Nanostructured molybdenum disulfide based catalysts for electrochemical hydrogen evolution reaction

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**NANOSTRUCTURED MOLYBDENUM DISULFIDE
BASED CATALYSTS FOR ELECTROCHEMICAL
HYDROGEN EVOLUTION REACTION**

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SCHOOL OF CHEMICAL AND BIOMEDICAL ENGINEERING

NANYANG TECHNOLOGICAL UNIVERSITY

2014

Nanostructured Molybdenum Disulfide Based Catalysts for Electrochemical Hydrogen Evolution Reaction

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Abstracts

Hydrogen related energy is expected to play a major role in the development of sustainable energy and protection of green environment. Electrocatalytic hydrogen evolution reaction (HER) is known as a successful and efficient method for hydrogen production with large scale. Efficient electrocatalysts, currently platinum (Pt), are necessary to this important electrochemical process. However, the scarce Pt resources with high cost limit its final large-scale proposition. Recent advances have revealed that nanostructured transition metal (VI) carbides and sulfides would be the promising non-precious alternatives to Pt for the electrochemical generation of hydrogen from water. The research work in this thesis was focused on the development of low-cost and efficient electrocatalytic materials for H₂ production from electrocatalytic HER.

In the first part of the research work, a unique nanorod-structured tungsten carbide (WC) material with high specific surface area of 198 m² g⁻¹ was synthesized by a template-free pseudomorphic carburization of carbon-coated tungsten trioxides (WO₃) nanorod, as an alternative support material for HER. Superior structural replication is achieved and the formation mechanism for the nanorod-structured WC material was proposed. An electro-catalyst composed of Pt nanoparticles supported on WC nanorods demonstrated higher electrocatalytic activity for the cathodic electrocatalytic hydrogen evolution than a Pt/C catalyst. Further work was carried by preparing well-defined WC nanoparticles by using WO₃ nanorods as a precursor under the methane-hydrogen (CH₄-H₂) mixtures. Then, the

as-prepared WC nanoparticles were used as a conductive dispersant to synthesize a novel electrocatalyst of layered MoS₂ supported on the reduced graphene oxide (RGO) decorated with nano-sized WC by a one-pot solvothermal process. The resultant MoS₂/WC/RGO composite with highly exposed reactive sites stabilized by the binary support showed an enhanced electrocatalytic activity for HER process with a Tafel slope as low as ~41 mV dec⁻¹ and a decent stability. This was mainly attributed to the synergism between the co-catalyst and high conductivity of the ternary composite.

Inspired by the above high efficient activity of layered MoS₂-based composite catalyst, a networked MoS₂/CNTs nanocomposite with high catalytic activity towards HER was developed by a facile solvothermal method, in which MoS₂ nanosheets are uniformly coated on carbon nanotubes (CNTs). It is found that both acid-treated CNTs and DMF play a critical role in the formation of this unique structure, and the low crystalline MoS₂ is identified as the actual catalyst for the enhanced HER due to the high number of exposed sites.

In the last part of this thesis work, a well-defined ultrathin MoS₂ nanoplate electrocatalyst was developed by a facile solvent-dependent control route from single source precursor. The obtained ultrathin nanoplate with a thickness of ~5nm features high density of basal edges and abundant unsaturated active S atoms. The multistage growth process is investigated and the formation mechanism is proposed. Ultrathin MoS₂ nanoplates exhibit an excellent activity for HER with a small onset potential of 0.09 V, a low Tafel slope of 53 mV dec⁻¹ and remarkable stability.

It is believed that the findings from this thesis work contribute towards a better understanding of the controllable synthesis of more efficient non-noble metal based electrocatalytic materials for hydrogen production.

Keywords: hydrogen evolution reaction, electrocatalysts, nanostructure, tungsten carbide, molybdenum sulfides.

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List of Abbreviation

BET	Brunauer-Emmett-Teller
BJH	Barret-Joyner-Halenda
CNTs	Carbon Nanotubes
CV	Cyclic Voltammogram
DI	Deionized
DFT	Density Functional Theory
EG	Ethylene Glycol
EDX	Energy-dispersive X-ray Spectroscopy
eV	Electron Voltage
FESEM	Field Emission Scanning Electron Microscopy
GO	Graphene Oxide
GCE	Glass Carbon Electrode
HER	Hydrogen Evolution Reaction
RGO	Reduced Graphene Oxide
MoS ₂	Molybdenum Disulfides
S	Sulfur
SCE	Saturated Calomel Electrode

TEM	Transmission Electron Microscopy
TOF	Turnover Frequency
TMCs	Transition Metal Carbides
TMSs	Transition Metal Sulfides
WO ₃	Tungsten Trioxide
WC	Tungsten Carbide
XPS	X-Ray Photoelectron Spectroscopy
XRD	X-Ray Diffraction
ΔG	Gibbs Free Energy Change

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Chapter I Introduction

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1.1 Background

The development of modern society has huge demand for the renewable and environmental-friendly energy source. Hydrogen (H_2), as an ideal energy carrier, is proposed to be a major energy resource for future world. Today, hydrogen is mainly produced from natural gas *via* steam methane reforming (i.e., the reaction of methane and water to form hydrogen and carbon dioxide).¹ Therefore, hydrogen manufacturing currently has a large greenhouse-gas footprint, which is neither renewable nor carbon-neutral. Compared with the widely employed steam reformed hydrogen, electrocatalytic production of hydrogen from water splitting can be more renewable, scalable and environment-friendly.

The water splitting reaction can be divided into two half-reactions: the oxygen evolution reaction (OER) and hydrogen evolution reaction (HER). HER is the reductive half-reaction of water spitting ($2H^+ + 2e^- \rightarrow H_2$), which needs a catalyst to reduce the overpotential and consequently increase the efficiency of this important electrochemical process.^{3,4} Compared with alkaline electrolytes, acidic electrolytes are more favorable as these units are more compact and could potentially run in reverse mode to produce electricity (i.e. in fuel cells).⁵ Currently, the most

effective catalyst for HER under acidic condition is well known to be Pt, which has near zero overpotential.⁵ But the high price and shortage of Pt prohibits its commercial application. Therefore, it remains challenging to develop highly effective HER electrocatalysts with high abundance and low cost and to replace the noble metal Pt-based catalysts. Recent advances in material science and nanotechnologies have revealed that transition metal carbides^{6,7} and chalcogenides,^{8,9} especially nanostructured molybdenum sulfides (MoS_x , $x \approx 2$ to 3),^{10,11} would be the promising and inexpensive alternatives to Pt for the electrochemical generation of hydrogen from water.¹²

1.2 Electrochemistry and Evaluation of HER

Figure 1-1 Scheme illustration of the mechanism of hydrogen evolution on the surface of an electrode in acidic solution.

As the half-reaction for water splitting, HER process would be explained by three possible reaction steps on various electrocatalysts in acidic media.^{3,13} The first Volmer step is

electrochemical hydrogen adsorption: $\text{H}_3\text{O}^+ + \text{e}^- + \text{M} \rightarrow \text{MH}_{\text{ads}} + \text{H}_2\text{O}$ (1); and followed either by Heyrovsky step (electrochemical desorption): $\text{MH}_{\text{ads}} + \text{e}^- + \text{H}^+ \rightarrow \text{M} + \text{H}_2$ (2) or Tafel step (chemical desorption): $2\text{MH}_{\text{ads}} \rightarrow 2\text{M} + \text{H}_2$ (3). Where M denotes an empty metal active site and MH_{ads} represents an adsorbed H intermediate. For a complete HER process, it must involve the bonding of hydrogen to the active sites on the surface of the catalysts in the first Volmer step (blue arrows in Figure 1-1). The second step is the release of molecular H_2 either by Heyrovsky reaction (green arrows in Figure 1-1) or Tafel reaction (red arrows in Figure 1-1).¹⁴ The HER activities of various catalysts can be summarized in the “volcano plot” as shown in Figure 1-2,¹⁵ where the exchange current density for different catalysts in acids are plotted as a function of the Gibbs free energy of adsorbed atomic hydrogen on catalysts.¹⁶ An optimal HER catalyst should provide catalytic surfaces that exhibit a Gibbs free energy of adsorbed hydrogen close to zero (e.g. $\Delta G_{\text{H}}^{\circ} \approx 0$). Thus, the promising catalyst lies at the top of the curve (Figure 1-2), which is neither binding the intermediate MH_{ads} too weakly nor too strongly.¹⁷ Accordingly, one can also easily understand why Pt is a most commonly choice of catalyst for the HER. Importantly, by comparison of the exchange current densities of the common metals at their corresponding free energy of adsorbed H, $\Delta G_{\text{H}}^{\circ}$, the value for MoS_2 just lies below those of the noble Pt group metals, suggesting the great potential of MoS_2 -based materials as an alternative to Pt for HER.

Figure 1-2 Volcano plot of the exchange current density as a function of the DFT-calculated Gibbs free energy of adsorbed atomic hydrogen for nanoparticulate MoS₂ and the pure metals.

As seen, MoS₂ follows the same trend as the pure metals.¹⁵

There is a simple mathematical relationship between current density and overpotential and is known as Butler-Volmer equation. It is given by

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

Where j is the current density and η is the overpotential, which is defined as the difference between the reversible potential and the operating potential. The value is specific to each cell design and will vary between cells and operational conditions even for the same reaction, it often lies in the range of 0.1 - 0.5 V for the HER.¹¹ Whereas α known as transfer coefficient and $f = F/RT$ (F is the Faraday constant, R is the gas constant, and T is the temperature in Kelvin). The combination of α and overpotential determine the magnitude of electrical energy supplied to the electrode in order to obtain the desired current. Overpotential at a specified apparent current density is an useful experimental parameter to characterize a given electrode in the working condition,³ whereas the onset overpotential, often namely as onset potential, refers to the

smallest potential where the catalyst starts to catalytically function or the HER process begins.¹¹

Specifically, at high overpotential ($\eta > 0.05$ V), the Butler–Volmer equation can be rearranged in the form,

$$\eta = a + b \log j$$

It is known as Tafel equation. The electrochemical evaluation for the HER at various catalytic materials are usually represented by the kinetic values of the constants a and b of the Tafel equation.¹⁸ The constant b , defined as Tafel slope, an inherent property of the catalysts, is related to the reaction mechanism of a catalyst and is determined by the rate-limiting step of the HER. The value depends on several factors, including the reaction pathway and the adsorption conditions of the active site.¹⁸ Because of a very high H_{ads} coverage ($\theta_H \approx 1$), the HER on a Pt surface is known to proceed via the Volmer-Tafel mechanism (eqs 1 and 3, Figure 1-1), and the Tafel step is the rate-limiting step at low overpotential, as attested by the measured Tafel slope of 30 mV dec^{-1} .¹⁸ In case of MoS_x, the Tafel slope may vary significantly for different structures and properties of MoS_x materials. Previous studies on MoS_x catalysts have shown a large spread of Tafel slopes ranging from 40mV to 120 mV dec⁻¹.¹⁹⁻²³

Another evaluation of intrinsic electrocatalytic activities for electrocatalysts has often been made in the basis of relative values of $\log j_0$ for the HER, which is an important kinetic parameter representing the electrochemical reaction rate at equilibrium. It may be understood as an indicator of the electron transfer rate of a catalyst and its magnitude determines how rapidly the electrochemical reaction can occur. Since MoS₂ is an intrinsic semiconductor with a marked

anisotropic behavior in conductivity,^{24,25} slow electron transport is likely the origin of the lower exchange current densities in certain molybdenum sulfide catalysts. Thus, optimizing the conductivity of those MoS_x-based materials is a very promising pathway for developing efficient HER electrocatalyst.²⁶ Here one important issue needs to be clarified is that the comparisons based on $\log j_0$ values alone give only a measure of kinetics at the equilibrium or zero-polarization condition, while the comparisons on the basis of b values provide a complementary mechanistic aspect of the kinetic behavior under the practical operating conditions.²⁷ An optimal and ideal catalyst is the material that has the highest exchange current density and lowest Tafel slope. These matters are of importance to optimize the operation and performance of electrolyzers for H₂ production and, especially for the selection of cathode materials for HER.

Besides, the intrinsic per-site activity of a catalyst is also an important metric necessary to assess the ceiling for further improvement and to guide catalyst development, which is often measured by the turnover frequency (TOF) for each active site, representing a chemical reaction rate. The value is closely related to the activity of each catalytic site of the catalysts. The difficulty in measuring a TOF is not only in determining the rate but in counting active sites. Besides, sites may not be all identical even for the same catalyst. Practically, for different MoS_x based catalysts, the comparison of the TOFs is only meaningful when the value is taken at the same overpotential. Thus, the comparison of TOF value at zero overpotential might be more reliable for this could be deduced from the j_0 .²⁸ In general, TOFs of transition metals range over 10 orders of magnitude, for example, Hg has a TOF as low as $\sim 10^{-9} \text{ s}^{-1}$.¹⁴ In this thesis, we will evaluate the HER catalytic activity for different MoS_x catalysts based on the onset potential, Tafel slope, exchange

current density, as well as the TOF.

1.3 Group-VI Transition-Metal Carbides (TMCs) as Electrocatalysts for HER

1.3.1 Overall Introduction

Transition metal carbides (TMCs) are produced by incorporating carbon atoms into the interstitial sites of their parent metals. In general, early TMCs possess unique physical and chemical properties.²⁹⁻³¹ For example, TMC compounds combine the physical properties of three different classes of materials: covalent solids, ionic crystals, and transition metals. As a result, TMC compounds often demonstrate the extreme hardness of covalent solids, the high melting temperature of ionic crystals, and the excellent electric and thermal conductivity of transition metals. Traditionally, the unique combination of these desirable physical properties has led to the commercial applications of TMCs as cutting tools³¹ and hard-coating materials.³²

Until to 1973, Levy and Boudart showed the resemblance between Pt and tungsten carbide in surface catalysis.³³ Since then, the catalytic properties of group VI carbides (mainly including tungsten carbides and molybdenum carbides) have been the subject of many investigations because of their potential application as the most promising candidates to replace or reduce Pt employment in catalysis reactions, such as HER.^{30,34,35} It was found that catalytic activity of group VI carbides for HER is attributed to the permeation of carbon atoms into the lattice of transition metal which lengthen the metal-metal distance and thus increase the *d*-band electron density at Fermi level of molybdenum or tungsten.³⁶ In addition, group VI carbides have been

often used as stable supports for precious metals over different ranges of pH in HER.^{37,38} By now, many effective approaches for the synthesis of group VI carbides have been reported, particularly the nanostructured carbides, including direct carburization of group VI metals or group VI metal-containing compounds at high temperature, solid state metathesis and mechanical milling.

1.3.2 Molybdenum Carbides

Molybdenum carbides (mainly referring to Mo₂C) are one important class of TMCs. In the past few years, studies have shown that molybdenum carbides are active in a variety of catalytic reactions including desulfurization,^{39,40} the water gas shift,⁴¹ and hydrogenation reactions.^{6,42} Vrabel and Hu reported that after removal of surface oxides, the commercial molybdenum carbide (Mo₂C) was a very active HER catalyst in both acidic and basic conditions.⁴³ However, the use of aggregated Mo₂C microparticles may hamper the transport of electrons or protons during the reaction, and thereby result in a loss of activity, given that the performance of HER electrocatalysts greatly depends on their compositions and structures.⁴³ Recently, Sasaki et al. demonstrated that Mo₂C nanoparticles on carbon nanotubes were indeed a highly active and durable electrocatalyst for hydrogen production.⁴⁴ Moreover, the nanopore-structured Mo₂C nanowires have also been developed to increase the specific surface area for HER.⁴⁵ The surface area was proved to play an important role in their performance for HER, thus it would be feasible and effective to improve the catalytic activity by increasing its specific surface area considering its high surface-area-to-performance ratio.

1.3.3 Tungsten Carbides

Another class of low-cost TMCs catalytic materials with great potential for replacing or reducing Pt in HER applications is tungsten carbides (including WC and W₂C), which are known to display similar electronic and catalytic properties to Pt-group metals due to the intercalation of C to the W lattice.^{46,47} Thus, they have shown sufficient HER activity to be considered as stand-alone HER electrocatalysts.^{7,48,49} Moreover, the good stability in acidic environments is also an important reason for choosing WC or W₂C electrodes as candidates for HER application.⁵⁰⁻⁵² Studies have showed that their catalytic properties strongly depend on its surface composition and conditions, such as the surface carbon coverage, the particle size, lattice defects and pseudometallic surfaces and so on.⁵³ Thus, it has been expected that a considerable improvement could be achieved by tailoring the electrocatalyst properties. However, the reported HER catalytic activities of WC and W₂C, expressed in terms of exchange current density (i_0), are still 2-3 orders of magnitude below many Pt-group metals. Therefore, there has been much interest in combining WC or W₂C with Pt-group metals as co-catalysts, with several studies reporting that WC/W₂C powder-supported Pt nanoparticles show significantly higher HER activity than conventional carbon supported Pt particle.⁵⁴⁻⁵⁶

1.3.4 Summary

In conclusion, group VI transition metal carbides (TMCs), including tungsten carbides (WC and W₂C) and molybdenum carbides (Mo₂C) have showed strong catalytic activity similar to those of the more expensive Pt-group metals for HER. By now, much effort has been done to explore and

prepare more efficient TMCs by controlling the morphology at the nanoscale as well as the modification of the host material (e.g. with noble metals). Future perspectives include further augmenting the exceptional catalytic activity of WC, W₂C or Mo₂C by *in situ* formation of their nanocomposites on functional matrices or by designing mesoporous structure with high specific surface area. Furthermore, more theoretical investigations into the electronic properties, crystal and surface structure as well as synergetic effects of TMCs/modified-TMCs nano-materials should be made based on first-principle calculations, which in combination with smart experimental strategies will greatly shorten the development process of highly efficient TMCs-based nanomaterials for HER applications.

1.4 Group-VI Transition-Metal Sulfides (TMSs) as Electrocatalysts for HER

1.4.1 Overall introduction

Transition metal dichalcogenides are layered materials that can exhibit semiconducting, metallic and even superconducting phases. In the past decades, nanostructures based on transition metal sulfides (TMSs) have been of special interest because of their diverse applications. Previously, they have been extensively studied due to their crucial role in the petroleum and chemical industry.⁵⁷ Among this big family, nanostructured MoS₂ and related metal sulfides such as WS₂ are the best studied electrocatalysts for HER, this has opened up an exciting new path for the sustainable generation of hydrogen.^{15,17,23,58} By now, much of the experimental work has stemmed from the theory that metallic edges⁵⁹ of 2H TMSs crystals are electrocatalytically

active.¹⁷ This has led to extensive investigations of nanostructured TMSs or its complexes with a high concentration of exposed edges as electrocatalysts for hydrogen evolution. Further improvements in the HER kinetics by placing TMSs nanostructure on a variety of substrates including reduced graphene oxide (rGO), carbon nanotubes (CNTs) have also been reported.^{22,60} It is known that MoS₂ and WS₂ belong to the layered transition-metal dichalcogenides (LTMDs) family of compounds that have a lamellar structure comparable to graphite in which the individual S-metal-S layers weakly interact with each other. They exhibit a variety of polymorphs.⁹ Their band-gap can be tunable, and the exfoliated sheets can gain metallic properties on a change in phase.⁶¹ TMSs can be prepared by several methods with different starting reagents, leading to materials with tunable stoichiometry, structure and morphology. In the past years, significant efforts have been made in the investigation and development of TMDs materials as HER catalysts. Research regarding the diverse properties of TMDs with variable structures and morphologies is highly important, and the catalytic activity of these materials for the HER needs to be explored further.

1.4.2 Molybdenum Sulfides

As one typical chemical composition of bulk molybdenum sulfides, MoS₂ naturally occurs as a lamellar hexagonally structure similar to graphite in which the individual S-Mo-S layers weakly interacts with each other by van der Waals forces, and each layer has a thickness of ~ 0.7 nm.^{62,63} Typically, MoS₂ occurs in two modifications, 2H and 3R. The hexagonal 2H-polytype has two layers per unit cell along the *c*-axis, the rhombohedral 3R-polytype has three layers per unit cell.

In nature, the 2H-type is dominant and more stable, and 3R will transform to 2H upon heating.^{13,64} While for those MoS₂ nanosheets produced from chemical Li-intercalation and exfoliation, the pure 2H phase will experience phase transformation to a metastable metallic 1T phase, which causes MoS₂ evolving from the semiconducting to metallic polymorphs.^{64,65} The conversion of 2H MoS₂ to 1T phase have been shown to be positive for its HER catalytic performance. Different from the hexagonal structure of its bulk form, the MoS₂ nanocrystals often exhibit a triangular morphology and are often reported as slightly truncated triangles.^{66,67} Figure 1-3a shows a typical scanning tunneling microscopy (STM) image of MoS₂ single sheet grown on Au(111).¹⁵ But only one edge type is energetically favored and presented due to the triangular shape.²⁵ The edges of the nanoplatelets are bright rims as seen from the STM images in Figure 1-3a, suggesting the conductivity at the edge. DFT calculations indicate that the free energy of adsorbed H (ΔG_H) on crystalline MoS₂ (10-10) edge sites with 50% S adsorption is close to those on a hydrogenase model and platinum (close to zero) (Figure 1-3b). It is found that for all types of MoS₂ edges, the electronic structure is dominated by metallic one-dimensional edge states, proving that fully sulfided Mo edges play an important role in the catalysis.^{17,68}

Figure 1-3 (a) STM on MoS₂ nanoplatelets on Au (111).¹⁵ (b) A molecular model of a platelet

exposing both Mo and S-edges from top and side view. Mo atoms are blue, S atoms yellow.^{25,69}

Studies on MoS₂ nanocrystals demonstrated that the ratio of basal plane sites to edge sites could be changed with the particle size without changing the nature of the edge, this is important for us to design efficient MoS₂ catalysts.¹⁵ After the heat treatment at different annealing temperatures (400 and 550 °C), the particle size changes and thus resulted in the predominance of the sulfided Mo-edge.¹⁵ Besides, the morphology between triangular and hexagonal form could be changed by varying sulfiding and reaction conditions.⁶⁷ Moreover, the incorporation of cobalt (Co) or nickel (Ni) into MoS₂ can tune the intrinsic catalytic activity,^{19,70} as the promoter atoms prefer to be located exclusively at the S edges. The presence of unsaturated sulfur atoms in these materials can engage in the discharge reaction and form S-H bonds and thus eventually lead to hydrogen formation.

The study on electrochemical hydrogen evolution on molybdenum sulfides can be traced back to 1970s,¹³ but the progress was very slow because of the poor activity for bulk MoS₂.⁷¹ Recent advances in material science and nanotechnologies have revealed that nanostructured MoS_x ($x \approx 2$ to 3),^{8,9} would be promising and inexpensive alternatives to Pt for the electrochemical generation of hydrogen from water.^{10-12,72} By analyzing the similarity between the metallic MoS₂ and the natural HER enzymatic catalysts, such as hydrogenases and nitrogenases that possess active centers consisting of Fe, Ni and Mo, Hinnemann et al. reported that the under-coordinated sulfur atoms at the edges of MoS₂ have very similar properties to those of the active enzymatic centers,¹⁷ and this was further verified experimentally for the nanoparticles of MoS₂ were shown

to be active catalyst for HER.¹⁵ Since then, MoS_x-based nanocatalysts have been extensively investigated for the HER.

From the above analysis, three ways are proposed to improve MoS_x-based electrocatalysts: (1) Increasing the number of the active sites per unit volume by tailoring progressively smaller nanostructures or engineering the surface structure at the atom scale or using discrete molecular units to make powerful molecular catalysts. (2) Increasing the conductivity and diffusion properties of MoS₂ materials by decreasing the restacking of the materials as well as stacking the layered structure to the conductive surface to improve the electron transfer among the catalysts. (3) Increasing the inherent activity of MoS₂ by appropriately tuning the electronic structure of the edge to increase the bond strength of the adsorbed H, this has been carried out by doping and adding substrate effects. Along these approaches, various MoS₂ based nanostructures have been primarily explored as electrocatalysts for HER.

1.4.3 Tungsten Sulfides

Another interesting TMSs compound is WS₂, in which the electrical properties can be varied from metallic and semiconducting by tuning the crystal structure and the number of layers.^{73,74} The structure is similar to that of MoS₂ and some of the other dichalcogenides, forming the same triangular shape as MoS₂ when prepared under similar conditions. Conventionally, mono- or few-layered WS₂ can be obtained by mechanical exfoliation or grown by chemical vapor deposition (CVD).^{73,75} In addition, chemical methods for large-scale synthesis of layered WS₂ have also been reported.⁷⁶ In the past few years, WS₂ has received intensive investigation as

photo- electrochemical catalysts^{77,78} and electrocatalysts¹⁹ due to its structural and electronic similarities to MoS₂. For example, WS₂ supported on SiO₂ has been synthesized and demonstrated as a good catalyst for the hydrogen evolution reaction.⁷⁸ Moreover, unprompted and Co-promoted WS₂ nanoparticle catalysts have also been tested, results demonstrated that Co is indeed promoting the HER compared with the unpromoted WS₂ NPs, which was also proved by DFT calculations.¹⁹ Recently, both chemically synthesized and exfoliated WS₂ nanosheets have been demonstrated enhanced catalytic activity toward HER.⁷⁹⁻⁸¹ Interestingly, different from the MoS_x, it was found that the HER active sites of WS₂ are related to its crystalline structures, that is, improved crystallinity of WS₂ showed improved catalytic activity, whereas, MoS_x gave the opposite result.⁸²⁻⁸⁴ But this still need to be further verified since there are many complex factors that could influence the HER activity of a catalyst.⁸⁵

1.4.4 Summary

In the past few decades, group VI transition metal sulfides (TMSs) have attracted great attention and been extensively investigated as promising electrocatalysts for HER. MoS_x/WS₂ electrodes consisting of various nanostructures (including nanoparticles, nanosheets, films and composites) have exhibited excellent HER efficiencies, which offer a suitable alternative to the expensive and scarce Pt. It is demonstrated that enhancing the active sites, the conductivity as well as the inherent activity of different MoS_x/WS₂ nanostructures are the common aims in designing effective electrocatalysts for HER. Firstly, the catalytic activity is greatly affected by the morphology, structure and density of active sites, thus a close attention should be paid to the

specific surface area and the composition of the designed MoS_x/WS₂ nanocatalysts. Further improvement of the conductivity of those materials is still highly desirable. In this sense, recent attempt on the more conductive 1T MoS₂ nanosheets holds immense promise for designing more active MoS₂ catalysts.

In addition, the improvement of the inherent activity of MoS_x catalysts is equally important. Potential strategies include element doping of the MoS_x host materials, and substrate effects stem from the interaction of substrate with the host catalyst.⁸⁶ Although the doping method has not been realized for the active Mo-edge, Co-doping the S-edges to be as active as the Mo-edges is a good example showing how such an effect could be realized. Specially, the study of the biomimetic and molecular catalysts has presented an alternative strategy using discrete molecular units as catalysts for the HER. Further study could focus on stabilizing the molecular catalysts with suitable substrates, such as the employing of the metal-organic-framework (MOF) and exploring other bimetallic organometallic complexes with terminal sulfur ligands synthesized from Mo, Co, W complexes.⁹

Owing to the demand for renewable hydrogen production, the field of the electrochemical HER using nanostructured MoS_x/WS₂ electrocatalysts has been experiencing a renaissance in recent years and will be of great interest in H₂ production.

1.5 Electrocatalytic Systems Developed in This Thesis

The electro-catalytic systems developed for H₂ production under acidic conditions in this work are discussed in the following four chapters. Chapter II describes a unique nanorod-structured

tungsten carbide material with high specific surface area of $198 \text{ m}^2\text{g}^{-1}$, which is successfully synthesized for the first time by pseudomorphic transformation of chemically synthesized WO_3 nanorods through a high-temperature method. An electrocatalyst composed of Pt nanoparticles supported on WC nanorods demonstrates higher electrocatalytic activity for cathodic electrocatalytic hydrogen evolution than a Pt/C catalyst. This work provides a novel method to synthesize high-surface-area nanorod-structured WC materials by preparing oxide precursors with the desired external morphology, thus offering great potential for a broad range of applications of these materials in related reaction systems.

In recent years, two-dimensional molybdenum disulfide (MoS_2) with exposed edges was demonstrated as a very promising electrocatalyst for HER in recent years. Previously, the reduced graphene oxide (RGO) was introduced to stabilize the layered structure of MoS_2 so as to increase the active sites. However, both RGO and MoS_2 /RGO are prone to restacking during the hydrothermal process, which shadows its potential applications. Additionally, the most important inherent problem of using MoS_2 in any kind of electrochemical reaction is the extremely low conductivity between two adjacent van der Waals bonded S-Mo-S sheets. Thus, Chapter III describes a novel electrocatalyst of layered MoS_2 supported on RGO decorated with nano-sized tungsten carbide (WC), which shows an enhanced catalytic performance in the hydrogen evolution reaction compared with MoS_2 /RGO. This good performance are attributed to the presence of a conductive and electrocatalytically-active nano-WC dispersant and the positive synergistic effect between nano-WC/RGO and layered MoS_2 . This study highlights the importance of using highly conductive WC as an effective co-catalytic support combined with the

layered composite material for electrochemical water splitting, which is a valuable attempt towards further development of the related composite materials to substitute noble-metal electrocatalysts for the HER.

As inspired by the conductive nano-WC/RGO support from the MoS₂/WC/RGO composite electro-catalyst, a networked MoS₂/CNT nanohybrid is synthesized and evaluated in Chapter IV.

The use of CNTs as support not only could increase the number of the exposed active sites on the edges, but also could improve the electrical conduction of MoS₂. In this work, we apply a facile solvothermal method to produce a networked nanocomposite consisting of low crystalline MoS₂ coated on carbon nanotubes (CNTs) for the HER. It is found that both acid-treated CNTs and DMF play a critical role in the formation of this unique structure, and the low crystalline MoS₂ is identified as the actual catalyst for the enhanced HER due to the high number of exposed sites. This study shows that the synthesis of low crystalline MoS₂ supported on inexpensive and conductive CNTs is feasible and has a great potential for electrocatalytic hydrogen evolution.

With the discovery that DMF acts as an effective solvent for mediating the formation of MoS₂ nanosheets, a well-defined ultrathin MoS₂ nanoplate catalyst is developed by a facile solvent-dependent control route from single source precursor in Chapter V. The obtained ultrathin nanoplate with a thickness of ~ 5 nm features high density of basal edges and abundant unsaturated active S atoms. The multistage growth process is investigated and the formation mechanism is proposed. Ultrathin MoS₂ nanoplates exhibit an excellent activity for hydrogen evolution reaction (HER) and remarkable stability. This work successfully demonstrates that the

introduction of unsaturated active S atoms into ultrathin MoS₂ nanoplates for enhanced electrocatalytic properties is feasible through a facial one-step solvent control method, and that this may open up a potential way for designing more efficient MoS₂-based catalysts for HER.

Chapter II Template-free Pseudomorphic Synthesis of Tungsten Carbide Nanorods

(This chapter is reproduced with permission from Yan, Y.; Zhang, L.; Qi, X.; Song, H.; Wang, J.-Y.; Zhang, H.; Wang, X.*, Template-Free Pseudomorphic Synthesis of Tungsten Carbide Nanorods. *Small*, 2012, 8, 3350-3356. Copyright 2012, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim)

2.1 Background Introduction

As introduced in chapter I, renewable hydrogen production from HER needs catalysts to reduce the overpotential and consequently increase the efficiency of this important electrochemical process. In recent years, Tungsten carbides (WC) have attracted considerable attention for catalytic and electro-catalytic applications since the discovery of its Pt-like characteristics as reported by Levy and Boudart.³³ It is well known that WC has high catalytic activity for hydrogenolysis and isomerization reactions.⁸⁷⁻⁹² Tungsten carbide is also reported to exhibit certain activity or synergistic effects with other metal for many electrochemical reactions of interest, including hydrogen oxidation,^{93,94} oxygen reduction,⁹⁵⁻⁹⁷ hydrogen evolution reaction (HER),⁹⁸ and oxidation of various organic molecules.⁹⁴ Although its electro-catalytic activity was usually not sufficient, the low cost and insensitivity to catalyst poisons such as CO make it an interesting alternative to noble metal catalyst. Other than direct use as catalyst, tungsten carbide has also been intensively studied as catalyst support for various reactions.⁹⁹⁻¹⁰¹ Particularly, the high corrosion resistance and superior electronic conductivity render WC suitable as

electro-catalyst support for various electrochemical applications, such as fuel cell.¹⁰²⁻¹⁰⁴ For example, higher catalytic activity has been reported for Pt/WC compared to Pt/C due to the synergistic effect between Pt and WC.^{105,106}

Conventionally, several routes have been adopted to synthesize WC powder, including direct carburization of tungsten or W-containing compounds at high temperature (typically, higher than 1400 °C), solid state metathesis and mechanical milling. However, these approaches often lead to low specific surface area, large particle size and poor morphology control. The surface areas of commercial WC and WC synthesized by these reported methods are normally lower than 10 m² g⁻¹ and the maximum value reported is ~ 100 m² g⁻¹.¹⁰⁷⁻¹¹⁴ On the other hand, the ability to control specific nanostructure is critical for the tuning of its physical and chemical property, especially when WC is to be used as catalyst support. Among various nanostructures, Tungsten carbide nanorod is of particular interest due to its unique properties. There are very limited studies on the synthesis of tungsten carbide nanorods or nanotubes, and the yielded nanostructures still suffer from low surface areas (≈10 m² g⁻¹).¹¹⁵⁻¹¹⁷ To synthesize nanostructured WC with high surface area and controlled morphology still remains a big challenge.^{54,118}

Inspired by Justin C. Lyte's work¹¹⁹ who demonstrated the pseudomorphoic fabrication of three dimensional ordered macroporous (3DOM) tungsten carbide from colloidal crystal templates. Herein, we report, for the first time, template-free synthesis of WC nanorods with high specific surface area of 198 m² g⁻¹ by size-controlled hydrothermal reaction of WO₃ nanorods and subsequent pseudomorphoic transformation of the WO₃ nanorods. The formation mechanism

was proposed based on the experimental results. Its application as electro-catalyst support for Pt nanoparticles was demonstrated using methanol electro-oxidation, CO stripping and HER.

2.2 Experimental Section

2.2.1 Reaction Apparatus

Our electrochemical reaction system is a three-electrode cell conducting at room temperature and connected to an on-line Autolab PGSTAT302 potentiostat (Eco Chemie, Netherlands). The sketch is shown in Figure 2-1.

Figure 2-1 Scheme of the three-electrode configuration cell for the electrochemical measurements.

2.2.2 Synthesis of WO_3 Nanorods and WC Nanorods

Preparation of WO_3 nanorods: WO_3 nanorods were synthesized by the recently reported

hydrothermal process with $(\text{NH}_4)_2\text{SO}_4$ (Sigma-Aldrich) as a capping agent.^{120,121} In a typical synthesis, $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (0.6597 g, Sigma-Aldrich) and $(\text{NH}_4)_2\text{SO}_4$ (0.5286 g) were dissolved in de-ionized water (15 ml), then HCl (3M, Merck, USA) aqueous solution was added to adjust the pH value to 2.0. Afterwards, the solution obtained was transferred into a Teflon-lined stainless autoclave where the reaction was maintained at 180 °C for 8 h. Then the precipitate were filtered, washed sequentially with water and ethanol for 3 times, respectively, and dried at 60 °C.

Preparation of WC nanorods: In a typical synthetic procedure of WC nanorods, a proper amount of as-prepared WO_3 nanorods and glucose (the molar ratios of W/C = 0.078) was dissolved in de-ionized water (15 mL) and was vigorously stirred for 20 min. The mixture was hydrothermally treated in a sealed Teflon lined stainless steel autoclave at 180 °C for 8 h to form carbon-coated WO_3 nanorod. The as-prepared precursors were calcined at 900 °C under a flow of H_2/Ar ($V_{\text{H}_2}/V_{\text{Ar}} = 1:3$, 300 mL min⁻¹) for 3 hours to finally form WC nanorods.

Preparation of (20 wt.%) Pt/WC-rods and (20 wt.%) Pt/C: Pt/WC-rods and Pt/C catalysts were synthesized by a modified Ethylene Glycol (EG) method. Briefly, 40 mg of WC-rods or XC-72 carbon powder (Gashub) was suspended in 10 mL of ethylene glycol solution and stirred with ultrasonic treatment for 30 min; 2.2 mL of hexachloroplatinic acid EG solution (4.6 mg Pt/mL EG) was added to the solution dropwise also under mechanically stirred conditions for 3 h. NaOH (2 M in EG solution) was added to adjust the pH of the solution to above 13, and then the solution was heated at 140 °C for 3 h to ensure that Pt was completely reduced. Thereafter,

in order to promote the adsorption of suspended Pt nanoparticles onto the support, hydrochloric acid was adopted as the sedimentation promoter. The resulting black solid sample was filtered, washed and dried at 60 °C for overnight in a vacuum oven.

2.2.3 Characterization

For XRD analysis, it was carried out on a X-ray diffractometer (Bruker AXS D8, Cu K λ , λ = 1.5406 Å, 40 kV and 20 mA), a concentrated solution of WC nanorods in ethanol was deposited on a glass slide, dried at 60 °C and mounted on the XRD sample stage for the analysis. The morphology was studied by a field emission scanning electron microscopy (FESEM, JEOL JSM 6700F). The composition of the samples was determined by using the FESEM equipped energy dispersive X-ray spectroscopy (EDS). For the crystalline analysis, a drop of solution containing WC nanorods was placed on a carbon-coated copper grid, and then dried naturally in air prior to be characterized by TEM (JEM 2100). The Brunauer–Emmett–Teller (BET) specific surface area and pore size distribution of the WC nanorods was measured in Autolab-6B (Quantachrome Instruments) using the liquid nitrogen adsorption method. Raman spectra were collected via a Renishaw Ramanscope in the backscattering configuration using 633 nm (1.96 eV) and 514 nm (2.41 eV) laser wavelengths over five random spots on WC nanorod powders. Thermal gravimetric analysis (TGA) was conducted on PerkinElmer Diamond TG/DTA equipment from 150 to 900 °C under air (20 mL min⁻¹) with a ramp rate of 5 °C min⁻¹.

2.2.4 Electrochemical Measurements

All electrochemical measurements were conducted on an Autolab PGSTAT302 potentiostat (Eco

Chemie, Netherlands) in a three-electrode cell at room temperature as shown in Figure 2-1. A Pt foil (4.0 cm^2) and a saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively. The working electrode was prepared on a glass carbon (GC) disk as the substrate. Typically, a mixture containing 2.0 mg catalyst, 2.5 mL ethanol and 0.5 mL Nafion solution (0.05 wt. %, Gashub) was ultrasonicated for 15 min to obtain a well-dispersed ink. The geometric area of the electrode was 0.1963 cm^2 . A certain amount of catalyst ink was then transferred onto the surface of the GC electrode and the solvent was slowly evaporated to obtain a catalyst thin film. The Pt loadings on the electrode were controlled at $20 \mu\text{g cm}^{-2}$ in this study. The aqueous solutions containing $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ or $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4 + 1.0 \text{ mol L}^{-1} \text{ CH}_3\text{OH}$ were used as electrolyte for the methanol oxidation. For CO-stripping tests, the electrode potential was held at -0.15 V (vs. SCE) in CO-saturated $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ solution for 20 min first. N_2 was bubbled into the solution for 20 min to remove dissolved CO in the solution while holding the potential at -0.15 V (vs. SCE). The CO-stripping was performed by cycling the potential from -0.15 V to 1.0 V (vs. SCE) at a scan rate of 15 mV s^{-1} . For the hydrogen evolution reaction (HER), $100 \text{ mM H}_2\text{SO}_4$ served as electrolyte solution. The working electrodes were mounted at a rotating disc electrode with a rotating rate of 1000 rpm during the test. In all experiments, the electrolyte solutions were purged with N_2 for 15 min prior to the experiments in order to remove oxygen. During the measurements, the headspace of the electrochemical cell was continuously purged with N_2 .

2.3 Results and Discussion

Figure 2- 2 (a) XRD pattern of as-prepared WO_3 nanorods ($\blacklozenge$ — WO_3). (b) FESEM image of as-prepared WO_3 nanorods.

Figure 2- 3 XRD patterns of (a) products obtained at 800 °C and (b) products obtained at 900 °C with a constant molar ratio (W/ C) of 0.078 for 3h [($\circ$)WC, ($\square$)W, ($*$) W_2C].

A sulfate-assisted hydrothermal method was used for the synthesis of WO_3 nanorods from a tungstic acid sol. Figure 2-2b shows that the hydrothermal product consists of uniform nanorods, with diameters of 50-70 nm and lengths of 200-300 nm. These nanorods exhibit hexagonal

phase of WO_3 ((8 ± 1) nm, PDF# 33-1378) (Figure 2-2a, Table 2-1). In addition, a few hexagonal nanorods aggregated through their side crystal planes during the reaction.

Table 2-1 Critical structural parameters of WO_3 nanorods and their solid-solid transformation products.

Sample name	Shape Size(nm) [a]	Crystallite Size(nm)[b]
WO_3 Nanorod (1) [c]	AD[d]: 60 AL[e]: 250	8 ± 1
Conversion of nanorod WO_3 , 3Ar:H ₂ , 800 °C	—	W: 55 ± 3
Conversion of nanorod WO_3 , 3Ar:H ₂ , 900 °C(2) [c]	AD[d]: 40 AL[e]: 200	W ₂ C: 11 ± 1 WC: 20 ± 3

[a] Average shape size values are estimated from FESEM images. [b] Crystallite size was estimated from line broadening of XRD reflections. [c] (1) refers to region shown in Figure 1b and (2) refer to region shown in Figure 3a. [d] AD refers to the average diameters. [e] AL refers to the average lengths.

The formation of tungsten carbide is known to depend on the amount of carbon sources, heating rate, and especially, temperature.²⁹ Typical XRD patterns of the as-prepared products in Figure 2-3 show that at a constant molar ratio of WO_3 to glucose (0.078) and reaction time (3h), temperature plays an important role. With the increase of the reaction temperature to 900 °C, a phase transition from W ((55 ± 3) nm, Figure 2-2a) to WC was observed (Figure 2-2b). The WC nanorods obtained at 900 °C can be indexed to that of the hexagonal phase with lattice constants $a = 2.90$, $c = 2.83 \text{ \AA}$ ((20 ± 3) nm, peak intensities and position are shown and confirmed from PDF# 51-0939). In addition, a small diffraction peak is obtained for hexagonal α - W_2C ((11 ± 1)

nm, space group $P3m1$) (marked with *), which was not anticipated in the final products, it is easily formed at the local undersupply of carbon under these reaction conditions, thus the adequate carbon source during the whole reaction was provided. The presence of tungsten at 800 °C and disappearance at 900 °C indicates carburization reaction is driven further to completion with the increase of temperature and that the extent of carburization is thermodynamically controlled.¹¹⁹

Pseudomorphism on a nano-scale (sub-100 nm) is achieved by reacting glucose/carbon coated WO_3 nanorods with flowing gas mixtures Ar (v) and H_2 (v) (3:1) at 900 °C for 3h. Figure 2-4 shows field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) images of the WC nanorods that were prepared by pseudomorphic transformation of chemically synthesized WO_3 nanorods at 900 °C. Individual nanorod morphology was still maintained and the diameters of WC nanorods are 30 - 50nm with varying lengths of 150 - 250 nm. This confirms the pseudomorphic transformation of WO_3 nanorods to WC nanorods. While there is a size shrinking by comparing with the WO_3 nanorod, this should be due to the gradual chemical conversion of WO_3 to WC.¹²² Besides, some sort of surface coating is also observed by the high resolution TEM imaging in Figure 2-4b, which is probably due to surface carbon and will be discussed in detail in later section. The bulk energy dispersive X-ray spectroscopy (EDS) analysis of the WC nanorods depicted in Figure 2-4a shows 0.89:1 molar ratio for W/C (Figure 2-5). It is worthy to note that the ratio of W to C is only a rough estimation, since EDS is often disturbed by the formation of adventitious carbons.¹²³

Figure 2-4 (a) FESEM image of WC nanorods. (b) TEM images of WC nanorods.

Inset: HRTEM image of an individual nanorod. (c) HRTEM image of the single WC nanorod, with the arrow showing lattice fringes of the WC (001) plane. Inset: FFT diffraction pattern of this section. d) SAEDX spectrum of the nanorods presented in (c).

The high resolution TEM micrographs were employed to explore the crystalline nature of the WC nanorods. As shown in the high resolution TEM image (Figure 2-4c), individual nanorod is highly crystalline. The measured distance between those (001) lattice planes is 0.274 nm, which closely matches the literature value of 0.28 nm for the hexagonal WC. The fast Fourier transform (FFT) diffraction pattern of this area (inset image) shows streaks along the (001) and (100)

directions, which can be indexed to the tungsten carbide planes. The SAEDX analysis of this rod gives a molar ratio of tungsten to carbon of 1:1 (Figure 2-4d). Besides, a small amount of oxygen was observed. This oxygen should come from the thin WO_x film formed in air at nanometer level, which is hardly detectable by XRD.¹²³

Figure 2-5 Bulk EDX spectrum of the WC nanorods sample.

In order to detect the possible presence of carbon coating on the surface of WC nanorods, Raman spectra was adopted to investigate the carbon species. Figure 2-6a shows the Raman spectra of the samples treated at 800 °C and 900 °C. The carbon-coated WO₃ nanorod heated at 800 °C have two obvious Raman peaks located at about 1345 and 1585 cm⁻¹, which are mainly attributed to the D-band and G-band of the disorder induced crystalline graphite, respectively.¹²⁴ This indicates the sample heated at 800 °C is still covered by a certain amount of carbon. These two peaks greatly depressed for the sample heated at 900 °C, indicating a significant decrease in carbon content.

Figure 2-6 (a) Raman spectra of the products obtained at the temperature of 800 °C and 900 °C.

(b) The nitrogen adsorption / desorption isotherms of WC nanorods sample. The inset is the pore size distribution curve.

Nitrogen adsorption experiment confirms the high porosity and specific surface area of the WC nanorods. As shown in Figure 2-6b, the nitrogen adsorption/desorption isotherm with a distinct hysteric loop at the relative pressure of P/P_0 ranging from 0.5 to 0.9 is identified as Type IV characteristic of mesoporous materials. Ganeson et al. previously reported mesoporous structure on tungsten carbide and attributed the mesoporosity to the tungsten carbide and not to excess surface carbon.¹²⁵ In this work, we believe the mesoporosity comes from the packing of WC nanorods. The pore size distribution was investigated by the Barrett–Joyner–Halenda (BJH) method, with an average pore size of 5.9 nm (inset of Figure 2-6b). The sample has a Brunauer–Emmett–Teller (BET) surface area of $198 \text{ m}^2 \text{ g}^{-1}$ with a total pore volume of $0.30 \text{ cm}^3 \text{ g}^{-1}$, exhibiting a high specific surface area in contrast to less than $20 \text{ m}^2 \text{ g}^{-1}$ for commercial WC products and those synthesized by other methods.^{102,126} The high BET surface area does not agree with the calculation based on geometry ($\sim 40 \text{ nm}$ in diameter). This could be explained by surface

roughness or the presence of micropores on the sample surface due to the unequal carburization of the non-uniform glucose/carbon coated WO_3 nanorods. The presence of amorphous carbon on the WC nanorod surface may also contribute to the high BET area. For example, Bosco et al. reported that the specific surface area appears to increase linearly with carbon impurity in the WC samples.¹²⁷

A proposed mechanism for the pseudomorphic transformation of WC nanorods is schematically illustrated in Figure 2-7. First, WO_3 nanorods were synthesized by hydrothermal method. Then carbon-coated WO_3 nanorods were used as the precursors for WC synthesis. This way of introducing carbon within nanorod-structured tungstic oxide facilitates the reaction by ensuring a uniform distribution of carbon onto WO_3 nanorods and improving their contact. In addition, the shrinking of both diameter and length (Table 2-1) of the obtained WC nanorods illustrates the gradual chemical conversion of WO_3 nanorod, beginning at the exterior surface and diffusing inward through solid-state carburization towards the nanorod center. From the perspective of the pseudomorphic transformation, solid-state carburization is preferred for the morphological retention of the WO_3 nanorods than the carburization by carbonaceous gases which had relatively high rates of nucleation and a certain etching ability. Besides, the excess surface carbon is also likely responsible for increased retention of the WC nanorods. From TEM image (Figure 2-4b), the amorphous carbon appears to completely cover the materials surface, which, to a certain extent, provided “cement” for holding the WC crystallite into the nanorod-structure.

Figure 2-7 Schematic illustration for the formation of WC nanorods.

The WC nanorods were first studied as electrocatalyst support for Pt nanoparticles. TEM images (Figure 2-8) show that the high surface area of the WC rods indeed allows uniform dispersion of Pt nanoparticles on its surface with an average particle size of 4 nm, which is in well agreement with the XRD results (Figure 2-9). The nanostructured WC rods supported Pt catalyst (Pt/WC-rods) was further characterized for methanol oxidation in a 0.5 mol L⁻¹ H₂SO₄ +1.0 mol L⁻¹ CH₃OH solution with cyclic voltammetry (CV). Its electrocatalytic activity was compared with carbon supported Pt catalyst with an equal amount of Pt and Nafion on the GC surface (Figure 2-10a). The results clearly indicate that WC nanorods itself has no characteristic peaks of methanol oxidation and Pt/WC-rods has a significantly higher electro-oxidation peak current than Pt/C. The calculated parameters of the electrochemical performance according to the Figure 2-10a are listed in Table 2-2. The current density of the methanol oxidation for Pt/WC rods reaches a value of 9.68 mA cm⁻²(*i*_a), which is much higher than that of Pt/C (3.97 mA cm⁻²). And the ratio of *i*_a to *i*_b of the Pt/WC rods also reaches a peak value of 2.42 by

compared with that of the Pt/C (1.73), this higher i_a / i_b of Pt/WC rods indicates better oxidation of methanol to carbon dioxide during the anodic scan.¹²⁸ This result is further supported by the CO-stripping experiments (Figure 2-11), where the onset potential for CO oxidation on Pt/WC rods is lower by 100mV compared to that of Pt/C. This demonstrates the improved CO electro-oxidation activity of the Pt/WC-rods catalyst. It is also observed that the pure WC-rods are inactive for the CO oxidation (Figure 2-11).

Figure 2-8 The TEM images of (a) Pt/WC-rods and (b) Pt/C. The inset images are the EDS patterns of Pt/ WC-rods and Pt/C, respectively.

Figure 2-9 XRD patterns of the as-prepared (a) Pt/C and (b) Pt/ WC-rods catalysts (○—WC, Δ —Pt).

The potential application of this material for hydrogen evolution reaction under acidic condition was also examined and compared to 20 wt.% Pt/C. Figure 2-10b clearly shows that WC nanorods itself exhibits certain activity towards hydrogen evolution reaction, which is slightly higher than Vulcan XC-72 carbon black. After the deposition of Pt nanoparticles, Pt/WC-rods again produces higher cathodic current of hydrogen evolution compared to Pt/C. Similar trends of catalytic activities of tungsten carbide supported Pt catalysts have been reported.⁵⁴⁻⁵⁶ Other than the intrinsic activity due to WC nanorods, a favorable interaction between tungsten carbides and Pt has been proposed for the observed high current density. This demonstrates the double role of nanostructured WC rods that works not only as the electrocatalyst but also as catalyst support.

Figure 2-10 Cyclic voltammograms of (a) methanol oxidation on WC nanorods, Pt/C and Pt/WC- rods in 0.5 mol L⁻¹ H₂SO₄ + 1 mol L⁻¹ CH₃OH solution, scan rate: 50 mV s⁻¹ and (b) hydrogen evolution reaction on WC naorods, Pt/C and Pt/WC-rods in 100 mM H₂SO₄, scan rate: 5 mV s⁻¹.

Figure 2-11 The CO-stripping curves on WC nanorods, Pt/C and Pt/WC-rods in a 0.5 mol L⁻¹ H₂SO₄ aqueous solution, scan rate: 15mV s⁻¹.

Finally we should admit that most techniques used to characterize the WC-nanorods point to the presence of residual carbon film on the surface of the samples. On one hand, the presence of surface carbon can improve the oxidation resistance of WC in an oxidizing atmosphere (e.g. air) under high temperature as pure WC can be oxidized at about 400 °C.¹²⁹ On the other hand, it was reported that the amorphous residual carbon have a negative effect on the catalytic activity of the pure WC toward methanol electro-oxidation. However, upon modification with Pt, the sample with carbon shows higher activities than that on pure WC,¹²⁷ which agrees with our experimental data. By now, a possible explanation for the improved activities could be that the surface carbon provides increased conductivity among WC crystallites, thus increasing the electro-catalytic activity. This effect is previously observed from the mesoporous WO₃ impregnated with carbon black for hydrogen oxidation activity. The addition of carbon into the WO₃ was found to decrease the electrical resistance of the samples.¹³⁰

Table 2-2 Electrochemical parameters of the catalysts in 0.5 M H₂SO₄ +1.0 M CH₃OH.

Sample name	$U_a(\text{V})$ [a]	$i_a(\text{mA cm}^{-2})$ [b]	i_a/i_b [c]
Pt/WC rods	0.65	9.68	2.42
Pt/C	0.65	3.97	1.73

[a] Potential of the methanol oxidation peak. [b] Anodic peak current density of the methanol oxidation. [c] Cathodic peak current density.

2.4 Conclusion

In summary, a unique nanorod-structured tungsten carbide material with high specific surface area of $198 \text{ m}^2 \text{ g}^{-1}$ was successfully synthesized by a template-free pseudomorphic carburization of carbon-coated WO₃ nanorod. Superior structural replication is achieved and the formation mechanism for the nanorod-structured WC material was proposed. This material was examined as electrocatalyst support for various reactions. An electro-catalyst composed of Pt nanoparticles supported on WC nanorods demonstrates higher electro-catalytic activity for methanol electro-oxidation, better tolerance to CO poisoning and superior performance for the cathodic electrocatalytic hydrogen evolution than a Pt/C catalyst. The material could become an alternative electro-catalyst for a range of reactions with potential to replace current Pt/C catalysts. Meanwhile, the potential influence of the presence of residual surface carbon was discussed. This work provides a novel thought to synthesize high surface area nanorod-structured tungsten carbide materials, thus offering great potential for a broad range of applications of these materials in the related reaction systems.

Chapter III Nano-Tungsten Carbide Decorated Graphene as Co-catalysts for Enhanced Hydrogen Evolution on Molybdenum Disulfide

(This chapter is reproduced with permission from Yan, Y.; Xia, B.; Qi, X.; Wang, H.; Xu, R.; Wang, J.-Y.; Zhang, H.; Wang, X.*, Nano-tungsten carbide decorated graphene as co-catalysts for enhanced hydrogen evolution on molybdenum disulfide. Chemical Communication, 2013, 49, 4884-4886. Copyright 2013, Royal Society of Chemistry)

3.1 Background Introduction

It is well known that conventional noble metal based electrocatalysts have very limited use in the water electrolysis due to their high cost and scarcity.^{55,131} Recently, several non-noble metal materials, such as transition-metal chalcogenides,¹⁵ carbides,^{35,132} and metal alloys¹³³ have been widely investigated as catalysts or supports for application in the hydrogen-evolving reaction. Particularly, two-dimensional molybdenum disulfide (MoS_2) with exposed edges was demonstrated as a very promising electrocatalyst for HER in recent years.¹³⁴⁻¹³⁶ To stabilize the layered structure of MoS_2 during the synthesis, various materials were employed as supports,¹³⁷⁻¹⁴³ in which hexagonal structured substrates, such as the reduced graphene oxide (RGO), were reported to be effective for the formation of MoS_2 nano-flakes.^{22,144} However, both RGO and MoS_2/RGO are prone to restacking during the hydrothermal process,^{145,146} which shadows its potential applications. Additionally, the most important inherent problem of using MoS_2 in any kind of electrochemical reaction is the extremely low conductivity between two

adjacent van der Waals bonded S-Mo-S sheets.¹¹ Although the electrical coupling to the underlying graphene sheets in an interconnected conducting network has been proven to provide rapid electron transport from the less-conducting MoS₂ to the electrode,^{22,147} if re-stacking happens, the re-stacked MoS₂ will exhibit low conductivity or the re-stacked RGO will possess low surface area and cannot afford uniform deposition of MoS₂ nanosheets.

With the objective of exploiting catalysts with high activity and stability, in this work, we propose a novel ternary composite based on two-dimensional MoS₂ supported on nanosized tungsten monocarbide (WC) decorated RGO which exhibits excellent HER catalytic performance. To our knowledge, such a ternary composite catalyst system has not been reported before for HER. To be specific, the shape-defined ternary MoS₂/WC/RGO composite is designed on the basis of the following considerations: (1) WC has high electrical conductivity (conductivity = 10^5 S cm^{-1} at 20 °C) among any interstitial carbides,^{148,149} and nano-sized WC can act as a good conductive dispersant which can effectively prevent GO and RGO from restacking and potentially improve the electrical conductivity, ion diffusion, and electrochemical properties of the final catalyst.¹⁵⁰⁻¹⁵² (2) Nano-sized WC materials have great potential to substitute noble-metals as catalysts or co-catalyst for HER, because of their Pt-like behavior.^{33,153} Its activity towards the cathodic HER has been widely reported.⁹⁴ (3) Highly active layered MoS₂ with increased edges can be obtained and maintained with the introduction of nanosized WC decorated RGO as support and co-catalyst. Synergistic effect may exist between MoS₂ and co-catalyst. (4) RGO can be obtained by solvothermal reaction of GO,¹⁵⁴ which is compatible with the solvothermal approach used for the synthesis of layered MoS₂. Therefore, Simultaneous formation of RGO and MoS₂ can be realized

in this one-pot process.

3.2 Experimental Section

3.2.1 Analytical Systems

In general, an electrochemical cell can be analyzed using an equivalent Randles circuit model.

For our system, it can be simplified as shown in the Figure 3-1. R_s represent the series resistance of the system. C_{dl} and R_{ct} represent the double layer capacitance and charge transfer resistance of the catalyst-electrolyte interface. R_s can be obtained from the impedance at the high frequencies of AC impedance spectroscopy, where the intercept of the semicircle on the real axis is assigned to the ohmic series resistance (R_s). iR correction to data with the series resistance (R_s) is performed by $\eta_{corr} = \eta - jR$.

Figure 3-1 Randles equivalent circuit model as applied for the electrochemical system of as-prepared catalysts supported on glass carbon (GC) electrode.

Figure 3-2 The Tafel plot of 70M/30(W-G) in the region of low current densities.

The onset potential for HER was decided from the semi-log (Tafel) plot. For example, the semi-log plot of 70M/30(W-G) in the region of low current densities as displayed in Figure 3-2 shows a linear relationship below -0.11V but starts to deviate above -0.10V. Therefore, -0.11 was chosen as the onset potential for 70M/30(W-G). The same method was applied on determining the overpotential for other samples in this thesis.¹⁵⁵

3.2.2 Synthesis of Nano-WC and GO

For a typical synthesis of nano-WC, a certain amount (50-80 mg) of as-prepared WO₃ nanorods as mentioned in section 2.2.1¹⁵⁶ was transferred into a tube furnace for reduction-carburization. The whole system was first purged with argon gas to completely remove any air before heating. The argon gas was then switched off and a mixture of CH₄ (20 mL min⁻¹) and H₂ (80 mL min⁻¹) was fed to the furnace. In the meantime, the furnace was first heated to 600 °C with a ramp rate of 5 °C min⁻¹ and then to 800 °C at a rate of 2 °C min⁻¹ and kept at this temperature for 3h. After that, the furnace was cooled down to a temperature of 700 °C. The supply of the carburizing agent was

switched off and argon was used to purge the furnace again. The furnace was further cooled down to room temperature.

Graphene oxide (GO) was synthesized from natural graphite powder by a modified Hummers' method.

3.2.3 Synthesis of Layered-MoS₂/WC/RGO Composite

Firstly, hybrid of WC/GO was obtained by adding as-prepared nano-WC to GO dispersed in 15 mL of Dimethylformamide (DMF) /H₂O (10:1) mixture. The mixture was sonicated in ice water bath for accumulated 30 min in a program of 1s on 1s off and then stirred at room temperature overnight. In order to investigate the effect of WC content in the WC/GO hybrid co-catalyst on the electrocatalytic hydrogen evolution activity of MoS₂, the weight percentages of WC to GO were varied from 0 to 100 (0, 20, 25, 33.3 and 100 wt.%) by varying the weight of nano-WC, the resulting samples were labeled as $xW(100-x)G$, where W and G refer to WC and graphene, respectively, and $x = 0, 20, 25, 33.3$ and 100, respectively.

Then, the composite samples were synthesized by a solvothermal method. (NH₄)₂MoS₄ (Sigma-Aldrich) was used as the MoS₂ source and was added to the 15 mL thoroughly mixed WC/GO hybrid GO. The mixture was sonicated at room temperature for approximately 20 min until a clear and homogeneous solution was achieved. Then, 0.2 ml of N₂H₄•H₂O was added and this obtained solution mixture was further sonicated for 10 min before transferred to a 50 mL Teflon-lined autoclave with a Teflon liner and kept at 210 °C for 18 h. The resulting precipitate was collected, washed thoroughly with distilled water followed by a rinse in ethanol, and then

dried at 60 °C for 12 h. Similarly, a series of the MoS₂/WC/RGO composites were prepared by using the x W (100- x) G as co-catalyst under the same conditions but replacing 25W75G with x W(100- x)G. Blank MoS₂ was also prepared following the same procedure as above except for the first addition of WC/GO hybrid co-catalyst. The detailed data are listed in Table 3-1. Moreover, in order to further investigate the content effect of the WC/RGO (25W75G) co-catalyst on the electrocatalytic hydrogen evolution activity of MoS₂, the weight ratio of 25W75G/MoS₂ was changed from 15 wt.% to 50 wt.% by varying the amount of 25W75G (see Table 3-2). For the purpose of comparison, 30%-25W75G/MoS₂ mixture was prepared by simple mechanical mixing of the pristine MoS₂ and 30 wt. % of 25W75G without the solvothermal process.

3.2.4 Characterization

All transmission electron microscopy (TEM), high-resolution (HR) TEM images and element mapping were taken from JEOL JEM 2100F, while the field emission scanning electron microscopy (FESEM) images and energy-dispersive X-ray spectroscopy (EDX) spectra were taken on a JEOL JSM 6700F. XRD analysis of different samples was carried out on a X-ray diffractometer (Bruker AXS D8, Cu K λ , λ = 1.5406 Å, 40 kV and 20 mA). Raman spectra were collected via a Renishaw Ramanscope in the backscattering configuration using 514 nm (2.41 eV) laser wavelengths over five random spots on the powers. X-ray photoelectron spectroscopy (XPS) spectrum was measured on a VG Escalab 250 spectrometer equipped with an Al anode (Al K α = 1846.6 eV). The specific surface area and pore size distribution of the samples were evaluated in

Autolab-6B (Quantachrome Instruments) using the liquid nitrogen adsorption/desorption method.

All the samples were degassed at 120 °C for 2 hours before the measurements. The BET surface area was determined using adsorption data in the relative pressure (P/P_0) range of 0.05-0.25. The desorption branch was used to determine the pore size distribution *via* the Barret-Joyner-Halender (BJH) method. The nitrogen adsorption volume at the relative pressure (P/P_0) of 0.95 was used to determine the single-point pore volume and the average pore size. Thermo gravimetric analysis (TGA) and the derived differential thermogravimetric (DTA) experiments were conducted on PerkinElmer Diamond TG/DTA equipment. The sample was first kept at 100 °C for 30 min to remove moisture and then was heated up to 1000 °C under high purity air flow (50 sccm) in a ramp of 10 °C min⁻¹ while its weight was monitored. Atomic force microscope (AFM) with a MPF3D microscope from Asylum Research was used in this paper.

3.2.5 Electrochemical Measurements

All electrochemical measurements were conducted on an Autolab PGSTAT302 potentiostat (Eco Chemie, Netherlands) in a three-electrode cell at room temperature. The reaction apparatus can be referred in section 2.2.1. Typically, a mixture containing 2.0 mg catalyst, 2.5 mL ethanol and 0.5 mL Nafion solution (0.05 wt. %, Gashub) was ultrasonicated for 15 min to obtain a well-dispersed ink. Then 20 µL of the catalyst ink (containing 13 µg of catalyst) was loaded onto a glassy carbon electrode of 4 mm in diameter (loading ~ 0.104 mg cm⁻²). The presented current density refers to the geometric surface area of the glass carbon electrode. Linear sweep voltammetry with scan rate of 5 mV s⁻¹ was conducted in 0.5 M H₂SO₄. The working electrodes

were mounted at a rotating disc electrode with a rotating rate of 1000 rpm during the test. In all experiments, the electrolyte solutions were purged with N₂ for 15 min prior to the experiments in order to remove oxygen. During the measurements, the headspace of the electrochemical cell was continuously purged with N₂. AC impedance measurements were carried out in the same configuration at $\eta = 0.15$ V from 10⁵-0.02 Hz with an AC voltage of 5 mV. Commercial Pt/C (20 wt. %) from E-TEK was measured as received. All the potentials reported in our manuscript were referenced to a reversible hydrogen electrode (RHE) by adding a value of (0.241+ 0.059 pH) V.

3.3 Results and Discussion

The as-prepared WC nanoparticles exhibit an interesting string-like morphology with average size of 35 nm as shown in Figure 3-3a. XRD pattern (Figure 3-3b) demonstrated the material was a hexagonal WC (PDF# 25-1047). From XPS spectrum of Figure 3-3c, the W4f_{7/2} and the W4f_{5/2} peaks corresponding to the binding energy of 31.6 and 33.7 eV are assigned to the tungsten carbide.¹⁵⁷ It also demonstrates the oxygen-modified W on the particle's surface at 35.7 and 37.2 eV which could come from the thin WO_x film that was formed in air at nanometer level, which is hardly detectable by XRD.¹⁵⁸ TG analysis (Figure 3-3d) of the nano-WC under air shows that there is a very slight weight loss (~ 0.5 %) during the heating range of 150-500 °C, which could be from undesirable amorphous carbon. Beyond this temperature range, an obvious weight increase caused by the oxidation of WC is observed from 500-600 °C, which is consistent with the reported fact that oxidation of WC starts at 500–600 °C.¹²⁹ The above results could indicate the relatively high purity of the nano-WC precursor.

Figure 3-3 FESEM images (a), XRD pattern (b), XPS W_{4f} spectra (c) and TGA-DSC (d) of the nano-WC obtained in the CH₄/H₂ mixtures at 800 °C for 3h.

The MoS₂/WC/RGO composite was synthesized by mixing the pre-synthesized WC nanoparticles with GO (see Figure 3-4) in a *N,N*-dimethylformamide (DMF)/water (10:1) mixture solution¹⁵⁹ via sonication, followed by a solvothermal reaction of (NH₄)₂MoS₄ and hydrazine in the co-catalyst solution at 210 °C for 18 h which led to the simultaneous reduction of (NH₄)₂MoS₄ precursor to MoS₂ and GO to RGO by hydrazine, forming the MoS₂/WC/RGO composite (see Figure 3-5). Various weight ratios were adopted for the synthesis of the ternary composites (for details, see Table 3-1 and Table 3-2). A typical one contains 70% of MoS₂ and 30% of co-catalyst consisting of WC (25%) and RGO (75%), which is denoted as 70 M/30(W-G).

Figure 3-4 AFM image (a), Raman spectrum (b) and XRD pattern (c) of the prepared graphene oxide sheets as starting material.

Figure 3-5 Schematic illustration of the synthesis of MoS₂/WC/RGO composite.

Table 3-1 Effects of WC/RGO co-catalyst content in the MoS₂/WC/RGO electrocatalysts on the HER activity according to polarization measurements.

Sample[a]	Composition	Tafel slope [mV / decade][b]	Onset potential [V] [c]
100M/0(W-G)	100MoS ₂ +0(WC/RGO)	106	-0.14
85M/15(W-G)	85MoS ₂ +15(WC/RGO)	74	-0.13
80M/20(W-G)	80MoS ₂ +20(WC/RGO)	78	-0.13
70M/30(W-G)	70MoS ₂ +30(WC/RGO)	41	-0.11
60M/40(W-G)	60MoS ₂ +40(WC/RGO)	60	-0.15
50M/50(W-G)	50MoS ₂ +50(WC/RGO)	51	-0.16

[a] W-G samples contains 25%WC and 75% of RGO in the co-catalyst. [b] Calculated from the linear portion of the plot in the potential range of 150 mV-200 mV. [c] The onset potential at which the hydrogen evolution occurred measured versus RHE.

Table 3-2 Effects of WC/RGO weight ratio on the HER activity according to polarization measurements.

Sample[a]	Composition	Tafel slop [mV / decade][b]	Onset potential [V] [c]
M/0W-100G	MoS ₂ +RGO	47	-0.13
M/33.3W-66.7G	MoS ₂ +33.3WC-66.7RGO	47	-0.12
M/25W-75G	MoS ₂ +25WC-75RGO	41	-0.11
M/20W-80G	MoS ₂ +20WC-80RGO	45	-0.13
M/100W-0G	MoS ₂ +WC	54	-0.12

[a]All composite samples contain 70% of MoS₂ and 30% of co-catalyst in the composite electrocatalyst. [b] Calculated from the linear portion of the plot in the potential range of 150 mV-200 mV. [c] The onset potential at which the hydrogen evolution occurred measured versus RHE.

The field emission scanning electron microscopy (FESEM) image (Figure 3-6a) clearly shows

that the resulting MoS₂/WC/RGO composite has a morphology of layered MoS₂ uniformly supported on the nano-WC decorated RGO nanosheet, in which the large transparent area together with uniformly WC nanoparticles can be also observed. TEM observation was carried out to further investigate this MoS₂ nanosheet on RGO decorated with WC nanoparticles structure and the MoS₂ nanosheet has a length of about 100 nm which agree with SEM observation (Figure 3-6b). High-resolution (HR) TEM image (Figure 3-6c) displays the presence of two structures in close proximity with an interlayer spacing of ca. 0.62 nm and 0.28 nm (Figure 3-6c inset, up-right corner), which correspond to the (002) and (001) plane of hexagonal MoS₂¹⁴⁰ and WC,¹¹⁵ respectively. Also, Figure 1c inset (lower left corner) revealed the hexagonal atomic lattices of the MoS₂ basal planes on the RGO surface and the lattice spacing of 0.27 nm matches the (100) spacing of MoS₂.^{22,140,144} More interesting, besides its deposition on RGO nanosheets, some MoS₂ nanosheets also deposited around nano-WC. Figure 3-6d further confirmed the uniform distribution of MoS₂ on WC-decorated RGO by energy dispersive X-ray spectroscopy (EDX) mapping of the four components in a selected-area of composite (Figure 3-7). Therefore, the nano-WC decorated RGO hybrid can be served as a good support for the deposition and uniform dispersion of layered MoS₂, and thus the formation of MoS₂/WC/RGO composite with the close contact between MoS₂, WC and RGO components could be realized in this one-pot solvothermal process. This contact would be beneficial for the subsequent electrocatalytic application with their interconnection and potential synergetic effect.

Figure 3-6 FESEM image (a) and high-resolution (HR) TEM images (b, c) of MoS₂/WC/RGO composite. The insets of Figure 2c show the lattice fringes of MoS₂ and WC in the enlarged images of the selected-area.(d) Elemental mapping analysis.

Figure 3-7 TEM image of the selected area of the MoS₂/WC/RGO composite for element mapping.

Figure 3-8 Component analysis of MoS₂/WC/RGO composites of (a) XRD patterns, the inset is the enlarged pattern of MoS₂/WC in the degree about 14.4 °. (b) Raman spectra and (c) XPS spectrum, the inset is the high resolution Mo 3d spectrum. (d) N₂ adsorption/desorption isotherms for MoS₂/RGO and MoS₂/WC/RGO composite. The inset is the corresponding pore diameter distribution.

The MoS₂/WC/RGO composite was characterized by X-ray diffraction (XRD). Most of the diffraction peaks (Figure 3-8a) match the hexagonal phase of WC (PDF# 51-0939). The very weak peaks of MoS₂ may indicate its small size and well dispersion due to the use of WC-RGO support (inset of Figure 3-8a). Raman spectroscopy of MoS₂/WC/RGO composite in Figure 3-8b revealed the characteristic peaks¹⁶⁰ of MoS₂ at 373 and 400 cm⁻¹ and nano-WC at 267, 716 and

805 cm^{-1} (Figure 3-9). The X-ray photoelectron spectroscopy (XPS) shows the peaks of Mo, S, W, C and O elements, and the atomic ratio of Mo/S is approximately 1:2 (Figure 3-8c). The high-resolution XPS spectrum confirmed the reduction of Mo (VI) to Mo (IV) (inset of Figure 3-8c).¹⁶¹ In addition, the high-resolution XPS spectrum of C 1s (Figure 3-10) further proved the reduction of GO to RGO. It agreed with XRD result with the absence of C (002) peak at about 12° and presence of C (002) at about 25° . Finally, the oxygen peak observed should result from the residual oxygen-functionalized groups from the reduced GO¹⁶² and oxygen-modified W at the nanometer level due to air exposure.¹⁵⁸

Figure 3-9 Raman spectra of self-prepared WC and commercial WC. The characteristic peaks of the as-prepared WC are consistent with the commercial one.

Nitrogen adsorption/desorption experiments were carried out to analyze the porosity and pore size distribution in the composite samples (Figure 3-8d). When RGO alone is used as support to deposit MoS_2 , the 70M/30G sample exhibits a Brunauer–Emmett–Teller (BET) area of only $9 \text{ m}^2 \text{ g}^{-1}$ with an average pore size of 4.97 nm. However, with the addition of nano-WC (BET area of 10

$\text{m}^2 \text{g}^{-1}$, Figure 3-11) as dispersant to form the ternary composite, the BET surface area of 70M/30(W-G) reaches $116 \text{ m}^2 \text{g}^{-1}$, which is almost 13 times of that of 70M/30G. Additionally, the average pore size increases to about 9.56 nm with a wide pore size distribution ranging from 2 to 100 nm. It indicated that the introduction of nano-WC can effectively prevent the restacking of RGO and would create large amount of voids between RGO layers (Figure 3-6 and 3-12), and thus provide much more accessible area for the deposition of MoS_2 nanosheets. The increased pore size of 70M/30(W-G) would also be helpful for the subsequent catalytic HER process with improved mass transfer. However, with the use of RGO as support only (Sample 70M/30G), large amounts of aggregated MoS_2 nanoparticles were observed on the RGO sheets due to the low surface area of the RGO as a result of the re-stacking, while no MoS_2 particles can be observed when nano-WC decorated RGO was used as the support, suggesting that they may exist as well-dispersed layered structure (Figure 3-13).

Figure 3-10 High-resolution XPS spectra of $\text{MoS}_2/\text{WC}/\text{RGO}$ composites. (a) C 1s, (b) S 2p and

(c) W 4f spectrum.

Figure 3-11 N₂ adsorption/desorption isotherms and the corresponding BJH pore-size distribution (inset) of nano-WC. The pore diameter distribution was determined from the desorption branch.

Figure 3-12 FESEM images of (a) nano-WC/RGO, (b) MoS₂/nano-WC hybrid.

The HER electrocatalytic activities of MoS₂/WC/RGO composite was investigated in a rotating disk electrode system in 0.5 M H₂SO₄ solution by employing a typical three-electrode setup. As shown in Figure 3-14a, the polarization curve (with correction for ohmic potential drop (iR) losses, referring to 3.2.1) recorded with 70M/30(W-G) showed an onset potential of -0.11 V versus a reversible hydrogen electrode (RHE) for the HER (determined from the semi-log plot as shown

in Figure 3-2), beyond which the cathodic current rose rapidly under more negative potential. In sharp contrast, either MoS₂ particles or 70M/30W hybrid showed little HER activity with a small current density. A Tafel curve is normally used to evaluate the efficiency of the catalytic reaction. Figure 3-14b shows that the Tafel plot of 70M/30(W-G) yielded Tafel slope of $\sim 41 \text{ mV dec}^{-1}$, which was much smaller than that of the MoS₂ alone ($\sim 106 \text{ mV dec}^{-1}$) but comparable with the Tafel slope ($\sim 30 \text{ mV dec}^{-1}$) of a commercial Pt catalyst (E-TEK 20% Pt/XC-72). This observed Tafel slope of 70M/30(W-G) in current work demonstrated that the HER follows the Volmer-Heyrovsky mechanism and the rate determining step is the electrochemical desorption of Hads.¹⁸

Figure 3-13 FESEM images and EDS spectra of MoS₂/WC/RGO composites (70M/30(W-G)) (a, c) and MoS₂/RGO hybrid (70M/30G) (b, d), respectively.

Figure 3-14 (a) Polarization curves, (b) Tafel plots, (c) AC impedance spectroscopic at overpotential of 0.15 V, and (d) stability tests for the MoS₂/WC/RGO electrocatalyst.

Three main reasons were proposed for the high HER activity of MoS₂/WC/RGO composite electrocatalysts. First is the “dual-catalyst” effect generated by the close neighborhood of the MoS₂, WC and RGO (Figure 3-15). The obtained MoS₂/WC/RGO electrocatalyst is a combination of layered MoS₂/nano-WC with layered MoS₂/RGO, which exhibit higher HER activity than a simple physical mixture of WC/RGO (30%) and MoS₂ (70%) (Figure 3-16). This fact demonstrates that a simple mechanical mixing cannot create effective interfacial contacts among the ternary components. Meanwhile, the synergistic effect of nano-WC decorated RGO sheets as co-catalysts on the improved HER activity of MoS₂ was observed experimentally in this work. As shown in Figure 3-17a, the composite electrocatalysts with the use of either RGO or WC as support show much improved HER activity in comparison to the MoS₂ alone, Though WC

has a much lower surface area, but nano-sized WC itself has certain HER activity (Figure 3-17b).

When both RGO and WC are incorporated as co-catalytic support, the resulting ternary catalysts show better activity than single supported one, since the WC decorated RGO co-catalyst provides an excellent substrate for the formation and stabilization of the layered MoS_2 with increased abundance of exposed edges that could serve as active catalytic sites for the HER.

Figure 3-15 Schematic illustration of the MoS_2 /WC/RGO composite on HER with dual-catalyst effect.

The second factor is the promoted electron transfer rate of the composition (70M/30(W-G)) with the presence of the co-catalyst. Due to the high electrical conductivity, the nano-WC in the co-catalyst could serve as a good conductive dispersant for enhanced electron transfer rate. AC impedance measurement was performed at overpotential of 0.15 V to prove this effect (Figure 3-14c). The HER charge transfer resistance (R_{ct}) in the case of 70M/30(W-G) is the smallest among the three catalysts at the investigated potential. It indicated that the incorporation of nano-WC could greatly improve electron transport and reaction kinetics during the HER. Finally, large amounts of the void created by the addition of nano-WC into the hybrid (70M/30G) may also contribute a lot to the enhanced hydrogen evolution activity by facilitating the ion exchange

and mass transfer.

The catalytic stability would be another important issues in the practical HER application. The stability of the 70M/30(W-G) composite electrocatalyst was conducted for 2000 potential cycles. As shown in Figure 3-14d, the catalyst after 2000 cycles retained a similar polarization curve to initial one, indicating that the 70M/30(W-G) composite catalyst maintained its unique stable catalytic HER performance in an acidic environment because both WC and RGO have good stability in such an environment.^{157,163}

3.4 Conclusion

In conclusion, a novel MoS₂ supported on nano-WC decorated RGO hydrogen-evolving electrocatalyst was successfully prepared in one-pot sovothermal process. The resultant MoS₂/WC/RGO composite with highly exposed reactive sites (layered MoS₂) stabilized by the binary support showed an enhanced electrocatalytic activity for HER process because of the synergism between the co-catalyst and high conductivity of the ternary composite. This study highlights the importance of using highly conductive WC as an effective co-catalytic support combined with the layered composite material for electrochemical water splitting, which is a valuable attempt for further development of the related composite materials to substitute noble-metal electrocatalysts for HER.

Figure 3-16 (a) FESEM image of the MoS₂ (70%) particles physically mixed with WC/RGO (30%) and (b) the corresponding polarization curve.

Figure 3-17 Polarization curve of (a) MoS₂/WC/RGO composites with different WC/RGO ratio in the WC/RGO co-catalyst and (b) nano-WC (MoS₂ was used as a reference).

Chapter IV Facile Synthesis of Low Crystalline MoS₂

Nanosheet-coated CNTs for Enhanced Hydrogen Evolution Reaction

(This chapter is reproduced with permission from Yan, Y.; Ge, X.; Liu, Z.; Wang, J.-Y.; Lee, J.-M.; Wang, X.*, Facile synthesis of low crystalline MoS₂ nanosheet-coated CNTs for enhanced hydrogen evolution reaction. Nanoscale, 2013, 5, 7768-7771. Copyright 2013, Royal Society of Chemistry)

4.1 Background and Introduction

Studies on molybdenum sulfides catalysts have indicated that nanometer-scaled molybdenum disulfide (MoS₂) with exposed edges has been identified as a promising electrocatalyst for the HER due to their low cost, high chemical stability and excellent electrocatalytic properties.¹⁶⁴ Increasing the number of the exposed active sites in the edges, as well as the improvement of the electrical conduction of MoS₂ material by choosing suitable substrates or supports, are crucial to effectively improve the HER electrocatalytic efficiency.¹¹ This is well demonstrated by a recent work where the reduced graphene oxide sheets serve the function of hosting MoS₂ to increase exposed edges and enhance the conductance of the hybrids.²² Another attempt has shown that controlling the surface structure of MoS₂ at the atomic scale can preferentially expose edge sites.²¹ In addition, some recent works have reported that amorphous molybdenum sulfide, MoS₃ and MoS_x prepared by electrochemical method, wet chemistry process or the thermolysis of ammonium thiomolybdates show high catalytic activity toward HER.¹⁶⁵⁻¹⁶⁷ Previously, CNT-

MoS₂ hybrid materials by solvothermal synthesis,¹⁶⁸ glucose or L-cysteine assisted growth of MoS₂ nanosheets on the CNT backbone by a hydrothermal method^{169,170} have been reported.

Herein, we apply a facile solvothermal method to produce a networked nanocomposite consisting of low crystalline MoS₂ coated on carbon nanotubes (CNTs) for HER. To the best of our knowledge, the nano-composite of MoS₂ nanosheet-coated CNTs with similar structures has not previously been applied in the field of HER.

4.2 Experimental Section

4.2.1 Calculation of Active Sites and Turnover Frequency (TOF)

Figure 4-1 Cyclic voltammograms of the MoS₂/CNTs and MoS₂ catalysts recorded in 0.5M

H₂SO₄; scan rate: 50 mVs⁻¹.

The absolute components of voltammetric charges (cathodic and anodic) can be obtained from CV, Figure 4-1 above. Assuming a one electron redox process, the total amount charge was divided by two. The value was further divided by the Faraday constant to get the number of active sites of the film.

When the number of active sites is obtained, the per-site turnover frequencies (in s^{-1}) were calculated with the following equation:

$$\text{TOF} = \frac{I}{Fn} \frac{1}{2}$$

I —Current (in A) during the linear sweep measurement.

F —Farady constant (in C mol^{-1}).

n —Number of active sites (in mol).

The factor $1/2$ in the equation represents that two electrons are required to form one hydrogen molecule from two protons ($2\text{H}^+ + 2e^- = \text{H}_2$).

4.2.2 Synthesis of MoS_2/CNTs

In a typical synthesis of MoS_2/CNTs composite, acid-treated CNTs (4 mg) were dispersed in N,N -dimethylformamide (DMF, 15mL, Sigma-Aldrich) by ultrasonication for 30 min, and then 15 mg ammonium thiomolybdate ($(\text{NH}_4)_2\text{MoS}_4$, 15 mg, Sigama-Aldrich) was added and ultrasonically dispersed for another 30min in the DMF solution. Then the mixture was transferred into an autoclave, and maintained at $210\text{ }^\circ\text{C}$ for 18 h, and was cooled to room temperature naturally. The black precipitate was collected by centrifugation and washed subsequently with DI-water and anhydrous ethanol several times, and finally dried at $60\text{ }^\circ\text{C}$ for 24 h. The preparation process of bare MoS_2 and the CNTs connected MoS_2 particles was similar to that described above, but without adding CNTs and replacing the DMF with H_2O . The high-crystallinity MoS_2/CNTs was prepared by further treating the as-prepared MoS_2/CNTs materials at $800\text{ }^\circ\text{C}$ in an atmosphere of H_2 balanced by N_2 for 2 h ($1\text{ }^\circ\text{C min}^{-1}$).

4.2.3 Characterization

All transmission electron microscopy (TEM), high-resolution (HR) TEM images and element mapping were taken from JEOL JEM 2100F, while the field emission scanning electron microscopy (FESEM) images and energy-dispersive X-ray spectroscopy (EDX) spectra were taken on a JEOL JSM 6700F. XRD analysis of different samples was carried out on a X-ray diffractometer (Bruker AXS D8, Cu K λ , $\lambda = 1.5406 \text{ \AA}$, 40 kV and 20 mA). Raman spectra were collected via a Renishaw Ramanscope in the backscattering configuration using 514 nm (2.41 eV) laser wavelengths over five random spots on the powers. X-ray photoelectron spectroscopy (XPS) spectrum was measured on a VG Escalab 250 spectrometer equipped with an Al anode (Al K $\alpha = 1846.6 \text{ eV}$).

4.2.4 Electrochemical Measurements

All electrochemical measurements were conducted on an Autolab PGSTAT302 potentiostat (Eco Chemie, Netherlands) in a three-electrode cell at room temperature. The reaction apparatus can be referred in section 2.2.1. Typically, a mixture containing 2.0 mg catalyst, 2.5 mL ethanol and 0.5 mL Nafion solution (0.05 wt. %, Gashub) was ultrasonicated for 15 min to obtain a well-dispersed ink. Then 40 μL of the catalyst ink (containing 26.6 μg of catalyst) was loaded onto a glassy carbon electrode of 5 mm in diameter (loading $\sim 0.136 \text{ mg cm}^{-2}$). The presented current density refers to the geometric surface area of the glass carbon electrode. Linear sweep voltammetry with scan rate of 5 mV s^{-1} was conducted in 0.5 M H_2SO_4 . The working electrodes were mounted at a rotating disc electrode with a rotating rate of 1000 rpm during the test. In all

experiments, the electrolyte solutions were purged with N₂ for 15 min prior to the experiments in order to remove oxygen. During the measurements, the headspace of the electrochemical cell was continuously purged with N₂. AC impedance measurements were carried out in the same configuration at $\eta = 0.15$ V from 10⁵-0.02 Hz with an AC voltage of 5 mV. All the potentials reported in our manuscript were referenced to a reversible hydrogen electrode (RHE) by adding a value of (0.241+ 0.059 pH) V.

4.3 Results and Discussion

The synthesis follows a facile one-step solvothermal approach. Briefly, 4mg of the acid-treated single wall CNTs and 15mg ammonium thiomolybdate ((NH₄)₂MoS₄) were dissolved in 15mL *N,N*-dimethylformamide (DMF). Then the mixture was well dispersed by sonication for 30 min, transferred into an autoclave, and reacted at 210 °C for 18 h. The resulting products were collected by centrifugation and washed subsequently with DI-water and anhydrous ethanol several times. The final products were obtained after drying at 60 °C for 24 h (see 4.2.2 for details).

Figure 4-2a show the morphology of the as-prepared MoS₂/CNTs observed from scanning electron microscopy (SEM), which has a one-dimensional network structure with a diameter of ~100nm, where the sheet-like MoS₂ subunits are uniformly coated on the CNTs (Figure 4-3). A further observation by transmission electron microscopy (TEM) indicates that the MoS₂ in the composites are in the form of stacked nanosheets uniformly grown on the outer surface of the CNTs, thus CNTs with a 'hairy' structure are formed (Figure 4-2b). It can be observed that the

MoS₂ sheets are composed of few MoS₂ layers (6 to 10 layers) with an interlayer spacing of 0.65 nm (inset of Figure 4-2c). The energy-dispersive X-ray (EDX) mapping analysis further confirms the good-distribution of MoS₂ nanosheets on the CNTs (Figure 4-4).

Figure 4-2 (a) FESEM image and (b,c) TEM images of MoS₂/CNTs composite. The inset shows a high-resolution (HR) TEM image of MoS₂ nanosheets; (d) FESEM image of the MoS₂ nanospheres without CNTs.

Figure 4-3 SEM image of the acid-treated CNTs.

Figure 4-4 TEM image of the selected area of the MoS₂/CNTs composite for element mapping, showing the uniform distribution of Mo (blue), S (green) on the CNTs.

Additionally, we also investigated the effect of CNTs and DMF on the morphology of the products. As shown in Figure 4-2d, the sample prepared without acid-treated CNTs is composed of MoS₂ nanospheres with sheet-like subunits. It is also important to note that replacing DMF

with water as solvent affords only a mixture of MoS₂ nano-particles and CNTs (Figure 4-5), in which the CNTs just serve as connecting wires for the aggregated MoS₂ particles. Before, it was reported that rGO sheets can serve a good substrate for the interactions between functional groups on GO sheets and Mo precursors in the DMF.²² In current work, the acid-treated CNTs serve as roles similar to rGO. The drastic morphological difference highlights the important role of DMF as a solvent for mediating the formation of MoS₂ nanosheets,¹⁷¹ while in this solvent environment, the acid-treated CNTs acted as a binder itself as well as a substrate to facilitate the growth of the MoS₂ sheets with uniform coverage along the longitudinal axis.

Figure 4-5 SEM image of the MoS₂/CNTs hybrid by replacing the DMF with water as solvent.

Figure 4-6a shows the X-ray diffraction (XRD) patterns of the as-prepared MoS₂/CNTs composite and bare MoS₂ without CNTs. The peaks at 25.2 ° and 44.6 ° are indexed to (002) and (100) planes of CNTs in the MoS₂/CNTs hybrid. In comparison to the bare MoS₂, the (002) peak of MoS₂ cannot be found in the composite, instead only two XRD peaks attributed to the (100) and (110) planes of MoS₂ could be observed. The absence of (002) diffraction peak indicates the restacking of MoS₂ nanosheets in the composite is not significant.

Raman spectroscopy was employed to further investigate the MoS₂ structure, where the appearance of two peaks at 380.0 and 407.6 cm⁻¹ corresponds to the E_{2g}¹ and A_{1g} vibrational modes of hexagonal MoS₂, respectively (Figure 4-6b). It is known that the E_{2g}¹ and A_{1g} correlate with atom displacements that are orthogonal to each other, in which A_{1g} involves out-of-layer symmetric displacements of sulfur atoms along the c-axis while the E_{2g}¹ involves in-layer symmetric displacements of Mo and S atoms (inset Figure 4-6b).¹⁷² The relatively larger E_{2g}¹ peak width and the weaker intensity suggest that the crystal structure of MoS₂ may contain substantial defect sites.¹³⁸ At these sites, it is hypothesized that there are many coordinately and structurally unsaturated sulfur atoms, which could contribute a lot to the enhanced HER activity.¹⁰

Figure 4-6 (a) XRD patterns of the MoS₂/CNTs and bare MoS₂. (b) Raman spectrum of the E_{2g}¹ and A_{1g} vibrational modes. The inset shows the atomic displacement of the E_{2g}¹ and A_{1g} vibrational modes in bulk MoS₂ as viewed along the [1000] direction.

Figure 4-7 (a) XPS survey spectra and (b-d) high-resolution XPS spectra of MoS₂/CNTs composites.

The chemical states of Mo, S and C in the as-prepared MoS₂/CNTs were investigated by the X-ray photoelectron spectroscopy (XPS). Figure 4-7a confirms the element composition of MoS₂/CNTs with the peaks of Mo, S, C and O elements. The high-resolution XPS spectra (Figure 4-7b) show that the C1s core level can be deconvoluted mainly into two peaks. The main peak at 284.6 eV is assigned to sp²- hybridized graphite-like carbon atom whereas the peak around 286.0 eV is attributed to the carbon atom bound to one oxygen atom, which are consistent with the reported values for acid-treated CNTs.¹⁷³ As shown in Figure 4-7c, the strongest Mo signal arises from 3d_{5/2}= 229.0 eV characteristic of a +4 oxidation state; shoulders corresponding to higher +6

oxidation states remain, probably due to the formation of MoO₃ in the process of the catalyst preparation and exposure to air.¹⁷⁴ This is further confirmed by the presence of a primarily single doublet in the S 2p region (Figure 4-7d) at lower binding energies, which corresponds to the S 2p_{3/2} and 2p_{1/2} orbitals of divalent surfide ions (S²⁻) at 161.71 and 162.74 eV, respectively. Additionally, the S 2p_{1/2} and 2p_{3/2} energies at 164.02 and 163.17 eV suggest the existence of bridging S₂²⁻.¹⁷⁵ Although it is difficult to exclusively identify the ratio between these sulfur species due to their similar binding energies, the presence of these higher energy peaks indicate that the active HER species are likely related to those species,¹⁶⁶ in good agreement with the Raman results of the existence of the unsaturated sulfur atoms. Finally, the analysis of the Mo (3d) and S (2p) peak intensities yields an S/Mo atomic ratio of 2.05 - 2.15, suggesting that the structure is close to MoS₂. It can also be inferred that the calculated weight content of the MoS₂ in the hybrid is approximately 70 %.

The HER electrocatalytic activities of MoS₂/CNTs composite was investigated in a rotating disk electrode system in 0.5M H₂SO₄ solution by employing a typical three-electrode setup. Figure 4-8a shows the polarization curves (with correction for ohmic potential drop (*iR*) losses, referring to 3.2.1& Figure 4-9) for the as-prepared catalysts. It is observed that the MoS₂/CNTs exhibits excellent activity for the HER with a low onset potential of ~0.09 V (determined from the semi-log plot, referring to 3.2.1), which surpasses the activity seen for bare MoS₂. A Tafel slope is normally used to evaluate the activity of the catalyst. The inset of Figure 4-8a show Tafel slope of 44.6 and 56.4 mV dec⁻¹ for MoS₂/CNTs and MoS₂, respectively. From the classical theory of hydrogen generation, a Tafel slope of around 40 mV dec⁻¹ indicates the rate determining step is

the electrochemical desorption of H_{ads} and H_3O^+ to form hydrogen and the HER occurs through a Volmer-Heyrovsky mechanism. In this work, the enhanced electrical conductivity could contribute a lot to the higher HER efficiency of $MoS_2/CNTs$ hybrid by comparison with bare MoS_2 because the presence of CNTs in the composite lead rapid electron transport from the less-conducting MoS_2 nanosheets to the electrode (see schematic illustration of Figure 4-10). AC impedance was then performed to prove this. As shown in Figure 4-8b, with the use of the same amount of catalyst, the $MoS_2/CNTs$ exhibits a lower charge-transfer impedance (R_{ct}) of $\sim 90 \Omega$ than that of the bare MoS_2 ($R_{ct} \approx 160 \Omega$). This reduced R_{ct} could afford much faster HER kinetics with the $MoS_2/CNTs$ hybrid catalyst.

Figure 4-8 (a) Polarization curves (the inset shows the corresponding Tafel plots), (b) AC impedance spectroscopy at overpotential of 0.15 V, (c) Calculated turnover frequencies and (d) stability tests for the $MoS_2/CNTs$ electrocatalyst.

On the other hand, it is noted that highly crystalline MoS₂/CNTs catalyst obtained at 800 °C shows very low HER activity with much higher Tafel slope ($\sim 107.4 \text{ mV dec}^{-1}$) than that of the as-prepared MoS₂/CNTs (Figure 4-11). The XRD pattern for the annealed sample (Figure 4-12) shows sharp peaks with very high intensity in comparison with the as-prepared MoS₂/CNTs, and especially the strong (002) peak at $2\theta = 14.4$ signifies a well-stacked layered structure, which demonstrates the high crystallinity of MoS₂ in the hybrid after annealing. Moreover, the XPS spectra of the S 2p region (Figure 4-13) exhibits a single doublet consistent with a -2 oxidation state for sulphur and no shoulder peak at higher energy (bridging S₂²⁻) is observed for the annealed sample. Additionally, as stated earlier, the Raman analysis reveals that the freshly-prepared MoS₂/CNT exhibits site defects which probably stemmed from the unsaturated sulfur atoms. All these evidences imply that the higher HER activity for the as-prepared MoS₂/CNTs is likely related to those defect sites or the bridging S₂²⁻ existent in amorphous state in the MoS₂ structure, which is in good agreement with previous report.¹⁶⁶

To estimate the intrinsic activity, the turnover frequency (TOF) is then calculated by quantifying the active sites through electrochemical approach.²³ Assuming a one-electron process for both reduction and oxidation, the upper limit of the active MoS₂ sites could be calculated for each catalyst from cyclic voltammograms (referring 4.2.1 & Figure 4-1). Figure 4-8c shows the polarization curves normalized by the active sites, which are expressed in term of TOF (referring 4.2.1 for details). When $\eta > 0.1 \text{ V}$, the distinct TOFs between the two catalysts probably reveal the improved substrate diffusion of MoS₂/CNTs composite catalyst because of the incorporation of CNTs. The TOF numbers per active site for the as-prepared MoS₂/CNTs is calculated to be

0.06 s⁻¹ at $\eta = 0$ mV (vs. 0.05 s⁻¹ for MoS₂). This TOF is lower than that of platinum (TOF=0.9 s⁻¹ at $\eta = 0$ mV and pH= 0).¹⁵ There is still room to improve the inherent activity by tuning the electronic structure of the edge to increase the bond strength of the adsorbed H.¹⁵

To assess the long-term stability of the MoS₂/CNTs catalyst, potential sweeps were conducted from - 0.3 to + 0.2 V vs. RHE for 2000 cycles. As shown in Figure 4-8d, the catalyst retained a polarization curve similar to the initial one after the continuous long-time cycling in an acidic environment.

4.4 Conclusion

In conclusion, a networked MoS₂/CNTs nanocomposite with high catalytic activity towards HER have been synthesized by a facile solvothermal method, in which MoS₂ nanosheets are uniformly coated on carbon nanotubes (CNTs). It is found that both acid-treated CNTs and DMF play a critical role in the formation of this unique structure, and the low crystalline MoS₂ is identified as the actual catalyst for the enhanced HER due to the high number of exposed sites. This study shows that the synthesis of low crystalline MoS₂ supported on inexpensive and conductive CNTs is feasible and has a great potential for electrocatalytic hydrogen evolution.

Figure 4-9 AC impedance spectroscopy of MoS₂/CNTs and bare MoS₂ performed in the same configuration at $\eta = 0.15\text{V}$ from $10^6 - 0.02\text{ Hz}$ with an AC voltage of 5 mV.

Figure 4-10 Schematic illustration of the electrocatalytic mechanism of HER on MoS₂/CNTs.

Figure 4-11 The polarization curves and the Tafel slop (inset) of as-prepared MoS₂/CNTs and MoS₂/CNTs annealed at 800°C.

Figure 4-12 XRD pattern of the MoS₂/CNTs composite after annealed at 800°C for 2h.

Figure 4-13 (a) XPS survey spectra and (b-d) high-resolution XPS spectra of annealed

MoS_2/CNTs composites.

Chapter V Ultrathin MoS₂ Nanoplates with Rich Active Sites as Highly Efficient Catalyst for Hydrogen Evolution

(This chapter is reproduced with permission from Yan, Y.; Xia, B.; Ge, X.; Liu, Z.; Wang, J.-Y.; Wang, X.*, Ultrathin MoS₂ Nanoplates with Rich Active Sites as Highly Efficient Catalyst for Hydrogen Evolution. ACS Applied Materials & Interfaces, 2013, 5, 12794-12798. Copyright 2013, American Chemical Society)

5.1 Background and Introduction

Over the past few years, molybdenum disulfide (MoS₂) has been extensively studied as the catalysts for HER owing to their special structures and electronic properties.^{86,176,177} Recent studies have shown the HER activity of MoS₂ is highly dependent on the exposed edges.^{171,178} Thus, designing MoS₂ nanosheets with more edge sites is one effective strategy to enhance activity and a lot of efforts have been focused on achieving this.^{20,179,180}

As shown in our earlier chapters, two kinds of layered MoS₂ composites have been developed. It is found that the S content in MoS₂ also plays an important role in HER process, as indicated by the traditional hydrodesulphurization (HDS) process.^{181,182} The unsaturated sulfur atoms on the surface of MoS₂ materials can engage the discharge reaction and easily form S-H bonds, thus leading to hydrogen formation eventually. For example, Hu's group reported that amorphous MoS₃ particles, which contain catalytically active S₂²⁻ ligands, show superior catalytic activity towards HER.¹⁶⁵ This result was further validated by Li's group recently,¹⁶⁶ where the higher HER efficiency of the MoS_x materials is related to the presence of bridging S₂²⁻ or apical S²⁻ in

amorphous states. However, the amorphous MoS₂ structure may lead to relatively poor electrochemical stability in the acid electrolyte and most of the reported methods involve complicated manipulation. Therefore, it is still a big challenge to prepare MoS₂ nanocatalysts with high HER activity and good stability by a facile method.

Herein, a well-defined MoS₂ nanocatalysts with abundant active unsaturated S atoms is developed by a novel and facile solvent-dependent method. This highly tunable synthesis offers three advantages: (i) the ultrathin MoS₂ nanoplates are rich with basal edges, thus increasing the density of active sites; (ii) the active S ligands can be introduced into the ultrathin plate-like MoS₂ structure, leading to a more efficient MoS₂ catalyst for HER than simple MoS₂ and (iii) the direct growth of the ultrathin MoS₂ nanoplates by a solvent dependent method with single source precursor is very facile and controllable. The obtained MoS₂ nanoplates have been characterized by various techniques. As expected, the ultrathin MoS₂ nanoplates show outstanding catalytic performance for HER. Moreover, the growth mechanism of ultrathin MoS₂ nanoplates is also first explained.

5.2 Experimental Section

5.2.1 Synthesis of Ultrathin MoS₂ Nanoplates

In a typical synthesis of ultrathin MoS₂ nanoplates, 20 mg ammonium thiomolybdate ((NH₄)₂MoS₄, Sigma-Aldrich) was dispersed in the mixture (15 mL) of *N,N*-Dimethylformamide (DMF) and water (H₂O) with volume ratio of 2:1 mixture by ultra-sonication for 30 min. The mixture was then transferred into the autoclave, and maintained

at 210 °C for 18 h. After cooling to room temperature naturally, the black precipitate was collected and washed by DI-water and ethanol several times, and finally dried at 60 °C for 24 h. The preparation process of MoS₂ nanoplate assemblies and thick MoS₂ nanosheet assemblies was similar to that described above, but only with DMF or H₂O as solvent. The high-crystallinity MoS₂ nanoplates was prepared by further treating the as-prepared ultrathin MoS₂ nanoplates materials at 800 °C in an atmosphere of H₂ mixed with N₂ for 2 h at a heating rate of 1 °C min⁻¹. The morphology evolution experiment was performed at 210 °C where autoclaves were removed from the reaction electronic oven at times of 40 min, 60 min, 1.5 h and 2 h and quenched immediately in an ice bath.

5.2.2 Characterization

All transmission electron microscopy (TEM), high-resolution (HR) TEM images and elemental mapping were taken from JEOL JEM 2100F, while the field emission scanning electron microscopy (FESEM) images were taken on a JEOL JSM 6700F. XRD analysis of different samples was carried out on a X-ray diffractometer (Bruker AXS D8, Cu K λ , λ = 1.5406 Å, 40 kV and 20 mA). Raman spectra were collected via a Renishaw Ramanscope in the backscattering configuration using 514 nm (2.41 eV) laser wavelengths over five random spots on the powers. X-ray photoelectron spectroscopy (XPS) spectrum was measured on a VG Escalab 250 spectrometer equipped with an Al anode (Al K α = 1846.6 eV). N₂ adsorption/desorption isotherm was conduct to analyze the pore structure. The BET surface area was determined using adsorption data in the relative pressure (P/P_0) range of 0.05-0.25.

5.2.3 Electrochemical Measurements

All electrochemical measurements were conducted on an Autolab PGSTAT302 potentiostat (Eco Chemie, Netherlands) in a three-electrode cell at room temperature. The reaction apparatus can be referred in Section 2.2.1. The electrocatalytic reaction details, the catalysts loading method and the potential calculation method are similar to those described in Section 4.2.4.

5.3 Results and Discussion

Figure 5-1 FESEM (a), TEM (b), High-resolution (HR) TEM (c) images and XRD pattern (d) of ultrathin MoS₂ nanoplates.

The ultrathin MoS₂ nanoplates are obtained by solvothermal treating (NH₄)₂MoS₄ in the mixture

of *N,N*-Dimethylformamide (DMF) and H₂O ($V_{\text{DMF}}: V_{\text{H}_2\text{O}} = 2:1$) at 210 °C for 18 h. The field-emission scanning electron microscopy (FESEM) image (Figure 1a) clearly shows the well-defined plate-like morphology of the MoS₂, where the lateral size of the plates is in the range of 200-300 nm. Figure 5-1b is a representative transmission electron microscopy (TEM) image, showing good agreement with SEM observation (Figure 5-1a). The light contrast in various areas of the TEM image indicates the thin two-dimensional (2D) nature of the plate-like nanostructures. Besides, dense interconnected ripples and corrugations can also be observed, suggesting the basal-edge-rich feature of the ultrathin MoS₂ nanoplates. The high-resolution (HR)TEM image (Figure 5-1c) of the curled edge shows the MoS₂ plates are composed of 7-10 layers (4-6 nm) with an interlayer spacing of 0.65 nm, further verifying the ultrathin nature of the MoS₂ plates. Importantly, the absence of the interplanar lattice (001) observed from the HRTEM image as indicated by the white circle, suggests that the nanoplate material is low crystallinity. This is further confirmed by the X-ray diffraction (XRD) pattern (Figure 5-1d), where all the diffraction peaks match the hexagonal phase of MoS₂ (2H-MoS₂), but the weak (00 l) diffraction illustrates the low crystallinity. Especially, the low intensity of the (002) diffraction of the *c* axis suggests the MoS₂ plates consist of a few layers nanosheets. While the slightly (002) peak shift could be attributed to the distortion of lattice among the as-prepared MoS₂ nanoplates. Finally, the energy-dispersive X-ray (EDX) mapping images (Figure 5-2) confirm the homogeneous distribution of Mo and S elements across the whole nanoplates.

Figure 5-2 TEM image (a) of the selected area of the ultrathin MoS₂ nanoplates for element mapping, showing the uniform distribution of S (b), Mo (c) across the whole nanoplates.

The chemical states of Mo and S in the ultrathin nanoplates are analyzed by X-ray photoelectron spectroscopy (XPS) technique. It can be observed that two characteristic peaks arising from 229.0 and 232.2 eV are attributed to the Mo 3d_{5/2} and 3d_{3/2} binding energies for a Mo (IV) oxidation state (Figure 5-3a), while the corresponding peaks for the S 2p_{3/2} and 2p_{1/2} orbitals of divalent sulfide ions (S²⁻) are observed at 161.8 and 163.1 eV (Figure 5-3b).¹⁷⁴ In addition to the XPS peaks for the pure MoS₂ structure, another set of small peaks for S and Mo are also presented (Figure 5-3a&b). The observation of Mo 3d_{5/2} and 3d_{3/2} peaks at lower binding energies suggests the presence of Mo (V),¹⁶⁶ while the peaks for S 2p_{3/2} and 2p_{1/2} at 162.6 and 163.9 eV indicate the presence of bridging S₂²⁻ or apical S²⁻ which result from the unsaturated S atoms, as indicated in Figure 5-3a and 5-3b.¹⁷⁵ To further verify the XPS results, Raman spectra is performed to have further detailed insight on the structure of the nanoplates. As shown in Figure 5-3c, the

characteristic Raman shifts at 377 and 404 cm^{-1} expected for the E_{2g}^1 and A_{1g} vibrational modes of hexagonal MoS_2 are clearly observed (inset of Figure 5-3c), respectively. Moreover, compared with the Raman spectrum of calcined MoS_2 nanoplates (Figure 5-4), the relatively larger peak width and weaker intensity of E_{2g}^1 peak of the ultrathin MoS_2 nanoplates indicate that the crystal structure of MoS_2 is not perfect and in-layer disorder or defects exist between the Mo and S atoms. Meanwhile, the lower intensity of E_{2g}^1 peak compared with A_{1g} peak further reveals the basal-edge-rich feature of the ultrathin MoS_2 nanoplates,¹⁸³ in good agreement with TEM observation (Figure 5-1b). Based on the above analysis, we accordingly suspect that certain amount of “defect sites” may exist on the surface of the nanoplates, which in turn provide sites for the formation of unsaturated S atoms. Thus, a model of MoS_2 nanoplate with unsaturated S atoms on the surface is proposed and schemed in Figure 5-3d, where those unsaturated S atoms exist either on the basal edges or the defect sites of the basal planes. As suggested by the atomic composition and binding energies measured from XPS and the low crystalline structure observed from TEM and XRD, the as-prepared nanoplate material is predominately composed of low crystalline MoS_2 with unsaturated sulfur atoms.

Figure 5-3 XPS spectra of Mo 3d (a) and S 2p (b), Raman spectrum (c) for ultrathin MoS₂ nanoplates. Inset of (c) shows the atomic displacement of the E_{2g}¹ and A_{1g} vibrational modes in bulk MoS₂. d) Illustration for the ultrathin MoS₂ nanoplates with unsaturated S atoms.

Figure 5-4 Raman spectra of the MoS₂ samples.

It has been discovered that the ratio of DMF and H₂O plays an essential role in determining the final morphology of the ultrathin MoS₂ nanoplates. When only DMF is used, the as-formed thick nanoplates aggregate and assemble into large particles, which are denoted as thick MoS₂ nanoplate assemblies (Figure 5-5a). With the addition of H₂O into the reaction solution, the aggregation phenomenon becomes less severe and the samples exhibit plate morphologies (Figure 5-5b). With the further increase of the volume ratio of H₂O to DMF, the as-formed plates become thinner such that eventually the plates curled up and shielded its basal edges, as shown in Figure 5-5c&5e. Thin conglomerated nanosheets are formed with the presence of H₂O only (Figure 5-5f). These results obtained in our work might illustrate that DMF play a role for the formation of the plate-like shape while the amount of H₂O in the mixture could adjust and control the thickness of the nanoplates. More importantly, H₂O would also take part in the dispersion and crystallinity for the final MoS₂ nanostructures (Figure 5-1 and 5-5). A suitable concentration of (NH₄)₂MoS₄ in the starting solvent ($V_{\text{DMF}}: V_{\text{H}_2\text{O}}=2:1$) would result in MoS₂ nanoplate with uniform dispersion (Figure 5-6). With the further increase of (NH₄)₂MoS₄ amount gradually from 20 mg to 40 mg, the morphology of the products evolves from well-defined nanoplates to nano-plate assemblies followed by flower-like nanostructure, and eventually to large nano-flowers. The formation of the nano-flowers morphology at high (NH₄)₂MoS₄ concentration might be due to the self-assembly of the nanoplate building blocks to minimize the total surface energy.

Figure 5-5 FESEM images of the products prepared with a) DMF b) DMF/ H₂O= 4:1 c) DMF/ H₂O=1:3 d) DMF/ H₂O=1:4 e) DMF/ H₂O=1:14 and f) H₂O. The transformation of the shape and thickness of the plates are indicated by the white arrows.

Figure 5-6 FESEM images of the as-prepared MoS₂ nanoplates with different concentrations of (NH₄)₂SO₄: a) 20 mg, b) 30 mg, c) 40 mg and d) 50mg.

Figure 5-7 FESEM images of the products obtained at different growth stages: a) 40 min, b) 60 min, c) 1.5h and d) 2h; e) Schematic illustration of the 2H-type structure of MoS₂.

The morphology evolution of MoS₂ nanoplates during the solvothermal process is further examined by FESEM techniques. In the first stage for 40 min, large amounts of MoS₂ nanoparticles are formed with a size ~10 nm (Figure 5-7a). Subsequently, these nanoparticles spontaneously aggregate into spherical cores of size ~200 nm with sawtooth-structured protuberances growing from the core (Figure 5-7b). After reaction for 1.5 h, the randomly aligned nanopetals originating from the sawtooth-structured protuberances are observed (Figure 5-7c), which are so large that the originally spherical core is no longer evident. As the reaction continues (Figure 5-7d), the inner amorphous spherical core diminishes gradually and the growth occurs on randomly aligned nanopetals as those petals grow into well-defined interconnected nanoplates with smooth basal plan and edges. Reactions for longer time are also found to form similar plate-like nanostructures, suggesting they are the final thermodynamically stable products. These observations agree with previous reports of the growth mechanism involving a multistage growth process.¹⁸⁴⁻¹⁸⁶ Thus, the growth and morphology of the plate-like MoS₂ nanostructures may be understood as follows. The particles initially formed are amorphous and thus adopt a spherical shape. The surface of the spheres acts as nucleation sites for the formation of sawtooth-structured protuberances consisting of small crystalline particles of MoS₂. As the reaction proceeds, it is energetically more favorable for the crystalline MoS₂ protuberances to grow, where they evolve from small nanopetals to well-defined interconnected MoS₂ plates with the protuberances on the surface of these spheres providing high-energy sites for crystal growth. The plate-like 2D shape of the protuberances and interconnected lamellars originate from the layered structure of MoS₂, which grows preferentially along the [100] and [010] directions compared to the longer [001]

direction as showed in Figure 5-7e.

Figure 5-8 Polarization curves (a), corresponding Tafel plots (b) and calculated turnover frequencies (c) of various samples. Stability test for the ultrathin MoS₂ nanoplates (d).

Featured by rich basal edges and active unsaturated sulfur atoms, the ultrathin MoS₂ nanoplates are expected to show better HER performance than conventional MoS₂ nanoplates. Figure 5-8a shows the polarization curves for the various catalysts (with correction for ohmic potential drop (iR) losses, see 3.2.1 and Figure 5-9). For comparison purpose, electrochemical measurements are also conducted on thick MoS₂ nanoplate assembly with less edge sites and calcined ultrathin MoS₂ nanoplates with high crystallinity (Figure 5-10). The ultrathin MoS₂ nanoplates exhibits excellent activity for the HER with a low onset potential of ~ -0.09 V (determined from the

semi-log plot, see 3.2.1), which surpasses the activities for the rest both MoS₂ samples. To obtain further insight into the HER on ultrathin MoS₂ nanoplates, Tafel plots of various catalysts are investigated (Figure 5-8b). The resulting Tafel slope of the ultrathin MoS₂ nanoplates is 53 mV dec⁻¹, which matches with several earlier reports for the MoS₂ catalysts.^{23,180} By contrast, this value is significantly lower than that of the calcined MoS₂ nanoplates. Maintaining similar morphology (Figure 5-10a), the calcined sample shows much higher crystallinity as confirmed by XRD results (Figure 5-10b). XPS spectra exhibits only a single doublet for Mo 3d and S 2p (Figure 5-10c&d), suggesting the lack of bridging S₂²⁻ or apical S²⁻. These observations indicate that the ultrathin MoS₂ nanoplates prepared are featured with more active sites stemming from the coordinately unsaturated sites and sulfur atoms, which are suspected to be the reasons why the ultrathin MoS₂ nanoplates are more active than MoS₂ with higher crystallinity. Moreover, compared to the thick MoS₂ nanoplate assemblies in terms of Tafel slope, the comparatively smaller value for MoS₂ ultrathin nanoplates may be explained by the fact that more accessible catalytically active edges are created due to the unique ultrathin morphology, as described below.

Figure 5-9 AC impedance spectroscopy of as-prepared MoS₂ catalysts performed in the same

configuration at $\eta = 0.15\text{V}$ from 10^6 - 0.02 Hz with an AC voltage of 5mV.

Figure 5-10 (a) FESEM image, (b) XRD pattern and (c-d) high-resolution XPS spectra of the calcined MoS₂ nanoplates.

To directly investigate the effect of the additional active edges brought in by the ultrathin shape, the turnover frequency (TOF) is then calculated over the ultrathin MoS₂ nanoplates and the thick MoS₂ nanoplate assemblies by quantifying the active sites through electrochemical approach (see 4.2.1).⁶⁰ The calculated active edge sites of ultrathin MoS₂ nanoplates is larger than that of thick MoS₂ nanoplate assemblies, giving the direct evidence of the enhanced active edge sites brought in by the ultrathin nature of the nanoplates and the abundant exposed S active atoms. This view could further be supported by the larger Brunauer-Emmett-Teller (BET) surface area of the ultrathin MoS₂ nanoplates (56 cm² g⁻¹) in comparison to the thick MoS₂ nanoplate assembly (28

$\text{cm}^2 \text{g}^{-1}$) (Figure 5-11), since higher surface area of the ultrathin nanoplate morphology can result in a higher density of accessible reactive sites. Figure 4c shows the polarization curves normalized by the active sites, which are expressed in term of TOF. The calculated TOF number per active site for the MoS_2 ultrathin nanoplates reaches 0.15 s^{-1} at $\eta = 0 \text{ mV}$, which is higher than the value (0.10 s^{-1}) for thick MoS_2 nanoplate assemblies, suggesting the improved intrinsic activity of the active sites due to the unsaturated active S atoms existed on the surface of ultrathin nanoplates. Hence, the high hydrogen-evolving activity of MoS_2 ultrathin nanoplates can be attributed to the combined presence of active unsaturated S ligands and additional edge sites generated in this ultrathin nanoplate morphology.

Figure 5-11 The nitrogen adsorption/desorption isotherms of ultrathin MoS_2 nanoplates and MoS_2 nanoplate assemblies.

Finally, the catalytic stability of the ultrathin MoS_2 nanoplates catalyst towards the HER is assessed. Figure 5-8d displays the polarization curves of ultrathin MoS_2 nanoplate before and after 2000 cycles. The negligible decay of the cathodic currents indicates the good stability of the

ultrathin MoS₂ nanoplates in a long-term electrochemical process. Previous reports for active MoS_x nanoparticles demonstrated a high S/Mo atomic ratio in the range of 2.5-3.0 and were basically amorphous.^{166,175} Therefore, poor stability of these MoS_x materials is expected during the HER under acidic condition. In contrast, the analysis of the Mo (3d) and S (2p) peak intensities for our material yields an S/Mo ratio of ~ 2.10, suggesting that the structure is close to MoS₂ while retaining abundant active S atom but that the as-prepared nanoplates are not standard MoS₂ maybe more close to MoS_x. It is worth noting that the stability performance obtained in our work is better than that of the amorphous MoS₂ reported previously, which may suggest that the crystalline MoS₂ in the structure could stabilize the catalytically active S-S bonds, thus leading to a low solubility of MoS₂ nanoplates in the acidic solution.^{23,165}

5.4 Conclusion

In conclusion, we report a facile solvent-dependent control route for the synthesis of ultrathin MoS₂ nanoplates with unsaturated active S atoms from single source precursor. The growth mechanism of ultrathin MoS₂ nanoplates is proposed. The existence of unsaturated active sulfur ligands and edge-rich ultrathin layers results in the exposure of additional catalytically-active sites, leading to outstanding catalytic performance for the HER. This study successfully demonstrates that introducing unsaturated sulfur ligands to ultrathin MoS₂ nanoplates is feasible by a facile solvent-dependent control route and this may open up a potential pathway for designing more efficient MoS₂-related catalyst for HER.

Chapter VI Conclusions and Outlook

6.1 Conclusions

The electrochemical splitting of water to produce hydrogen is expected to be one of the most attractive processes to alleviate the energy and environmental challenges we are currently facing. Currently, the successful utilization of hydrogen evolution reaction (HER) for hydrogen production depends critically on new efficient materials. Recent advances in material science have revealed that nanostructured transition VI metal (Mo and W) carbides or sulfides, are very promising alternatives to Pt for the electrochemical generation of hydrogen from water. To contribute to this great project, several successful electrochemical catalysts for HER have been developed and evaluated in this thesis work systematically.

First, a unique nanorod-structured tungsten carbide material with high specific surface area of $198 \text{ m}^2 \text{ g}^{-1}$ was successfully synthesized by pseudomorphic transformation of chemically synthesized WO_3 nanorods through a high-temperature method. In addition, an electrocatalyst composed of Pt nanoparticles supported on WC nanorods demonstrated higher electrocatalytic activity for cathodic electrocatalytic hydrogen evolution than a Pt/C catalyst. Next, a novel electrocatalyst of layered MoS_2 supported on reduced graphene oxide (RGO) decorated with nano-sized tungsten carbide (WC) was prepared. The resultant $\text{MoS}_2/\text{WC}/\text{RGO}$ composite with highly exposed reactive sites stabilized by the binary support showed an enhanced electrocatalytic activity in the HER process because of the synergism between the co-catalyst and high conductivity of the ternary composite. Following this, a networked MoS_2/CNT

nanocomposite with high catalytic activity towards HER was synthesized by a facile solvothermal method, in which MoS₂ nanosheets are uniformly coated on carbon nanotubes (CNTs). Moreover, it was found that both acid-treated CNTs and DMF play a critical role in the formation of this unique structure, and the low crystalline MoS₂ is identified as the actual catalyst for the enhanced HER due to the high number of exposed sites. Subsequently, a facile solvent-dependent control route was developed to synthesis ultrathin MoS₂ nanoplates with active unsaturated active S atoms from single source precursor. The growth mechanism of ultrathin MoS₂ nanoplates was proposed. It was proved that the existence of unsaturated active sulfur ligands and edge-rich ultrathin layers results in the exposure of additional catalytically-active sites, leading to outstanding catalytic performance for the HER. This study successfully demonstrates that introducing unsaturated sulfur ligands to ultrathin MoS₂ nanoplates is feasible by a facile solvent-dependent control route and this may open up a potential pathway for designing more efficient MoS₂-related catalyst for HER.

6.2 Outlook

Aiming to solve the global energy problem, the electrocatalytic H₂ production must be efficiently and economically acceptable for industrial application. Thus the development of highly active and low cost electrocatalytic systems will be highly desirable for any researchers in this project. Several research directions are suggested and elaborated in the following sections.

6.2.1 Modification of the Molybdenum Sulfides Catalysts

As stated earlier, improving the intrinsic reactivity of the MoS₂ catalyst is an efficient way to

optimize the catalyst. This has begun only recently, and one most potential strategy is doping, through optimizing the binding energy of the hydrogen. This strategy has not been realized for the active Mo-edge, but Co-doping the S-edges to be as active as the Mo-edges is an example of how such an effect could be realized. Doping studies of the Mo-edge of MoS_x remain to be undertaken but maybe that computational chemistry will provide a powerful tool in this effort.

6.2.2 Development of Molecular MoS₂ Edge Site Mimic

Recent year, the study of the biomimetic and molecular catalysts has presented an alternative strategy using discrete molecular units as catalysts for HER, which in principle can be tailored to give a high density of catalytically active metal sites without the rest of the inactive bulk material. Further study could focus on stabilizing the molecular catalysts with suitable substrates, such as the employing of the metal-organic-framework (MOF) and exploring other bimetallic organometallic complexes with terminal sulfur ligands synthesized from Mo, Co, W complexes.

6.2.3 Optimizing the Conductivity of Molybdenum Sulfides Host Materials

Apart from synthesizing molybdenum sulfides at the nanometer scale, new, optimized and enhanced properties can also be achieved by the modification of the host material, especially the improvement of the conductivity of the host materials. For example, by means of controllable disorder engineering and oxygen incorporation, an optimized MoS₂ catalyst with a moderate degree of disorder was developed recently, which exhibits superior activity for electrocatalytic hydrogen evolution. Furthermore, the attempt on the more conductive 1T MoS₂ nanosheets has also been vigorously pursued recently and holds immense promise for improvements of MoS₂

6.2.4 Cathodic Hydrogen Evolution Test in Microbial Electrolysis Cells (MECs)

Apart from systems producing H_2 in the presence of electron donors in a half cell, recently, MECs provide a scalable way to produce H_2 , see Figure 6-1. It is known that in the cathode of a typical MECs, the HER proceeds that requires an applied voltage. Thus, to achieve a high volumetric H_2 production rate at low electrical energy input, the potential losses need to be minimized. In this project, our work mainly focuses on preparing the non-noble metal based cathodic electro-catalyst so as to decrease the cathode over-potential. Therefore, in the future work, it will be more attractive to scale-up of synthetic methods and evaluate the catalysts in the target electrolyzer, such as MECs shown in Figure 6-1.

Figure 6-1 Schematic representation of a typical configuration of the microbial electrolysis cell (MEC) for hydrogen production.

It is expected that with continuous research efforts from the scientific communities around the

world, H₂ production from water splitting will experience a renaissance and reach satisfactory efficiencies for practical applications to meet our future energy needs.

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Publications Related to This Thesis

Journal Papers

- (1) **Yan, Y.**; Zhang, L.; Qi, X.; Song, H.; Wang, J.-Y.; Zhang, H.; Wang, X.*; Template-Free Pseudomorphic Synthesis of Tungsten Carbide Nanorods. Small, 2012, 8, (21), 3350-3356.
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