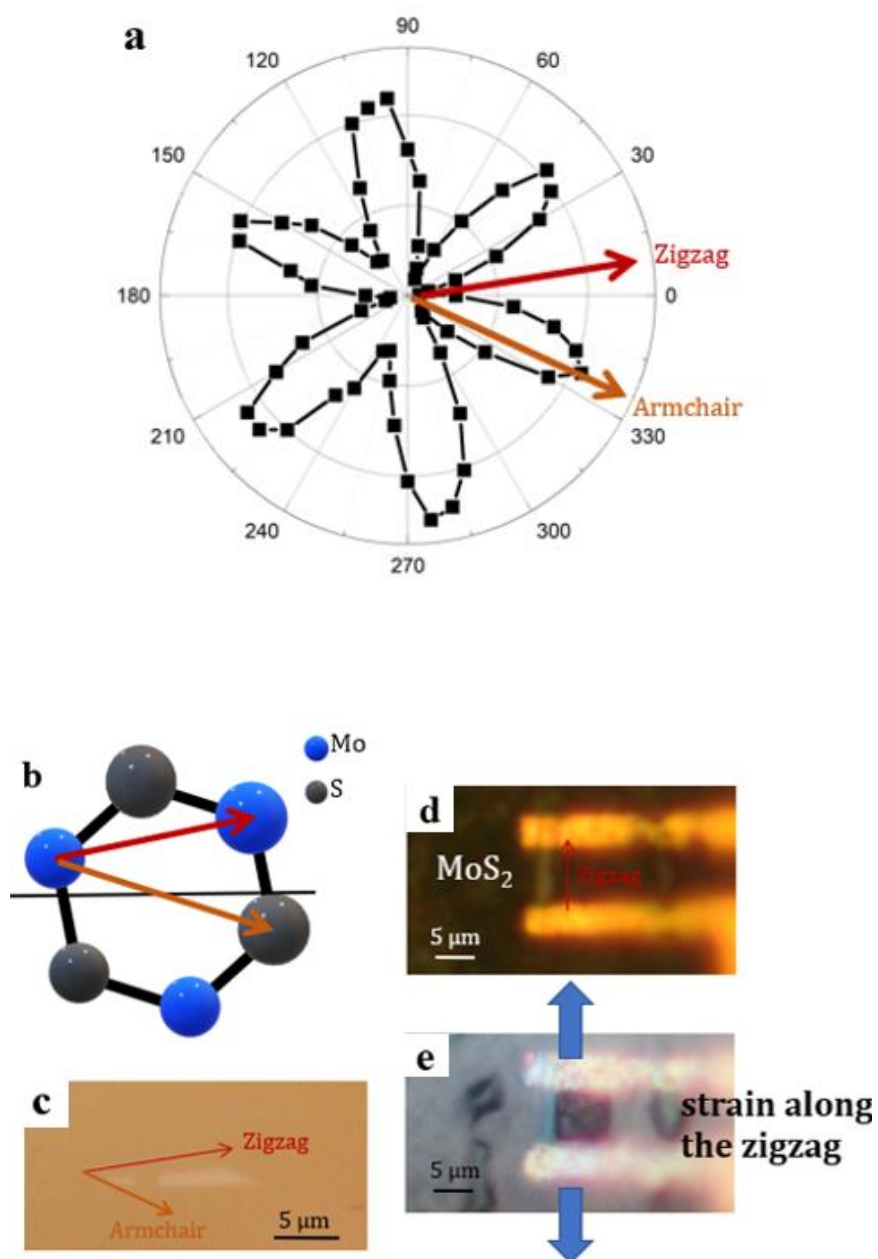


Figure 4-15. SHG result and testing device of zigzag direction monolayer MoS₂: (a) SHG map of an armchair monolayer MoS₂, (b) schematic of MoS₂ atom arrangement, (c) optical image of a zigzag direction monolayer MoS₂ sample, (d, e) HER device on a zigzag MoS₂ sample

After setting the direction of strain, the electrochemical tests along the zigzag direction were performed on these samples. After adding strain, the electrochemical capacitance was observed to increase. And a new capacitance peak emerges at around -0.4 eV vs. SCE. This peak may be caused by an S vacancy defect energy level. Also, the most attractive observation is that the width between the conduction band and valence band is smaller in a strained sample than in an unstrained MoS_2 . This confirms that the applied strain can effectively change the electronic structure of materials. These results also match the calculation result. The strain in the zigzag direction of the MoS_2 will elongate the distance between 2-Mo atoms and results in a weaker bonding between Mo-S bonds. After showing some defects, the materials' capacitance will be changed.

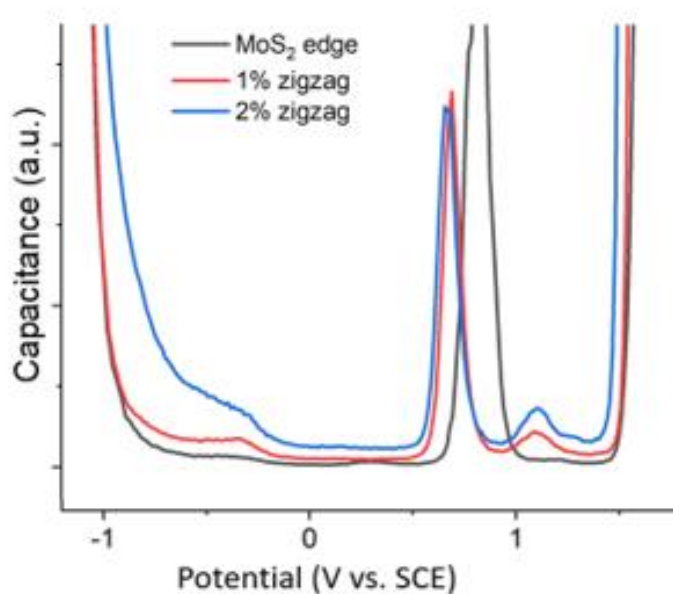


Figure 4-16. Electrochemical capacitance of monolayer MoS_2 under zigzag direction strain conditions

4.4 CONCLUSION

In conclusion, we have demonstrated an electrochemical method to measure the DOS and defect states of 2D materials under an ambient environment. This work highlights the opportunities in (i) conveniently estimating the band structure evolution originated from chemical reactions; (ii) directly investigating the 2D materials on insulating substrates (e.g., SiO_2/Si) to eliminate the impacts from different substrates, for example, different surface potential and dielectric screening effect, which could determine the interfacial energy-level alignments at the interfaces and hence the energy/carrier transport properties of the devices. This work paved the way towards an electrochemical platform for understanding the intrinsic DOS, as well as the tunable electronic structure of 2D materials with defects, layer thickness, and substrate. Also, this work can help us understand the electronic properties of monolayer materials easier. And this technology will be used in the later catalyst experiment in the next chapter.

5 HYDROGEN EVOLUTION REACTION STUDY

5.1 INTRODUCTION

Due to the continued population growth and limited storage of fossil fuel energy, the development of alternative clean energy sources has attracted increasing interest in recent decades [1, 7]. Among the various types of resources, hydrogen energy obtained from water splitting shows great promise [10, 137]. An efficient catalyst is usually required to achieve water splitting. Platinum (Pt) and its alloys, which can work as a powerful catalyst in the water-splitting process or/and hydrogen evolution reaction (HER), have catalysis property over a potential of 0.1 V and a TOF range of 1-1000 [11, 12, 64]. Pt, however, is limited by its scarce storage and high cost. With its exclusive catalysis property and low cost, MoS₂ has been recognized as an HER catalyst, potentially substituting Pt in clean energy supplements [25, 26, 33, 138-140]. As a quasi-two-dimensional transition metal dichalcogenide (TMD) with a layered structure, the catalysis property of MoS₂ for HER reaction has attracted a lot of attention [26, 32, 35, 37, 76, 94, 141, 142]. Different from the inert basal plane, the edge of MoS₂ has sufficient active sites and a low theoretical overpotential (0.08 V) [7]. Thus, for exposing more edge areas, some literature reported the catalysis of MoS₂ based on the different structure stacks and layer numbers [36, 142, 143]. However, this increasing-active-sites strategy will decrease the electronic transportation ability on the surface of the electrode. On the other hand, enhancing the TOF/intrinsic-activity is an effective method to increase the MoS₂ catalysis performance linearly [11]. The intrinsic activity can also evaluate the catalyst on a per-site-level and provides a molecular-level understanding of the catalyst. Introducing a mechanical strain has been shown as an effective method to control the intrinsic property, such as its bandgap width, electron transportation, and piezoelectricity [69, 144-151].

Previous research showed a lower overpotential in HER when adding tensile strain to MoS₂ due to the lower bonding energy of H atoms to the MoS₂ surface [32, 44, 152, 153]. At the same time, shown in Error! Reference source not found.a, the theoretical result confirmed a bandgap shrinkage of MoS₂ after applying tensile strain. This phenomenon is also confirmed by previous literature [69, 147, 154]. Furthermore, at the K point, the conduction band minimum is reaching -4.4 eV, close to the H⁺/H conversion energy level (4.44 eV [155]). However, the catalysis properties of strained monolayer MoS₂ have not been fully understood. With the lowering of the conduction band, strained MoS₂ should be easier to contact the H⁺/H conversion energy level at the K point than the unstrained one (Error! Reference source not found.b & c). That means a tensile-strained MoS₂ will have available electrons to involve in the HER reaction earlier. Thus, we postulate that the HER catalysis will happen at a smaller overpotential with strained MoS₂ than the unstrained counterpart.

After obtaining the electrochemical capacitance of the MoS₂, we have demonstrated that it can characterize the electronic property of monolayer 2D materials, even under tensile strains. This can help us to reveal the strain effect on monolayer MoS₂ in the HER process by clarifying its electronic states.

The catalysis property of a catalyst is majorly valued by its active-sites number and the turnover frequency (TOF). While increasing the active-site number will finally meet a limitation, enhancing the TOF can theoretically increase the catalysis linearly. On the other hand, the TOF is closely related to the eigen property of a given material. Therefore, how to define a method to reveal the relationship between the electronic structure and TOF is essential. In work described in this chapter, we aimed to discover this missing puzzle piece through strain engineering. We

demonstrate that tensile strain contributes to a spin-orbital coupling in monolayer molybdenum disulfide, which results in an enhanced electronic state at its conduction band edge. This exotic electronic structure in the strained monolayer MoS₂ induces an unexpected 3-zone catalysis process and an ultrahigh TOF of 27.75 s⁻¹ in hydrogen evolution reaction.

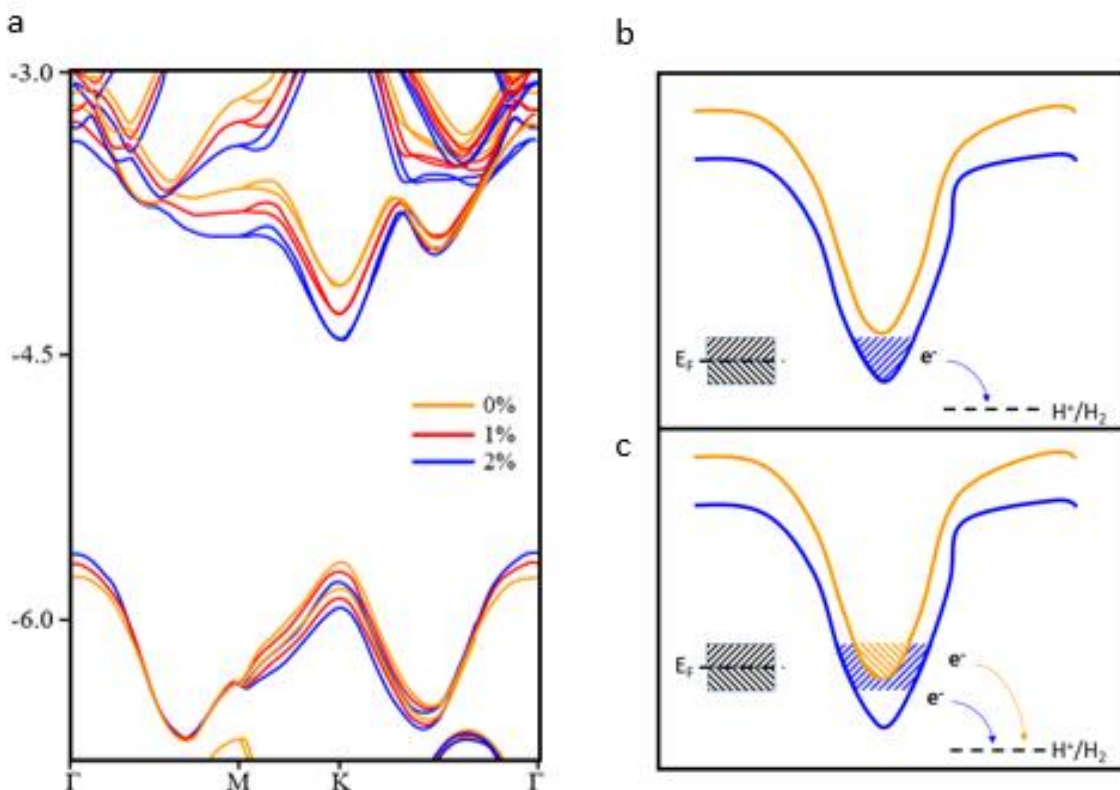


Figure 5-1. Band structure and schematic of electrons jump at the different potential: (a) band structure of 0%, 1%, and 2% strained MoS₂, (b, c) schematic of how the electrons in catalyst jump to H^+/H conversion level at different potential

In this work, the HER catalysis property of monolayer MoS₂ was investigated under different strain conditions to reveal the band structure of strained monolayer MoS₂. Based on the experimental

results, the applied tensile strain stretches the band structure of MoS₂, which is reflected in the HER reaction. The applied strain leads to a 3-zone process in HER and shows a 0.08 V vs. RHE overpotential in the 2% strained sample. The turnover frequency (TOF) of the 2% strained sample reached a value of 27.75 s⁻¹, close to that of Pt. The catalysis test provides the band structure shape of monolayer MoS₂ under different strain conditions. Also, the conduction band structure matches the 3-zone phenomenon in HER results. This reflects the intrinsic property of a catalyst, and for the first time, we are able to link the band structure with catalysis in a monolayer material.

5.2 EXPERIMENT SETUP

In this experiment, the mechanical exfoliation method is used to obtain the monolayer MoS₂ flake from bulk crystal. Then the monolayer MoS₂ was placed on the PET substrate. The layer number of the MoS₂ flake is confirmed by Raman spectroscopy. The distance between E_{2g}¹ and A_{1g} will shrink to each other as the layers reducing. A 1%, 2% biaxial strain was applied using a biaxial beam bending method, similar to that used in the literature [69, 156]. The HER tests are conducted in the 0.5 mol/L H₂SO₄ solutions with a saturated calomel reference electrode and carbon counter electrode. The band structure study was performed by the electrochemical capacitance test within an ionic liquid environment (BMIM-BF₄).

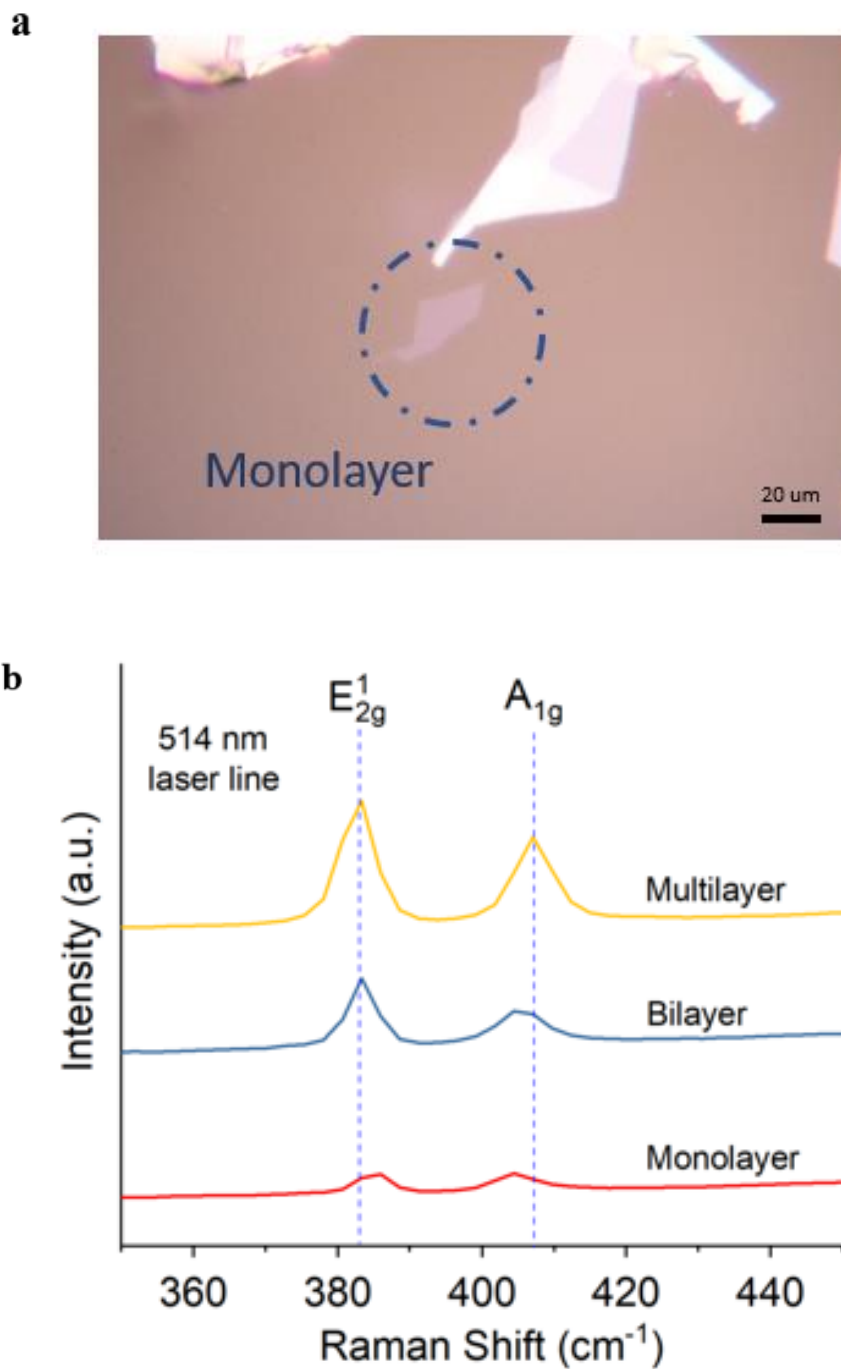


Figure 5-2. Monolayer MoS₂ sample and Raman spectroscopy results: (a) optical image of a monolayer MoS₂ flake, (b) Raman spectra of monolayer and multilayer MoS₂

Error! Reference source not found. presents the step by step micro device fabrication process. The three layers of PMMA were spin-coated onto the PET substrate. Then a 50 nm layer of Cr was coated with a magnetron sputtering system for improving the conductivity in the coming E-beam step. The electrodes were developed through E-beam and thermal evaporator. The electrodes are 80 nm thick Au and 5 nm Ti as the bonding material. Then, another two layers of PMMA were spin-coated onto the substrate for opening the test window, which can expose the desired catalysis area. A rubber container was fabricated to the window position to contain the electrolyte. At last, the whole device was attached to a designed biaxial beam for further applying the tensile strain.

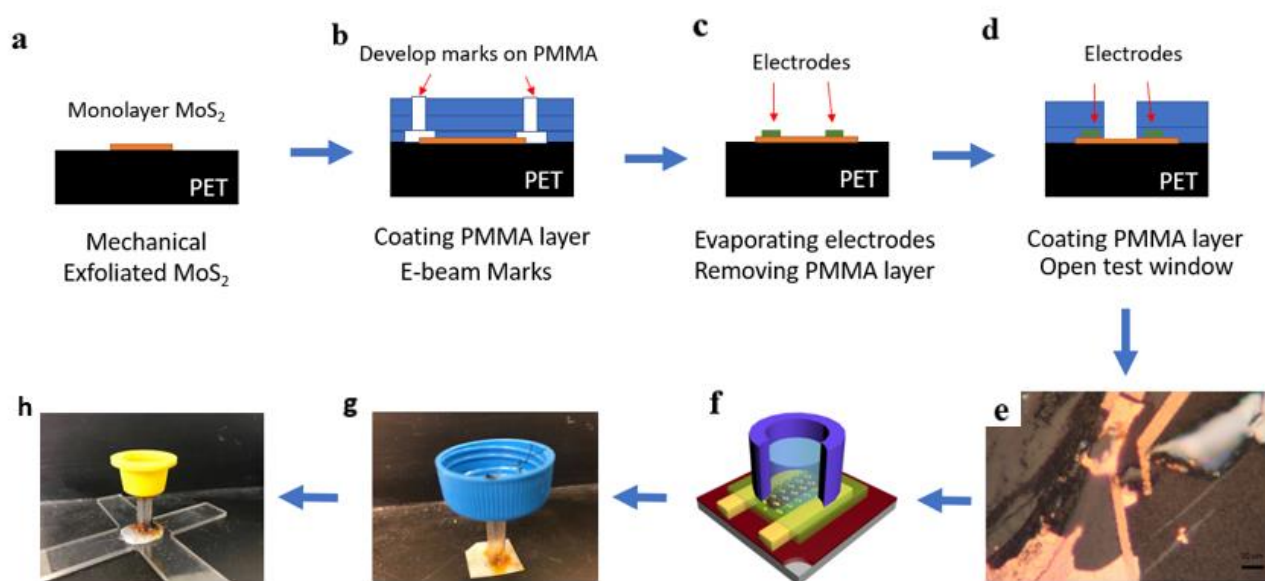


Figure 5-3. The process of device fabrication : (a) *mechanically exfoliated* monolayer MoS_2 sample on PET substrate, (b) two layer PMMA with Cr conductive layer on MoS_2 sample, (c) deposited electrodes on the monolayer MoS_2 sample, (d) electrochemical test window on the monolayer MoS_2 , (e) top view photo of Au electrode on the monolayer MoS_2 , (f) HER testing device, the container with electrolyte sitting on the monolayer MoS_2 with an opened test window, (g) photo of an HER test device, (h) HER test device sitting on the beam bending strain applying device

The strain application based on biaxial plate bending is illustrated in Error! Reference source not found. **a.** The previous PET substrate with MoS₂ and electrode is attached to another PET cross by superglue. And a dome-shaped watch glass is selected as a curvature controller for bending the PET cross-beam to the desired curvature. By measuring the total thickness of the PET cross and PET electrode substrate, the substrate's neutral axis can be defined

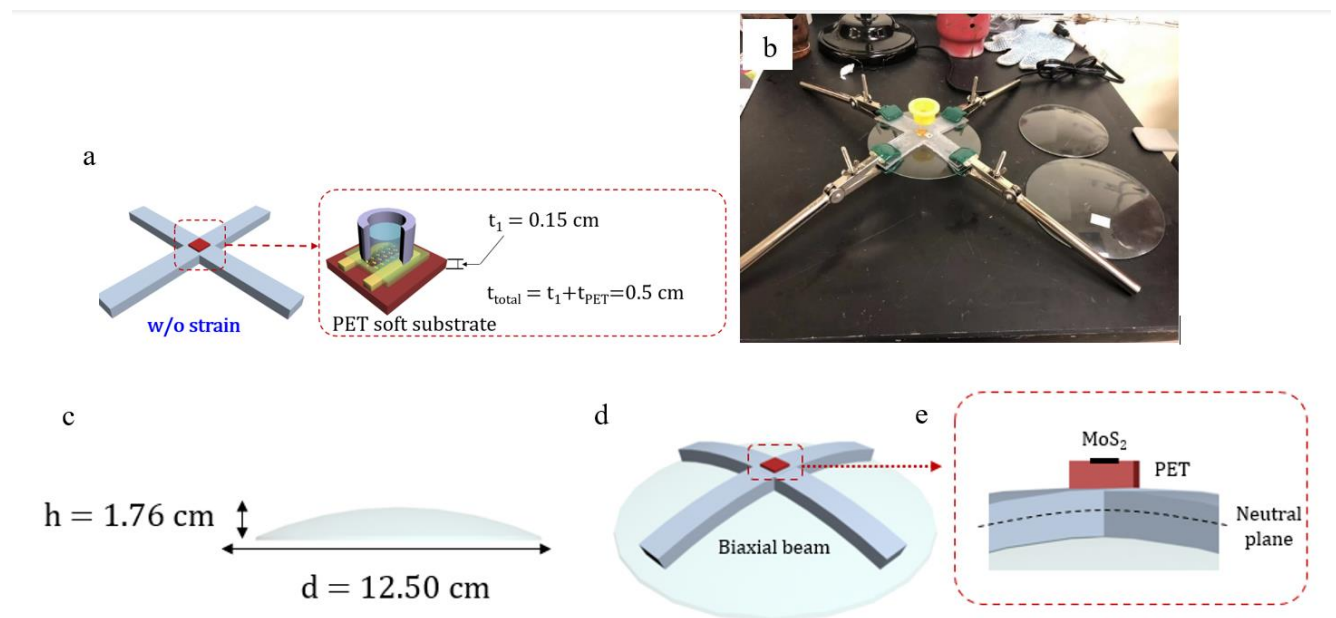


Figure 5-4. Strain applying device (2% tensile strain): (a) schematic of the MoS₂ sample on the biaxial beam, (b) photo of applying strain to MoS₂, (c) schematic with parameters of a beam bending arch for achieving 2% strain, (d, e) schematic of applying strain through biaxial beam bending on the arch.

The strain can be expressed with the following equation.

The radius of the arch can be expressed as a function of the arch height h and the chord length d .

$$R = \frac{(h + 0.5t_{total})^2 + (0.5d + 0.5t_{total})^2}{2(0.5t_{total} + h)} \quad (2)$$

The strain on the curved beam outer layer:

$$\varepsilon = \frac{t_{total}/2}{(t_{total}/2 + R)} \quad (3)$$

where R is the dome's radius, and t is the total thickness of the two PET substrates (the small thickness of the MoS₂ monolayer sample is ignored). By using this method, domes with different radius R are used to apply different amounts of strain. In the 2% strain case, the d of dome is 12.5 cm, while the h is 1.76 cm. In 1% strain case, the d is 16.74 cm, while the h is 1.3 cm.

For example, the strain applied on the MoS₂ (ε) in **Error! Reference source not found.** equals to:

$$\frac{t_{total}/2}{(t_{total}/2 + R)} = 2.0\% \quad (4)$$

After the assembly of the device and application of strain, the test is conducted with a 3-electrode setup (**Error! Reference source not found.**). A probe stage and an electrochemical workstation (BioLogic SP-300) are used to measure the HER catalysis activity. The whole system includes one saturated calomel electrode as the reference electrode, one carbon electrode as the counter electrode, 0.5 mol/L sulfuric acids as the electrolyte. The electrolyte is in a rubber container attached to the opened test window on the top PMMA layer.

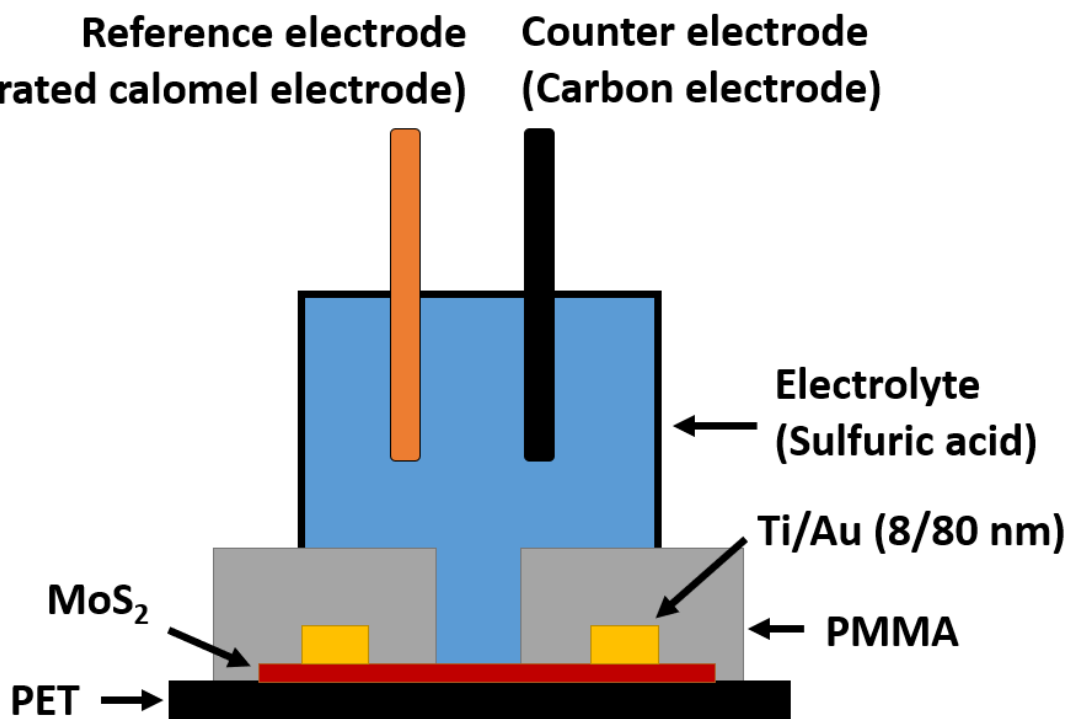


Figure 5-5. Schematic of the electrochemical test setup

The working electrode is made of a bilayer Ti/Au, which is deposited using a thermal evaporator with a base vacuum around 1×10^{-7} mbar and the temperature under 45°C to prevent the softening of the PET substrate. The Ti layer is designed as a bonding layer between PET and gold. The probe contacting the gold working electrode is connected with a potentiostat. And the current vs. voltage, impedance, and capacitance results can be obtained from the test.

Experiments were run under different test potentials to get different currents to reflect the HER reaction speed in MoS_2 . The scanning step is 5mV/s . By drawing the current vs. potential plot, the overpotential of reaction can be found. Also, the HER activities on the same sample under different strain conditions can be compared. The Tafel slope even is extracted to reveal the electrochemical

reaction mechanism of HER under different strained MoS₂. An impedance test is used to measure the interface resistance between the electrode and electrolyte. The electrochemical capacitance test was run using a similar setup with the HER test, with the only difference of using Ag/AgCl as the reference electrode and BMIM-BF₆ as the electrolyte. The whole capacitance structure under different potentials was obtained to further analyze the material's density of states. The scan rate in this test was 5mV/s.

5.3 HYDROGEN EVOLUTION REACTION TEST RESULTS

5.3.1 Polarization Curve and Tafel Slope and Turnover Frequency

As shown in Error! Reference source not found.a, the current density increases with increasing potential and the increasing amount of strain. Under the strained situations, the polarization curve shows an unusual plateau that divides the HER reaction into three distinct zones. The polarization curve, at -0.2 V vs. RHE, shows a 28 mA/cm² current density for the unstrained, 58 mA/cm² for the 1% strained, and 90 mA/cm² for the 2% strained MoS₂ samples, respectively. It is evident that the applied tensile strain improved the catalysis property of the monolayer MoS₂. The current density increasing speed slows down after around -0.3 V vs. RHE in the two strained samples and shows a plateau from -0.3 V to -0.6 V. After -0.6 V, the current density rapidly increases again. A similar plateau is also reported in the literature with the neutral electrolyte (PH = 4 – 9) due to the mass transportation limitation near the solid-liquid surface [157, 158]. However, in our experiment (electrolyte PH = 1), the plateau is considered to be caused by the intrinsic property variation under the tensile strain.

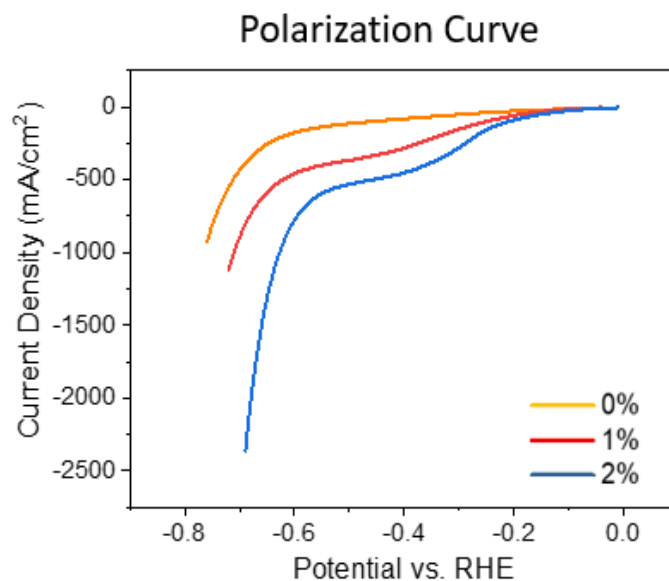
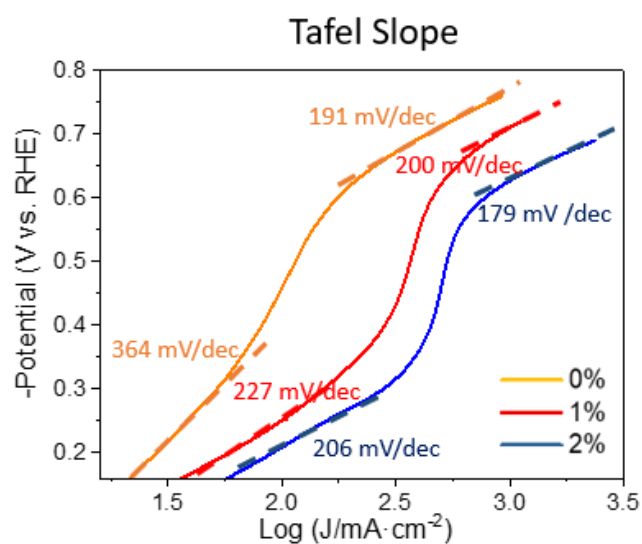
a**b**

Figure 5-6. Electrochemical testing results of MoS_2 based HER: (a) current vs. potential plot of the unstrained, 1% strained, and 2% strained monolayer MoS_2 sample, (b) Tafel slope of the unstrained, 1% strained, and 2% strained monolayer MoS_2 sample.

The turnover frequency (TOF) is also calculated based on the assumption that each Mo atom works as the active site in the HER. The area of a unit cell is given in **Error! Reference source not found.** after considering the effect of the tensile strain. The lattice constant of unstrained MoS₂ is $a = 0.318$ nm, $b = 0.550$ nm. The tensile strain will change the a and b by 1% or 2% at the same time.

TOF is calculated based on the following equation:

$$TOF = \frac{\text{Total number of hydrogen atoms per second}}{\text{Total number of active sites per unit area}} = \frac{j}{2qN} \quad (5)$$

Where j is the current density (mA/cm²), the number 2 in the equation represents two electrons transfers per H₂ molecule generated, q is the elementary charge (1.6×10^{-19} C), and N is the active site density in the catalyst (cm⁻²). In this work, we assumed that each surface layer Mo atom has an active site. In each unit cell, there are 2 Mo atoms. Thus, the number of active sites can be calculated for each strain condition as 1.14×10^{15} for 0%, 1.12×10^{15} for 1%, and 1.10×10^{15} for 2%. After calculation, in the first zone, the TOF of monolayer MoS₂ without strain yielded a value of 20.23 s^{-1} . The 1% and 2% strained MoS₂ showed an extraordinary TOF of 21.61 s^{-1} and 27.75 s^{-1} , respectively, much higher than that of the bulk Pt (0.94 s^{-1}) [35]. In the third zone, the TOF is calculated to be 0.34 s^{-1} for the unstrained, 1.06 s^{-1} for the 1% strained, and 1.79 s^{-1} for the 2% strained MoS₂ samples, respectively. This indicates that the applied tensile strain affects the H bonding property of the active sites.

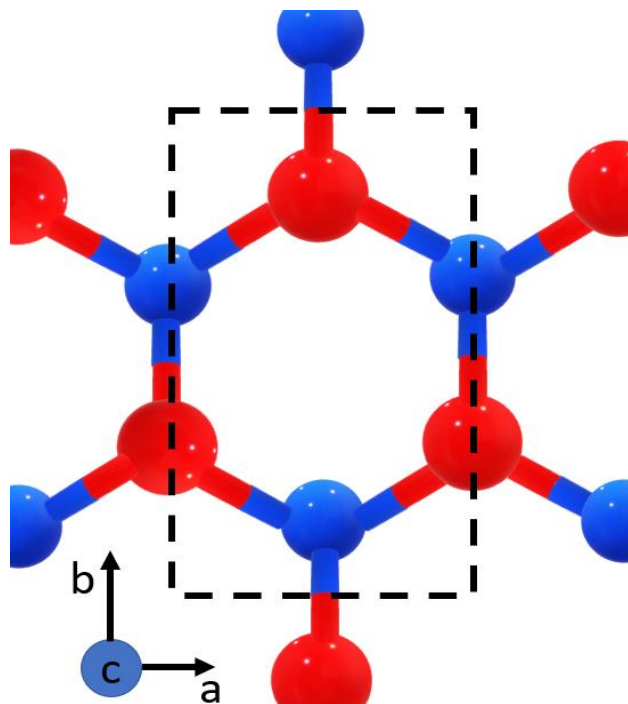


Figure 5-7. The schematic of a unit cell in MoS₂

The three distinctive zones are also reflected in the Tafel slope plots (Error! Reference source not found.**b**). In the first zone (the initial current density increasing part with potential below -0.3 V), the plots show a Tafel slope of 364 mV/dec for the unstrained, 227 mV/dec for the 1% strained, and 206 mV/dec for the 2% strained MoS₂, respectively. In the second zone (with the potential between -0.3 V and -0.6 V), the increasing speed of the current density is slower and shows a plateau in the 1% and 2% strained samples. In the third zone, the current density increase dramatically in all three samples. And the Tafel slope shows similar results for all three samples, i.e., 191 mV/dec for unstrained, 200 mV/dec for 1% strained, and 179 mV/dec for 2% strained samples, respectively.

Also, based on the polarization plot, there are two plateaus on the 1% and 2% strained samples. In the 1% strained sample, it is from ~ -0.24 V to -0.42 V. In the 2% sample; the plateau region moves to ~ -0.34 - -0.49 V. This plateau is due to the limited active electrons in this scanned potential range. From the polarization curve, there is a forward and reverse scanning difference. The area between the forward and back scanning range is the capacitance stored during the test process.

5.3.2 Impedance Test Results

These HER and Tafel results confirm the tensile strain can affect the property of MoS_2 and further improve the HER. However, we still lack an understanding of the reason causing this change. Thus, some further impedance test was conducted on the strained MoS_2 samples. The electrochemical Impedance test is a test method to test the whole system configuration by getting the resistance and capacitance values under different potentials and frequencies. It refers to an electrical circuit element's ability to resist the flow of current. Resistance is defined by Ohm's law as the ratio of voltage to current, E to I . While this is a well-known relationship, it is applicable only to one type of circuit element: the ideal resistor. Numerous simplifying properties exist for an ideal resistor: at any current or voltage level, it obeys Ohm's Law. Resistance is frequency-independent. Through a resistor, the alternating current and voltage signals are phase-locked. The real world, on the other hand, has circuit elements with significantly more complex behavior. These elements require us to abandon the straightforward concept of resistance in favor of impedance, a more general circuit parameter. Impedance, like resistance, is a measure of a circuit's ability to resist the flow of electrical current. However, unlike resistance, it is not constrained by the simplifying properties listed above. The impedance of an electrochemical cell is typically determined by applying an alternating current through the circuit and then measuring the current

flowing through. Assume that a sinusoidal potential is used to excite the system. AC current is generated in response to this potential. This current signal can be examined mathematically as a sum of sinusoidal functions (a Fourier series). In most cases, electrochemical impedance is determined using a low excitation signal. This results in a pseudo-linear response from the cell. The current response to a sinusoidal potential in a linear (or pseudo-linear) system is a sinusoid with the same frequency but phase-shifted (**Error! Reference source not found.**).

Figure 5-8. Sinusoidal current response in a linear system

Based on Ohm's Law, an expression analogous to allows us to calculate the impedance of the system as:

$$Z = \frac{E_t}{I_t} = \frac{E_0 \sin(\omega t)}{I_0 \sin(\omega t + \Phi)} = Z_0 \frac{\sin(\omega t)}{\sin(\omega t + \Phi)} \quad (6)$$

The impedance is expressed in terms of a magnitude, Z_0 , and a phase shift, Φ .

When the applied sinusoidal signal $E(t)$ is plotted on the X-axis of a graph and the sinusoidal response signal $I(t)$ on the Y-axis, an oval is obtained (Error! Reference source not found.). This oval shape is referred to as a "Lissajous Figure".

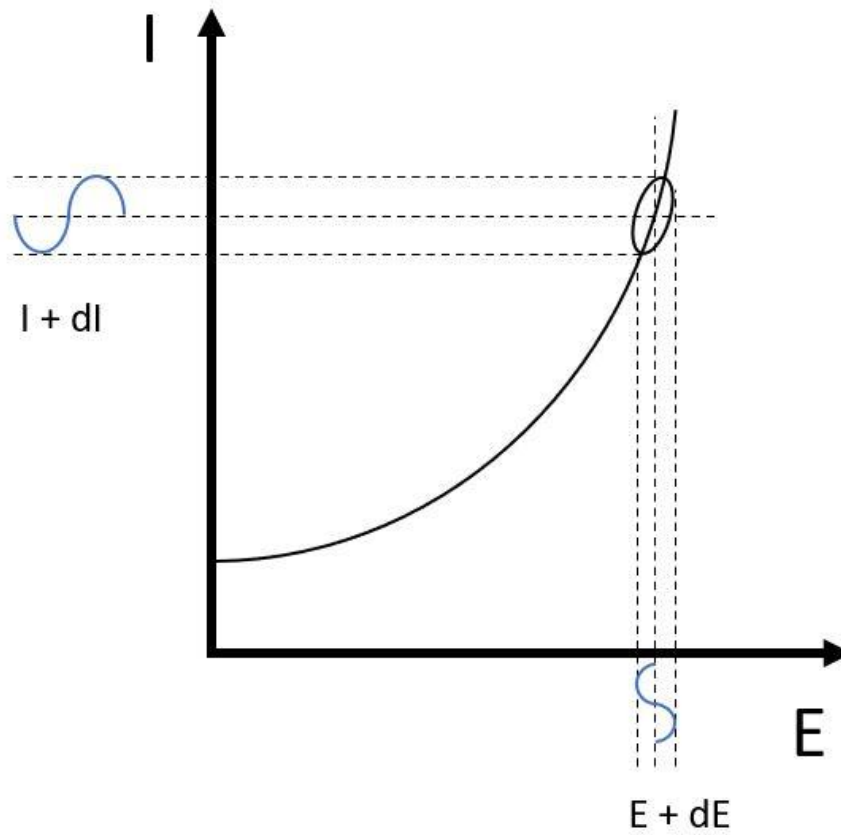


Figure 5-9. Schematic of Lissajous figure

With the Eulers relationship,

$$\exp(j\Phi) = \cos \Phi + j\sin \Phi \quad (7)$$

The impedance can be written as a complex number,

$$Z(\omega) = \frac{E}{I} = Z_0 \exp(j\Phi) = Z_0(\cos \Phi + j\sin \Phi) \quad (8)$$

$Z(\omega)$ is a two-part expression consisting of a real and an imaginary part. When we plot the actual part on the X-axis and the imaginary part on the Y-axis of a chart, we obtain a "Nyquist Plot" (Error! Reference source not found.**a, b, c**). Take note that the Y-axis is negative in this plot and that each point on the Nyquist Plot represents the impedance at a single frequency. The Nyquist Plot has been annotated to indicate that data with a low frequency are on the right, and data with a greater frequency are on the left. The Nyquist Plot can be used to show impedance as a vector (arrow) of length $|Z|$. The angle formed by this vector and the X-axis is frequently referred to as the "phase angle." It is equal to $\angle Z$ ($\arg Z$). However, Nyquist Plots contain one significant flaw. When viewing any data point on the plot, it is impossible to determine the frequency at which the point was recorded. The semicircle is the shape associated with a single "time constant." Frequently, electrochemical impedance charts contain many semicircles. Occasionally, only a piece of a semicircle is visible. The Nyquist Plot shown in Error! Reference source not found., depicted in is the outcome of the electrical circuit modeled in Error! Reference source not found.**b**. Also, because of the complexity of our electrode-electrolyte testing system, the multiple "time constant" is considered. Thus, in Error! Reference source not found.**b**, a multibody model is established.

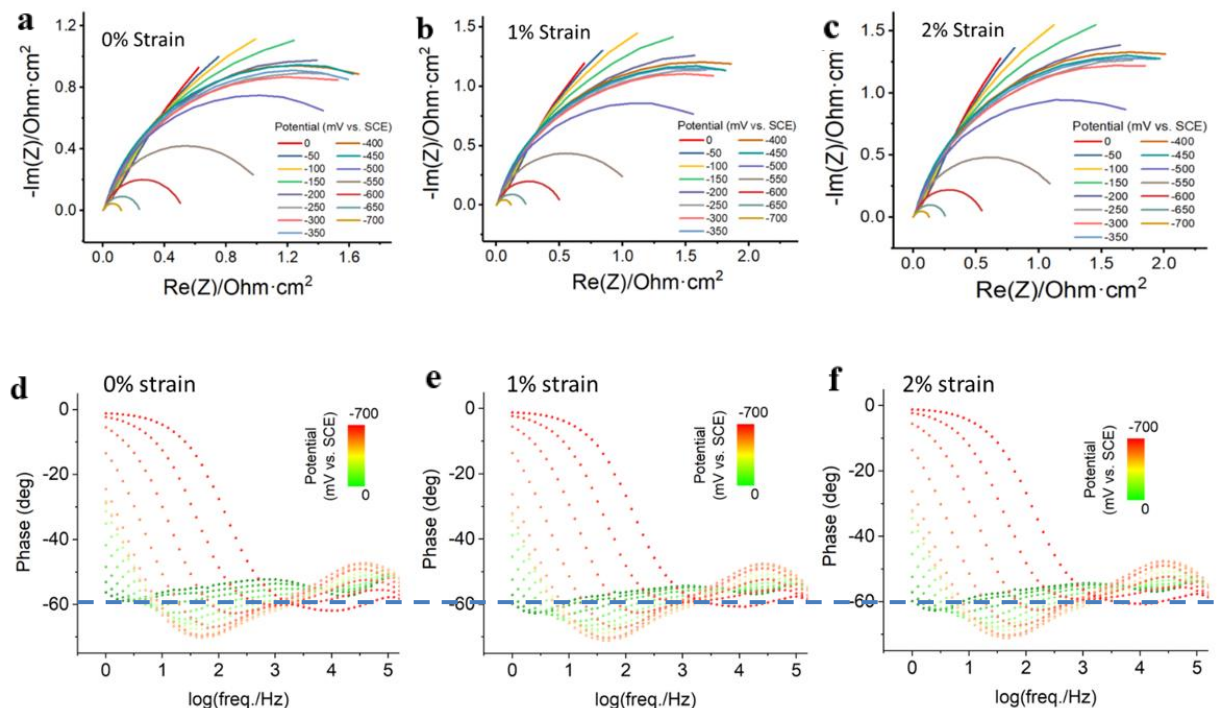


Figure 5-10. Impedance test results of HER test: (a) Nyquist Plot of 0%, (b) 1%, and (c) 2% strained monolayer MoS₂ electrode; Phase vs. frequency plot of (d) 0%, (e) 1%, and (f) 2% strained monolayer MoS₂ electrode, under different potential

In Error! Reference source not found. **d, e, f**, under different strain conditions, the MoS₂ sample shows different impedance and phases in the EIS test. In the phase shift plot, we can find at 4 $\log(\text{freq./Hz})$, phase of 0% strain sample < 1% strain sample < 2% strain sample. This change can lead to a difference in the electrical ability of the system.

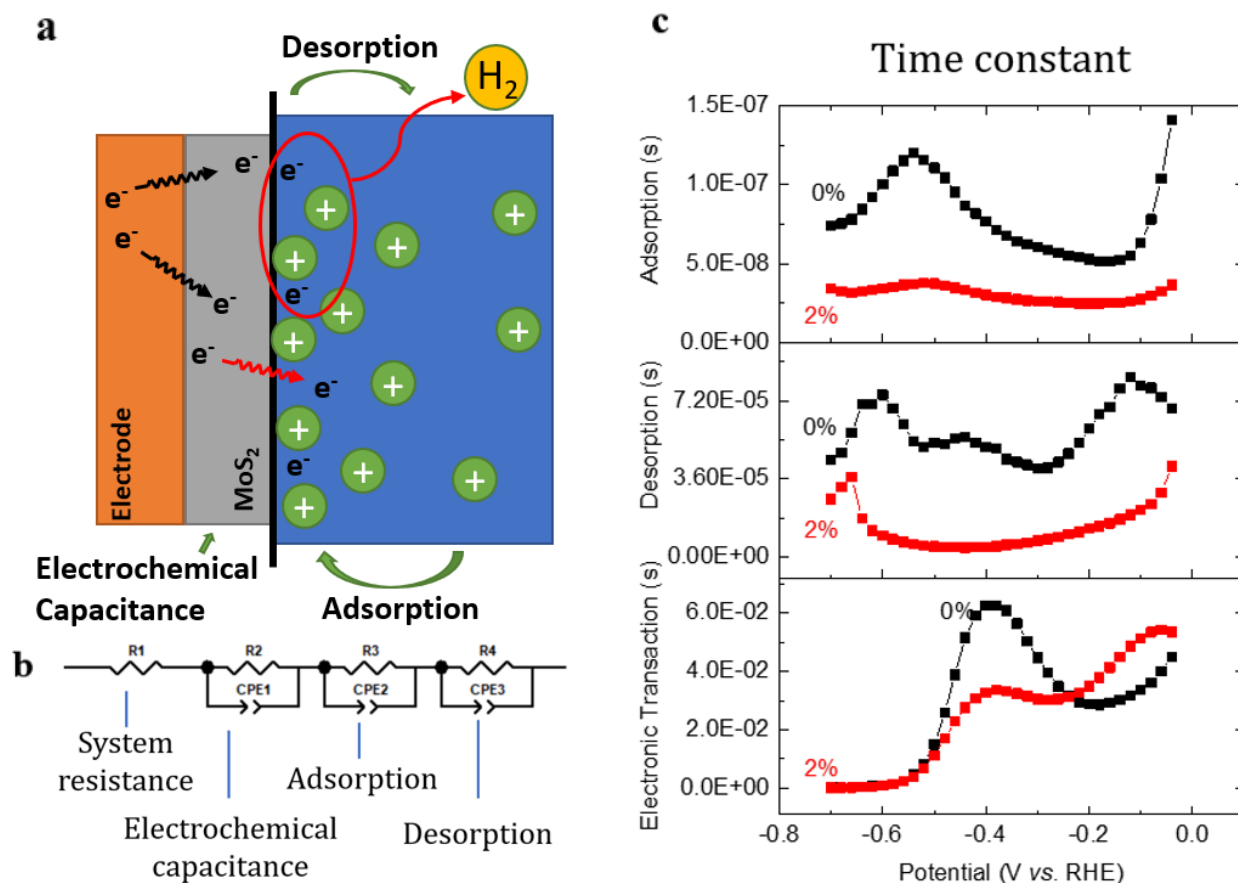


Figure 5-11. Impedance simulation model and simulation results of monolayer MoS₂ under different strain conditions: (a) schematic of the electron transaction and the adsorption/desorption processes at the electrode-electrolyte interface, (b) Simulation model for the impedance results, (c) corresponding equivalent circuit.

Error! Reference source not found. **a & c** show the different EIS results under 0% and 2% strain. Based on the three-part model in other researcher's work [76], simulation work also is conducted based on the EIS test. A four-part model is used to fitting the results for more accurate analysis (Error! Reference source not found. **a & b**). In the simulation process, four separate electrical parts were established. This model includes one single resistance part and three capacitances-resistance

groups, presenting the adsorption layer, desorption layer, and electronic transaction part. By separating the adsorption and desorption parts from the traditional three-part model, the configuration of the system will be explained in detail. R1 is for the system resistance. R2 and CPE1 present the quantum capacitance and resistance in the MoS₂ sample. R3 and CPE2 mean the resistance from the interface of electrode and electrolyte and the capacitance in adsorption. R4 and CPE3 are the resistance in diffusion and capacitance of desorption. The simulation results show that the adsorption and desorption time constants are on the order of 10^{-6} s. This means even the time constants of the 2% strained sample are smaller than the unstrained sample in the adsorption and desorption part, and these are still not the primary factors of HER. And due to the slow mobility of electrons in mechanical exfoliated MoS₂, the electronic transaction is the rate-limited part of the whole model. Based on the electron mobility in mechanical exfoliated MoS₂ is low to 1×10^{-4} m²/V*s, the time constant of the electronic part is on order around 10^{-2} s. The fitting results also show a 3-zone property that matches the 3-zone polarization curve and Tafel slope in the electronic component. This match between the electronic property of MoS₂ and the reaction speed also confirms that the electronic part dominates the HER speed. In the first zone (0 V to -0.25 V), the time constant decreases. This reflects a faster reaction time of electrons. In the second zone (-0.25 V to -0.5 V), the time constant increases. This may relate to the plateau shown in the Tafel slope and polarization plot. In the third zone (less than -0.5 V), the time constant decreasing matches the current density increases in the polarization curve.

The simulation results show that the applied strain can affect the time constant of MoS₂, adsorption, and desorption effectively. The time constant of adsorption and desorption of 2% strained MoS₂ is around 1/3 of unstrained MoS₂ in the HER process. However, in the 0 to -0.2 V area, the 2% strained MoS₂ has a higher time constant in quantum capacitance. In the -0.2 V to -

0.5 V area, the time constant of quantum capacitance of the 2% strained sample is lower than the unstrained MoS₂. When the potential goes further than -0.5V, there is no significant difference in time constant between the 2% strained MoS₂ and unstrained one.

5.3.3 Theoretical Result of Strain Effect on Monolayer MoS₂

The polarization plot shows the change in the HER test after applying strain. The EIS plot shows the time constant changing after strain. However, the strain effect on atomic and electronic levels is still not well understood. Thus, density functional theoretic calculation is used to help to understand the strain-induced change in electronic levels. Density-functional theory (DFT) is a computational quantum mechanical modeling technique used in physics, chemistry, and materials science to study the electronic structure (or nuclear structure) (most notably the ground state) of many-body systems, especially atoms, molecules, and condensed phases. Based on the famous Hohenberg and Kohn theorems, DFT provided a sound basis for the development of computational strategies for obtaining information about the energetics, structure, and properties of (atoms and) molecules at much lower costs than traditional ab initio wave function techniques. This technique has strongly influenced the evolution of quantum chemistry during the past 15 years.

In this work, the first-principles calculations are performed using the fully relativistic density functional theory (DFT) within the generalized gradient approximation (GGA), as implemented in the Quantum ESPRESSO [159] package. The norm-conserving pseudopotential is employed [160]. The monolayer MoS₂ structure is relaxed until forces on each atom are below 0.00001 Ry/a.u. A $20 \times 20 \times 1$ Monkhorst-Pack k-point grid is used for self-consistent calculation with a kinetic energy cutoff of 90 Ry. For calculating the density of states, a non-self-consistent calculation is performed using a $120 \times 120 \times 1$ Monkhorst-Pack k-point grid. Based on the

calculation results, the DOS of MoS₂ is shown in Error! Reference source not found.. The x-axis is the potential vs. vacuum. And the y-axis is the intensity of the DOS. The density of states can reflect the possible open sites for the electron in a material at a certain energy level. From the DOS plots, we can see that the strain changes the shape of the conduction band significantly. The width of the bandgap is changed by the applying of strain. The bandgap widths of 0%, 1%, and 2% strained samples are 1.75 eV, 1.6 eV, and 1.5 eV in DFT calculation results. In the valence band, the strain causes a peak shift closer to the vacuum energy level from unstrained MoS₂. The valence band edge of the 2% strained sample is around 0.1 eV closer to the vacuum than the unstrained sample. In the conduction band, the peak is shown at -4.2 eV position of 0% strain sample shifts to -4.4 eV under 1% strain. In 2% strained MoS₂, the intensity of DOS peaks changes a lot from the unstrained sample. There are two major peaks in the conduction band of 2% strained sample. One is at -4.1 eV while another locates at -3.6 eV. In the 0% strained sample, there are three major peaks which are around at -3.75 eV, -3.5 eV, and -3.4 eV, respectively. These differences can prove the strain effect on the DOS theoretically.

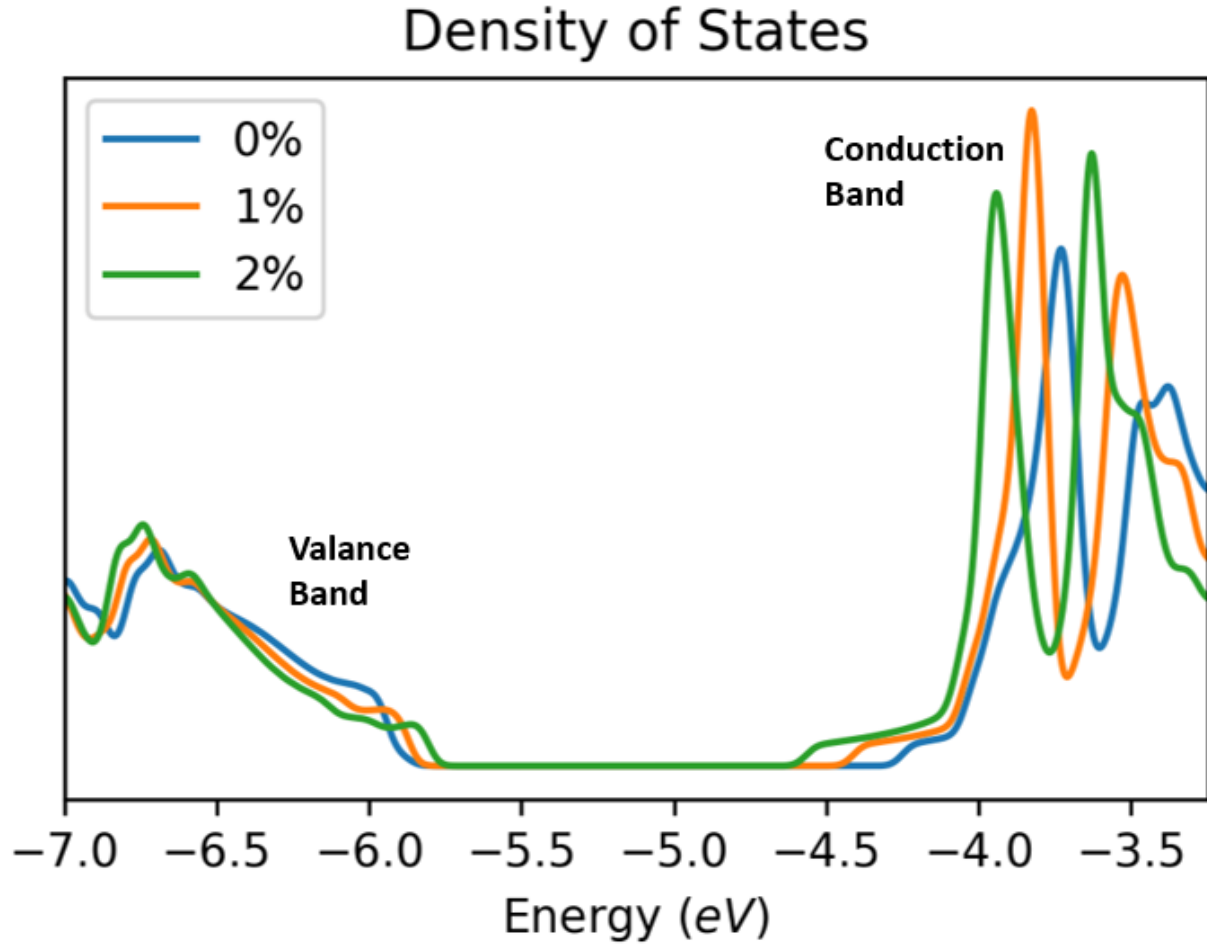


Figure 5-12. DFT calculation results of the density of states of MoS₂ under different strain conditions

Also, the band structure of strained and unstrained MoS₂ obtained by the DFT calculation is shown in Error! Reference source not found.. As shown in the calculation results, both the conduction and valance bands drop lower with increasing strain. And the applied strain narrows the bandgap at the K point. Another attractive point is after applying 2% tensile strain; the monolayer MoS₂ transitioned from a direct bandgap semiconductor to an in-direct semiconductor. The smallest bandgap in 2% strained monolayer MoS₂ is from the Γ to K.

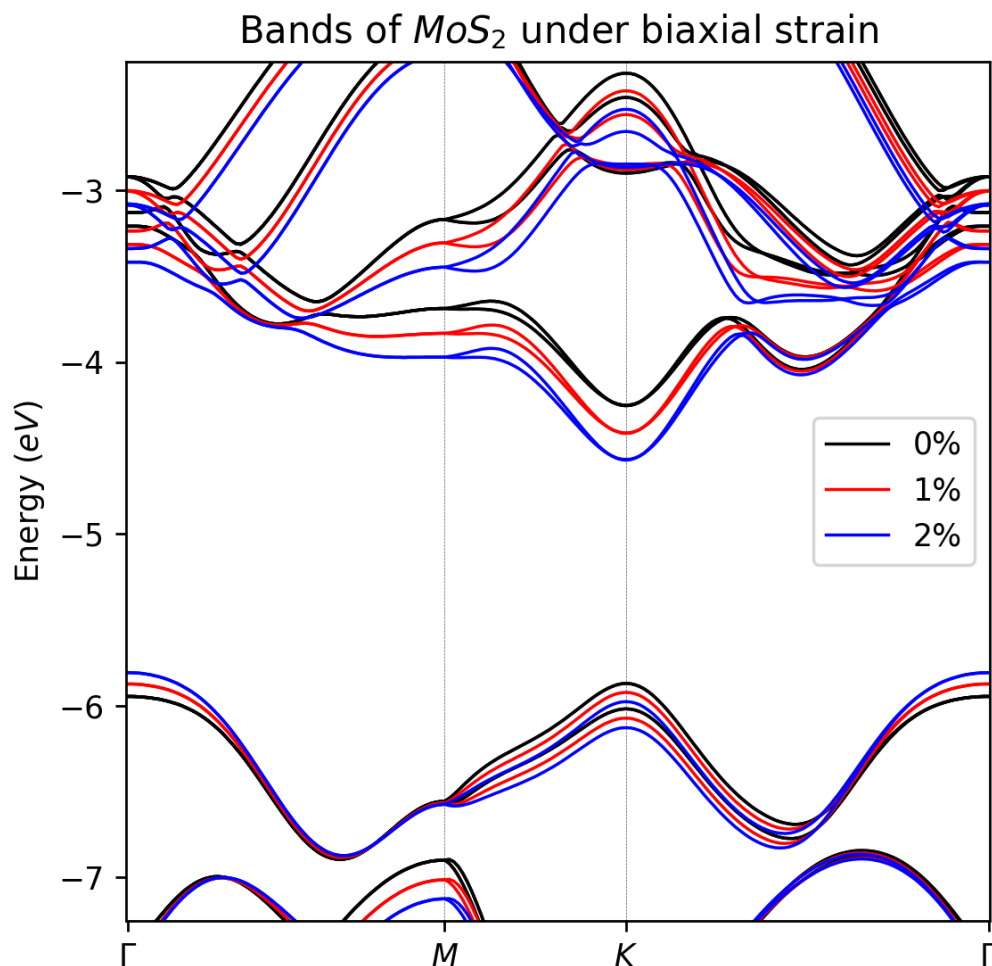


Figure 5-13. DFT calculation results of band structure of monolayer MoS_2 under different strained conditions

5.3.4 Correlation of HER, Theoretical Calculation, and QCS of MoS_2

Through the common concept in condensed matter physics, the key point of catalysis property is that the potentially useable electrons at a certain energy level in a catalyst material can be involved in the HER reaction. That can be reflected by its DOS plot. The shifting of the conduction band edge peak in the DOS plot of the 2% strained sample can explain the better catalysis property of

HER. In the HER process, the overpotential can bring the Fermi level of material to the conduction band. And a higher DOS peak means more active-able electrons at that energy level. These potential electrons can involve in the HER catalysis and bring a better catalysis property. In the HER process, the free electrons on the catalyst can make the kinetic barrier of the reaction lower; and in this way, the HER process will be smoother. Also, shown in the EIS test, the time constant of adsorption and desorption is much shorter after adding strain. This can make the transportation of electrons between electrode and electrolyte much faster and lead to a fast HER process. On the other hand, in electrochemistry, the catalyst's active sites are the major factor in the HER process. The ability to turnover electron to H in each active site can affect the catalysis property significantly. After applying tensile strain, defects are introduced to the surface of MoS₂ and generates more active sites. These active sites can provide more free electrons to the HER. The change of density of states between unstrained and 2% strained samples can be used to explain the phenomenon. The detailed discussion will be in the following content.

On the other hand, the 3-zone HER process is unexpected and has never been reported before. However, it is tough to be elucidated just through the electrochemical side. Thus, a new test method was run under the potential state to dig deeper into the electronic property of MoS₂. As shown in Error! Reference source not found.a, the electrochemical capacitance of monolayer MoS₂ was tested by the potential state under an ionic liquid environment. The bandgap width of unstrained and 2% strained MoS₂ is measured to be 1.78 eV and 1.63 eV, respectively, matching the previous theoretical results [70]. And a relative position difference of CBM between 0% and 2% strained sample is revealed (around 0.08 eV).

For easier analysis, the HER and band structure results are aligned to the vacuum energy level. The work function of unstrained MoS₂ has been reported to be around 4.3 eV [161], and 2% tensile strained MoS₂ around 4.4 eV [162]. The balance energy level of the conversion between H⁺/H is 4.4 eV vs. vacuum energy [155]. After the alignment, the conduction band, density of states, and current density are plotted on the same Y-axis in Error! Reference source not found.**b**. The CB position difference of strained and unstrained MoS₂ leads to the overpotential difference in HER. Moreover, when the scanning potential reaches the second valley in CB, the DOS and polarization curves reach the third zone, which correlates with the newly available electrons in the second valley.

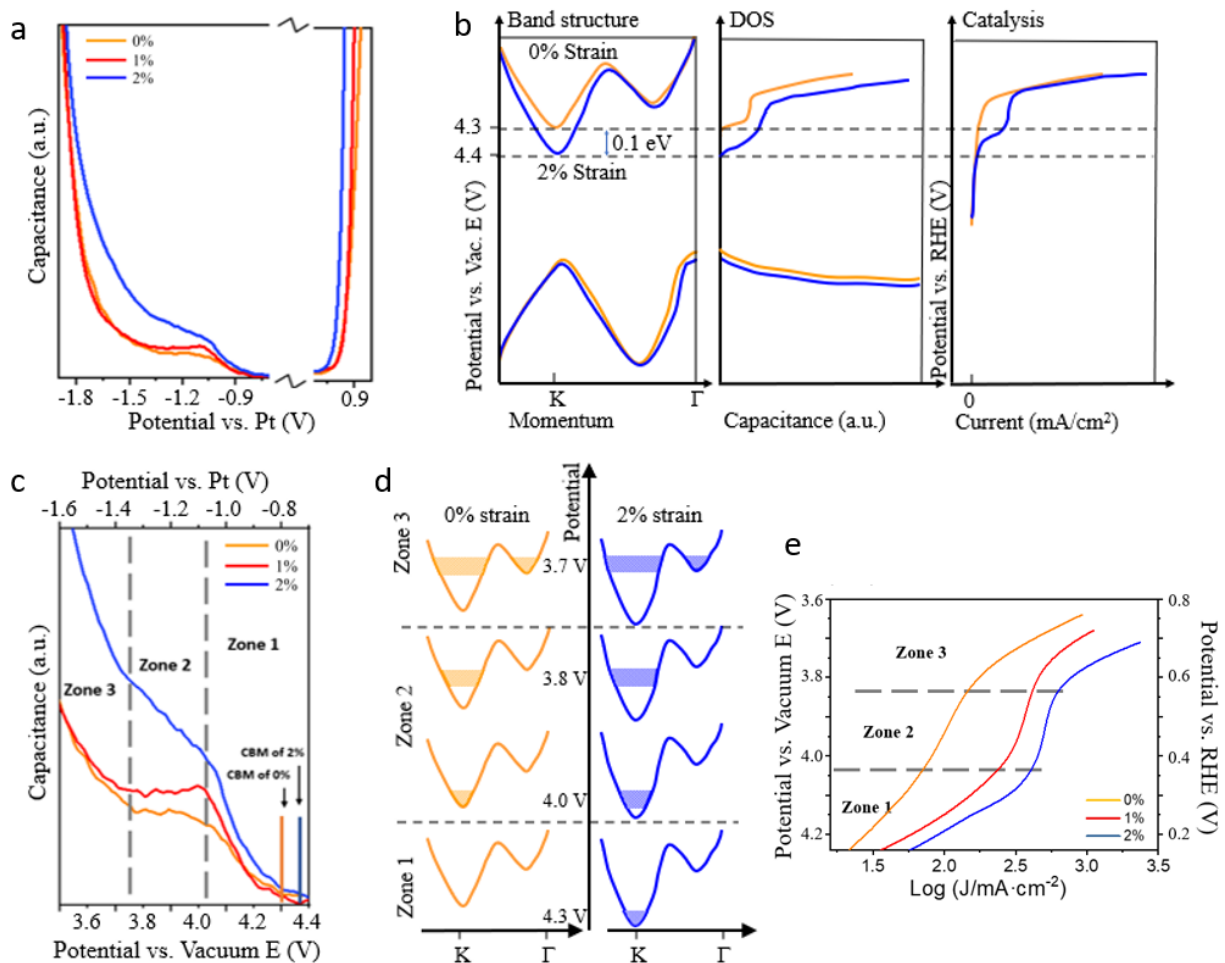


Figure 5-14. Electrochemical capacitance test results and schematic of comparison between band structure, DOS, and electrochemical test results: (a) *electrochemical capacitance* of MoS₂ under different strain conditions, (b) correlation between band structure, DOS, and current density in catalysis, (c) conduction band structure of MoS₂ under different tensile strains after potential alignment to vacuum energy level, (d) schematic of electrons' filling status in CB of unstrained and 2% strained MoS₂ at K point *corresponding to the 3-zones*, (e) Tafel slope of HER after potential alignment to vacuum.

As shown in Error! Reference source not found. **c, d, & e**, after the potential alignment, the conduction band of MoS₂ and Tafel slope can both be divided into three zones. In zone 1, due to

the lower CB bottom, the 2% strained MoS₂ has a higher capacitance than the unstrained MoS₂ when the scanning position reaches 4.3 V (zone 1 Error! Reference source not found.**d**). The higher capacitance can provide more available electrons in the CB band of MoS₂ and more available positions for the electrons, resulting in faster response speed and faster electron transaction in HER. This explains the better catalysis property of strained MoS₂ in zone 1 of the Tafel slope and polarization curve. On the other hand, an apparent plateau is shown in zone 2 of all samples. This slow electronic capacitance increasing zone limits the reaction speed and causes the plateau in the polarization curve and Tafel slope. The plateau width on the capacitance plot fits the HER polarization and Tafel plots width. This further proves that when the increase of capacitance slows down, the HER speed meets a plateau due to the insufficient supplement of electrons. A similar correlation also shows in the 1% strained MoS₂ sample. In zone 3, the capacitance increasing fast again, which means the MoS₂ can provide sufficient electrons to the active sites for HER. This matches the greater catalysis property in zone 3 of the polarization curve and Tafel slope.

5.3.5 Electrochemical/Quantum Capacitance of MoS₂ under Different Strain Conditions

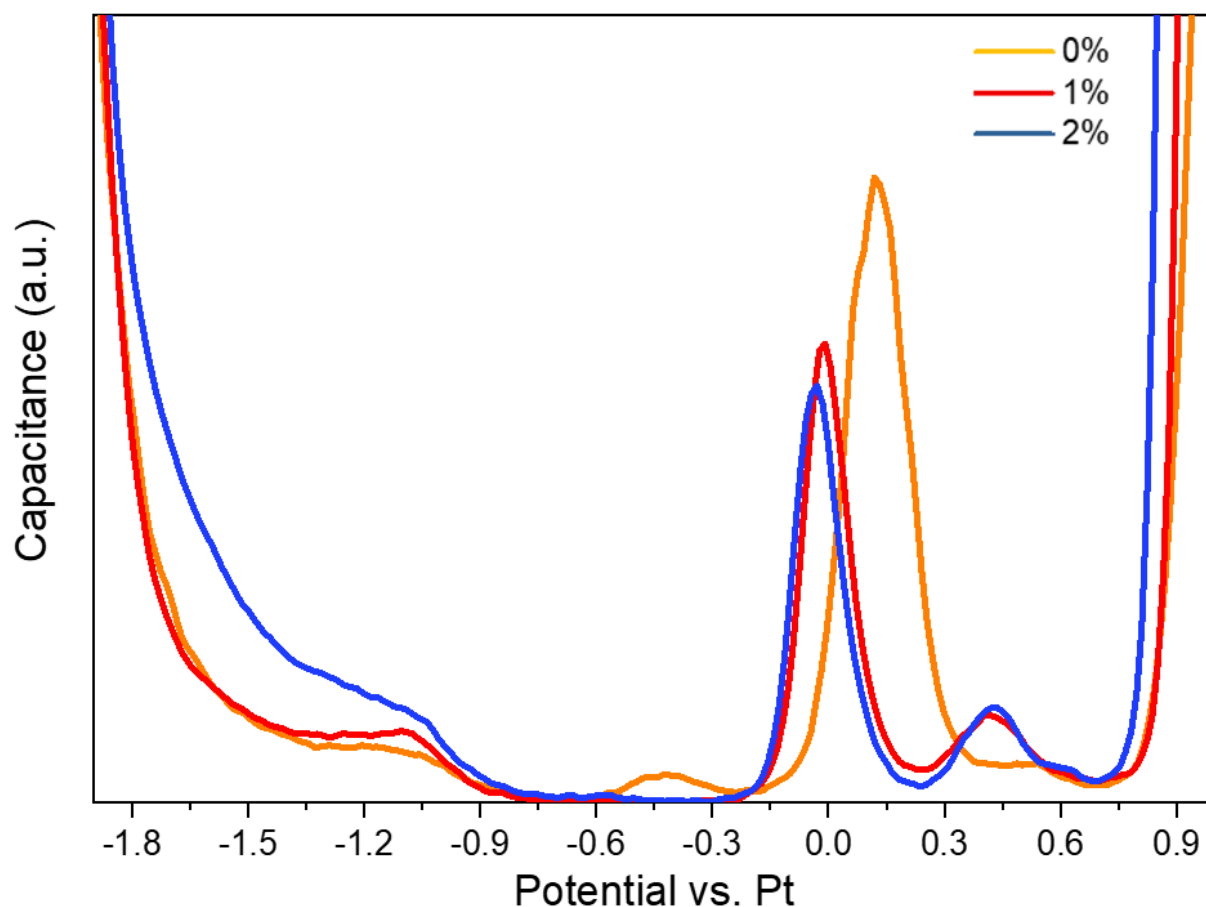


Figure 5-15. The complete band structure plot obtained from the electrochemical *capacitance* test

Error! Reference source not found. shows the complete band structure plot of strained and unstrained monolayer MoS₂. Except for the previously discussed characteristics, the biggest difference between unstrained and strained MoS₂ is the peak shifting at 0 eV. Also, there are peaks different at – 0.45 eV and 0.45 eV positions. The causes of these differences are still not fully

understood. One potential reason could be that the strain causes defective energy states and further leads to these energy peaks. For example, at the zigzag edge of monolayer MoS₂, the possible energy position of a Mo vacancy from CB is a range between 0.11 eV and 0.69 eV. This is also the range of peak shifts in our plot. This may indicate that the reason for peak shift is due to the status change of Mo vacancy after applying strain. Under the strained condition, there are also new peaks forming either close to VB or CB. This may be due to the formation of new vacancies.

5.4 CONCLUSION

The catalysis property of monolayer MoS₂ in HER under different strains was studied in this work. The biaxial tensile strain enhances the current density in HER and also the TOF. An unexpected 3-zone process was observed in the Tafel and polarization curves of the HER test. To further understand the unique 3-zone reaction behavior, an electrochemical capacitance test was innovated to investigate the band structure of the monolayer MoS₂. Under the applied biaxial tensile strain, the bandgap width of the monolayer MoS₂ has changed from the unstrained condition as well as the conduction band structure. This change in the conduction band of MoS₂ shows a similar trend to the 3-zone phenomenon in the polarization curve and Tafel slope. The conduction band difference between the unstrained and strained MoS₂ is responsible for the different electronic properties of MoS₂, which further leads to the different catalysis properties. Based on the test method in this study, a new way of elucidating the connection between the physical property and electrochemical performance of 2D TMD material is established. The method can be readily adapted to study the band structure of a broad range of materials to explain more phenomena in the electrochemical field.

6 CONCLUSIONS AND OUTLOOK

A reliable method of fabricating the flexible circuit system for strain engineering the band structure of 2D material is established in this project. In the electrochemical capacitance test, the electronic property and band shape of monolayer MoS₂ under different strain conditions were obtained. In the HER test, strained MoS₂ showed a better catalysis property than the unstrained sample (indicating the band structure change). The impedance test showed an effect from strain on the interface between the MoS₂ and the electrolyte. Also, the bandgap shrinkage and the electrochemical/quantum capacitance change provide compelling evidence for this change. All these achievements can be a precursor to the exploration of 2D materials in the future, not only in the catalyst field, but also in other fields such as semiconductors.

In the future, based on the flexible device fabrication process developed in this project, we may be able to apply strain engineering to other kinds of van der Waals materials to discover the HER activity and other properties. One example of such materials could be WSe₂, a TMD material that attracts researchers' attention by its characteristic features of electronic structure and preference. The applied strain may lead to changes in the HER activity in WSe₂ due to the evolution of band structure. On the other hand, in addition to the catalyst area, the Fe₃GeTe₂ (FGT) has itinerant ferromagnetism and can be used in memory devices. The Curie Temperature (T_c) of bulk FGT is about 220-230 K. However, the transition temperature of monolayer FGT is only around 140 K. By applying strain on very thin FGT flakes, we may study the relationship between the strain and magnetic ordering. Due to the high resolution shown in the electrochemical capacitance test, we can potentially develop a pollution or biomedical sensor. There will be new strong peaks formation after the adsorption process happening on the electrode's vacancy. The adsorbed atom can either

be a protein molecular or any pollution atom. Also, with the development of the semiconductor industry, especially in logic circuits, the structure size is becoming smaller and smaller. The scale of the newest generation chip is 3 nm, while the 1.4 nm fabrication process is under development which only contains less than ten atoms in a transistor. This extremely small size posts an ultra-high challenge to the materials in the transistor, such as the bonding layer, the gate material, etc. With probably only several atoms included in the structure, the material's electronic property is important at this angstrom-scale. However, it is hard to determine the electronic property of materials at this small scale with traditional methods. With our electrochemical/quantum capacitance test, we can get the band structure in the 4 eV range, which can cover most of the semiconductor materials. This provides a potential way to develop new materials for the fast-developing semiconductor industry. Also, based on our HER test, applying a strain may change the electronic property and further lead to an unexpected high on-off ratio in a transistor. With this concept, if we can build an angstrom-scale sample and apply a strain through its substrate, this sample may show some unusual properties.

In summary, strain engineering of 2D materials is an exciting research topic. When adapted to a wider range of materials, it could help reveal many new properties and exciting phenomena.

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VITA

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