The Synthesis and Electrocatalytic Activities of Molybdenum Sulfide for Hydrogen Evolution Reaction

Thesis by
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EXAMINATION COMMITTEE APPROVALS FORM

This thesis of Zhengxing Li is approved by the examination committee

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In the context of the future hydrogen economy, effective production of hydrogen (H₂) from readily available and sustainable resources is of crucial importance. Hydrogen generation via water splitting by solar energy or electricity has attracted great attention in recent years. In comparison with photocatalytic water-splitting directly using solar light, which is ideal but the relevant technologies are not yet mature, electrolysis of water with catalyst is more practical at the current stage. The Pt-group noble metals are the most effective electrocatalysts for hydrogen evolution reaction (HER) from water, but their high costs limit their applications.

Due to the earth-abundance and low price, MoS₂ is expected to be a good alternative of the Pt-group metals for HER. Plenty of researches have been conducted for improving the HER activities of MoS₂ by optimizing its synthesis method. However, it remains challenging to prepare MoS₂ catalysts with high and controllable activity, and more investigations are still needed to better understand the structure-performance correlation in this system.

In this thesis, we report a new strategy for fabricating MoS₂ electrocatalysts which gives rise to much improved HER performance and allows us to tune the electrocatalytic activity by varying the preparation conditions. Specifically, we sulfurized molybdenum oxide on the surface of a Ti foil electrode via a facile chemical vapor deposition (CVD) method, and directly used the electrode for HER testing. Depending on the CVD temperature, the MoO₂-MoS₂ nanocomposites show different HER activities. Under the
optimal synthesis condition (400°C), the resulting catalyst exhibited excellent HER activity: an onset potential (overpotential) of 0.095 V versus RHE and the Tafel slope of 40 mv/dec. Such a performance exceeds those of most reported MoS$_2$ based HER electrocatalysts. We demonstrated that the CVD temperature has significant influence on the catalysts in crystallinity degree, particle size and dispersion, morphology, and density of the edge sites etc., and these factors in turn determine the HER activity.
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<th>Description</th>
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<tbody>
<tr>
<td>CVD</td>
<td>Chemical Vapor Deposition</td>
</tr>
<tr>
<td>HER</td>
<td>Hydrogen Evolution Reaction</td>
</tr>
<tr>
<td>DFT</td>
<td>Density Functional Theory</td>
</tr>
<tr>
<td>$\Delta G^\circ_{\text{H}}$</td>
<td>Free Energy of Adsorbed H</td>
</tr>
<tr>
<td>3D</td>
<td>Three-dimensional</td>
</tr>
<tr>
<td>RHE</td>
<td>Reversible Hydrogen Electrode</td>
</tr>
<tr>
<td>MoS$_2$</td>
<td>Molybdenum Disulfide</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
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<tr>
<td>XRS</td>
<td>X-ray Photoelectron Spectroscopy</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
</tr>
<tr>
<td>HRTEM</td>
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1. INTRODUCTION

1.1 Energy Technologies

1.1.1 Energy Sources

With the high-speed development of the society, the supply of energy has becoming more and more important for the daily life of the human beings. People’s lifestyles have a huge demanding of energy, as the transportsations, daily comforts and properties would lose its colors without the energy supply.\(^1\) So the security of the energy is vital for sustainable development of the society, we could not take it for granted. Normally, the energy sources could be divided into five broad categories: Coal, Natural gas, Petroleum, Nuclear and Renewable energies (Figure 1)\(^18\), the Coal, Natural gas, Petroleum are called fossil fuels and the Renewables include Wind, Biofuels, Wood, Geothermal, Solar energy, Hydrogen power etc..\(^{19}\)

Each source of the energy has some drawbacks and disadvantages. The fossil fuels are the main sources for the energy consumptions, but their rapid depletion has generated enormous problems, such as the greenhouse effect and the contaminations, in particular the air pollutions. The Nuclear energy could produce the radioactive fission productions, which is harmful to the mankind health. And also the solar energies are limited to the geography and the large space.\(^1,20\)

However, compared with the fossil fuels and nuclear energies, most of the renewable energies have plenty of advantages, such as, Cleanliness, abundance and Environmental friendliness, in particular, the Hydrogen energy, which is the most environmental friendly fuel and has the highest energy density.\(^{21}\). Thus, sustainable hydrogen production has been
becoming increasingly important for solving the energy crisis and environmental issues and gotten the great attention.\textsuperscript{20, 22}

\textbf{Figure 1:} Energy flow graph for United States, 2012\textsuperscript{1}

1.2 \textbf{Hydrogen Energy}

1.2.1 \textbf{Hydrogen Energy Carrier}

Hydrogen is of the highest mass energy density, which is of course larger than any other fuel all over the world. The hydrogen burning reaction could be described as the following:

\[ 2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{l}) \quad (\Delta H = -286.0 \text{ kJ/mol}) \] \textsuperscript{1}

The formula has the meaning that we could get 286kJ energy from the 1mol reaction of the hydrogen and the oxygen. Thus, it could be easily seen from the formula that the mass hydrogen energy density is 143.0 kJ/g (\( E = 286.0 \text{ kJ/mol} \times 0.5 \text{ mol/g} \)), exhibiting the
largest energy density value comparing with all the other fuels\textsuperscript{23}. Based on properties of the higher energy density and the lower weight, hydrogen (mainly the liquid hydrogen) has been used in many areas, especially the transportations and space technologies\textsuperscript{21, 24}.

1.2.2 Hydrogen Production

As an ideal energy carrier, the clean and renewable hydrogen could be created efficiently and cost-effectively by two ways:

(1) In industry, the hydrogen could be produced by the steam reforming of natural gas (CH\textsubscript{4}), which is shown as the follows:

\[
\text{CH}_4(g) + \text{H}_2\text{O}(g) \rightarrow \text{CO}(g) + 3\text{H}_2(g) \quad \text{................................. ②}
\]

Nowadays, 95% of the standard production for the hydrogen in the United States is produced by the reforming of natural gas in the large central plants, which is a procedure that would generate numerous releases of carbon dioxide, and even carbon monoxide, although not as much as the outright burning of the natural gas. Though this method is a vital route for large amount of hydrogen production, the consumption of the fossil fuels could not be avoided\textsuperscript{25}.

(2) Another pathway to produce the hydrogen is to conduct the water splitting. The water splitting cells for hydrogen evolution reaction can be divided into two categories: (i) Solar water splitting cells by solar energy (Figure 2 & 3); (ii) Electrocatalytic water splitting cells by electricity (Figure 4 & 5).
Compared with the method of reforming of natural gas (Method 1), the methods of water splitting for hydrogen evolution reaction by both solar energy and electricity (Method 2) are renewable, clean and environmental friendly. Therefore, study on the water splitting for the hydrogen evolution reaction is of great meaning and importance, and thus deserves great attentions.

As the water splitting by electricity cells could be less influenced by the light, weather and regions, so it is more practical and convenient to produce the hydrogen by this kind
of cells. Therefore, we focused our research on the development of the electrocatalytic water splitting cells.

1.3 Hydrogen Evolution Catalysts

For the hydrogen evolution reaction (HER) from water by electricity, the efficiency could be increased greatly by the good catalysts. And the performance of the catalysts could be attributed to three factors:

(1) Set off potential (Overpotential)

(2) The current density (at the same potential value)

(3) Tafel slope

In general, a good catalyst could have the capability to lower the set off potential and Tafel slope value, and also current density could be increased.

1.3.1 Pt Group Electrocatalysts

Typically, Pt-group metals exhibit the highest activities of electrocatalysis toward hydrogen evolution reaction (HER), such as Pt$^{26}$, Ir$^{12, 26b}$, Pd$^{12, 26b}$, Rh$^{12, 26b}$ etc.

Among them, Pt has the best performance and wide usage. it can be got that the Pt electrocatalyst could significantly lower the overpotential with the lowest Set off potential value of about 0.2-0.4, and the Tafel slope value is around 30 mv/ decade$^{6, 12}$

However, due to the scarcities and high expenses, the widespread application of the Pt-group electrocatalysts might be limited. Thus, the future development direction of highly
activity electrocatalysts for HER is focused on the materials which are cheap and earth-abundant\textsuperscript{22b}.

1.3.2 Few Layered Electrocatalytic Activity Materials

In recent years, two-dimensional (2D) layered materials have attracted considerable attention in both the fundamental and application science, because of their unique chemical and physical properties\textsuperscript{17, 27}. The layered bulk materials are formed by the stacking of planes via weak interlayer van der Waals interactions\textsuperscript{28}. Due to their anisotropic structure, the ultrathin flakes can be obtained by chemical or mechanical processes, as well as the thin films, nanosheets, nanoribbons, nanoparticles and nanotubes etc\textsuperscript{17, 28}.

MoS\textsubscript{2} is a brilliant star in the 2D layered materials’ group, which is a silvery black solid that occurs as the cheap and earth-abundant mineral molybdenite\textsuperscript{7-8}.

For the buck MoS\textsubscript{2}, each Mo is being connected to the nearest six sulfide atoms, by occupying the center of the sphere with trigonal prismatic coordination. And each sulfur atom is bound to three Mo centers, with a pyramidal shape\textsuperscript{9, 29}.

In this way, the bulk MoS\textsubscript{2} of the layered structures is formed by the interconnection of trigonal prisms. And so, the sulfide atoms layers are interacted by the weak van der Waals force\textsuperscript{9}. 


Based on the special layered structure and stable properties of MoS$_2$, which is an relatively unreactive material, being unaffected by dilute acid, alkali, organic solvent, plenty of applications have been put into practice.

(1) Lubricant

Because of the interactions of the near sulfide atoms layers conducted by the weak van der Waals force, MoS$_2$ has the properties of lubricants, due to the low coefficient of friction. In general, MoS$_2$ is commonly used as a dry lubricant with particle sizes range from 1 µm to 100 µm. Likewise, some other layered materials, such as graphite, hexagonal boron nitride etc., exhibit the similar lubricating properties.$^{30}$

(2) Petroleum refining

MoS$_2$ is commonly well known as a good catalyst for hydrodesulfurization reaction to conduct the desulfurization in petroleum refineries.$^{31}$ Recently, Smith etc.$^{32}$ have made the exfoliated MoS$_2$, which gave the better performance for the reaction. And also, the effectiveness of the MoS$_2$ catalysts has already enhanced by doping with small amounts
of cobalt or nickel and the intimate mixture is supported on alumina\textsuperscript{33}, which made the MoS\textsubscript{2} application on industry benefit the mankind a lot.

(3) Electronic and optical properties

People found that the properties of single or few layer MoS\textsubscript{2} is different from the bulk MoS\textsubscript{2}, in particular the Electronic and optical properties. Whereas the band gap of Bulk MoS\textsubscript{2} is 1.2 eV, the band gap of single layers Mos\textsubscript{2} is 1.8 eV\textsuperscript{34}, which make it possible for the production of sensitive photodetectors\textsuperscript{35} and the switchable transistors\textsuperscript{9}.

The recent studies of MoS\textsubscript{2} have shown that it is one of the best electrocatalysts for the Hydrogen Evolution Reactions, and both the calculations and the experimental results have given the certificates that MoS\textsubscript{2} might be the most promising alternatives of platinum.\textsuperscript{14,17}

The electrocatalytic property of molybdenum sulfides for the hydrogen evolution reactions could stem from 1970s.\textsuperscript{36} In the year of 1977, Tributsch, H first reported the electrochemical performance of molybdenum sulfides layer crystals.\textsuperscript{36} However, the bulk molybdenum sulfides had the lower electrocatalytic activities, thus few attentions had been attracted on this research topic, so the research progress is very slow during the past decades.\textsuperscript{37}

In 2005, Berit etc. conducted the biomimetic electrocatalytic hydrogen evolution process of the Hydrogenase and Nitrogenase by using density functional theory (DFT) calculations\textsuperscript{11}, they reported that $\Delta G_{\text{f}}$ (free energy of adsorbed H) is a good indicator of
the electrocatalysts for HER and could be applied to many material systems, range from metals to enzymes, including the system of MoS$_2$.\textsuperscript{11}

![Calculated free energy for HER at a potential U=0 (RHE) at PH=0](image-url)

**Figure 8** Calculated free energy for HER at a potential U=0 (RHE) at PH=0\textsuperscript{11}

And also Berit etc. claimed that it was the sulfur edges of MoS$_2$ that had the electrocatalytic activities for the hydrogen evolution, due to the similar properties of the uncoordinated sulfur edges and the active enzymatic centers.\textsuperscript{11}

Later in 2007, Thomas and co-workers future certificated experimentally that it is the edge sites of MoS$_2$ that has the electrocatalytic actives rather than the inert basal plane.\textsuperscript{12}

Thomas etc. found that the particle size increased at the high temperature, and for all the samples, the reaction rate, which was proportional to the length of the edge, had nothing to do with the size of the particles. So they confirmed that the edge sites of MoS$_2$ were indeed the active sites by the experiment. After the DFT calculations, MoS$_2$ got the position in the volcano-type relations for HER catalysts.\textsuperscript{12}
After that, in the year of 2011, Hemamala etc. reported the synthesis of a disulfide-terminated well-defined inorganic compound \([(\text{PY}_5\text{Me}_2)\text{MoS}_2]^{2+}\). Hemamala etc. use the compound \([(\text{PY}_5\text{Me}_2)\text{MoS}_2]^{2+}\) to mimic the sulfide-terminated edge sites of MoS$_2$ for the electrocatalytic hydrogen evolution reactions. They verified once again that the active sites of MoS$_2$ was the disulfide-terminated edges, and supplied a route to prepare the powerful electrocatalytic molecular complexes.

After the previous published work of Au (111) supported MoS$_2$, carbon paper supported MoS$_2$ was also reported by Chorkendorff and coworkers. They firstly dropped the aqueous ammonia heptamolybdate solution on the Toray carbon paper, and then MoS$_2$ was gotten after the sulfurization conducted by H$_2$S. The value of Tafel slop is around 120 mv/dec. And the performance of MoS$_2$ was promoted by the co-impregnation of Cobalt. Though, compared with that of the bulk one, the performances of MoS$_2$ had improved a lot, it is still not good enough to be regarded as a good electrocatalysts for HER. In 2011,
Dai etc. reported a solvothermal approach for the synthesis of MoS$_2$/Graphene hybrids. The MoS$_2$/RGO hybrids were synthesized by the excellent coupling of MoS$_2$ nano particles on the Gaphene sheets via a facile solvothermal method. The as prepared catalysts of MoS$_2$/RGO hybrids exhibited great electrocatalytic activities for the hydrogen evolution reaction with the low value of the setoff potential ($\sim 0.1$ V) and Tafel slope (41mv/dec). Later the hybrids of MoSx with CNTs and other mesoporous carbons etc. were prepared for the hydrogen evolution reactions.

In 2013, Li and co-workers prepared the three-dimensional (3D) MoS$_x$ foams. They firstly synthesized the 3D-Graphene foam on the 3D-Ni foam skeleton via chemical vapor deposition (CVD), and then the foams were immersed in the (NH$_4$)$_2$MoS$_4$ solution; after the MoS$_x$ layers were formed on the surface of 3D-Gaphene foams by the reduction by the Hydrogen via the CVD method, the 3D-MoS$_x$@graphene foams electrode were formed. These kinds of foams could load more MoS$_x$ catalysts and have the excellent performance for the hydrogen evolution. And also they reported that the 3D MoS$_x$@Graphene electrode had the highest electrocatalytic activities for the hydrogen evolution at the temperature of 120 °C with the Tafel slop around 43 mv/dec.

In order to get more exposed active edge sites of MoS$_2$ for improving the efficiency for the hydrogen evolution reactions, Thomas Jaramillo etc. reported a method to control the surface structure of MoS$_2$. They firstly deposited the Molybdenum on the silica template by the electro-deposition. And the DG morphology MoS$_2$ was formed by the sulphidization with H$_2$S, followed by the etching of silica template with 2% HF. It could be seen that the surface area, HER
performance and active sites were gravely improved by the engineering mesoporous MoS₂ films with DG morphology. ¹⁶

Another route to improve the performance of the MoS₂ electrocatalyst for the HER is to make the MoS₂ into small particles or few layers (or single layers) to get more exposed active edge sites. Li and coworkers enhanced the electrocatalytic activities of MoS₂ for hydrogen evolution reaction by the ultrasonication of the bulk MoS₂. ¹⁷ The diameter of the as-prepared MoS₂ nanoparticles was around 1.5 nm. And the test electrode was fabricated in two ways: ① the assembling of as-prepared MoS₂ nanoparticles on the Au electrode. ② the drop-casting of as-prepared MoS₂ nanoparticles on the Au electrode. And they found that the assembling ones had the better performances. ¹⁷

Recently, there have been papers reported that the layers of the molybdenum sulfides have the influence on their efficiency for the hydrogen evolution reactions. The few layer or single layer molybdenum sulfides have the better performance on HER. ⁴¹

From the above, it could be seen that many efforts have been taken to obtain the higher electrocatalytic activity MoS₂ catalyst for HER from both calculations and experiments, and it has also certificated that it is the sulfur edges of the plates rather than the inert basal planes of MoS₂ which are the active catalytical sites of MoS₂ for HER, and the conductivity that have the great influence on the performance of the MoS₂ catalyst.

In the past years, many researches have been conducted to improve the imposed edges and conductivity of MoS₂. Some of them took the attention on the engineering of the surface structures of MoS₂ ¹⁶ and the different synthesizing methods to MoS₂ (PVD or CVD ¹²-¹³, ¹⁵ & Hydrothermal or solvothermal ¹⁴, ⁴⁰ etc.); and some researches focused on
the growing of MoS$_2$ on a variety of good conductive supported substrates, such as gold$^{12}$, graphite$^{11}$, carbon black$^{15}$, carbon paper$^{13}$, glassy carbon$^{14,28}$, CNTs$^{40c}$ and graphene$^{14}$ etc.

However, up to now, the efficiency of the MoS$_2$ electrocatalysts is not good enough and there are currently no ideal ways to get the MoS$_2$ electrocatalysts in the large amount under the low costs. So during my studying in the period of Master Degree, my main tasks were to make the development of the MoS$_2$ electrocatalysts, and finally we succeed in finding the ways to solve the problems facing the MoS$_2$ electrocatalysts and improved the performance of MoS$_2$ electrocatalysts for the hydrogen evolution reactions.

The researches are mainly about the synthesis of the MoS$_2$ via the CVD method with the low price materials.

There are many advantages for this method: ① the synthesizing materials are sulfur and MoO$_3$, which are easy to obtain and abundant in the earth; ② the preparing process is very easy and the catalysts could be produced in large amount; ③ the efficiency is excellent.
2. EXPERIMENTS

2.1 The Electrocatalytic Activities of MoS$_2$ Synthesized by the CVD Method for HER

2.1.1 The Synthesis of the MoS$_2$ via the CVD Method

2.1.1.1 The Facilities and Experimental Parameters

The Electrode Parameter

Titanium foils (Ti)

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<th>Thickness</th>
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<tr>
<td>Assay</td>
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</tr>
<tr>
<td>Form</td>
<td>Foil</td>
</tr>
<tr>
<td>Products</td>
<td>SIGMA-ALDRICH</td>
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Table 1 The properties of Titanium foil

<p>| | | |</p>
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<tr>
<th></th>
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<tbody>
<tr>
<td>1</td>
<td>•Model</td>
<td>NBD-O1200-80IIC</td>
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<tr>
<td>2</td>
<td>• Limiting Temperature</td>
<td>1400℃</td>
</tr>
<tr>
<td>3</td>
<td>• Chamber size</td>
<td>Φ 80×1000mm</td>
</tr>
<tr>
<td>4</td>
<td>• Temperature Zone</td>
<td>double zone</td>
</tr>
<tr>
<td>5</td>
<td>• Accuracy</td>
<td>± 1℃</td>
</tr>
<tr>
<td>6</td>
<td>• Heating rate</td>
<td>20℃/Min</td>
</tr>
<tr>
<td>7</td>
<td>• Flowing gas</td>
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<td>8</td>
<td>• Flowing rate</td>
<td>15 sccm</td>
</tr>
<tr>
<td>9</td>
<td>• Company products</td>
<td>Nobody Material Science and Technology Co., Ltd (NBD)</td>
</tr>
</tbody>
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Table 2 The parameters of the CVD Furnaces
The reagents parameters

Molybdenum (VI) oxide (MoO₃)

<table>
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<tr>
<th>Grade</th>
<th>ACS reagent</th>
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<tbody>
<tr>
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<tr>
<td>Form</td>
<td>Powder</td>
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<tr>
<td>Products</td>
<td>SIGMA-ALDRICH</td>
</tr>
</tbody>
</table>

Table 3 The properties of MoO₃

Sulfur (S)

<table>
<thead>
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<th>Grade</th>
<th>Purum p.a.</th>
</tr>
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<td>Assay</td>
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<td>Form</td>
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</tbody>
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Table 4 The properties of Sulfur

2.1.1.2 The Experimental Details

2.1.1.2.1 The Preparation of Primary Electrodes

The primary Ti electrodes were prepared by the tiny Titanium foils with the appearance size 3 mm (width) × 15 mm (long) × 0.25 mm (thickness). We firstly selected the end of the Ti electrode foil as the working zone (only one face) with the area of 3 mm (width) × 3 mm (long) × 0.25 mm (thickness). After that, the foils were covered by the epoxy resin with the end (opposite to the working zone) of the foils and the working zone uncovered. Then the Ti foil electrodes were prepared.

As the precursor of MoS₂, MoO₃ powder was dissolved in the water with the concentration of 20 mg/ml. And then the growth of the MoO₃ on the working zone (3 mm (width) × 3 mm (long) × 0.25 mm (thickness)) of the electrodes were carried out by
annealing the 18 μl as-prepared MoO₃ water solution on the surface of Ti foil under 120°C for 5 minutes. In order to decrease the influence of the final products, the epoxy resins were removed before the sulfurization of the MoO₃ annealed Ti foil electrode. And after that, the primary electrodes were well prepared.

2.1.1.2.2 The Sulfurization of the Primary Electrodes.

Sulfur powder was used as sulfuric source to conduct the sulfurization process of the primary electrodes. As it is shown in the Figure 10, the sulfurization process was conducted in a double heat zone finances.

In the CVD experiment, 1 g sulfur powder in the crucible was putted on the left temperature zone, and the as-prepared primary electrodes were putted on the right temperature zone by placing on the quartz boat with the majority part of the body exposed in the space.

![Figure 10 Sulfurization process in the CVD Furnaces](image)

The tube chamber was pumped to vacuum, and filled with argon gas. After the repeating of the process for three times, the argon gas flow was controlled accurately at the speed
of 15 sccm. So the sulfurization process of primary electrodes could be conducted in the inert environment; and also in the tube chamber, the sulfur in the left zone could be evaporated under the high temperatures and transferred to the right zone to completed the sulfurization process of MoO$_3$.

In order to make the study of the influence of the temperature and crystalline, the sulfurization process of primary electrodes were conducted at the different temperatures; and the temperatures were set on 300ºC, 400ºC, 500 ºC and 600 ºC separately.

During the synthesis of the reaction, the chamber was heated to 300 ºC form the initial 20 ºC with a heating rate of 20 ºC min$^{-1}$ in the environment of Ar flow at the both heating zones of the CVD Furnaces, and the tube chamber was kept at 300 ºC for 30 minutes. The processes are the same with 400ºC, 500 ºC and 600 ºC.

After the naturally cooling down process, the sulfurization was finished, and as well, the electrodes covered with ideal products were prepared.
3. Results and Analysis

3.1 The Characterization of the As-prepared Electrodes.

3.1.1 XRD and XPS Characterization of the MoS$_2$ Deposited Electrode.

The as prepared MoS$_2$ deposited Ti foil electrodes were characterized by the powder X-ray diffraction (XRD).

From the graph, it could be clearly seen that the Ti characteristic peaks at 38.6 °, 40.4 °, 53.2 ° and 70.8 ° etc. appeared in all the samples. We could confirm the source of the above peaks were from the Ti substrates. So we only need to take the rest peaks in the graph into consideration.

The X-ray diffraction (XRD) graphs shown in Figure 11 illustrated that the synthesized products were various at the different temperatures. The graph of the product obtained at 300°C showed that the main peaks were corresponded to molybdenum oxide (MoO$_3$), the peaks corresponding to MoS$_2$ could be hardly seen. So we could get the conclusion that the as 300°C prepared electrode was mainly composed with MoO$_3$.

In the 400 °C one, the all peaks that were corresponded to the MoO$_3$ had disappeared, particularly the characteristic peak at 26°. Meanwhile the weak peaks at corresponding to 2H-MoS$_2$ for the (002) and (101) planes reflection had appeared at 14.4° and 33.5° in the graph, which is consistent to the characteristic peak of MoS$_2$; so It could be clear seen that MoS2 had successfully grown on the Ti foil electrodes with no MoO3 left after the sulfurization for 30 minutes at 400°C. But we could see additional peaks in the graph, such as peaks at 26.3° and 37.3° etc., which were corresponded to MoO$_2$ compound.
And also it could be seen from the Graph 29, the electrodes prepared at 500°C and 600°C also had been transferred to MoS$_2$ and the MoO$_2$. The difference between the electrodes prepared 400°C 500°C and 600°C was that the sharpness of the characteristic peaks of bulk MoS$_2$ and MoO$_2$ varied from each other. For the MoS$_2$ characteristic peaks, the 400 °C one was weaker while the 500°C and 600°C ones, while for the MoO$_2$ characteristic peaks, the 400 °C one was the strongest one.

And also, it could be supposed that the products sulfurized above 400°C (400°C, 500°C, 600°C) could be of the MoO$_2$-MoS$_2$ composites Ti foil electrocatalyst while the sulfurized at 300°C could be the MoO$_3$-MoS$_2$ composites Ti foil electrocatalyst.
**Figure 11** XRD graph of the as prepared MoS$_2$ Ti foil electrodes. The black, red green blue, cyan and magenta lines were the electrodes which were fabricated at the temperature of 300 °C, 400 °C, 500 °C and 600 °C separately.
Figure 12 XPS spectra of the as prepared MoS$_2$ Ti foil electrodes. (a) Mo 3d and S 2s peaks; (b) S 2p peaks. The peaks were from the electrodes which were fabricated at the temperature of 300 °C, 400 °C, 500 °C and 600 °C separately; (c), (d), (e), (f) were the graph of O 1s peaks at 300 °C, 400 °C, 500 °C and 600 °C separately.

X-ray photoelectron spectroscopy (XPS) was used to study the chemical state of Mo and S in the as prepared MoS$_2$ deposited Ti foil electrodes, as shown in Figure 12.

The high-resolution XPS spectra in the Figure 12 illustrate that, for the unsulfidized precursor, the bonding energies of Mo 3$d_{3/2}$ and Mo 3$d_{5/2}$ peaks are located at 236eV 232.8 eV respectively, revealing the Mo$^{4+}$ oxidation state in the of compound, which also confirm that the chemical state of the precursor compound of MoO$_3$ is +6.$^{40a}$

For the as prepared MoS$_2$ electrodes sulfurized at 400°C, it could be seen that Mo (IV) 3$d_{3/2}$ and Mo (IV) 3$d_{5/2}$ peak at 232.4 eV and 229.3 eV respectively, which indicates that the comical state of the as prepared electrode at 400°C has been changed to the oxidation
state of +4 for Mo, along with the appearance of the S 2s peak at 226.5 eV. And it is similar to as prepared MoS$_2$ electrodes sulfurized at 500°C and 600°C.

However, for the 300°C sulfurized MoS$_2$ electrodes, we could see the peaks of Mo in both +6 oxidation state and +4 oxidation state, with the Mo (VI) 3d$_{3/2}$, Mo (IV) 3d$_{3/2}$ and Mo (IV) 3d$_{5/2}$ peaks located at 235.9 eV, 232.7 eV and 229.3 eV respectively, which illustrates that the 300°C sulfurized MoS$_2$ electrodes still have the initial reactant chemical state of Mo$^{4+}$, so the product could be confirmed to be the MoO$_3$-MoS$_2$ nanocomposites Ti foil eletrocatalyst.

From the Figure 12(b), it could be clearly seen that S 2p$_{1/2}$ and S 2p$_{3/2}$ are located at 163.5 eV and 162.3 eV respectively, which shows that the appearance of sulfur with the oxidation state of -2, at all the synthesized temperatures, which could also confirm that the as synthesized compounds is really MoS$_2$.\textsuperscript{43}

From Figure 12 (c), (d), (e), (f), O 1s could show that the chemical state of the oxygen is -2 in the products sulfurized at 300°C, 400°C, 500°C and 600°C.

So the products prepared above 400°C could be the MoO$_2$-MoS$_2$ nanocomposites Ti foil eletrocatalysts.
3.1.2 SEM Characterization of the MoS$_2$ Deposited Electrode.

The prepared MoS$_2$ Ti foil electrodes were characterized by the SEM (Figure 13), and the images were conducted in Quanta 600.

**Figure 13** SEM images of MoS$_2$ on the Ti foil electrodes at the higher magnification. (A) SEM image of MoS$_2$ synthesized at 300 ºC for 30 min. (B) SEM image of MoS$_2$ synthesized at 400 ºC for 30 min. (C) SEM image of MoS$_2$ synthesized at 500 ºC for 30 min. (D) SEM image of MoS$_2$ synthesized at 600 ºC for 30 min.
From the SEM images, we could figure out that:

(1) The products are nanoflakes with the thickness below to 100 nm.

(2) The dispersions of the nanoflakes varied from the products sulfurized at different temperatures. It could be clear seen that the one sulfurized at 400°C showed a good dispersion. The aggregations of the as-synthesized nanoflakes appeared at the products sulfurized at 500°C and 600°C. The eutectic growth was severe in the samples sulfurized at 500°C and 600°C, especially the 600°C one.
3.1.3 Hydrogen Evolution Reaction Activities of the As-prepared MoS$_2$ Electrodes.

The electrocatalytic Hydrogen Evolution Reaction activities of the as-prepared MoS$_2$ electrodes were future evaluated directly in the 0.5 M H$_2$SO$_4$ water solution by using the three-electrode electrochemical workstation.

Just as the described in table 5, the parameter of the electrochemical workstation is suitable for the testing of MoS$_2$ for the HER.

<table>
<thead>
<tr>
<th>Key features</th>
<th>Properties</th>
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</thead>
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<tr>
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<tr>
<td>Potential accuracy</td>
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<tr>
<td>Potential resolution</td>
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<tr>
<td>Control software</td>
<td>NOVA</td>
</tr>
</tbody>
</table>

Table 5 The parameter of the electrochemical workstation (Data from Mettrohm Autolab)

The MoS$_2$ Ti foil electrodes were measured by the Linear Sweep Voltammetry procedure (using the potentiostatic procedure) with a scan rate of 2 mv s$^{-1}$. In the measurement, the MoS$_2$ electrodes were conducted as the working electrodes, while the commercial Pt electrode was used as the counter electrode, the Saturated Silver Chloride Electrode as the reference electrode. And the value of the Saturated Silver Chloride Electrode is 0.197 V.
In all the measurements, all the potential values were calibrated to the Reversible Hydrogen Electrode (RHE).

\[ V\text{ (RHE)} = V\text{ (Saturated Silver Chloride Electrode)} +0.197\ V. \]

So all the potential values in the thesis are against with Reversible Hydrogen Electrode (RHE).

In order to minimize the influence of the Ohmic Drops for HER activities of the electrocatalysts, we conducted the measurement of the Ohmic Resistances, the Ohmic Resistances was tested to be around 9 Ω in 0.5 M H₂SO₄ water solution.

In the experiments, all the as-prepared MoS₂ electrodes were measured, and thus all the data in the thesis has been iR corrected. And as well, the background current has been eliminated, so that the real current density from the catalyst could be shown in the graph.

![Figure 14](image.png)

**Figure 14** The polarization curves of prepared MoS₂ Ti foil electrodes.
As can be seen from the polarization curves (i–V plot) in Figure 14, all the prepared MoS$_2$ electrodes had the performance for the Hydrogen Evolution Reaction, and the electrode that was made in 300°C, 400°C, 500°C had the relative higher efficiency than those in other temperatures. And among all the five as-prepared electrodes, the one prepared in 400°C showed the highest activities. The Figure 14 showed that for the electrocatalytic performances of the as-prepared electrodes, there was a ranking and regulation for the six electrodes.

The MoS$_2$@400°C exhibited a small onset potential of ~ 0.095 V for HER (Figure 14) and the tafel slop is of a relatively small value of ~ 40 (Figure 15), which were of great enhancement in efficiency, compared with the natural bulk MoS$_2$.

![Figure 15](image-url) The Tafel curves of prepared MoS$_2$ Ti foil electrodes.
From polarization curves in Figure 16, we could see that the Ti foil electrode (after the sulfurization) showed an low activity for HER at working range of MoS$_2$, thus we could confirm that the functional matter was the as-grown compounds (MoS$_2$) on the working zone of the Ti foil electrode.

![Polarization Curves](image)

**Figure 16** The polarization curves of Ti electrodes (after sulfurization), MoS$_2$@400°C Ti foil electrodes and commercial Pt electrode.

The ranking and the rule for the performance of hydrogen evolution reactions were as the following:

MoS$_2$@400 °C > MoS$_2$@500 °C > MoS$_2$@300 °C > MoS$_2$@600 °C > MoO3
The reasons analysis for the ranking and the rule:

(1) From the polarization curves in Figure 15, we could see that the MoO$_3$ electrode had a very poor electrocatalytic activity for the HER, and after been partly transferred to MoS$_2$ electrodes, the HER electrocatalytic performance increased greatly.

(2) The performance ranking of the electrodes is as the following:

$$\text{MoS}_2@400\text{C} > \text{MoS}_2@500\text{C} > \text{MoS}_2@300\text{C} > \text{MoS}_2@600\text{C} > \text{MoO}_3$$

We need more proofs to certificate the reasons why the performance ranking is like this, such as the HRTEM characterization, ICP-OES etc.

(3) Figure 15 & 16 also show the performance of commercial Pt electrode for HER, which has already been well known as the best electrocatalytic catalyst for the Hydrogen Evolution Reactions.$^{39}$ Also, we could get the conclusion from the Figure 15 & 16 that MoS$_2$ is really a promising electrocatalysts which has the biggest possibility to replace the Pt-group electrocatalysts.
3.1.4 Conclusions and Summaries

In this experiment, we designed and prepared a new MoO₂-MoS₂ nanocomposites Ti foil electrodes for the first time, which has the relative high electrocatalytic activity for the HER, with a new route for the preparing the high efficient MoS₂ electrocatalysts via CVD method, which could be synthesized with the low cost materials (earth-abundant Sulfur and Molybdenum oxide) in the large amount and greatly improve the performance for the hydrogen evolution reactions.

The electrocatalysts were the prepared by directly conducting the sulfurization of the deposited MoO₃ on the working zones of Ti foil electrodes, which were sulfurized at a series of temperatures from 300°C to 600°C (300°C, 400°C, 500°C and 600°C) in the double zones of CVD tube Furnaces.

The as-prepared products deposited on the Ti foil electrodes could be confirmed that the products sulfurized at 300°C could be the MoO₃-MoS₂ nanocomposite Ti foil electrocatalyst, while the ones sulfurized above 400°C (400°C, 500°C, 600°C) would be the MoO₂-MoS₂ nanocomposites Ti foil electrocatalysts.

The as-obtained Ti foil electrodes were directly used as the electrochemistry electrodes to conduct the test of the efficiency of the electrocatalysts, which were sulfurized at different temperatures.

The ranking and the rule for the performance of hydrogen evolution reactions were as the following:

$$\text{MoS}_2@400^\circ C > \text{MoS}_2@500^\circ C > \text{MoS}_2@300^\circ C > \text{MoS}_2@600^\circ C > \text{MoO}_3$$
The MoS$_2$ nanoflakes sulfurized at 400$^\circ$C had the best performance for the HER with the small onset potential of ~ 0.095 V versus reversible hydrogen electrode (RHE) and Tafel slope of 40 mV/dec, which were highly comparable with (even better than) the most excellent previous reported results,$^{14-15}$ while the electrocatalysts had the advantages of using the abundant and low cost precursor materials and being produced in the large amount via the easier methods.

MoS$_2$ could be for sure a real promising electrocatalysts which has the biggest advantages to be the alternative of the Pt-group electrocatalysts.
4 Conclusions

In this thesis, we prepared the MoS2-based electrocatalysts using CVD synthesis, and systematically investigated their HER performance.

The first set of catalysts was prepared by in-situ sulfurization of MoO3 on the surface of a Ti foil electrode via a CVD process. With increasing the CVD temperature from 300ºC to 600ºC, gradual evolution of MoS2 and the phase transition of MoO3 to MoO2 were observed. The catalysts prepared at different temperature showed rather different HER activities, among which the best catalyst was a MoO2-MoS2 nanocomposites prepared at 400ºC. Further increasing the CVD temperatures resulted in dramatically decreased HER efficiency of the as-prepared electrocatalysts. It is worth noting that despite a facile process that can be accomplished within 30 min, the HER performance of the optimized MoO2-MoS2@Ti electrodes was excellent (an onset potential of 0.095 V versus RHE and the Tafel slope of ~ 40 mv/dec), surpassing those of most reported MoS2-based electrocatalysts. We speculate that the optimized composite has a MoO2/MoS2 core/shell structure, which may account for the outstanding HER activity. However, detailed structural characterization and mechanism study has not been accomplished within the scope of this thesis and is still ongoing.

The synthetic strategies are facile and cost efficient. The as-synthesized MoS2 catalysts have excellent and adjustable HER activities. Our preliminary results demonstrate the significant influence of synthetic condition on the structure and catalytic performance of the catalyst. This study confirms the great potential of MoS2 as an alternative to Pt-group
metals for hydrogen generation through water splitting, and provides new insights into the structure control and performance optimization of MoS$_2$-based electrocatalysts.


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