Mo-S Chemistry: From 2D Material to Molecular Clusters

DISSEPTION

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Lu Ma

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Dissertation Committee:

Dr. Yijing Wu, Advisor
Dr. Patrick Woodward
Dr. Joshua Goldberger
Abstract

Layered transition metal dichalcogenides (TMDs), especially molybdenum disulfide (MoS₂), have been of great interest for a long time. MoS₂ naturally occurs as the mineral molybdenite, which has been involved in diverse research fields, such as electronics, optoelectronics, spintronics, energy storage, lubrication, and catalysis.

In MoS₂ crystals, a sheet of molybdenum atoms is sandwiched between sheets of sulfur atoms. The covalent Mo-S bonding is strong, but the interaction between the sandwich-like tri-layers is weak van der Waals force, resulting in easy exfoliation of a single layer or a few layers. These MoS₂ ultrathin layers (less than 10 atoms thick) belong to the family of two-dimensional (2D) materials. As dimensionality reduced, these MoS₂ ultrathin layers have unique charge transport properties, which solve the limitation of conventional Si and other bulk materials as scaling down to microelectronic and nanoelectronic devices. However, the synthesis of orientated single- or few-layer TMDs with large area remains challenging. The first part of this dissertation focuses on the design and controlled synthesis of 2D TMDs and study of their electronic device applications. A facile vapor-solid method was employed to get single crystalline few-layer MoS₂ films on (0001)-oriented sapphires with excellent structural and electrical properties over centimeter length scale. A carrier density of ~2×10¹¹ cm⁻² and a room temperature mobility as high as 192 cm²/Vs were extracted from space-charge limited transport regime in the films. In addition, transition
metal doped 2D MoS₂ films were successfully synthesized by one-step process. These doped films enable the tuning of the properties 2D MoS₂ films. By substituting to other substrates or film transferring, 2D/3D heterojunction diodes have also been made with excellent rectification.

MoS₂ has also been explored as catalysts such as for hydrogen evolution reaction (HER). The edges of MoS₂ has been identified as the active sites for HER, but the basal planes are catalytically inert. The second part of this dissertation focuses on the design and characterization of Mo-S clusters and study of their HER catalytic activities. Different Mo-S clusters that contain the edge structures of MoS₂ have been made to understand and improve the HER efficiency. X-ray photoelectron spectroscopy (XPS), Raman spectroscopy and X-ray absorption spectroscopy (XAS) has been used to reveal the properties of Mo and S atoms at different sites.

The synchrotron X-ray based XAS is one of the most useful technique to determine the local geometric and electronic structure of materials. The XAS technique can characterize both bulk sample in transmission mode, and ~ 100 nm surface in total electron yield mode regardless of the crystallinity of the materials. The XAS includes X-ray absorption near edge structure (XANES) and Extended X-ray absorption fine structure (EXAFS). The XANES is sensitive to the charge transfer, orbital occupancy and symmetry. The bond length and coordination details can be extracted from Fourier transform of EXAFS. The third part of this dissertation focuses on the application and improvement of XAS technique.
Dedication

This document is dedicated to my family.
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Vita

2011……………………… B.S. with Honor, Physical Science;

B.S., Material Physics

University of Science and Technology of China (USTC), China

2014……………………… M.S., Inorganic Chemistry, The Ohio State University

Publications of Graduate Study


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* Equal Contribution

Fields of Study

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Chapter 1: Introduction

1.1 Two-dimensional (2D) Materials and 2D Electronics

Since the isolation of graphene in 2004,[1] there has been a great deal of interest in the 2D materials. Similar to graphene, a lot of layered materials have been cleaved into individual free-standing atomic layers-2D materials. One of the most common source for 2D materials is the family of layered Van der Waals materials, with strong in-plane bonds providing the stability of 2D Van der Waals materials and weak Van der Waals forces between layers making them ready to exfoliate.

The amazing properties of graphene, such as excellent electric conductivity,[2] good thermal conductivity[3] and extremely high carrier mobility of ~10000 cm$^2$V$^{-1}$s$^{-1}$[2] spark a material revolution around the world. A wide range of graphene-based applications have been reported, such as biosensor,[4] supercapacitors[5] and batteries.[6] The research of graphene established a model of methods to study 2D materials experimentally in synthesizing, transferring and characterizing,[7, 8] theoretically in electronic structure, quantum Hall effect and spintronics,[9, 10] and practically in real-life applications.[11-15] Despite of these outstanding merit, the zero bandgap in graphene limits its application in logical circuits, since it does not have an off state.
The 2D materials have drawn significant interest in electronics since they have the possibility to solve the scaling down issue for the conventional electronic devices. The reducing of the thickness of conventional Si and other bulk materials increases the surface roughness and causes the mobility degradation. The operation issues, such as current leakage due to electron tunneling also arise. The 2D materials do not have such degradation with thin channels, promising for the micro- and nano- electronics. On one hand, researchers tried different methods to introduce a bandgap in graphene: chemical functionalization,[16] nanostructuring [17-19] or introducing an external perpendicular electric field (in bilayer graphene).[20] However, these methods either sacrifice the high mobility of graphene (150 meV bandgap cause mobility down to 200 cm²V⁻¹s⁻¹[21]) or require very high voltage (100V can open a 250 meV bandgap[20]). On the other hand, new 2D materials, such as 2D TMDs with comparatively low mobility, but a very high on/off ratio, have been obtained.

1.2 2D Transition Metal Dichalcogenides (TMDs)

Layered TMDs are one big family of layered Van der Waals materials, which are formed by early transition metals and chalcogenides with stoichiometry formula MX₂ (M=Ti, Zr, Hf, V, Nb, Ta, Re; X=S, Se, Te). The transition metal atoms are sandwiched between two layers of chalcogen atoms. One transition metal atom is coordinated by six chalcogen atoms to form either octahedral or trigonal prismatic MX₆ polyhedrons. These MX₆ polyhedrons share edges to form one layer of TMDs. The surface energy of MoS₂,
MoSe$_2$ and WS$_2$ (65-75 mJ m$^{-2}$ [22, 23]), which are comparable to the surface energy of graphene (65-120 mJ m$^{-2}$ [24, 25]) and the calculation results indicate the stability of single-layer TMDs (summarized in Figure 1.1 [26]). Among them Mo and W dichalcogenides have sizable band gaps around 1-2 eV (summarized in Table 1.1). In addition, the abundance of Mo and W dichalcogenides also makes them possible for industrial application with a low cost.

Figure 1.1 Summary of the calculation results of stability of MX$_2$ (M=transition metal atoms, X= chalcogen atoms) compounds. In each box, the lower-lying structure (H or T) is the most stable phase and the upper-lying structure is the less stable phase. White color means only one phase is stable. Orange color indicates 1H phase and Green color indicates 1T phase. Grey color means neither 1T nor 1H phase is stable. “+” means half-metal; “*” means metal and “***” means semiconductor. [26]
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Table 1. 1 Summary of band gaps of single-layer and bulk molybdenum and tungsten dichalcogenides (E=experimental result, T=theoretic calculation result).

Bulk Mo and W dichalcogenides have a variety of stacking polytypes. The most common three are the 1T, 2H and 3R phases (as shown in Figure 1. $^{2[33]}$). The 1T phase has a tetragonal symmetry with octahedral coordination; the 2H phase has a hexagonal symmetry with trigonal prismatic coordination; and the 3R phase has a rhombohedral symmetry with trigonal prismatic coordination. The 2H phase is the most stable phase for MoS$_2$. 


Figure 1. The structures of the (a) 2H, (b) 3R and (c) 1T phases of molybdenum and tungsten dichalcogenides. The metal atoms (M) are grey and the chalcogen atoms (X) are yellow.\cite{33}

As the number of layers decreases to one, there is no variety of stacking different layers. Thus, single-layer Mo and W dichalcogenides only have two phases, 1H and 1T. The coordination of metal atoms is trigonal prismatic in the 1H phase and octahedral in the 1T phase (Figure 1. 3). The 1H phase is the most common phase for molybdenum and tungsten dichalcogenides. According to the calculation result in Figure 1 .1, the 1H phase is the only stable phase for Mo and W dichalcogenides. Experimentally the 1T phase can also be obtained by lithium intercalation\cite{34}. Both the 1T and the 1H phases have been found in the
lithium intercalation product. The 1H and 1T phases of Mo and W dichalcogenides have similar thickness of around 6-7 Å\[35].

Figure 1. 3 (a) 1H and (b) 1T phases of single layer molybdenum and tungsten dichalcogenides. The metal atoms are purple and the chalcogen atoms are yellow.

From bulk to single layer, the band gaps of MoS\textsubscript{2} and WS\textsubscript{2} change from indirect to direct as shown in Figure 1. 4. Bulk MoS\textsubscript{2} and WS\textsubscript{2} have indirect band gaps from the Γ point to the point between K and Γ points in Brillouin zone. While, in the case of single-layer MoS\textsubscript{2} and WS\textsubscript{2}, the direct band gap is located at the K point. There are also indirect band gaps in single-layer MoS\textsubscript{2} and WS\textsubscript{2}, from the Γ point to the K point.
Figure 1. 4 Calculated band structure of bulk and single-layer (a) MoS$_2$ and (b) WS$_2$ (the 2H phase for bulk and the 1H phase for single-layer materials)$^{[36]}$. The black arrows indicate the lowest energy transition.

Single- or few-layer Mo and W dichalcogenides are promising materials for electronic devices. There are three key factors for materials used to make digital logic devices: high charge carrier mobility for fast operation, high on/off ratio ($10^4$-$10^7$) for effective switching and low off-state conductance for low power consuming$^{[37]}$. 1-2 eV bandgaps of Mo and W dichalcogenides can provide high on/off ratio$^{[38]}$ with low power dissipation. The first top-gate single-layer MoS$_2$ field-effect transistor (FET) (Figure 1. 5a) with excellent on/off
ratio (\( \sim 10^8 \)) and mobility (\( > 200 \text{ cm}^2\text{V}^{-1}\text{s}^{-1} \)) excited the interest in research on syntheses and applications of TMDs.\[39\] Single-layer MoS\(_2\) amplifier\[40\] and logic operations\[41\] have also been demonstrated. Majumdar et al. point out that when the gate lengths are less than 5 nm, direct source–drain tunneling will be an issue and materials with carriers having large effective mass perform better.\[42\] Compared to other 2D materials, Mo based 2D TMDs are the most suitable materials for the logical electronics will gate length less than 5nm.\[43\]

Figure 1. 5 Scheme of (A) top gated\[39\] and (B) back gated single layer MoS\(_2\) transistor.\[44\]

However, the high mobility is still controversial. Dielectric environment (e.g. HfO\(_2\)) influence the mobility a lot due to the screening effect on the impurities in single- or few-layer MoS\(_2\)[45]. The mobility can be overestimated by 10-50 times due to the increase of capacitive coupling of the channel by the dielectric of the top-gate with the back-gate (Figure 1. 5b). The carrier mobility of single- or few- layer MoS\(_2\) FETs on SiO\(_2\)/Si substrate (SiO\(_2\) as gate) was only \( \sim 10 \text{ cm}^2\text{V}^{-1}\text{s}^{-1} \) without the high-\( \kappa \) environment at room
temperature\textsuperscript{[46]}. The interface between MoS\textsubscript{2} and SiO\textsubscript{2} has been considered as one of the main limit\textsuperscript{[47]}. The mobility has been increased to 200 or 500 cm\textsuperscript{2}V\textsuperscript{-1}s\textsuperscript{-1} by HfO\textsubscript{2}\textsuperscript{[39]} or Al\textsubscript{2}O\textsubscript{3}\textsuperscript{[48]} top-gate due to the high-\(\kappa\) dielectric screening of charged impurities. Fuhrer and Hone emphasized that the gate not in use should be grounded in order to well define the capacitances\textsuperscript{[49]}. On the other hand, the mobility of MoS\textsubscript{2} FETs has also been underestimated, which is caused by the Schottky barriers at the interface of MoS\textsubscript{2} and metal contacts\textsuperscript{[45, 50]}. The mobility was enhanced from \(\sim\)100 to \(\sim\)220 cm\textsuperscript{2}V\textsuperscript{-1}s\textsuperscript{-1} by reducing the contact resistance and thinning the Schottky barrier\textsuperscript{[51]}.

These new 2D materials open the door to new realms of the fundamental science and the practical applications. In addition to a simple atomic 2D plane, doping in 2D TMDs and restacking various 2D Van der Waals materials layer by layer to form Van der Waals heterostructures would reveal new phenomena. These Van der Waals heterostructures would also be promising for novel devices with multilayers in a precisely chosen array since there is no requirement of lattice match\textsuperscript{[52]}.

1.3 MoS\textsubscript{2} and Mo-S Clusters as Catalysts for Hydrogen Evolution Reaction (HER)

Hydrogen, the environmentally friendly fuel with the largest energy density, is pursued as future energy carrier to replace fossil fuels. Using electrolysis of water to generate hydrogen is not a new idea, which can be tracked to 1890s\textsuperscript{[53]}. The most popular electrocatalyst for HER is platinum, which exhibits extremely high exchange current density with a small Tafel slope\textsuperscript{[54]}. MoS\textsubscript{2} has been reported as an promising electrocatalyst
for HER. Both theoretical DFT calculations\cite{55, 56} and experimental result by scanning tunneling microscopy\cite{57} identified the edges of the MoS\textsubscript{2} are active sites for catalyzing HER but the basal plane is inert. As a result, exposing more edges of MoS\textsubscript{2} is a strategy to enhance the HER catalytic activity. The 2D MoS\textsubscript{2} layers can expose more edge sites, but the layered structures usually expose the basal planes as the terminal surface with small amount of dangling bond. Kong et al. made vertically aligned layers to increase the edge sites on the surface.\cite{58} Nanostructured MoS\textsubscript{2} with large surface curvature was also reported.\cite{59} Xie et al. used hydrothermal method to fabricate MoS\textsubscript{2} nanosheets with rich defects.\cite{60} However, these MoS\textsubscript{2} still left a large amount of inert basal planes in the structures. Another approach is to synthesize the well-defined molecular analog of the MoS\textsubscript{2} edge structure, which can not only help study the catalytic process but also get superior catalytic activity through increasing the active sites. Karunadasa et al. first synthesized Mo\textsuperscript{IV}-disulfide complex [(PY5Me\textsubscript{2})MoS\textsubscript{2}]\textsuperscript{2+} (Figure 1.6), which represented the MoS\textsubscript{2} edge structure to study the catalytic process. With these molecular clusters, different kinds of edge site structures can be studied so as to identify the most active structures for HER.
Figure 1. 6 Structure of [(PY5Me₂)MoS₂]²⁺ molecule.

1.4 Chapter Outlines

This introduction in Chapter 1 is followed by Chapter 2, which discusses the synthesis and the growth mechanism of single crystal 2D MoS₂ layers. The high quality of the MoS₂ films was obtained through control the precursors supersaturation through the growth at high temperature. The commercial MoS₂ powder, which can decompose and release sulfur at high temperature was used as sulfur source. The controlled amount of sulfur enabled the smooth growth of MoS₂ layers without forming small separate domains.

Chapter 3 will discuss the diodes and transistor made by the single crystalline 2D MoS₂ films. The space charge mobility of the pristine 2D MoS₂ films was as high as 192 cm²V⁻¹s⁻¹. The natural MoS₂ is always n-type semiconductor, due to the strong Fermi level pinning near the conduction band. With Nb doped in the precursor, p-type MoS₂ with controlled doping density was also synthesized. Through direct growth MoS₂ on SiC
substrate, 2D p-MoS$_2$/3D n-SiC and 2D p-MoS$_2$/3D n-GaN heterojunction diode was fabricated was obtained with excellent rectification.

In Chapter 4, the properties of the Mo-S clusters will be discussed. A lot of characterization techniques were used to understand the S atoms at different sites, especially the XPS and XAS techniques. A dimeric molecular analog [Mo$_2$S$_{12}$]$^{2-}$ was designed as the smallest unit that have the edge structure of MoS$_2$. The electrochemical investigations showed that [Mo$_2$S$_{12}$]$^{2-}$ clusters had superior HER catalytic activity under acidic conditions. The [Mo$_2$S$_{12}$]$^{2-}$ and the reported [Mo$_3$S$_{13}$]$^{2-}$ clusters were compared.

Chapter 5 and Chapter 6 will focus on the synchrotron X-ray based technique, XAS. The XAS contains X-ray absorption near edge structure (XANES) and Extended X-ray absorption fine structure (EXAFS). The XANES is sensitive to the charge transfer, orbital occupancy and symmetry. The bond length and coordination details can be extracted from Fourier transform of EXAFS. In Chapter 7, the XAS study of the Mo-S clusters will be summarized.

The conclusions and the outlook of this thesis are summarized in Chapter 8.

References


Chapter 2: Synthesis of Single Crystalline 2D MoS$_2$ Films

2.1 Introduction

2.1.1 Methods for synthesizing 2D materials

Various methods have been studied to synthesize 2D materials including top-down methods and bottom-up methods. Top-down methods are the methods to get single- or few-layers of TMDs from their corresponding bulk materials. The most common top-down method is mechanical exfoliation. Single-layer molybdenum dichalcogenides have been successfully exfoliated by adhesive tapes\cite{1}. This method provides the highest quality single layer MoS$_2$. However, the mechanical exfoliation is difficult to scale up and the reproducibility is low. In fact, there are lots of defects in the bulk material, so the exfoliated layers still contain defects. Another top-down method is thermal ablation by lasers\cite{2}. Single-layer MoS$_2$ can be obtained by this method but the use of lasers hindered the scale-up process. The third top-down method is lithium intercalation, which can be traced back to 1975\cite{3}. Single layer of MoS$_2$\cite{4}, WS$_2$\cite{5}, MoSe$_2$\cite{6} has been obtained by lithium intercalation with high yield\cite{7}, but the product loses the semiconductor properties as it changes phase to the metallic 1T phase. The 1H phase would be recovered by heating at 300°C. Since this method needs reaction for several days, modifying this method by electrochemical cell were used to make it more efficient\cite{8}. Whereas, the flammability of
lithium and the requirement of an inert atmosphere are still challenging this method. Liquid exfoliation by direct sonication in different solvents has also been studied, such as in organic solvents\textsuperscript{[9]}, mixed solvent of water and ethanol\textsuperscript{[10]}, aqueous surfactant solutions\textsuperscript{[10]} and a mixture of solvent and polymer\textsuperscript{[11]}. This method is easy to carry out, but the yield is very low.

Bottom-up methods are the methods to get single- or few- layer TMDs from the molecules or atoms. The most common method is chemical vapor deposition (CVD). Several CVD methods for large-scale MoS\textsubscript{2} ultrathin films have been reported recently. A typical process follows these two steps: first, different Mo and sulfur precursors are heated to a high temperature to let them evaporate; second, products deposit on the substrates at the cold zone. For example, MoO\textsubscript{3} and sulfur powder\textsuperscript{[12]}, MoCl\textsubscript{5} and sulfur powder\textsuperscript{[13]}, one precursor (NH\textsubscript{4})\textsubscript{2}MoS\textsubscript{4} containing both molybdenum and sulfur\textsuperscript{[14]}, or molybdenum metal thin film on substrate and sulfur powder\textsuperscript{[15]} have been used. The products of these methods are all polycrystalline single- or few- layer MX\textsubscript{2} with grain size 10-30nm\textsuperscript{[12,13,15]}. Recently, the mechanism of CVD method by MoO\textsubscript{3} and sulfur powder has been systematically studied\textsuperscript{[16]}, showing that the nucleation concentration was higher near the grain boundaries. The precursor concentration and the chamber pressure played key roles in controlling the quality of the product. By modifying the process, the CVD method using MoO\textsubscript{3} ribbons as a precursor can produce single- or few- layer MoS\textsubscript{2} on micrometer scale.
2.1.2 Few-layer MoS₂

Compared to single-layer MoS₂, few-layer MoS₂ may be more attractive, since large-scale synthesis is much easier and the devices still perform quite well[17, 18]. Another advantage of few-layer MoS₂ is its density of state (DOS), which is three times of the DOS of single-layer MoS₂. As shown in Figure 1.4, the CBM of MoS₂ moves from the K point to a lower symmetry point between Γ and K as the number of layers increases. The lower symmetry point for bulk MoS₂ has a higher valley degeneracy (gᵥ=6) than the K point for single-layer MoS₂, resulting in higher DOS. The high DOS will drive high currents in the ballistic limit[17]. Thus, the few-layer MoS₂ FETs can offer higher on-state current than the single layer-MoS₂ FETs and maintain high on/off ratios at the same time[19].

Few-layer MoS₂ based electronic devices are promising, but the synthesis of high quality few-layer MoS₂ films is still challenging. In this chapter, a new vapor-solid growth method will be presented to get larger area epitaxial (0001)-orientated single-crystal MoS₂ films on sapphire substrate. After that the special characterization technique for the ultrathin MoS₂ films will be introduced and the characterization results will be discussed.

2.1.3 High-resolution X-ray Diffraction (HRXRD) for 2D material characterization

Conventional XRD use θ-2θ scan to determine the inter-planar distance of the planes parallel to the sample surface. In a typical symmetric θ-2θ scan, incident angle ω is varied,
while keeping the detector at 2θ angle (ω = θ). However, this mode isn’t suitable for thin film due to poor sensitivity and interference from substrate.

Sensitivity or resolution of XRD can be represented by Divergence (Figure 2. 1). Divergence δθ is expressed as

$$\delta \theta = \frac{h+s}{a},$$

(2. 1)

Where “h” is the size of the X-ray source, “s” is the slit size, “a” is the source-specimen distance. Typically, δθ is around 500 arc sec (1 deg = 3600 arc sec) for the conventional XRD, but the width of rocking curve for a highly perfect crystal is only a few arc seconds. Smaller divergence can be obtained by reducing the size of X-ray source. Conventional XRD usually use CuKα as the X-ray source. CuKα is actually a doublet composed of CuKα1 (λ = 1.540562 Å) and CuKα2 (λ = 1.54439 Å). HRXRD use only CuKα1 as the source to reduce the size of X-ray source and increase monochromaticity to improve the resolution.

Figure 2. 1. Scheme of X-ray irradiated on sample (h is the size of the X-ray Source, “s” is the slit size, “a” is the source-specimen distance, “δθ” is the divergence)
HRXRD has both double-axis scan and triple-axis scan. The two axes in double-axis scan are first axis adjusting the beam conditioner and second axis scanning the sample through Bragg angle. Beam conditioner is one of the most essential part for X-ray diffractometer. Beam conditioner is used to increase flux, improve spectral purity and control the divergence. Since these three properties can hardly be tuned separately, beam conditioner always contains pinhole or slit system, reflection optics and monochromator. Compared to double-axis system, triple-axis system has the third axis adjusting the analyzer. An analyzer is either a crystal or a slit to narrow the range of angles that detector can receive. The analyzer constrains the detector so that there is only one 2θ angle can be observed. Thus, the sensitivity of XRD can be improved. The comparison of the double-axis scan and the triple-axis scan is shown in Figure 2. 2.

![Double-axis and triple-axis system](image)

Figure 2. 2 (a) Double-axis and (b) triple-axis system.

When incident beam penetrates through the film into substrate, as the film is thin, a large amount of signal comes from substrate, overlaying the signal from film. Glancing
incidence XRD uses a small incident angle to increase the absorption path within thin film and reduce the interference from substrate (Figure 2. 3b). The glancing incidence scan is always used for poly-crystal thin films. If the thin film is a single crystal, diffraction peaks can only be obtained at a specific orientation. The glancing incident angle cannot satisfy the Bragg condition, so diffraction peaks cannot be observed.

Figure 2. 3 Scheme of symmetric and asymmetric XRD scan: (a) symmetric scan; (b) Glancing Incidence scan; (c) Glancing exit scan (ω: incident angle, θ: diffracted angle, φ: tilt angle).

To get X-ray diffraction peaks from an orientated thin film, coupled scan is used to measure the Bragg diffraction angles. Different from powder XRD θ-2θ scan, in a coupled scan, the ω and 2θ angles change in a coupled manner, so that the direction being measured doesn’t change. The 2θ angle is linked to the ω angle by the equation

\[ \omega = \frac{1}{2} \times 2\theta + \text{offset}. \]  

\[ (2.2) \]
The 2θ angle changes with ω so that peaks with different 2θ positions but identical tilts can be observed. If there is lattice mismatch, impurity or relaxation in the film, the positions of the diffraction peaks will be influenced. In a double-axis coupled scan, the detector can see different 2θ angles, so the shift of 2θ angle due to defects can be observed. In a triple-axis scan, only one exact 2θ angle can be observed because the detector is constrained by the analyzer.

Another useful scan in HRXRD is the rocking curve scan, especially for thin film characterization. Peaks will appear where Bragg condition is satisfied in XRD spectra. In a rocking curve scan, the incident angle is fixed at the θ angle and the detector is fixed at the 2θ angle. The tilting angle of the sample is varied around its equilibrium position. The sample is tilted along the axis which is perpendicular to the X-ray beam plane. Rocking curve refers to the range of the angles where the crystal will reflect a given wavelength. A perfect crystal will produce very sharp rocking curve peaks exactly at the Bragg angles. Defects such as mosaicity, dislocation and curvature will influence the positions and widths of the rocking curves. The effects of different defects of the thin film on rocking curve are summarized by Pietsch et al. [20]

2.2 Experimental Section

2.2.1 Reagents, materials and instruments

Molybdenum disulfide powder (99.98%) was purchased from Sigma-Aldrich. The sputtering instrument was AJA Orion RF/DC Sputter Deposition Tool. A Bruker AFM
system with carbon tips operating at 300 kHz resonant frequency was used for all scans. Raman characterizations were done using a Renishaw spectrometer at 514 nm laser excitation (laser power 6 mW). High resolution X-ray diffraction was done using a Bruker X-ray diffractometer with Cu Kα1 source. A Technai F20 Philips instrument operated at 200 keV was used for TEM imaging.

2.2.2 Vapor-solid growth of 2D MoS2 films

2D MoS2 films were synthesized vapor-solid growth method. The process is illustrated in Figure 2. 4. Single-crystal (0001)-orientated sapphire substrates were solvent cleaned and 5 nm of molybdenum was deposited by sputtering using AJA Orion RF/DC Sputter Deposition Tool. Atomic Force Microscopy (AFM) images of Mo metal (Figure 2. 5) were taken to check the thickness and uniformity before sulfurization. The Mo layer was scratched to expose the sapphire substrate. The thickness difference between the Mo layer and the substrate was about 5nm (Figure 2. 5c). After checking the thickness, the substrate with Mo layer and 8.0mg MoS2 powder in a small quartz tube were placed in a larger quartz tube. The larger quartz tube was pumped down by a mechanical pump, sealed and heated to 1100 °C for 4.5 h and then cooled down to room temperature at a rate of 0.5 °C/min.
Figure 2. 4 The schematic picture of growth setup.

Figure 2. 5 The AFM image of Mo deposited on substrate. (a) 10×10 μm AFM image; (b) 50×50 μm AFM image; (c) a line scan of image b indicated by a blue line.
2.3 Results and Discussion

2.3.1 Control the nucleation process

Nucleation is the first step in the crystallization process. Nuclei formed in this step can continue to grow into crystalline domains. In order to get single-crystal MoS$_2$ films with good crystalline nature, the nuclei density should be minimized, which can be achieved by a controlled low supersaturation. In our vapor-solid synthesis, initially sulfur vapor reacts with the surface Mo metal and creates the seed crystal. Sulfur pressure needs to stay at a low value to reduce the nucleation density. It is difficult to control the amount of sulfur by using elemental sulfur itself because the super saturation is very high compared to the small amount of Mo metal on the substrate. We reduced the sulfur pressure by using MoS$_2$ powder as a sulfur source to get a low sulfur pressure during the synthesis. Thermogravimetric analysis (TGA) of MoS$_2$ shows that above 950 °C, sulfur can be gradually released and detected by mass spectrometer.$^{[21-24]}$ The decomposition of MoS$_2$ powder at high temperature can provide sulfur to sulfurize the Mo metal on sapphire substrate. The equilibrium between MoS$_2$ powder and sulfur vapor inside the quartz tube would provide a sulfur vapor pressure of 0.023Pa at 1100 °C.$^{[22]}$ According to the pressure-temperature phase diagram of Mo-S system (Figure 2. 6),$^{[25]}$ this pressure is the lowest sulfur pressure at which pure MoS$_2$ phase can be produced. The total amount of sulfur that MoS$_2$ can release under vacuum at ~1000°C for 4.5 hours is about 0.099%,$^{[22]}$ which is calculated to be the amount of sulfur that the Mo layer on substrate needed to get MoS$_2$ phase.
Figure 2. 6 Temperature-pressure phase diagrams of Mo-S system. [26] The red star indicates the reaction condition.

During the synthesis, the following reactions occur:

\[
\text{MoS}_2 \text{ powder (surface) } \rightarrow \text{MoS}_x (x < 2) + \frac{2-x}{2} S_2 \quad \text{(2.3)}
\]

\[
\text{Mo (on sapphire) } + S_2 \rightarrow \text{MoS}_2 \text{ (on sapphire)} \quad \text{(2.4)}
\]

The (0001)-orientated sapphire was chosen to be a good Van der Waals epitaxy substrate due to its atomically flat surface without dangling bonds on the surface. Both theoretical\cite{27}.
and experimental [29, 30] study show that the surface of (0001)-orientated sapphire is
terminated by one Al layer because in this situation the dangling bonds on the surface are
either completely filled or empty to form an auto-compensated neutral surface. Thus, the
lattice matching condition has been relaxed dramatically.

2.3.2 Single crystallinity of the 2D MoS₂ films

Figure 2. 7a is a digital image of the as-grown MoS₂ film with mirror-like appearance
due to its atomically smooth surface (The RMS roughness of the MoS₂ film was ~ 0.53 nm
in a 5 µm x 5 µm area by an AFM scan). Figure 2. 7c is an SEM image of the MoS₂ film,
which demonstrate the uniformity and continuity of the film in a large scale. The inset of
Figure 2 .4c is the SEM image of the area scratched by tweezers, which shows the lateral
layered structure of the MoS₂ film. In fact, the surface of as-grown MoS₂ sample reported
here appeared to be smoother compared to that of 4-5nm MoS₂ film exfoliated from
geological MoS₂.[31] The thickness of the MoS₂ film from sulfurizing 5nm Mo is
approximately 7.0 nm based on AFM measurement (Figure 2. 7b).
Figure 2. 7 (a) Digital image of the MoS$_2$ film; (b) AFM images of the MoS$_2$ film near the edge to measure the thickness; and (c) SEM image of the MoS$_2$ film. The inset is an SEM image of a scratched area.

The 2-θ/ω XRD scan (Figure 2. 8a) exhibits only the (0001) family diffractions of MoS$_2$ and the diffraction of sapphire (0006) peak, which indicates a preferred growth orientation
of MoS$_2$ with the c-axis parallel to that of sapphire substrate. Thickness fringes near the MoS$_2$ (0002) peak suggest a sharp interface (Figure 2. 8a) and confirmed the thickness ~ 7 nm estimated from AFM scan by the following calculations:

![XRD scan of MoS$_2$ film on sapphire](image)

Figure 2. 8 (a) $2\theta/\omega$ XRD scan of MoS$_2$ film on sapphire (blue index: MoS$_2$ diffraction peaks, black index: sapphire (0006) diffraction peak.) and (b) zoom-in picture of $2\theta/\omega$ XRD scan of MoS$_2$.

The thickness fringes should also obey Bragg equation:

$$2L \sin \omega_1 = n_1 \lambda$$  \hspace{1cm} (2.5)

$$2L \sin \omega_2 = n_2 \lambda$$  \hspace{1cm} (2.6)
Where \( n_1 \) and \( n_2 \) are the integer number of the fringe peak positions; (the one closest to the diffraction peak has \( n_1=1 \) and the next has \( n_2=2 \)); \( \omega_1 \) and \( \omega_2 \) are the corresponding angles; \( \lambda =0.154056\text{nm} \), the wavelength of Cu K\(_{\alpha 1}\) and \( L \) is the thickness of the film.

\[
\text{so, } L = \frac{(n_1-n_2)\lambda}{2(\sin \omega_1 - \sin \omega_2)}. \tag{2.7}
\]

By this calculation, the thickness of MoS\(_2\) film was 7.0nm, which is consistent with the AFM result.

![Figure 2.9](image)

Figure 2. 9 (a) XRD Scan at MoS\(_2\) (10–13) position; (b) Phi Scan at MoS\(_2\) (10–13) diffraction position and sapphire (01–12) position.

The off-axis (10-13) 2-\( \theta/\omega \) XRD scan (Figure 2. 9a) across the full range of \( \Theta=360^\circ \) shows six peaks at MoS\(_2\) (10-13) position (Figure 2. 9b) due to the six-fold symmetry of the hexagonal phase of MoS\(_2\) and indicates the single-crystalline nature of as-grown MoS\(_2\) film. A full range \( \Theta=360^\circ \) scan of the sapphire (01-12) substrate taken with the sample in
the same position showed three peaks of single-crystalline sapphire corresponding to its three-fold symmetry. The Ø-scans showed that the unit cell of MoS$_2$ was rotated by 30° with respect to that of sapphire substrate.

To understand the in-plane orientation between MoS$_2$ and sapphire, the relative orientations of the two basal planes is shown in Figure 2. 10. The MoS$_2$ film and the sapphire substrate are rotationally commensurate: the length of 7 MoS$_2$ unit cells equals to the length of 8 sapphire unit cells after 30° rotation. The 30° rotation between the epi-layer and the substrate reduces the in-plane lattice mismatch to 13.0% with $\sqrt{3}a$(MoS$_2$) = 5.47 Å, a(sapphire) = 4.758Å. For the unrotated case, the lattice mismatch of MoS$_2$ and sapphire with a(MoS$_2$) = 3.16Å and a(sapphire) = 4.758Å would have been 50.5%. The lattice mismatch of 13% is still relatively high, but as shown previously,[32] Van der Waals epitaxial materials can tolerate a higher degree of lattice mismatch than that expected in traditional epitaxy.
Figure 2. 10 Relative in-plane orientation of MoS$_2$ to sapphire substrate with MoS$_2$ axis 30° with respect to sapphire: (a) top view and (b) side view. (Black-aluminum atom, blue-oxygen atom, purple-molybdenum atom, yellow-sulfur atom; purple dashed line-unit cell of MoS$_2$, black dashed line-unit cell of sapphire).

Figure 2. 11 Triple-axis rocking curve scan at MoS$_2$ (0002) diffraction position.
Triple-axis rocking curve scan was also measured to confirm the single crystalline nature (Figure 2. 11). A full width at half maximum (FWHM) of 15.552 arc sec at MoS$_2$ (0002) diffraction was found to be about one-half of that of exfoliated single-crystalline MoS$_2$.[33] The narrow rocking curve FWHM suggests that the MoS$_2$ films grown by vapor-solid method had high crystalline quality with relatively low density of defects.

![Figure 2.12](image.png)

**Figure 2.12** (a) HAADF-STEM image and (b) SAED pattern of free standing MoS$_2$ layer.

Scanning transmission electron microscopy (STEM) was also used to determine the structural quality and crystallinity of the transferred MoS$_2$ film. For STEM characterization, MoS$_2$ films were transferred directly to Cu-mesh TEM grids. The high angle annular dark field (HAADF) image in Figure 2. 12a confirms that the quality of the film. Selected area electron diffraction (SAED) patterns were also acquired. The patterns consistently showed single crystal diffraction patterns.
The two characteristic Raman peaks of MoS$_2$ were observed with E$_{2g}^1$ at 381.2 cm$^{-1}$ and A$_{1g}$ at 406.5 cm$^{-1}$ with a peak separation of 25.3 cm$^{-1}$ confirming the film had the characteristics of bulk (or several-layer) MoS$_2$ (Figure 2.13).$^{[34]}$

2.3.3 Transport properties of unintentionally doped (UID) MoS$_2$ films

The carrier mobility, which is strongly dependent on the crystalline quality as well as on the background impurity of the 2D film, plays a critical role in transport properties and hence on device performance. Theoretical calculations$^{[35]}$ and experiments$^{[36, 37]}$ show that
while charge impurity limited scattering in single-layer MoS\textsubscript{2} is \(\sim 17 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}\) without the high-\(\kappa\) dielectric screening effect, the intrinsic phonon-limited mobility of single-layer as well as multilayer MoS\textsubscript{2} is expected to be as high as 320-410 cm\(^2\)V\(^{-1}\)s\(^{-1}\).\(^{[38, 39]}\) Without the high-\(\kappa\) dielectric, few-layer MoS\textsubscript{2} films have been shown to have mobility from 10 to 100 cm\(^2\)V\(^{-1}\)s\(^{-1}\) \(^{[17, 40, 41]}\) which can be enhanced to several hundred cm\(^2\)V\(^{-1}\)s\(^{-1}\) with a high-\(\kappa\) dielectric environment.\(^{[40-42]}\) However, the high mobility values reported were on exfoliated samples, rather than on large area synthetic MoS\textsubscript{2}. The high space charge mobility approaching the phonon-limited values has been achieved using the vapor-solid synthesis method.

Transport properties of MoS\textsubscript{2} films were investigated by transmission line measurement (TLM). The devices were made by depositing Ti/Au contacts using photolithography, metal evaporation and lift-off. The Current-Voltage (I-V) characteristics for different contact spacing (L) are shown in Figure 2. 14. The I-V characteristics had two different region: \(I \propto V\) at low current density and \(I \propto V^2\) at higher current density. This phenomenon is typical for space charge limited transport.\(^{[43]}\) When the background carrier density is relatively low, this two-region I-V curve will be observed. Low background carrier density is good for FET devices. Quantitative calculation of space charge transport in semiconductors can be described by Mott-Guirney law

\[
I = \frac{9\varepsilon_0\varepsilon_r\mu V^2}{8L^2},
\]

Where, \(\varepsilon_0\varepsilon_r\) = permittivity \(\mu\) = mobility, \(L\) = contact spacing.
However, Mott-Guirney law is only suitable for bulk material, where one-dimensional electrostatics is valid (Figure 2. 14a). It is not correct for our devices since the field was applied laterally (Figure 2. 14b). Previous work\cite{44, 45} on the analysis of space charge transport in thin film with lateral contact used the equation

\[ I = \frac{2\varepsilon_0\varepsilon_r\mu V^2}{\pi L^2}. \] (2. 9)

This equation is suitable for the “2D” thin film situation. The current still has quadratic dependence on voltage similar to the situation in Mott-Guirney equation, but the current dependence on contact spacing changes from \( I \propto 1/L^3 \) to \( I \propto 1/L^2 \).

![Figure 2. 14 Configuration of (A) bulk contact (Mott-Guirney) and (B) “2D” contact.](image)

The equation used for fitting the I-V curve is

\[ I = \frac{q n \mu t L}{d} V + \frac{2 \varepsilon_S \mu L}{\pi d^2} V^2 \] (2. 10)

Where, q: electron charge, \( \mu \): electron mobility, t: thickness of MoS\(_2\) film, L: width of TLM pads, d: TLM pad spacing, \( \varepsilon_S \): dielectric constant of bulk MoS\(_2\) (=7.6).\cite{17, 46}
Figure 2. 15 (a) I-V log-log scale, showing two distinct slopes for linear and quadratic dependence on bias. The inset shows the device configuration. (b) I-V measured at room temperature for various TLM spacing, along with the fit to \( I = BV + CV^2 \). (c) Temperature dependent I-V for pad spacing of 3.5 \( \mu \)m. The inset shows the device configuration. (d) Theoretical estimates of temperature dependent electron mobility limited by POP, ADP, and remote impurity scattering compared with experimentally extracted mobility.

From the resulting fit (Figure 2. 15b), an electron mobility of 120 (±20) cm\(^2\)/Vs and a carrier density of 2x10\(^{11}\) cm\(^{-2}\) were extracted. Interestingly, from the I-Vs measured in a direction perpendicular (in-plane) to the direction of measurement as reported above, an
electron mobility of 65 cm$^2$/Vs and a carrier density of 2x10$^{11}$ cm$^{-2}$ were extracted by fitting I-Vs to equation 2. 10.

This observation of anisotropic electron mobility (with a mobility-ratio of ~ 1.8) in few-layer MoS$_2$ in the two mutually perpendicular directions is in agreement with prior theoretical predictions$^{[47]}$ of anisotropic electron effective mass (0.53$m_0$ vs 0.73 $m_0$) for transport in ($\Lambda_{\text{min}}$) and in (⊥$\Lambda_{\text{min}}$) directions of the crystal.

To reduce the effect of surface-related defects and impurities on the mobility, the films were covered with 20 nm of Al$_2$O$_3$ by atomic layer deposition (ALD). The ALD Al$_2$O$_3$ can passivate some of the interface charge leading to less remote impurity scattering. The I-Vs measured at various temperatures between two device pads separated by 3.5 µm are shown in Figure 2. 15c, and displayed typical characteristics of space charge transport. The extracted electron mobility showed weak temperature dependence while the carrier density was found to increase slightly from 1.3x10$^{11}$ cm$^{-2}$ at 10 K to 1.7x10$^{11}$ cm$^{-2}$ at 290 K. The room temperature electron mobility was found to be ~ 192 cm$^2$/Vs with ALD Al$_2$O$_3$ on MoS$_2$, an improvement from 120 cm$^2$/Vs which was extracted without dielectric on MoS$_2$.

A simple estimation of the electron mobility in few-layer MoS$_2$ was made based on polar optical phonon (POP) scattering,$^{[48]}$ acoustic deformation potential (ADP) scattering$^{[49]}$ and remote ionized impurity scattering in 2-dimensional electron gas,$^{[49]}$ assuming an electron effective mass of 0.53$m_0$. For remote impurity scattering, we assumed that the remote interface charge density ($n_{\text{fix}2D}$) is located at the ALD/MoS$_2$ interface, and that the 2D carriers are in the middle of the few-layer film. Since the 2D sheet carrier in our MoS$_2$ film
is non-degenerate \((2 \times 10^{11} \text{ cm}^2)\), the carrier conduction does not take place predominantly at the Fermi Level. The scattering time was therefore estimated at any energy ‘E’ and weighed with density of states and Fermi-distribution over the entire energy range (see mobility calculation in supplementary material\(^{[50]}\)).

Figure 2. 15d shows the temperature dependent electron mobility calculated using POP, ADP and remote impurity scattering times compared with experimentally extracted mobility from our MoS\(_2\) films. For a fixed remote impurity \((n_{\text{fix}2D})\) of \(1 \times 10^{11} \text{ cm}^2\), the theoretically estimated mobility seems to have a close fit to those measured data points, validating our scattering time estimates. The \(n_{\text{fix}2D} = 1 \times 10^{11} \text{ cm}^2\) which gives a good fit between theory and experiment, is also close to the actual carrier density \((1.3 \times 10^{11} - 1.7 \times 10^{11} \text{ cm}^2)\) extracted after ALD layer on MoS\(_2\).

2.3.4 Temperature effect on the growth of MoS\(_2\) films

MoS\(_2\) films were synthesized at different temperatures \((850^\circ C, 900^\circ C\) and \(1100^\circ C\)) at the same temperature ramping rate, the same cooling rate and with the same amount of MoS\(_2\) powder. The XRD and AFM characterization results are shown in Figure 2. 16 and 2. 17. From the XRD spectra, though the MoS\(_2\) phase can be obtained at lower temperature, only the spectra of films grown at \(1100^\circ C\) showed thickness fringes. That means the lower temperature product didn’t have such a flat surface as the \(1100^\circ C\) films. The AFM images of the lower-temperature films also show higher roughness RMS value, 2.68nm and
1.93nm for 850°C and 900°C sample, respectively. The high temperature of 1100°C contributed to the high quality of the MoS₂ films.

Figure 2. 16 2θ/ω XRD scans of MoS₂ films grown at different temperatures.

Figure 2. 17 AFM images of MoS₂ films grown at different temperatures.
2.3.5 Influence of cooling rate on MoS$_2$ films

Instead of cooling down the furnace at a rate of 5°C/min, the MoS$_2$ films was directly taken out of the furnace and cool down to room temperature within 5 min. The 2-θ/ω XRD scan is shown in Figure 2. 18, which still exhibits only the (0001) family diffractions of MoS$_2$ and the diffraction of sapphire (0006) peak. The preferred growth orientation of MoS$_2$ with the c-axis parallel to that of sapphire substrate did change. In the zoom-in picture, thickness fringes can be observed, but not as obvious as the slow cooling MoS$_2$ films.

Figure 2. 18 (a) 2θ/ω XRD scan and (b) zoom-in picture of 2θ/ω XRD scan of fast-cooling MoS$_2$ film on sapphire.
Figure 2. 19 Phi Scan of fast-cooling MoS$_2$ films at MoS$_2$ (10–13) diffraction position and sapphire (01–12) position.

The off-axis (10-13) 2-0/ω XRD scan across the full range of $\Theta=360^\circ$ shows six peaks at MoS$_2$ (10-13) position (Figure 2. 19), indicating the six-fold symmetry of the hexagonal phase of MoS$_2$ and the single-crystalline nature of as-grown MoS$_2$ film.
As shown in Figure 2.20, there were a lot of thick particles on the surface of the MoS$_2$ films. The RMS roughness was ~4.56nm, which was much larger than that of the slow cooling one. The fast cooling may suddenly increase the supersaturation of the sulfur and cause the increasing of the nuclei density and grow into small thick particles on the surface of the MoS$_2$ films.

2.4 Conclusion

In conclusion, via the vapor-solid growth method, high-quality few-layer MoS$_2$ films were obtained at 1100 °C using sulfur vapor by decomposing MoS$_2$ powder. The as-grown surface was found to be atomically smooth and high resolution XRD scans and Raman
spectroscopy indicated excellent out-of-plane ordering and epitaxial registry of the films over centimeter length scales. The film was found to exhibit space-charge transport and an electron mobility of 192 cm²/Vs was extracted at room temperature. The anisotropic electron mobility (with a mobility ratio of ~1.8) was also demonstrated in measurement directions mutually perpendicular to each other. ALD Al₂O₃ on MoS₂ was found to enhance the electron mobility which showed very weak temperature dependence from 10 to 290 K. A simple scattering model based on optical phonon, acoustic phonon and remote impurity scattering was found to exhibit a good match with the experimentally extracted mobility. This demonstration of record high electron mobility for synthetic large area few-layer MoS₂ films is highly promising for enabling a wide variety of large-scale electronic device fabrication based on layered 2D materials.

Reference


[50] Supporting Information for Epitaxial Growth of Large Area Single-Crystalline Few-Layer MoS2 with High Space Charge Room Temperature Mobility of 192 cm²V⁻¹s⁻¹.
3.1 Introduction

MoS\textsubscript{2} is n-type semiconductor in nature due to the strong Fermi level pinning near the conduction band, intrinsic defects and ambient interactions.\[^{[1]}\] It is challenging to dope 2D MoS\textsubscript{2} films, especially p-type doping. Several works on p-type MoS\textsubscript{2} through charge transfer, surface functionalization, plasma treatment and substitutional CVD doping have been reported.\[^{[2-5]}\] The use of Niobium (Nb) as a substitutional impurity on the metal site to get p-type conductivity was suggested several decades ago\[^{[6-8]}\] for bulk MoS\textsubscript{2} and WSe\textsubscript{2}. Hole mobility of 10 cm\textsuperscript{2}/Vs in Nb-doped MoS\textsubscript{2} flakes obtained by transport reaction had been reported earlier,\[^{[9]}\] but such MoS\textsubscript{2} flakes were few microns to few hundred microns thick. Besides, no detailed investigations into the material quality of such thick Nb-doped MoS\textsubscript{2} were reported. P-type conductivity has also been electrostatically achieved on MoS\textsubscript{2} mechanically exfoliated from geological samples using back-gating and liquid-gating approaches.\[^{[10]}\] However, no report exists for \textit{in situ} p-doping using an acceptor dopant in epitaxial (and even mechanically exfoliated) MoS\textsubscript{2} thin films, which is necessary for demonstration of MoS\textsubscript{2}-based bipolar devices such as heterojunction bipolar transistors (HBT), light emitting diodes (LEDs), and photodetectors.
The integration of 2D semiconductors with the conventional three-dimensional (3D) substrates could enable semiconductor heterostructures with unprecedented properties. Direct growth of \( p \)-type MoS\(_2\) films on SiC was demonstrated using vapor-solid growth method. The resulting heterojunction was found to display rectification and current-voltage characteristics consistent with a diode for which forward conduction in the low-bias region is dominated by multi-step recombination tunneling. Capacitance-voltage measurements were used to determine the built-in voltage for the \( p \)-MoS\(_2/\)n-SiC heterojunction diode.

3.2 Experimental Section

3.2.1 Reagents, materials and instruments

Molybdenum disulfide powder (99.98%) was purchased from Sigma-Aldrich. The sputtering instrument was AJA Orion RF/DC Sputter Deposition Tool. A Bruker AFM system with carbon tips operating at 300 kHz resonant frequency was used for all scans. Raman characterizations were done using a Renishaw spectrometer at 514 nm laser excitation (laser power 6 mW). High resolution X-ray diffraction was done using a Bruker X-ray diffractometer with Cu K\( \alpha \)l source. A Technai F20 Philips instrument operated at 200 keV was used for TEM imaging. Cross-section samples for study were prepared using a focused ion beam nano manipulator (Quanta 3D FEG, FEI).
3.2.2 Synthesis of p-type MoS$_2$ film on sapphire

Niobium (Nb), which has one less valence electron than Mo was doped into MoS$_2$ to get p-type semiconductor. Mo and Nb layers were first deposited on sapphire substrate by sputtering (AJA Orion Radio Frequency/Direct Current (RF/DC) Sputter Deposition Tool) to form a 2.5nmMo/0.2nmNb/2.5nmMo sandwich structure. Then, Nb doped MoS$_2$ films were obtained by the same vapor-solid process. Doping was successful due to the diffusion of Nb into MoS$_2$ lattice (Figure 3.1).

![Diagram showing the Nb doping process](image)

Figure 3.1 Schematic of Nb-doping in MoS$_2$ through vapor-solid method.

3.2.3 Synthesis of p-type MoS$_2$ film on SiC

The 4H-SiC with hexagonal symmetry is in the space group $P6_3mc$ with $a=3.073\text{Å}$ and $c=10.053\text{Å}$. The lattice mismatch of “a” with that of MoS$_2$ is only 2.75% (Figure 3.2).
Figure 3. 2 Schematic of MoS$_2$ on SiC (yellow-sulfur atoms, purple-molybdenum atoms, blue-Si atoms and black-carbon atoms).

Nb-doped MoS$_2$ was grown directly on commercially available nitrogen-doped 4H-SiC substrates with 4° miscut (n-type carrier concentration of approximately $8.6 \times 10^{18}$ cm$^{-3}$). The substrates were degreased using acetone, isopropanol, and deionized water with ultrasonic agitation, then baked at 120 °C for 5 min. 2.5nmMo/0.2nmNb/2.5nmMo layers were deposited on the n-SiC substrates by sputtering. 90 mg of MoS$_2$ powder was used as sulfur source and placed in a small quartz tube. The small quartz tube and the metalized substrate were inserted in a larger quartz tube. The open end of the large quartz tube was pumped down by a mechanical pump for 30 min, sealed and heated to 1100 °C for 4.5 h, and then cooled down to room temperature at a rate of 0.5 °C/min.
3.3 Results and Discussion

3.3.1 Nb-doped MoS₂ films on sapphire

For Nb-doped MoS₂ on sapphire, two samples with different thickness of Nb were prepared to control the doping density. Sample A was made with 0.3nmNb and sample B was made with 0.2nmNb. The material and structural quality of the Nb doped MoS₂ films on sapphire were assessed using Raman spectroscopy, high resolution XRD scans, aberration-corrected STEM imaging, and optical absorbance measurements. Figure 3. 3 shows the on-axis XRD scans for the samples A, and B. The (002) peak of MoS₂ was observed in all the three scans although the intensity for sample A was lower, indicating degradation of material quality under such high doping levels \(1.5 \times 10^{21} \text{ cm}^{-3}\). Sample B exhibited high intensity (002), (004), and (006) peaks, indicative of good crystalline quality of MoS₂.

![Figure 3. 3 2θ/ω XRD scan of Nb doped MoS₂ films on sapphire.](image-url)
The comparison of 2θ/ω XRD scan of sample B and the UID MoS\(_2\) films indicates that the high quality of the film was preserved after Nb doping (Figure 3. 4a). The six-fold symmetry can also be observed in the Phi scan (Figure 3. 4b). AFM measurements of sample B with RMS of 1.3 nm is shown in Figure 3. 5.

Figure 3. 4 (a) 2θ/ω XRD scan and (b) Phi scan of Nb doped MoS\(_2\) films on sapphire (sample B).
Figure 3. 5 AFM of Nb doped MoS$_2$ (sample B).

Figure 3. 6a shows the Raman spectra of the samples taken with a Renishaw, 514 nm laser (with 60mW power). Characteristic in-plane ($E_{12g}$) and out-of-plane ($A_{1g}$) vibrational modes were observed at 381 and 407 cm$^{-1}$, respectively, for all the three samples. This indicates that the phonon spectrum of MoS$_2$ remains unchanged despite the addition of Nb.
Figure 3. 6 (a) Raman spectra on p-type MoS$_2$ sample A ($p = 1.5 \times 10^{21} \text{ cm}^{-3}$), sample B ($p = 3.1 \times 10^{20} \text{ cm}^{-3}$), and UID MoS$_2$ film. (b) Absorbance measurements for samples A ($p = 1.5 \times 10^{21} \text{ cm}^{-3}$), B ($p = 3.1 \times 10^{20} \text{ cm}^{-3}$), and UID MoS$_2$ film.

Optical absorbance measurements were performed on all the samples using a broad UV-VIS-NIR deuterium-tungsten-halogen white light source. The absorbance spectra was taken for a reference piece of sapphire in order to determine a reference intensity $I_0(\lambda)$. The MoS$_2$ sample was measured and the absorbance was determined using $A = I(\lambda)/I_0(\lambda)$, where $I(\lambda)$ is the intensity collected by the monochromator after the light is transmitted through the MoS$_2$ grown on sapphire. The normalized absorbance spectra (Figure 3. 6b) show that all three samples A, B, and UID MoS$_2$ exhibit an absorption edge at 1.8 eV indicative of a
direct band-to-band transition in these semiconductors. DFT calculations show that although the lowest energy transition in bulk MoS$_2$ is approximately 1.2 eV, the direct transition of approximately 1.8 eV still exists at the $K$ point.\textsuperscript{[11]} This is verified by the fact that both PL as well as absorbance measurements on bulk MoS$_2$ have been found to exhibit a prominent transition or peak around 1.8–1.9 eV which has been attributed to direct-gap transitions between split valence band maxima ($v_1$ and $v_2$) and conduction band minima all located at $K$ point of Brillouin zone.\textsuperscript{[12]} For the Nb-doped samples A and B, the 1.8 eV direct gap is found to exhibit clear band tails, which is a good indicator of the shallow Nb states. The multiple blue/UV peaks are possibly due to transitions involving higher bands.

STEM imaging was performed on an aberration-corrected Nion Ultra STEM-100\textsuperscript{TM} electron microscope operating at an acceleration voltage of 60 kV. The atomic resolution Z-contrast STEM image of the Nb-doped sample B is shown in Figure 3.7. The Z-contrast image reveals that the ordered crystalline nature of the MoS$_2$ layers stacked in the [0001] direction on a sapphire substrate is preserved even with degenerate p-type doping.
The carrier density was studied by Hall measurement. A Ni (30 nm)/Au (50 nm)/Ni (30 nm) metal stack was deposited by e-beam evaporation to form Ohmic contacts to Nb-doped MoS₂. Devices were isolated by etching MoS₂ using BCl₃/Ar-based inductively coupled plasma/reactive ion (ICP-RIE) etch chemistry. Hall measurements were performed using standard van der Pauw pads, and both samples A and B had positive Hall coefficients indicating hole transport. Temperature dependent Hall measurements for sample A showed no carrier freeze-out even at 20 K (Figure 3. 8a), indicating that degenerate p-type doping had been achieved. Negligible dependence of hole mobility on temperature was observed for sample A. The room temperature hole mobility measured for sample A was 0.5 cm²/Vs with a hole density of $N_A = 1.5 \times 10^{21}$ cm⁻³. Sample B with a lower Nb concentration was
found to exhibit a room temperature hole mobility of 8.5 cm$^2$/Vs with a corresponding p-type charge density of $3.1 \times 10^{20}$ cm$^{-3}$. From transfer length method (TLM) measurements, a low contact resistance of 0.6 Ω mm was extracted for sample B (Figure 3. 8b). The sheet resistance extracted from TLM was 1.8 kΩ/□ which was found to match that obtained from Hall measurement. The significant improvement in hole mobility (8.5 cm$^2$/Vs from 0.5 cm$^2$/Vs) with a reduction in p-doping density indicates that the mobility is limited mainly by ionized impurity scattering at such high degenerate doping densities.

![Figure 3. 8(a) Temperature-dependent Hall measurement on degenerately doped p-type MoS$_2$ film (sample A) showing no carrier freeze-out at 20 K. (b) TLM fitting to extract sheet and contact resistance on p-type MoS$_2$ film (sample B).](image)

Figure 3. 8 (a) Temperature-dependent Hall measurement on degenerately doped p-type MoS$_2$ film (sample A) showing no carrier freeze-out at 20 K. (b) TLM fitting to extract sheet and contact resistance on p-type MoS$_2$ film (sample B).
3.3.2 Nb-doped MoS$_2$ films on SiC

The crystalline orientation and quality of Nb-doped MoS$_2$ films on SiC were evaluated using double-axis high-resolution X-ray diffraction (XRD) measurements (Figure 3.9). The XRD spectra show the characteristic (002), (006), and (008) peaks for MoS$_2$ as well as the (004) peak of 4H-SiC. The crystallinity of MoS$_2$ on SiC suggests that, similar to the previous work on sapphire, optimal growth conditions lead to high quality growth of layered TMDs, this time on electrically active substrates. Figure 3.10 shows a 5 $\mu$m $\times$ 5 $\mu$m atomic force microscope scan of Nb doped MoS$_2$ on nitrogen-doped 4H-SiC with 1.66 nm RMS roughness.

![Figure 3.9 High resolution 20/ω XRD spectra of Nb doped MoS$_2$ grown on SiC with (002), (006), and (008) peaks of MoS$_2$ and (004) peak of 4H-SiC.](image-url)
Figure 3. 10 AFM image of Nb doped MoS$_2$ on SiC.

Lateral transport measurements performed on Nb doped MoS$_2$ on SiC between two Ni/Au/Ni contacts on a mesa were linear, confirming Ohmic conduction in the film. A contact resistance of 0.78 $\Omega$-mm (specific resistivity $3.6 \times 10^{-6}$ $\Omega$-cm$^2$) and sheet resistance of 1.7 k$\Omega$/□ were extracted from transfer length method (TLM) measurement. The sheet resistivity is lower than achievable in Nb doped MoS$_2$ films on sapphire substrate.
Current decreases with decreasing temperature and the transport in the exponential region of the I-Vs is found to be dominated by multi-step recombination tunneling. The inset shows the fabricated device structure.

The vertical current-voltage (I-V) characteristic was measured between an Ohmic contact to Nb doped MoS$_2$ (contact area 2500 $\mu$m$^2$) and indium metal dots pressed into the backside of the SiC substrate (inset of Figure 3. 11). Bias was applied to the Nb doped MoS$_2$ Ohmic contact with respect to the $n$-SiC contact. The room temperature I-V characteristic showed 6 orders of rectification ($+/\sim 2.0$ V) and a characteristic slope of 112 mV/decade. The temperature dependent I-V characteristics for the MoS$_2$/SiC diode is also shown in Figure 3. 11. Current density only varies slightly over a wide range of
temperatures, indicating that the diode current is relatively temperature independent. At room temperature, the diode has an ideality factor, $\eta$, greater than 2 (2.1), and the ideality factor increases with decreasing temperature.

3.3.3 Transferred Nb-doped MoS$_2$ films on GaN

The Nb doped MoS$_2$ has also been transferred to GaN substrate to form p-MoS$_2$/n-GaN diode. Since the GaN can will decompose at the high temperature for MoS$_2$ synthesis. The GaN templates onto which the p-MoS$_2$ films were transferred were obtained from Lumilog and were n-type doped ($N_D = 3 \times 10^{18}$ cm$^{-3}$). An additional 200 nm of lightly doped n-type GaN ($N_D = 7 \times 10^{17}$ cm$^{-3}$) was grown by molecular beam epitaxy on the GaN/sapphire templates to reduce band-to-band tunneling leakage in the transferred p-MoS$_2$/n-GaN diodes. Vertical current-voltage (J-V) characteristics of the MoS$_2$/GaN heterojunction diode were measured by applying bias to the Ni/Au/Ni contacts on p-MoS$_2$ (Figure 3.12). The room temperature J-V characteristics showed 9 orders of magnitude rectification at $+/−$2 V and exhibited an ideality factor of approximately 2 in the exponential region before series resistance became dominant. This indicates that transport in the MoS$_2$/GaN heterojunction diode is likely dominated by recombination current.
The current-voltage characteristic of p$^+$-MoS$_2$/n-GaN diode exhibits 9 orders of magnitude rectification. The ideality factor extracted from the room temperature characteristic is approximately 2, indicating the forward biased transport is dominated by recombination current. (Inset: Linear scale).

3.4 Conclusion

In conclusion, Nb can act as an efficient acceptor in MoS$_2$ leading to high hole density and relatively high mobility. For a hole concentration of $3.1 \times 10^{20}$ cm$^{-3}$, a hole mobility of 8.5 cm$^2$/Vs was measured at room temperature and was found to be limited by ionized impurity limited scattering. The use of Nb substitutional impurity for p-type doping demonstrated here for MoS$_2$ could be extended to other dichalcogenides and could
therefore have wider applications. A large-area heterojunction between \textit{p-type} 2D layered MoS$_2$ and \textit{n-type} 4H-SiC has been demonstrated. MoS$_2$ grown on SiC was found to have good structural and surface quality. The MoS$_2$/SiC heterojunction is rectifying and that the built-in voltage is approximately 2.2 V. The \textit{p-type} MoS$_2$/\textit{n-type} GaN diodes were formed by film transfer. The diodes exhibited excellent rectification. This work demonstrates the potential of 2D/3D heterojunctions for novel device applications.

Reference


4.1 Introduction

4.1.1 Mo-S system for HER

Hydrogen is the chemical fuel with the largest energy density in the world. Generating hydrogen from water splitting has drawn great interest for decades. To date, the best hydrogen evolution reaction (HER) electrocatalysts are the Pt-group metals. However, the low abundance and high cost hinder their applications. Therefore, searching for alternative HER catalyst is of crucial importance. According to Sabatier principle, the requirement for the optimal HER catalyst is the “moderate” binding of hydrogen on the catalytic sites, which is reflected by “close to zero” Gibbs free energy for atomic hydrogen adsorption ($\Delta G_{\text{ads}}(H) \approx 0$). The volcano-type relations between the exchanged current density and $\Delta G_{\text{ads}}(H)$ have been observed for various metallic HER catalysts. The state-of-the-art HER catalyst such as Pt (111) has a close-to-zero $\Delta G_{\text{ads}}(H)$ of only -0.09 eV.

MoS$_2$ has been discovered as an alternative to the Pt-group catalysts for HER. Both computational and experimental studies prove that the under-coordinated sulfur atoms on the sulfur edges of the MoS$_2$ plates have excellent catalytic activity for HER, while the (0001) basal planes are inert. Thus, developing MoS$_2$ material with more exposed edge
is one strategy to enhance its catalytic property. Considerable efforts have been made in synthesizing different MoS$_2$ nanostructures to expose more edges.$^{[7-12]}$

Designing Mo-S based clusters with analog of MoS$_2$ sulfur edges is another promising way to improve the catalytic activity. The amount of the active and inert sites in the material can be precisely controlled, and the sulfur edge density can be maximized. Different analogs of the MoS$_2$ edges can potentially be designed. Karunadasa et al., have integrated the single “Mo-S$_2$” triangular functional unit into a molecular catalyst for homogeneous HER.$^{[13]}$ The cluster [Mo$_3$S$_{13}$]$^{2-}$, trimer analog of MoS$_2$ edge sites, has also been reported to be an advanced heterogeneous HER catalyst very recently.$^{[14]}$ Whereas, compared to the nanostructuring of MoS$_2$, few studies about the Mo-S clusters have been reported.

4.1.2 Possible active sites in Mo-S systems

As shown in Figure 4.1, there are two kinds of sulfur-rich edge sites in MoS$_2$ structure. The sulfur atoms covering the (10-10) Mo edges are the terminal sulfur atoms and the sulfur atoms on the surface of the (-1010) Mo edges are the bridging sulfur atoms. The binding energy of these two kinds of sulfur are different, so they can be distinguished by XPS. The well-defined Mo-S clusters are also crucial for identifying and understanding the function of the active sites and the catalytic mechanism.
Figure 4. 1 Schematic of MoS$_2$ with edge sites highlighted.

Figure 4. 2 shows the structure of the reported [PY5Me$_2$MoS$_2$]$^{2+}$ and [Mo$_3$S$_{13}$]$^{2-}$ clusters and their relationship with the MoS$_2$ edges. We report designed another Mo-S cluster, a dimer analog, (NH$_4$)$_2$[Mo$_2$(S$_2$)$_6$]-2H$_2$O, with bridging S$_2$ and terminal S$_2$. The comparison of the turnover frequency at 200 mV overpotential proves the superiority of our (NH$_4$)$_2$[Mo$_2$(S$_2$)$_6$]-2H$_2$O catalyst over all the other non-noble metal supported Mo-S based HER catalysts.
Figure 4. 2 The relationship of the Mo–S based molecular HER catalysts to the monolayer MoS$_2$ with sulfur-rich edges: the discrete analogue [(PY5 Me$_2$)MoS$_2$]$^{2+}$, the trimeric analogue [Mo$_3$S$_{13}$]$^{2-}$ cluster, and our dimeric analogue [Mo$_2$S$_{12}$]$^{2-}$ cluster.

4.2 Experimental Section

4.2.1 Reagents and materials and instruments

All chemicals were used as received: (NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O and NH$_2$OH·HCl were purchased from Sigma-Aldrich; 200 proof ethyl alcohol and ACS grade isopropyl alcohol from Fisher Scientific; de-ionized water (18MΩ-level) from the Barnstead E-Pure system. Fluorine-doped tin oxide (FTO) glass pieces from Hartford Glass Co.
The X-ray photoelectron spectroscopy (XPS) analyses were performed on a Kratos Axis Ultra XPS with monochromatic Al X-ray source, at an operation voltage as 12 kV and a current as 10 mA. All the XPS spectra were calibrated with C 1s at 284.6 eV. The SEM (FEI/Philips Sirion Field Emission SEM) was used to obtain the morphology of the crystal. The elemental mapping was acquired by Energy Dispersive Spectrometer using X-rays (EDS) that incorporated on the SEM. The Raman spectra were collected on Renishaw microscope Raman spectrometer with a 514 nm excitation wavelength at 50X zoom. The power of the laser was 0.6 mW to avoid sample damage, and the acquisition time was 20s. Raw data were used without further data processing.

Submonolayer of catalyst was loaded via lay-by-layer deposition method with the help of a commonly used polycation poly(diallyldimethylammonium chloride) (PDDA). Glass pieces (2.5×2.5×0.3 cm³) coated with fluorine-doped tin oxide (FTO) were cleaned by sonication in soap water, DI water, ethanol and acetone solution, respectively. After being dried, the FTO substrates were soaked in diluted PDDA solution (MW<100000, 0.035 w.t.% in water) for 8 min, washed by H₂O (4 min), and then soaked in 0.05 mM methanolic Mo2 solution for another 8 min, washed by methanol (2 min) and H₂O (2 min), and then completely dried for electrochemistry test. Massive loading on FTO was done by directly drop-casting 1 mM [Mo₂S₁₂]²⁻ DMF solution and vacuum-dried. To determine the amount of sub-monolayer loading, the loaded catalysts on FTO was washed off by sonicating in 15 ml 0.1 M NaOH solution for 1 hr and immersing in the solution for overnight. The concentration of Mo in the resulted solution was measured by inductively coupled plasma (ICP) measurement. The amount for sub-monolayer loading of [Mo₂S₁₂]²⁻ is determined
to be 0.17 nmol cm$^{-2}$ on FTO. The Glassy carbon (GC) electrode (CHI, $d=3.0$ mm, $A=0.071$ cm) to a mirror finish with aqueous slurry of 0.05 µm alumina powder on a polishing microcloth (BUEHLER), cleaned with deionized (DI) water and acetone, and dried before each use. A homogeneous ink was made from fresh DMF solution, 30 mg/mL of Super P® Li carbon and 80 µL/L of 5 wt% Nafion solution. The paste was drop-casted on the GC electrode surface through micropipette, and then dried in the vacuum oven. Various amount of $[\text{Mo}_2\text{S}_{12}]^{2-}$ was loaded by control the concentration of the paste and the loading volume.

The glassy carbon (GC) electrode (CHI, $d=3.0$ mm, $A=0.071$ cm) to a mirror finish with aqueous slurry of 0.05 µm alumina powder on a polishing microcloth (BUEHLER), cleaned with deionized (DI) water and acetone, and dried before each use. A homogeneous ink was made from fresh DMF solution, 30 mg/mL of Super P® Li carbon and 80 µL/L of 5 wt% Nafion solution. The paste was drop-casted on the GC electrode surface through micropipette, and then dried in the vacuum oven. Various amount of $[\text{Mo}_2\text{S}_{12}]^{2-}$ was loaded by control the concentration of the paste and the loading volume.

The electrochemical tests were carried out by Reference 600 potentiostat (Gamry Instruments, Warminster, PA) in a custom made three-electrode electrochemical cell, with 0.5 M H$_2$SO$_4$ (pH~0) as the electrolyte solution sparged with Ar gas. GC electrode modified by different catalyst/loading was used as the working electrode, and the counter electrode was a graphite rod. The Ag/AgCl reference electrode (3 M NaCl, BASI) was calibrated to the reversible hydrogen electrode (RHE) potential with Pt meshes being both working and counter electrodes in the same 0.5 M H$_2$SO$_4$ solution purged with high purity. The shift was -0.239 V vs. RHE. The polarization curves were measured by LSV with a scan rate of 5 mV s$^{-1}$. The $j-V$ curve shown in the paper are all $iR$ corrected. The EIS were performed at different DC bias with the frequency range of $2 \times 10^5 \sim 1 \times 10^3$ Hz and the AC amplitude of 10 mV. The accelerated stability test was applied through cyclic voltammetry at 0.2 V $\sim$ –0.25 V vs. RHE with a scan rate of 100 mV/s. The chronocoulometry (CA) test was performed using a GC rotating disk electrode (Pine Instrument, $d=5.0$ mm, $A=0.196$ cm$^2$) with a rotating rate of 2500 r.p.m, which can help
remove the in-situ generated H₂ bubble. The electrochemical tests with FTO working electrode were carried out in a custom made three-electrode electrochemical cell with FTO sealed by the O-ring.

4.2.2 Synthesis of (NH₄)₂[Mo₂(S₂)₆]·2H₂O

The (NH₄)₂[Mo₂(S₂)₆]·2H₂O clusters were prepared based on the method of Müller et al. [15-18], but with some important modifications. 2.0g of (NH₄)₆Mo₇O₂₄·4H₂O and 1.5g of NH₂OH·HCl were dissolved in 30 ml deionized (DI) water (> 18.0 MΩ cm) to form a reddish brown solution, to which a 30 ml of dark red (NH₄)₂Sₓ solution was added afterwards. The mixed solution was warmed at 50°C for 1 hr, then cooled to room temperature and filtered. The filtrate was heated at 90°C for another 4 hrs and filtered again after being cooled down. Then, 10 ml (NH₄)₂Sₓ solution was added to the reddish brown filtrate under magnetic stirring at room temperature. The resulting solution in a 100 ml Erlenmeyer flask was transferred to a sealed box filled with Ar gas. After overnight reaction, the black rod-shaped crystals of (NH₄)₂[Mo₂(S₂)₆]·2H₂O precipitated out from the solution, which were collected by filtration afterwards. The black crystals were further purified by wash with 10 ml ice-cold water, 20 ml 2-propanol, 15 ml carbon disulfide, and 20 ml diethyl ether for a couple of times. The sample was dried in the vacuum oven at room temperature, and then stored in the glovebox. The identity and purity of the sample were confirmed by XRD measurements.
4.2.3 Synthesis of (NH₄)₂[Mo₃S(S₂)₆]·H₂O

(NH₄)₂[Mo₃S(S₂)₆]·H₂O was prepared according to the method of Müller et al.¹⁵,¹⁷ 4.0 g (NH₄)₆Mo₇O₂₄·4H₂O dissolved in 30 ml DI water was mixed with 80 ml of (NH₄)₂Sₓ solution, and then heated at 90°C in a glass Erlenmeyer flask for 15 hrs. The Dark-red crystals of (NH₄)₂[Mo₃S(S₂)₆]·H₂O were collected by filtration, and then washed successively with 300 ml water, 25 ml ethanol, 20 ml carbon disulfide (three times), and 20 ml diethyl ether, and finally dried in the vacuum oven at room temperature. The identity of the crystals confirmed by powder XRD.

4.3 Results and Discussion

4.3.1 Characterization of the (NH₄)₂[Mo₂(S₂)₆]·2H₂O and (NH₄)₂[Mo₅S₁₃]·H₂O

The crystal structure was first extracted from the single-crystal XRD data (Figure 4.3). The single-crystal XRD analysis shows that (NH₄)₂[Mo₂(S₂)₆]·2H₂O crystallizes in the orthorhombic space group Pnna with a =21.2927(11) Å, b =13.0408(7) Å, c = 12.6064(7) Å. The two bridging S₂ have a shorter S–S bond length of 2.034(5) Å, and the bond length of the two terminal S₂ is 2.053(2) Å.
The powder XRD was also measured, which is consist with the simulated result from the \((\text{NH}_4)_2[\text{Mo}_2(\text{S}_2)_6]\cdot2\text{H}_2\text{O}\) crystal structure (Figure 4. 4). Similarly, the experimental XRD data of \((\text{NH}_4)_2[\text{Mo}_3\text{S}_{13}]\cdot\text{H}_2\text{O}\) agrees well with simulated one (Figure 4. 5).
Figure 4. 4 Powder X-ray diffraction data of (NH₄)₂[Mo₂(S₂)₆]·2H₂O.

Figure 4. 5 Powder X-ray diffraction data of (NH₄)₂[Mo₃S₁₃]·H₂O.
Due to the difference of S-S bond length in bridging and terminal S$_2$ ligand (The bridging S$_2$ is 0.02 Å shorter than the terminal one), these two kinds of S$_2$ ligand were detected by Raman at different frequency (550 cm$^{-1}$ for bridging S$_2$ and 520 cm$^{-1}$ for terminal S$_2$). Figure 4. 6 shows the Raman spectra of (NH$_4$)$_2$[Mo$_3$S$_{13}$]·H$_2$O using different laser power. The sample is easily oxidized to be MoO$_3$ if the laser power is larger than 1% in the air (514nm, 50x zoom), as indicated by the black line. The Raman spectra of (NH$_4$)$_2$[Mo$_3$S$_{13}$]·H$_2$O qualitatively resembles that from the literature, but the intensities are not exactly the same.$^{[19]}$ The intensity of v(S-S)$_{br}$ is larger than v(S-S)$_{t}$, which is also observed in the earlier literature$^{[19]}$, but different from the recent report.$^{[14]}$

![Figure 4. 6 Raman spectra of (NH$_4$)$_2$[Mo$_3$S$_{13}$]·H$_2$O.](image)
The Raman spectra of (NH$_4$)$_2$[Mo$_2$S$_{12}$]·2H$_2$O is shown in Figure 4.7. Compared to the reported value of $\nu$ (S-S) for different type of S$_2$ ligand (725 cm$^{-1}$ for neutral S$_2$, 589 cm$^{-1}$ for S$^-$ and 446 cm$^{-1}$ for S$^{2-}$ due to the difference of S-S bond length, 2.00 Å for S$^-$ and 2.13 Å for S$^{2-}$), the charge distribution of the S$_2$ unit in our [Mo$_2$S$_{12}$]$^{2-}$ should be between -1 and -2.
Figure 4. 8 XPS spectra of $[\text{Mo}_2\text{S}_{12}]^{2-}$ solid powder and the deposited film. (a) Deconvolution of the Mo 3d region. (b) The S 2p spectra consist of three different doublets (S 2p1/2 and S 2p3/2).
The clusters can be deposited on an electrode surface by facile drop-casting methods. Figure 4.8 shows the X-ray photoelectron spectroscopy (XPS) spectra of Mo 3d and S 2p region for the as-synthesized crystalline powder sample and the deposited film on FTO by drop-casting fresh 1 mM [Mo$_2$S$_{12}$]$_{2^{-}}$ dimethylformamide (DMF) solution. The binding energy (BE) is 229.4 eV and 232.6 eV for Mo 3d5/2 and Mo 3d3/2, respectively. In the literature of (NH$_4$)$_2$[Mo$_2$(S$_2$)$_6$]·2H$_2$O, the BEs of Mo 3d doublets were reported to be 230.3 eV and 233.4 eV.$^{[20]}$ The separation between the two peaks is similar for our study and reference$^{[20]}$. However, it is hard to compare the absolute BE value because the reported study calibrated N 1s of NH$_4^+$ to 403.0 V, which should normally appear at lower binding energies.$^{[21-23]}$ The broad S 2p spectra consist of three different doublets (S 2p3/2 and S 2p1/2): (i) one at (161.8 eV, 163.0 eV) ascribed to the terminal S$_2$ ligands, (ii) one at (163.1 eV, 164.2 eV) due to the bridging S$_2$ ligands, and (iii) one at higher BE contributed from trace amount (<5%) of residual polysulfides. The clear separation of the spectra of the terminal and bridging S$_2$ ligands differentiate it from those MoS$_2$ and amorphous MoS materials. The ratio of terminal to bridging sulfur at the surface was slightly lower than the theoretical value (2:1), but remained the same for both the crystalline powder and the deposited film sample. Therefore, we conclude that the structure of the anionic cluster on the electrode surface is unchanged.
4.3.2 Electrochemical test

The electrocatalytic activities were investigated on GC electrode in 0.5 M H$_2$SO$_4$ solution, via linear sweep voltammetry (LSV) with a scan rate of 2 mV s$^{-1}$ using a typical three-electrode setup. The polarization curve of [Mo$_2$S$_{12}$]$^{2-}$ and [Mo$_3$S$_{13}$]$^{2-}$ is displayed in Figure 4. The catalytic activity of [Mo$_2$S$_{12}$]$^{2-}$ is superior to that of [Mo$_3$S$_{13}$]$^{2-}$ with the equivalent mole of catalyst loading.

![Polarization curves of [Mo$_2$S$_{12}$]$^{2-}$ and [Mo$_3$S$_{13}$]$^{2-}$](image)

Figure 4. Polarization curves of [Mo$_2$S$_{12}$]$^{2-}$ and [Mo$_3$S$_{13}$]$^{2-}$. 
Figure 4. 10 XPS spectra of [Mo$_2$S$_{12}$]$^{2-}$ film before and after HER test: (a) Mo 3d region and (b) S 2p region.
<table>
<thead>
<tr>
<th>Mo 3d</th>
<th>position (eV)</th>
<th>FWHM (a.u.)</th>
<th>Area (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>solid</td>
<td>Mo 3d 5/2</td>
<td>229.45</td>
<td>0.987</td>
</tr>
<tr>
<td></td>
<td>Mo 3d 3/2</td>
<td>232.58</td>
<td>1.187</td>
</tr>
<tr>
<td></td>
<td>S 2s</td>
<td>226.87</td>
<td>3.023</td>
</tr>
<tr>
<td>film</td>
<td>Mo 3d 5/2</td>
<td>229.41</td>
<td>0.927</td>
</tr>
<tr>
<td></td>
<td>Mo 3d 3/2</td>
<td>232.55</td>
<td>1.129</td>
</tr>
<tr>
<td></td>
<td>S 2s</td>
<td>227.04</td>
<td>2.906</td>
</tr>
<tr>
<td>film after HER</td>
<td>Mo 3d 5/2</td>
<td>229.42</td>
<td>1.827</td>
</tr>
<tr>
<td></td>
<td>Mo 3d 3/2</td>
<td>232.54</td>
<td>1.774</td>
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<tr>
<td></td>
<td>S 2s</td>
<td>226.28</td>
<td>1.7161</td>
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Table 4. 1 Summary of the Mo 3d XPS result of [Mo$_2$S$_{12}$]$^{2-}$.

<table>
<thead>
<tr>
<th>S 2p</th>
<th>position (eV)</th>
<th>FWHM (a.u.)</th>
<th>Area (a.u.)</th>
<th>Terminal /bridging</th>
</tr>
</thead>
<tbody>
<tr>
<td>solid</td>
<td>terminal</td>
<td>S 2p 3/2</td>
<td>161.86</td>
<td>0.906</td>
</tr>
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<td></td>
<td></td>
<td>S 2p 1/2</td>
<td>162.96</td>
<td>1.059</td>
</tr>
<tr>
<td>bridging</td>
<td>S 2p 3/2</td>
<td>163.04</td>
<td>0.84</td>
<td>440.2</td>
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<td></td>
<td></td>
<td>S 2p 1/2</td>
<td>164.18</td>
<td>1.0004</td>
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<tr>
<td>bridging</td>
<td>S 2p 3/2</td>
<td>164.45</td>
<td>1.015</td>
<td>356.18</td>
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<td></td>
<td></td>
<td>S 2p 1/2</td>
<td>164.6</td>
<td>0.973</td>
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<tr>
<td>bridging</td>
<td>S 2p 3/2</td>
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<td>316.88</td>
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<tr>
<td></td>
<td></td>
<td>S 2p 1/2</td>
<td>163.34</td>
<td>0.807</td>
</tr>
<tr>
<td>bridging</td>
<td>S 2p 3/2</td>
<td>164.33</td>
<td>1.069</td>
<td>350</td>
</tr>
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<td></td>
<td></td>
<td>S 2p 1/2</td>
<td>164.81</td>
<td>1.131</td>
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<tr>
<td>film</td>
<td>terminal</td>
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<td>162.75</td>
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<td>bridging</td>
<td>S 2p 3/2</td>
<td>164.13</td>
<td>0.706</td>
<td>316.88</td>
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<tr>
<td></td>
<td></td>
<td>S 2p 1/2</td>
<td>163.34</td>
<td>0.807</td>
</tr>
<tr>
<td>bridging</td>
<td>S 2p 3/2</td>
<td>164.33</td>
<td>1.069</td>
<td>350</td>
</tr>
<tr>
<td></td>
<td></td>
<td>S 2p 1/2</td>
<td>164.81</td>
<td>1.131</td>
</tr>
<tr>
<td>bridging</td>
<td>S 2p 3/2</td>
<td>162.82</td>
<td>1.25</td>
<td>357.16</td>
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<td></td>
<td></td>
<td>S 2p 1/2</td>
<td>163.06</td>
<td>1.304</td>
</tr>
<tr>
<td>bridging</td>
<td>S 2p 3/2</td>
<td>163.96</td>
<td>1.37</td>
<td>178</td>
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<tr>
<td></td>
<td></td>
<td>S 2p 1/2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>bridging</td>
<td>S 2p 3/2</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>S 2p 1/2</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 4. 2 Summary of the S 2p XPS result of [Mo$_2$S$_{12}$]$^{2-}$.
After HER test, the Mo 3d spectra remained similar. For S 2p spectra, the doublet of polysulfide residue disappeared, which consists with what was reported for $[\text{Mo}_3\text{S}_{13}]^{2-}$.[14]

The peak positions of terminal and bridging $\text{S}_2$ remained the same. The Mo to S ratio from XPS changed slightly, which clearly demonstrates that sulfur was not kicked out in the HER catalytic cycle. The detailed analysis are shown in Table 4.1 and Table 4.2.

4.4 Conclusion

In conclusion, a novel incomplete cubane cluster $(\text{NH}_4)_2[\text{Mo}_2(\text{S}_2)_6]\cdot2\text{H}_2\text{O}$ has been reported as an excellent HER catalyst. The crystal structure of $(\text{NH}_4)_2[\text{Mo}_2(\text{S}_2)_6]\cdot2\text{H}_2\text{O}$ was well characterized by synchrotron-radiated single-crystal X-ray diffraction. The catalyst can be loaded on GC and FTO electrodes by drop-casting of its methanol solution. The comparison of the turnover frequency at 200 mV overpotential proves the superiority of our $(\text{NH}_4)_2[\text{Mo}_2(\text{S}_2)_6]\cdot2\text{H}_2\text{O}$ catalyst over all the other non-precious metal supported Mo-S based catalysts. These results suggest that out $[\text{Mo}_2\text{S}_{12}]^{2-}$ cluster has promising HER applications in the electrolysis and photoelectrolysis of water.

The properties of the $[\text{Mo}_2\text{S}_{12}]^{2-}$ cluster is still unclear. For example, based on the XPS result, the Mo in $[\text{Mo}_2\text{S}_{12}]^{2-}$ have the same oxidation state as the Mo in $[\text{Mo}_3\text{S}_{13}]^{2-}$ and MoS$_2$. That means the oxidation state of Mo in $[\text{Mo}_2\text{S}_{12}]^{2-}$ is 4+, different from the +5 as expected from the chemical formula. The Raman result also shows that the $\text{S}_2$ in the $[\text{Mo}_2\text{S}_{12}]^{2-}$ has an average oxidation state between -1 and -2. Whereas, the XPS and the
Raman are all surface sensitive techniques. It’s hard to tell if the bulk material have the same properties as the surface.

Reference


Chapter 5: X-ray Absorption and its Applications

5.1 Introduction of X-ray Absorption

There are several kinds of interactions between X-ray and matter, e.g. X-ray absorption, elastic scattering and inelastic scattering. In fact, these interactions can be considered as the same phenomena from different aspect. For X-ray absorption, the X-ray absorption dependent on energy is measured, without changing the angle. X-ray is absorbed by all matter through photo-electric effect. The X-ray occurs when a photon interacts with electrons and gives up all of the energy. This energy will cause the transition of the electrons from lower energy levels to higher energy level if the energy if higher than the binding energy of the electron (Figure 5.1 left). Then, there is a vacancy left in the lower energy level. The vacancy will be filled by an electron from the higher energy level and release its energy. There are several path to release the energy: by emitting fluorescence radiation at a lower energy than the incident energy or kicking out another electron, which is called Auger electron. These two decay pathways induce varies detection methods, e.g. fluorescence detection and electron yield detection.
The X-ray absorption obeys the Beer’s law for uniform homogenous samples, similar to the UV-vis absorption.

\[
\frac{I}{I_0} = \exp(-\mu x), \tag{5.1}
\]

Where, \(I\) is the X-ray intensity transmitted through sample, \(I_0\) is the incident X-ray intensity, \(\mu\) is the absorption coefficient and \(x\) is the sample thickness.

The transition follows the Fermi’s Golden rule, thus for the allowed electric dipole transition \(\Delta l = \pm 1, \Delta J = 0, \pm 1\) and \(\Delta M = 0, \pm 1\); and for spin-orbit coupling \(\Delta S = 0\) and \(\Delta L = 0, \pm 1\). Where \(l\) is the angular quantum number, \(J\) is the total angular momentum, \(L\) is the azimuthal quantum number, \(S\) is the spin quantum number and \(M\) is the secondary total angular momentum quantum number. The initial state is a bound state.
Above the absorption edge, the states are continuum states. Below the edge, there may be still some allowed localized transitions. The quantum numbers are summarized in Table 5.

The K and L₁ edges probe the final state with p symmetry and the L₂ and L₃ edges probe the final state with d and s symmetry.

<table>
<thead>
<tr>
<th>edge</th>
<th>Initial state</th>
<th>n</th>
<th>l</th>
<th>Final state l</th>
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</thead>
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<tr>
<td>K</td>
<td>1s</td>
<td>1</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>L₁</td>
<td>2s</td>
<td>2</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>L₂</td>
<td>2p (j=1/2)</td>
<td>2</td>
<td>1</td>
<td>0, 2</td>
</tr>
<tr>
<td>L₃</td>
<td>2p (j=3/2)</td>
<td>2</td>
<td>1</td>
<td>0, 2</td>
</tr>
</tbody>
</table>

Table 5. 1 Quantum number of the initial state and final state in X-ray absorption.

X-ray absorption spectra contains the X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) as show in Figure 5. 1. The charge state, orbital occupancy information may be obtained from the XANES. The EXAFS oscillation is caused by the electron wave scattered by the neighboring atoms. The outgoing and scattered parts of the final state wave interfere. The structure parameters can be extracted from EXAFS through fitting.

Unlike the X-ray diffraction, the XAS doesn’t required the sample to be crystalline. The amorphous materials, liquids and even gases since the short-range scattering contribute to most of the signal. The ambient condition for the middle and hard X-ray experiments (above 2k eV) makes it easy to be adapted for in-situ measurement for various systems,
such as for catalysis, electrochemistry and environmental science. The XAS measurement in bulk scale also avoid that the particular case in atomic or nanometer scale chosen by the techniques such as TEM, XPS and Raman cannot represent the properties of the materials without assuming a good uniformity. The small scale characterization combined with the bulk scale coadaptation will provide a comprehensive picture of the material properties.

In this chapter, we present two work that XAS technique coupled with atomic scale study by TEM and surface technique XPS. The first one is using ex-situ XAS to determine the structure of the bimetallic Pt-Cu core-shell catalysts, which demonstrates the catalytic mechanism. The second one is in-situ Li-ion battery characterization in Na-ion battery to study the partial reversible reaction of $\alpha$-MnO$_2$ during inserting/extracting sodium ions.
5.2 Pt-Cu Core-shell Nanostructures for Nonaqueous Oxygen Evolution Reactions

5.2.1 Introduction

Designing efficient catalysts for advanced energy applications is crucial for the effective and versatile use of energy. Particularly, the oxygen evolution reaction (OER) is a key step in many energy storage processes, such as water splitting\cite{1} and rechargeable metal-air batteries.\cite{2,3} However, due to the multiple electron transfer nature, the sluggish kinetics of the OER usually leads to large voltage polarization and hinders its practical applications in commercialized devices.\cite{4,5}

Owing to the electronic and geometric structures, bimetallic nanostructured catalysts typically exhibit unusual catalyzing properties.\cite{6} Through the rational compositional and structural design, the catalytic activity can be significantly tuned and improved towards specific reactions.\cite{7} In fact, bimetallic catalysts have already been widely applied to energy storage, such as the oxygen reduction reaction (ORR) in fuel cells\cite{8-17}, and the OER\cite{18} and hydrogen evolution reactions (HER)\cite{19} in water splitting.

In this work, we have systematically examined the catalytic activity and mechanism of the platinum-copper (Pt-Cu) core-shell bimetallic nanostructures in non-aqueous condition. A facile strategy to prepare Pt-Cu bimetallic catalysts with the core-shell structure was demonstrated. The composites in the catalyst was characterized by High-Energy X-ray Diffraction (HEXRD) and XANES spectroscopy, indicating that the Cu was oxidized to Cu(II) and Pt was partially oxidized in the whole particle level. The core-shell
structure of the Pt-Cu catalyst was determined by EXAFS spectroscopy in bulk quantity, as well as confirmed then by scanning transmission electron microscopy (STEM). The particle sizes of the Pt-Cu catalyst was analyzed by small angle X-ray scattering (SAXS), which showed narrow size distributions in the diameter range of 2-4 nm. Those nanostructures exhibited excellent catalytic performance towards the non-aqueous OER, as demonstrated by the substantially reduction of the charging overpotential in Li-O₂ batteries to less than 0.2 V, compared to a typical 1 V overpotential. The X-ray photoelectron spectroscopy (XPS) indicated that the robust catalytic activity can be attributed to the active surface Cu(I) sites which were stabilized by the Pt core. The results of this study have proved that such Pt-Cu core-shell nanostructures are efficient catalysts for non-aqueous OER and our protocol can be generalized to guide the design of other bimetallic catalysts.

5.2.2 Experimental Section

5.2.2.1 Synthesis of the Pt-Cu core-shell nanoparticles

Vulcan XC-72 carbon powder (Cabot Corporation) was used as support for preparing the carbon-supported Cu, Pt, or Pt-Cu catalysts. The Cu and Pt salts used were Cu(NO₃)₂·3H₂O and H₂PtCl₆, respectively. The precursors were dissolved in deionized water (Millipore, 18 MΩ) and then mixed with a pre-determined amount of Vulcan XC-72
to achieve the desired weight loading of metal(s) on the support. The volume of water used for dissolving the salts exceeded that necessary to fill the pores of the Vulcan XC-72 support (i.e., wet impregnation technique). After stirring for 2 hours, the slurry mixture was vacuum dried at 70°C for 3 hours. The final catalysts were formed by treating the dried samples for 2 hours in a dilute hydrogen atmosphere (3.5% H2 in an inert gas) at a temperature of 150-250°C.

5.2.2.2 High-energy X-ray Diffraction

The X-ray diffraction (XRD) measurement of the cathode laminates after discharge was carried out on beamline 11-ID-C at APS. The X-ray wavelength was 0.1725 Å. The XRD two-dimensional patterns were collected in the transmission mode using a Perkin Elmer large area detector, and then integrated into conventional one-dimensional patterns (intensity versus 2θ) for analysis using the Fit2d software.

5.2.2.3 Scanning Electron Microscopy

The field-emission scanning electron microscope (FESEM, Hitachi S-4700) was used to characterize the morphology of the discharge product and the cathode surface. The samples were protected from exposure to air during transferring to the SEM chamber by a conductive tape applied in the glove box.

5.2.2.4 Transmission Electron Microscopy
(Scanning) transmission electron microscopy was carried out using a FEI Titan 80-300 ST transmission electron microscope with a spherical and chromatic aberration-corrected image corrector operating at 80 keV. Thin specimens for TEM analysis were prepared by dispersing powders onto a holey carbon coated grid.

5.2.2.5 X-ray Absorption Data Collection.

X-ray absorption data was collected at the Advanced Photon Source (APS) on beamline 10-BM (MRCAT) with electron energy 7 GeV with average current of 100 mA. The radiation was monochromatized by a Si (111) crystal monochromator. The monochromator was detuned 50% for harmonic rejection. All spectra were recorded by transmission mode. For energy calibration, a piece of copper or platinum foil was measured simultaneously at the reference ionization chamber in transition mode at Cu K-edge and Pt L3-edge, respectively. The energy scale was adjusted to the tabulated values: Cu metal foil with \(E_0=8979\) eV and Pt metal foil with \(E_0=11564\) eV. The spectra of commercial Cu2O and CuO were also recorded as standard materials.

5.2.2.6 XAS Data Analysis

Athena software was used for data processing (energy calibration, background subtraction and normalization). The linear combination was also fitted with Athena. The structural information was obtained by fitting the EXAFS with Artemis. The scattering paths were calculated with feffv9. The EXAFS coordination parameters were obtained by fitting in k-space of the \(k^2\)-weighted Fourier transform data: \(k=2.0-13.4\) Å\(^{-1}\) for Cu K-edge
and \( k=3.0-14.5 \text{ Å}^{-1} \) for Pt L3-edge. The first-shell fitting was performed between 1.4 and 2.8 Å for the Cu K-edge and 1.5-3.2 Å for the Pt L3-edge.

5.2.2.7 SAXS measurement

Measurements were performed at 12-BM at the Advanced Photon Source (APS), Argonne National Laboratory. The 2D SAXS data were collected on the Mar165 CCD detector (Rayonix, LLC.), a \( q \) range of 0.01 – 0.4 Å\(^{-1}\) with an incident energy of 11.54 keV (\( \lambda = 1.074 \text{ Å} \)). The scattering vector, \( Q \), was calibrated using a silver behenate. Quantitative data analyses were performed using spheroid form factors with a Schulz–Zimm distribution implemented in the Irena package within Igor Pro.\(^{[20]}\)

5.2.2.8 Li-O\(_2\) cell assembling

All cells were assembled in an argon gas-filled glovebox. The cathode material (Pt-Cu on carbon) (80 wt\%) and polyvinylidene fluoride (PVDF, 20 wt\%) were mixed in a 1-methyl-2-pyrrolidinone (NMP, Aldrich) solution to make the slurry. The slurry was coated on carbon paper (TGP-H-030, Torray) and dried at 100 °C for 12 hours in a vacuum. The loading of the active material was 0.70 ± 0.15 mg. The cells were assembled in a Swagelok cell configuration with a piece of lithium foil (thickness, manufacturer?) as anode (7/16 inch diameter), a piece of glass fiber as separator (1/2 inch diameter, saturated by the electrolyte of 1M lithium triflate (LiCF\(_3\)SO\(_3,\) Aldrich) in a tetraethylene glycol dimethyl ether (TEGDME) solvent), the cathode and a piece of aluminum mesh as current collector. After assembling, the cell was purged with pure oxygen for 30 minutes before testing.
5.2.2.9 Electrochemical measurements

The Li-O₂ cells were tested by a MACCOR cycler within a voltage range between 2.2V and 4.5 V and the discharge and current was set to a constant current density of 100 mA/gcarbon. The observed capacity was normalized by the weight of the active material on cathode for comparison.

5.2.2.10 X-ray Photoelectron Spectroscopy (XPS)

The XPS spectra was calibrated by C 1s at 285 eV. Cu 2p line was fitted with GL(80) line-shape (Gaussian 20 %-Lorentzian80 %) by casaXPS. The fitting parameters were based on the reported values. [21]

5.2.3 Results and Discussion

The Pt-Cu catalyst (2.5% Pt+5% Cu, in weight percentage), pure Cu (5% Cu) and pure Pt (2.5% Pt) samples were prepared by wet-impregnation method. The crystalline components in Pt-Cu catalyst were characterized by HEXRD (Figure 5. 2a). The diffraction pattern was consistent with CuO. No peak related to Pt, PtO₂ or Pt-Cu alloy phases (e.g. Cu₃Pt and CuPt) was detected, which implies that Pt may exist either in an amorphous state or in a very small domain. XANES spectra, which are sensitive to the oxidation state of the elements, were then recorded at both Cu K and Pt L₃-edges. The oxidation state of Cu was determined by comparing the Cu K-edge positions of Pt-Cu catalyst to the standard Cu(I)
oxide and Cu(II) oxide (Figure 5. 2b). The Pt-Cu catalyst showed the same edge position corresponding to Cu(II), in agreement with the HEXRD result. Quantitative calculation of the bulk-scale oxidation state was performed by the linear combination fitting (LCF), which reveals that the Cu was oxidized to Cu(II) (Table 5. 2).

Figure 5. 2 (a) HEXRD of Pt-Cu catalyst; (b) Cu K-edge XANES spectra of Pt-Cu catalyst and the standard Cu(I) oxide and Cu(II) oxide; (c) Pt L3-edge XANES spectra of Pt-Cu catalyst and the standard Pt foil and PtO2.

<table>
<thead>
<tr>
<th>Cu K-edge (in air)</th>
<th>XANES fit (-10, +30eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu(I) oxide</td>
</tr>
<tr>
<td>5% Cu</td>
<td>0.307</td>
</tr>
<tr>
<td>2.5% Pt + 5% Cu</td>
<td>0</td>
</tr>
<tr>
<td>5% Pt + 5% Cu</td>
<td>0</td>
</tr>
<tr>
<td>10% Pt + 5% Cu</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 5. 2 LCF result of Cu K-edge XANES of Pt-Cu catalysts in air.

The oxidation state of Pt was determined by the white line intensities (Figure 5. 2c). The Pt L3-edge jump is attributed to the transition from 2p3/2 to 5d3/2 and 5d5/2. Since the oxidized Pt has more vacancy in the d-orbital, the white line intensity increased with the
platinum oxidation number. The linear relationship of the O/Pt ratio and the white line intensity has also been reported.[22] Here, the Pt in both the bimetallic Pt-Cu catalyst and the pure Pt samples had white line intensities between that of Pt and PtO$_2$, indicating that they still keep some metallic character even in air. The white line intensities were also quantitatively analyzed via curve fitting (Figure 5.3).

![Figure 5.3 Fitting result of XANES spectra of 2.5%Pt+5%Cu catalyst.](image)

<table>
<thead>
<tr>
<th>Samples</th>
<th>White line intensity (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5% Pt</td>
<td>4.868</td>
</tr>
<tr>
<td>2.5%Pt+5%Cu</td>
<td>4.970</td>
</tr>
<tr>
<td>Pt foil</td>
<td>2.348</td>
</tr>
<tr>
<td>PtO$_2$</td>
<td>12.949</td>
</tr>
</tbody>
</table>

The size distributions of the Pt-Cu catalyst, pure Pt and pure Cu samples were obtained through fitting the integrated 1D plot of the SAXS data that had the carbon background subtracted. Schulz-Zimm was chosen as the distribution shape with spheroid form factor in a dilute system. As shown in Figure 5.4, pure Cu sample had a broad size distribution from 1 nm to ~20 nm; while pure Pt sample has a very narrow size distribution (1-3 nm). Similar to the pure Pt sample, the size distribution of the Pt-Cu catalyst was also within a narrow range of 2-4 nm.
Figure 5.4 The size distribution results obtained from SAXS.

TEM was utilized to provide direct evidence on the structural and morphological characteristics of the catalysts. The Pt-Cu nanoparticles were uniformly distributed on the carbon support (Figure 5.5a). The particles with diameters of 2-4 nm were observed from the TEM images. The size histogram by statistical analysis of TEM images (Figure 5.6) was consistent with the SAXS results. Individual Pt-Cu nanoparticle was identified by high resolution TEM (HRTEM) with cuboctahedron shape (Figure 5.5b). Cuboctahedron (Figure 5.5b, inset) is one of the stable nuclei structures for platinum\textsuperscript{[23]} and copper\textsuperscript{[24]}, which is enclosed by the low-index \{100\} and \{111\} facets of the close packed cubic structure.
Because these as-prepared Pt-Cu bimetallic nanoparticles possess unique features on porous carbon matrix with high specific surface area, they can provide more active sites
for the electrochemical reactions. Consequently, catalytic activity for OER is expected to be increased, as demonstrated next in the tests with Li-O$_2$ cells.

The Pt-Cu catalysts were tested in Li-O$_2$ electrochemical cells. During charging, the desired discharge product, Li$_2$O$_2$, decomposes and releases oxygen with the following OER occurring:

$$\text{Li}_2\text{O}_2 \rightarrow 2\text{Li}^+ + 2e^- + \text{O}_2.$$ \hspace{1cm} (5.2)

Due to the sluggish kinetic of the OER, typical Li-O$_2$ batteries suffer from large overpotentials, which causes the low round-trip efficiency.$^{[25-31]}$ As shown in Figure 5.7a, the Li-O$_2$ cells with bare carbon, pure Pt or pure Cu on carbon as air electrode had a high charging voltage of above 4V (vs Li/Li$^+$). Surprisingly, with the Pt-Cu catalysts on the air electrode, the charge potential was dramatically reduced to about 3.2 V. The discharge product showed toroid shape (Figure 5.7b), which is typical for Li$_2$O$_2$ formed in a Li-O$_2$ cell.$^{[32-34]}$ After 36 cycles, the discharge product Li$_2$O$_2$ was still completely charged back, leaving a clean air electrode surface (Figure 5.7c). This result proves that the Pt-Cu catalysts can efficiently facilitate the decomposition of the Li$_2$O$_2$ during the charging process, i.e., facilitate the OER.
Figure 5. 7 (a) The comparison of voltage profile of Li-O₂ electrochemical cells with different Pt-Cu catalysts (b) SEM image of discharge product with 2.5% Pt+ 5% Cu on carbon as cathode. (c) SEM image after cycling under 5-hour time control till its specific capacity dropped to 100 mAh/g carbon and stopped at the end of charge (36 cycles).

Regarding the catalytic mechanism, since neither pure Pt nanoparticle nor pure Cu nanoparticle has the contribution to lowering the charge overpotential, it is believed that the unique core-shell structure of the Pt-Cu catalyst played a crucial role on the catalytic activity towards the OER.

The fact that in the Pt-Cu catalyst, all Cu was oxidized but the Pt maintains a certain degree of metallic property is attributed to the unique arrangement of the Pt and Cu atoms. In addition, the SAXS results indicate that the size distribution of the Pt-Cu catalyst was dominated by Pt. A plausible assumption is that Cu acted as shell to protect the Pt from
oxidation and the Pt core determined the size distribution of the Pt-Cu catalyst. To support our hypothesis, EXAFS was employed to determine the coordination structure of the Pt-Cu catalyst. The Pt-Cu catalyst, pure Cu and pure Pt samples were fully reduced by H₂ to avoid the influence of the oxygen on resolving the structure. Fourier transform (FT) of the EXAFS and the related scattering paths at Cu K-edge and Pt L₃-edge are shown in Figure 5. 8a and 5. 8b, respectively. The spectrum of the pure Cu sample contains one peak related to the Cu-Cu scattering path. With Pt in the bimetallic catalyst, the peak became slightly wider due to the emergence of the Cu-Pt scattering, resulting from the formation of Cu-Pt alloy at the interface. A similar trend was also observed at the Pt L₃-edge. The FT of the EXAFS of the pure Pt sample shows two peaks which associate with the Pt-Pt scattering. For the bimetallic catalyst, the intensity of the Pt-Cu scattering, which is located between the two Pt-Pt scattering peaks, increased and led to the evolution of the overall peak shape. Therefore, with the FT results we conclude that the Pt-Cu alloy was formed at the Pt/Cu interface in the bimetallic catalysts and the homoatomic interactions (Cu-Cu and Pt-Pt) are stronger than the bimetallic heteroatomic interaction (Pt-Cu).
Figure 5.8 (a, b) Magnitude of the Fourier transform of Pt-Cu catalysts: (a) At Cu K-edge in comparison with monometallic 5%Cu sample (orange dashed line: Cu-Cu patch and purple dash dotted line: Cu-Pt path); (b) At Pt L₃-edge in comparison with pure Pt sample (orange dashed line: Pt-Pt path and purple dash dotted line: Pt-Cu path). (c, d) First-shell model EXAFS fit of the k³-weighted Fourier transform of 5%Pt+5%Cu catalyst: (c) Cu K-edge (Δk=2.0-13.4 Å⁻¹ and ΔR=1.4-2.8 Å) and (d) Pt L₃-edge (Δk=3.0-14.5 Å⁻¹ and ΔR=1.5-3.2 Å). FT magnitude in solid line and imaginary in dashed line, data in black and fit in red.
The nearest-neighbor coordination numbers around Cu and Pt atoms were extracted from fitting the EXAFS of the Pt-Cu catalysts with first-shell model. Figure 5.8c and 5.8d show the typical fitting results for the Pt-Cu catalysts, the good fitting quality was verified by the R-factors of $\leq 0.001$ with k1 and k3 weightings for both Cu K and Pt L3-edges. The fitting parameters were summarized in Table 5.3. Since the amplitude reduction factor $S_0^2$ was maintained the same during the fitting, the changes in coordination numbers were compared. Here the nearest neighbor M’ atoms around M atom is denoted by $N_{MM'}$. Because neither $N_{Cu-Pt}$ nor $N_{Pt-Cu}$ was zero in our catalysts, Pt and Cu didn’t form separate monometallic particles. Instead, they should establish either intermetallic compound or core-shell structure. If an intermetallic compound was formed, the total coordination number of Pt ($N_{Pt-M} = N_{Pt-Cu} + N_{Pt-Pt}$) should equal to the total coordination number of Cu ($N_{Cu-M} = N_{Cu-Cu} + N_{Cu-Pt}$). But in our case, for the Pt-Cu catalyst, $N_{Pt-M} \neq N_{Cu-M}$. In fact, in a core-shell structure, the Pt was bonded to Cu only at the interface, thus one metal atom has significantly higher possibility to coordinate with the same type of metal atom than the other type. The distinct inequality of $N_{Pt-Pt}$ and $N_{Cu-Pt}$ provides an evidence supporting the formation of the core-shell structure in the Pt-Cu catalysts. In addition, since the surface atoms have smaller coordination numbers than the bulk, the fact $N_{Pt-M} \geq N_{Cu-M}$ indicates that Pt was acting as the core while Cu as the shell.
Table 5. 3 Fitting parameters of the Fourier Transform of the first shell of the k³-weighted EXAFS spectra, where N is the coordination number, S₀² is the amplitude reduction factor, R is the bond distance, σ² is the Debye-Waller factor and E₀ is the edge energy shift.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Edge</th>
<th>Scatter</th>
<th>N*S₀²</th>
<th>R (Å)</th>
<th>σ² (Å²)</th>
<th>E₀ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5%Pt+5%Cu</td>
<td>Cu K</td>
<td>Cu-Cu</td>
<td>7.40</td>
<td>2.536±0.002</td>
<td>0.0114±0.0003</td>
<td>-1.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cu-Pt</td>
<td>0.30</td>
<td>2.601±0.014</td>
<td>0.0009±0.0017</td>
<td>-5.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cu-M</td>
<td>7.70</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pt</td>
<td>Pt-Cu</td>
<td>5.66</td>
<td>2.601±0.014</td>
<td>0.0009±0.0017</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pt-Pt</td>
<td>4.96</td>
<td>2.707±0.011</td>
<td>0.0064±0.0013</td>
<td>3.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pt-M</td>
<td>10.62</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5%Cu</td>
<td>Cu K</td>
<td>Cu-Cu</td>
<td>7.50</td>
<td>2.534±0.002</td>
<td>0.0133±0.0004</td>
<td>-1.8</td>
</tr>
<tr>
<td>2.5%Pt</td>
<td>Pt</td>
<td>Pt-Pt</td>
<td>7.81</td>
<td>2.714±0.005</td>
<td>0.0104±0.0006</td>
<td>-0.66667</td>
</tr>
</tbody>
</table>

Cu K: Δk=2.0-13.4 Å⁻¹ and ΔR=1.4-2.8Å; Pt L₃: Δk=3.0-14.5 Å⁻¹ and ΔR=1.5-3.2Å.

ΔN=±10%

The extents of the alloying of Pt and Cu were also calculated from the EXAFS-derived coordination numbers and from the coordination numbers expected for the complete and random alloying (i.e., random dispersion of Cu and Pt throughout the particles). As defined by Hwang et al., the extent of alloying of Pt (JPt) is:

\[ J_{Pt} = \frac{P_{Pt, observed}}{P_{Pt, random}} \times 100\% \]  (5. 3)
where,

\[ P_{Pt,observed} = \frac{N_{Pt-Cu}}{N_{Pt-Pt}+N_{Pt-Cu}} \]  

(5.4)

\[ P_{Pt,random} = \frac{N_{Pt-Cu,random}}{N_{Pt-Pt,random}+N_{Pt-Cu,random}} = \frac{n_{Cu}}{n_{Cu}+n_{Pt}} \]  

(5.5)

The extent of alloying of Cu (\( J_{Cu} \)) is:

\[ J_{Cu} = \frac{P_{Cu,observed}}{P_{Cu,random}} \times 100\% \]  

(5.6)

where,

\[ P_{Cu,observed} = \frac{N_{Cu-Pt}}{N_{Cu-Cu}+N_{Cu-Pt}} \]  

(5.7)

\[ P_{Cu,random} = \frac{N_{Cu-Pt,random}}{N_{Cu-Cu,random}+N_{Cu-Pt,random}} = \frac{n_{Pt}}{n_{Cu}+n_{Pt}} \]  

(5.8)

where, \( n_{Pt} \) and \( n_{Cu} \) are the number of moles of Pt and Cu, respectively.

The mole fractions of Cu and Pt determined from the as-fabricated ratios were used to calculate \( P_{random} \). The \( P_{Pt,random} \) and \( P_{Cu,random} \) for the 2.5%Pt+5%Cu catalysts are 0.86 and 0.14, respectively. The \( P_{Pt,observed} = 0.524 \) and \( P_{Cu,observed} = 0.039 \) were calculated from the EXAFS fitting result. Thus, \( J_{Pt} = 60\% \) and \( J_{Cu} = 28\% \). \( J_{Pt} \) and \( J_{Cu} \) values are smaller than 100\%, which implies both Pt and Cu atoms were not preferred to be alloyed. The homoatomic Pt-Pt or Cu-Cu bonds are favoured over the heteroatomic Pt-Cu bonds. As \( N_{Pt-M} \geq N_{Cu-M} \) the Pt particles were in the core and the Cu particles were in the shell.
Apart from the bulk-scale characterizations of the structure of Pt-Cu catalysts by interpreting EXAFS spectra, the core-shell structure of Pt-Cu nanoparticles was further verified by high angle annular dark field scanning transmission electron microscopy (HAADF-STEM). Due to the Z-contrast effect of STEM (Z is atomic number), Pt have a higher intensity than that of Cu. As shown in Figure 5.9, the shells of the nanoparticles with a lower intensity than the core validated the core-shell structure of the Pt-Cu catalysts.

![Figure 5.9 HAADF-STEM images of 2.5%Pt+5%Cu sample.](image)

Since the electrocatalytic OER process only occurs on the electrode surface, X-ray Photoelectron Spectroscopy (XPS), a surface sensitive technique, was employed to investigate the interaction between Pt and Cu on the surface of Pt-Cu catalyst. The results showed a distinct Cu surface was formed, i.e., both Cu (II) and Cu (I) were found on the
surface through deconvolution of the Cu 2p peak (Figure 5. 10). Based on the STEM, XAS and XPS results, it seems that the Pt core was covered by the oxidized Cu (Cu₅O), and especially the Pt-Cu alloy was formed at the interface, as schematically shown in the inset of Figure 5. 9. It should be noted that the Cu (I) species typically are unstable at room temperature, as evident that only Cu (II) was detected on the pure Cu sample. However, the presence of Cu (I) on the surface of our Cu-Pt catalyst suggests that the unique core-shell structure may stabilize the Cu(I) through the Pt-Cu alloy interface in the particle. Based on the earlier studies on the catalytic activity of Cu (I) on OER in aqueous systems, we believed that such stabilized Cu(I) species on the catalyst surface played a crucial role to reduce the OER potential in non-aqueous Li-O₂ cell, as observed in this study. In fact, the distribution of the active Cu(I) sites were not as uniform as that of the atomically dispersed dopants in the traditional carbon-based catalysts, e.g. Fe/N/C. The dopants with atomic uniformity produce a higher interfacial boundary with the discharge product Li₂O₂ to help the electron and mass transfer process, leading to the low charge overpotential in Li-O₂ cells. Thereby, regarding the high catalytic activity of the Pt-Cu catalysts, the uniformity distribution of the active sites was not the main reason. As calculation results showed that the O₂(2-⁻) had a lower O₂ desorption energy, the charge-transfer from the O₂²⁻ to the catalytic surface may play a crucial role on the catalytic activity.
5.2.4 Conclusion

In summary, this study reports the electrocatalytic activity of a unique bimetallic Pt-Cu core-shell nanostructured catalyst towards the non-aqueous OER process. The structure characterizations of the catalysts were accomplished via XAS, revealing that the core-shell structure of the Pt-Cu particle and the oxidation state of each component. Benefiting from the unique Pt-Cu core-shell structure, Cu (I) has been stabilized on the surface and serves as the key to improve the OER catalytic activity. Consequently, the bimetallic Pt-Cu catalyst exhibited significantly reduced charging overpotential (< 0.2 V) in non-aqueous Li-O₂ cells. This interesting finding suggests that our protocol can be generalized to guide the design of other efficient bimetallic catalysts.
5.3 Study of (De)sodiation in K⁺-stabilized α-MnO₂ Nanowires by XAS

5.3.1 Introduction

Lithium ion batteries (LIB) have dominated the market of rechargeable energy storage devices for decades as a high-energy power source, especially for portable electronics. However, the limited storage of Li source makes it urgent to find new charge carriers to replace Li. Sodium ion batteries (NaIB) the ideal alternative to LIB due to its abundance. A substantial amount of research has been devoted to the development of electrode materials for NaIB, including nanostructured manganese oxides. However, these materials always suffer from poor cycling performance. The possible reason is that the relatively large size of Na⁺ will affects the host structure, but no experiment has been performed to identify it.

In this chapter, K⁺-stabilized α-MnO₂ nanowires are studied by monitoring the morphology and phase evolution during electrochemical (de)sodiation using in situ TEM. The coin cell level studied is conducted by in-situ XAS measurement. It is found that α-MnO₂ nanowire was fully sodiated to Mn₂O₃ and Na₂O. An intermediate phase Na₀.₅MnO₂ formed during the first sodiation. This Na₀.₅MnO₂ dominates the following cycles via a reversible conversion reaction with Mn₂O₃ polycrystals. The valence change of the Mn during cycling agrees well with the TEM observation. In addition, the changes of Mn-Mn and Mn-O bond length with cycles also extracted by fitting EXAFS. The results
demonstrated that the initial tunneled structure of $\alpha$-MnO$_2$ degraded before the sodiated to Na$_{0.5}$MnO$_2$, demonstrating the mechanism of the poor cyclability in Na-ion batteries.

5.3.2 Experimental Section

5.3.2.1 Material Synthesis.

The nanowires are synthesized via a hydrothermal method using KMnO$_4$ and MnSO$_4$ as the raw materials.[47] During the formation of the tunneled structure in solution, K$^+$ will be trapped inside the tunnels and function as the stabilizers to support the tunnels.

5.3.2.2 Open cell design in TEM.

The open cell is built using the in-situ STM TEM holder equipped with two dangling gold tips being connected to the outside circuit. The nanowires are glued to one Au tip by conductive epoxy, and the metallic sodium is attached to the other Au tip by scratching the tip across the surface of a sodium foil in glovebox. During the holder transfer into the TEM chamber, sodium metal is partially oxidized to Na$_2$O, which functions as the solid electrolyte in the open cell design. The piezo-controlled movement is operated at single nanowire level to make it connected to the Na/Na$_2$O on the other side, and an appropriate bias is then applied to initiate the sodiation process. The desodiation process is started by reversing the bias. Both ex-situ and in-situ TEM are performed inside the JEOL JEM-
ARM200CF equipped with a 200 KV cold field emission electron source. The elemental information is obtained using an Oxford X-max 100TLE windowless SDD X-ray detector.

5.3.2.3 Coin cell making.

The laminate contains $\alpha$-MnO$_2$ nanowires, PVDF and black P with the weight ratio of 8:1:1. The coin cell was assembled using $\alpha$-MnO$_2$ nanowires as the cathode, glass microfiber as the separator, NaPF$_6$ in EC/DEC as the electrolyte and metallic Na foil as the anode. Punched coin cell cases and spacers with Kapton window were used to guarantee X-ray transmission at Mn K-edge.

5.3.2.4 In-situ X-ray Absorption Spectroscopy.

The XAS measurement for the Mn K-edge was performed at the Advanced Photon Source (APS) on the bending-magnet beamline 9-BM-B with electron energy of 7 GeV and average current of 100 mA. The radiation was monochromatized by a Si (111) double-crystal monochromator. Harmonic rejection was accomplished with an Rh-coated mirror. All spectra were collected in transmission mode. For energy calibration, a Mn foil was measured simultaneously at the reference ionization chamber. The peak of the first derivative of Mn foil was adjusted to the tabulated value of 6539 eV. The coin cell was
first discharged to 1 V and then charged back to 4 V at 0.1 C rate. X-ray absorption near edge spectra (XANES) data reduction and analysis were processed by Athena software.

5.3.3 Results and Discussion

5.3.3.1 In-situ TEM result

The α-MnO$_2$ nanowires contain one-dimensional tunnel structure as shown in Figure 5. 11. The 2×2 tunnel structure is highlighted, which is stabilized by K$^+$. The accurate composition of the nanowire is K$_{0.25}$MnO$_2$.

Figure 5. 11 [001] HAADF-STEM image showing the atomic tunneled structure. One 2×2 tunnel is highlighted and the atomic model is in the inset (red dot-Mn and green dot-K).
Figure 5.12. (a) The diameter vs sodiation time for one α-MnO₂ nanowire being repetitively cycled; the numeric percentages are for the diameter expansion (positive) and contraction (negative) during each event; (b-g) the corresponding SAED patterns of the same nanowire at different (de)sodiation states.

The in-situ TEM images of the (de)sodiation of a single α-MnO₂ nanowire is shown in Figure 5.12. The nanowire expanded during sodiation and contracted during desodiation. The diameter change of the nanowire during this process is shown in Figure 5.12a. The first full sodiation results in about 50% radial expansion while the first desodiation only leads to 15% contraction. The expansion and contraction rates of the rest cycles are limited within 20%, indicating that the mechanism of the first sodiation was different from that of the rest (de)sodiation cycles. The phase evolution is tracked via the selected area electron diffraction (SAED) pattern (Figure 5.12b-g). During the first sodiation (Figure 4b-d), an
intermediate phase Na$_{0.5}$MnO$_2$ formed and covered to Mn$_2$O$_3$ and Na$_2$O finally. For the full desodiated phase, Na$_{0.5}$MnO$_2$ reformed rather than MnO$_2$. The reactions are showing as follow:

\begin{align*}
\text{MnO}_2 + 0.5\text{Na}^+ + 0.5e^- &= \text{Na}_{0.5}\text{MnO}_2 \\
\text{Na}_{0.5}\text{MnO}_2 + 0.5\text{Na}^+ + 0.5e^- &= 0.5\text{Mn}_2\text{O}_3 + 0.5\text{Na}_2\text{O}
\end{align*}

Some residual Na$_2$O polycrystals were detected, probably due to their poor electron conductivity, which made them difficult to decompose. During the 2$^{\text{nd}}$ sodiation, the Na$_{0.5}$MnO$_2$ totally converted to Mn$_2$O$_3$ and Na$_2$O, and formed again during the 2$^{\text{nd}}$ desodiation. Apart from the first cycle, the following cycles were reversible conversion reaction between Na$_{0.5}$MnO$_2$ and Mn$_2$O$_3$. Figure 5. 12g also shows that Mn$_2$O$_3$ cannot be totally converted back to Na$_{0.5}$MnO$_2$, which may be caused by the gradual pulverization of Mn$_2$O$_3$ polycrystals to make the electron path discontinuous inside Na$_2$O matrix. The partially irreversible conversion resulted in the capacity fading in the NaIBs.$^{[46]}

5.3.3.2 In-situ XAS result

To study the mechanism of the (de)sodiation process of MnO$_2$ nanowires in bulk scale, in-situ XAS data were collected during the battery cycling. The $\alpha$-MnO$_2$ nanowires were utilized as cathode and Na metal as anode. In-situ XANES spectra, which are used for identifying the oxidation state of Mn are shown in Figure 5. 13a with the spectra of the standard Mn, MnO, Mn$_2$O$_3$ and MnO$_2$. The initial oxidation state of $\alpha$-MnO$_2$ nanowires
(red solid line) is slightly lower than $4^+$, compared with the standard MnO$_2$ (blue dashed line). This is due to the K$^+$ in the structure. During the discharge process, the oxidation state of Mn continuously decreased to nearly $3^+$ when fully discharged to 1V (green solid line). During the charge, the oxidation state of Mn increased obviously (from green to purple solid line) but it was not totally recovered to its original state even at the fully charged stage (charge to 4 V). To quantitatively analyze the Mn oxidation state change, the liner combination fitting (LCF) of the in-situ XAS spectra with standard Mn$_2$O$_3$ and MnO$_2$ was conducted. The LCF result with the battery discharge-charge profile is shown in Figure 5. 12b. The initial oxidation state of the $\alpha$-MnO$_2$ nanowires was $\sim3.6^+$, which roughly matches the initial composition of the nanowires ($K_{0.25}$MnO$_2$). Then, it decreased to $\sim3.1^+$ at the end of discharge. During charge, the oxidation state of Mn increased to $\sim3.4^+$, which is probably in accordance with the state of charge observed in TEM when intermediate Na$_{0.5}$MnO$_2$ is the dominant phase. The fact that Mn cannot recover its oxidation state indicates that the first cycle is not totally reversible, which could be explained by the fact that the residual Na$^+$ left in the $\alpha$-MnO$_2$ nanowires that cannot be totally extracted out. The in-situ XAS results agree well with the in-situ TEM observation in terms of the Mn valence evolution and the reversibility of the host structure.
Figure 5. 13 (a) Normalized XANES spectra of one NaIB with $K^+$-stabilized $\alpha$-MnO$_2$ nanowire electrode and standard Mn, MnO, Mn$_2$O$_3$ and MnO$_2$; (b) Charge-discharge profile and the oxidation state of Mn during battery cycling.

The Fourier Transform of the EXAFS at Mn K-edge is shown in Figure 5. 14. During discharge, i.e. $Na^+$ inserted into $\alpha$-MnO$_2$, the Mn-O bond length increased and the Mn-Mn bond length decreased. That may be caused by the replacement of the $K^+$ stabilizer with the smaller $Na^+$, which resulting in the shrinking of the 2×2 tunnel and the reduction of the Mn-Mn bond length. This change of the bond length verfied the tunnel mechanism of the $Na^+$ insertion into the $\alpha$-MnO$_2$. During charge, the reverse evolution of the bond length of Mn-O and Mn-Mn was also observed. After fully charged back to 4V, the bond distance didn’t return to their original status, indicating that the irreversible reaction during the first cycle.
Figure 5. 14 FT of EXAFS showing Mo-O and Mn-Mn bond length with cycling.

5.3.4 Conclusion

The (de)sodiation mechanism in single K$^+$-stabilized $\alpha$-MnO$_2$ nanowire was studied by combining in-situ TEM in single-wire scale and in-situ synchrotron XAS in bulk scale. During first sodiation, $\alpha$-MnO$_2$ transformed to an intermediate phase, Na$_{0.5}$MnO$_2$, and then totally converted to Mn$_2$O$_3$ and Na$_2$O upon full sodiation. The 1$^{\text{st}}$ desodiation process and the following cycles are dominated by the partially reversible conversion reaction between Na$_{0.5}$MnO$_2$ and Mn$_2$O$_3$. The inserted Na$^+$ ions exert a stronger destructive effect on the tunnel structure of the $\alpha$-MnO$_2$ due to their near-centered diffusion path inside the 2×2 tunnels, which impedes a strong interaction with the tunnel stabilizers K$^+$. 
5.4 Conclusion

To summarize, the X-ray absorption technique can provide useful information for various research field. The combination of the bulk-scale XAS characterization with the atomic or surface techniques can provide a comprehensive picture of the material properties, which helps to understand the mechanisms. The electron spectroscopy, such as XPS, is surface sensitive since the inelastic mean free path of electron is less than 1nm for electron energies with 10-1000eV. The electron mean free path is also a key factor in XAS. Due to the limited range of the photoelectrons, the XAS is only sensitive to a range of 5-10Å around the central atom. Different from the long-range order needed by the diffraction techniques, the XAS is more versatile and can be applied for amorphous materials, glasses, solutions, liquids and even gases. The bimetallic Pt-Cu catalysts study shows that the XAS can provide information of the oxidation states, bond length and also coordination numbers. Through the analysis of the coordination environment, the nano-scale structure was extracted from the fitting the Fourier Transform of the EXAFS spectra. The (de)sodiation process of α-MnO₂ demonstrates the capability of operando characterization by XAS.

Reference


Chapter 6: Intermediate Energy X-ray Absorption

6.1 Introduction of Intermediate Energy X-ray Absorption

The X-ray with energy above 5-10 keV is called “hard” X-ray. As shown in Chapter 5, these characterizations are all at energies within the “hard” X-ray. The X-rays with lower energy is “soft” X-ray. Due to the absorption of X-ray by air or even the light He gas, soft X-ray experiments have to be conducted under vacuum, which limits its applications for non-solid samples and in-situ characterization. The XAS experiment at intermediate-energy of 2-3 keV is possible to conduct at ambient pressure. Since the energy is still low, though the system does not have to be under vacuum, He gas are needed to purge everything including beam path, ion chambers and sample chambers. The X-ray with energy of 2-3 keV covers the energy range for the K-edges of light element and L-edges of transition metals.

For a Si (111) monochromator, the d-spacing is 3.1356Å. Bragg’s law of diffraction is $2dsin\theta = n\lambda = n\frac{12.4}{E(keV)}$. Thus, at 2.1keV, angle of the monochromator crystal is ~70°, which is almost reach the limit of the monochromator. At this energy, due to the big difference of dtheta with energy, only XANES spectra can be taken. The poor penetration at lower energy make it impossible to measure sample in transmission mode. Fluorescence
or total electron yield detection can be used. The harmonic rejection has to be taken care by harmonic rejection mirror rather than detuning to avoid further reduction of the flux.

In this chapter, we will discuss the XANES measurement at P K (2149 eV) edge, which is the lowest energy can be obtained at the Advanced Photon Source.

6.2 P K-edge XANES to Study the Cathode in Sodium-ion Battery

6.2.1 Introduction

Lithium-ion batteries (LIB) have been dominated the battery market especially for portable electronics. However, to overcome the scarcity of lithium, alternative battery technologies, such as sodium-ion batteries (NIBs), are in demand. The remarkable successes of LIBs achieved by adopted graphite anodes, which exhibit a capacity of 360 mAh/g by forming LiC₆. Unfortunately, the sodium graphite intercalation compound cannot be formed because of the unfavorable thermodynamics between graphite and Na unless electrolyte solvents are cointercalated[1] or graphite goes through sequential treatments of oxidation and reduction to generate a more defective turbostratic structure.[2, 3]

Fortunately, nongraphitic carbons, for example hard carbon, as anodes can provide meaningful capacities for NIBs.[4-6] One strategy to improve the performance of the hard carbon anode is tuning carbon structures with heteroatoms.[7-14] These doped carbons exhibit unique properties; however, they often lose the advantages of hard carbon. To date, it remains challenging to significantly increase the capacity while maintaining the key desirable characteristics of hard carbon.
Herein, we doped phosphorus oxide (PO$_x$) in hard carbon to study the structure-capacity relationship of hard carbon anodes. The PO$_x$ makes the structure of hard carbon more favorable for Na-ion storage, thus increasing its reversible desodiation capacity from 283 mAh/g to 359 mAh/g with a low operation potential. We determine that the doped PO$_x$ is redox inactive by monitoring the oxidation state of phosphorus during cycling via X-ray absorption spectroscopy. Thus the PO$_x$ does not contribute to the higher capacity. We conclude that the doping caused the changes of the carbon local structures, which lead to the higher capacity.

6.2.2 Experimental Section
6.2.2.1 Synthesis of PO$_x$ doped hard carbon

Aqueous suspension of GO was prepared via modified Hummer’s method for the preparation for both hard carbon (HC) and PO$_x$ doped hard carbon (P-HC). Sucrose, H$_3$PO$_4$ and GO with the mass ratio of 80:4:1 were mixed in an aqueous solution before sonication. The obtained solution/suspension was dried at 80 °C for 48 h, dehydrated at 180 °C for 24 h and then pyrolyzed at 1100 °C for 5 h under Ar flow. The HC was prepared with the same conditions but without the addition of H$_3$PO$_4$.

6.2.2.2 Materials Characterizations

The morphology of HC and P-HC were obtained by an FEI NOVA 230 high resolution scanning electron microscopy (SEM). Energy-dispersive X-ray (EDX) mapping were
obtained on a FEI Titan 80-300 (S) transmission electron microscopy (TEM) with an EDX attachment. To reveal the doping dispersion inside hard carbon particles and eliminate the impact from surface species, a specimen (100 nm thick) was carved out of a large carbon particle by focused-ion beam (FIB) before EDX mapping. TEM images were recorded by a FEI Titan 80-200 TEM. Phosphorus K-edge XANES data were collected at the Advanced Photon Source (APS) on the beamline 9-BM-B with electron energy of 7 GeV and average current of 100 mA. The radiation was monochromatized by a Si (111) double-crystal monochromator. Harmonic rejection was accomplished with a Rh-coated mirror. The samples were measured in a He-purged sample chamber and data were collected in fluorescence mode using a four-element Vortex Si-Drift detector. The phosphorus pentoxide (P₂O₅) was used for energy calibration by setting the first derivative to 2149 eV. The high-energy synchrotron XRD was carried out at the 11-ID-C beamline of the Advanced Photon Source, Argonne National Laboratory. The wavelength was 0.11798Å. The XRD patterns were collected in the transmission mode using a Perkin Elmer large area detector. The collected two-dimensional patterns were then integrated into conventional one-dimensional patterns (intensity versus 2θ) for final data analysis using the Fit2d software.

6.2.2.3 Electrochemical Measurements

Coin cells (CR2032) are used for all the electrochemical measurements. The electrodes consisted of hard carbon, polyvinylidene fluoride (PVdF) and carbon black with a mass ratio of 80:10:10. For preparation of electrodes, electrode components are grounded in N-
Methyl-2-pyrrolidone (NMP), and the obtained slurry is coated onto Al foil by doctor blade and dried at 100 °C for 12 h under vacuum. The active mass loading for all electrodes are between 1.5 to 2 mg/cm². Sodium metal is used as the counter/reference electrode and 1.0 mol/L NaPF6 solution in ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1 in volume) is used as the electrolyte. Galvanostatic sodiation/desodiation tests are performed in the potential range of 0.01-2 V vs Na⁺/Na on Arbin BT2000 system at room temperature.

6.2.3 Results and Discussion

Graphene oxide (GO) was involved in the synthesis, which made the surface area of the pyrolyzed sucrose extremely low (7 m²/g). The doping level of phosphorus was determined to be 3 wt% in P-HC by inductively coupled plasma optical emission spectrometry (ICP-OES). The P was uniformly doped, which was confirmed by the energy dispersive X-ray (EDX) spectroscopy (Figure 6.1a). No P aggregation was formed in the P-HC. The transmission electron microscopy (TEM) images of both P-HC reveal typical turbostratic local structures (Figure 6.1b).
We employed XANES to study the oxidation state of P in P-HC (Figure 6. 2). Based on the edge positions of the standards, NaH$_2$PO$_2$ for P(I) and P$_2$O$_5$ for P(V)\textsuperscript{[15]}, the two peaks at 2146.4 and 2149.0 eV are assigned to P(III) and P(IV)/P(V), respectively, where there is no signal from phosphorus of zero oxidation state. Therefore, according to the XANES results, it is evident that most doped phosphorus species occur as PO$_x$ instead of elemental phosphorus.
P-HC does exhibit an impressive desodiation capacity of 359 mAh/g at a current density of 20 mA/g, which is much higher than the 283 mAh/g obtained by the HC (Figure 6. 3). Note that P-HC electrode retains well the key characteristic features of hard carbon: a low operation potential and a relatively high first cycle coulombic efficiency.
P-HC exhibits a much higher capacity than HC, which could be the result of two major factors: the possible redox reactivity POx and/or the favorable changes of carbon structures. For the reactivity of POx, it could be reduced a certain extent in the first sodiation, which may contribute to the higher capacity of P-HC. The monitor of the evolution of the oxidation state of phosphorus was monitored by XANES at different state of charge (Figure 6.2). After the first sodiation to 0.2V vs Na+/Na, the peaks at 2146.4 and 2149.0 eV became weaker. The peaks kept almost the same intensity without significant change upon further sodiation to 0.01V and the following desodiation process. Thus, the POx does not contribute to the higher desodiation capacity of P-HC and the higher capacity must be the result of the change of the local structure of hard carbon.
The structural change of hard carbon was verified by X-ray diffraction. As shown in Figure 6.4, with PO\textsubscript{x} doping, the (002) peak of hard carbon shifted from 1.78° to 1.76°, confirming the d-spacing enlargement. A larger d-spacing would facilitate intercalation of more Na-ions between the carbon layers inside the hard carbon.

![XRD of HC and P-HC](image)

Figure 6.4 XRD of HC and P-HC.

6.2.4 Conclusion

In summary, we increase the capacity of the low-surface-area hard carbon by PO\textsubscript{x} doping. The key electrochemical characteristics of hard carbon are kept. We confirm that the PO\textsubscript{x} does not contribute to the higher capacity by reactions. The enlargement of the interlayer d spacing is the main reason for the enhanced capacity. This study provides
important insights on the design principle of local atomic structures in hard carbon as an anode in NIBs.

Reference


Chapter 7: Study Mo-S Clusters by X-ray Absorption

7.1 Introduction

XAS is a powerful technique to study the Mo-S compounds. The hard X-ray at Mo K edge is possible to penetrate the sample and obtain good EXAFS data. The Mo K-edge is from the 1s to 5p dipole transition of molybdenum. The Mo electronic configuration with different oxidation states are: Mo metal: [Kr]4d⁵5s¹ (Figure 7. 1); Mo⁴⁺: [Kr] 4d²; Mo⁵⁺: [Kr] 4d¹; and Mo⁶⁺: [Kr] 4d⁰.

Electronic configuration of Molybdenum

Figure 7. 1 Electronic configuration of molybdenum.
The pre-edge is from the 1s to 4d transition, which is dipole forbidden. According to the dipole selection rule, the final state has to have p symmetry. Apart from very small quadrupole contribution, the strength of this pre-edge feature is proportional to the amount of Mo p-d mixing in the lowest unoccupied orbital. Thus, XAS has been used to study the Mo oxidation state and the bond details for Mo based catalysts,[1] proteins containing Mo,[2] as well as in-situ studies.[3, 4]

In addition to the hard X-ray, the XAS studies at intermediate energy, i.e. S K and Mo L₃ and Mo L₂ edges are also informative. The Mo L₂,L₃-edge absorption are originated from the 2p to 4d transition, which can probe the splitting of the 4d orbitals. For example, in Mo⁶⁺ species, both L₂ and L₃ edges show a split main peak, which corresponds to a transition to the empty valence orbitals of the tetrahedral ion. The S K-edge absorption is from the 1s to 4p transition. Additionally, the pre-edge feature due to the 1s to 3d transition may also be observed in some Mo-S compounds, such as thiosulfate. Thus, the charge distribution and the coordination environment in the Mo-S compounds can be determined through the XAS measurements.

7.2 Experimental Section

The XAS measurement at Mo K-edge was performed at the Advanced Photon Source (APS) on the bending-magnet beamline 20-BM-B with electron energy of 7 GeV and average current of 100 mA. The radiation was monochromatized by a Si (111) double-crystal monochromator. All spectra were collected in transmission mode by. For energy
calibration, a Mo foil was measured. The peak position of Mo foil was adjusted to 20000.36 eV. The XAS measurement at S K and Mo L2, L3 edges were performed on the bending-magnet beamline 9-BM-B. All spectra were collected in fluorescence mode by 4 element vortex detector and total electron yield detector. For energy calibration, sodium thiosulfate was measured. The peak position of pre-edge of sodium thiosulfate was adjusted to 2469.2 eV. The samples were diluted with polyethylene glycol and pressed to pellets to optimize the signal.

7.3 Results and Discussion

7.3.1 Mo K-edge X-ray absorption

The Mo K-edge XANES spectra of different Mo samples are shown in Figure 7.2a. The Mo5+ and Mo6+ samples show obvious pre-edge features due to the d-p mix in the unoccupied orbitals. The edge positions (first derivative peak position in Figure 7.2b of the Mo in (NH4)2Mo2S12 and (NH4)2Mo3S13 are the same as that in MoS2, indicating that the oxidation states of Mo in both (NH4)2Mo2S12 and (NH4)2Mo3S13 are 4+. This result is consistent with the XPS result in Chapter 4.

The Fourier transform of the EXAFS spectra of the MoS2, (NH4)2Mo2S12 and (NH4)2Mo3S13 are shown in Figure 7.3. The two peaks in the MoS2 spectra at about 2Å and 3Å are corresponding to the Mo-S and Mo-Mo bond, respectively.\textsuperscript{[5]} The average Mo-S distances in (NH4)2Mo2S12 and (NH4)2Mo3S13 are quite similar to that in MoS2. Similar distance of Mo-S in different Mo-S compounds has been observed by others.\textsuperscript{[6, 7]} The Mo-
Mo scattering in (NH$_4$)$_2$Mo$_2$S$_{12}$ and (NH$_4$)$_2$Mo$_3$S$_{13}$ is much weaker than that in MoS$_2$, which may result from the smaller amount of Mo than MoS$_2$. In addition, the Mo-Mo bond distances in (NH$_4$)$_2$Mo$_2$S$_{12}$ and (NH$_4$)$_2$Mo$_3$S$_{13}$ are smaller than that in MoS$_2$. The nearest Mo-Mo distance in MoS$_2$ is 3.16 Å. The Mo-Mo distance in (NH$_4$)$_2$Mo$_2$S$_{12}$ is 2.83 Å$^{[8]}$ $^{[9]}$ and the Mo-Mo distance in (NH$_4$)$_2$Mo$_3$S$_{13}$ is 2.72 Å.$^{[10]}$ The FT results agree well with the data from the bond distance extracted from the single-crystal diffraction.

Figure 7. 2 (a) XANES spectra and (b) its first derivative of various Mo samples.
7.3.2 Mo L₂, L₃ -edges XANES

The Mo L-edges from 2p to 4d transition are also sensitive to the oxidation state of Mo. When Mo got reduced, the Mo L₃ edge will shift to lower energy.[11, 12] The Mo L-edge XAS can also probe the splitting of the 4d orbital, which caused by the ligand field (Figure 7. 4).
Figure 7.4 Schematic representation of the contributions to the energy of the ligand K-edge and metal L-edge pre-edge features.

The XANES spectra at Mo L$_3$ and Mo L$_2$ edges are shown in Figure 7.5 and Figure 7.6, respectively. The Mo$^{6+}$ compounds are all show doublet peak at both Mo L$_3$ and Mo L$_2$ edges, indicating that the splitting 4d orbitals. No doublet peak is observed in MoS$_2$, (NH$_4$)$_2$Mo$_2$S$_{12}$ and (NH$_4$)$_2$Mo$_3$S$_{13}$. The Mo L$_3$ edges of MoS$_2$, (NH$_4$)$_2$Mo$_2$S$_{12}$ and (NH$_4$)$_2$Mo$_3$S$_{13}$ of significantly shift to lower energy compared to the Mo$^{6+}$ compounds. The position of the Mo L$_3$ edge of MoS$_2$, (NH$_4$)$_2$Mo$_2$S$_{12}$ and (NH$_4$)$_2$Mo$_3$S$_{13}$ are compared in Figure 7.7. The edge position slightly shifted to higher energy, which indicated a higher Mo oxidation state, from MoS$_2$ to (NH$_4$)$_2$Mo$_3$S$_{13}$ to (NH$_4$)$_2$Mo$_2$S$_{12}$. 

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Figure 7. 5 Mo L₃ XANES spectra of different Mo-S compounds.

Figure 7. 6 Mo L₂ XANES spectra of different Mo-S compounds.
7.3.3 S K-edge XANES

As shown in Figure 7.8, the oxidation state of sulfur in (NH₄)₂Mo₃S₁₃ and (NH₄)₂Mo₂S₁₂ are higher than the sulfur in MoS₂. That reasonable since (NH₄)₂Mo₃S₁₃ and (NH₄)₂Mo₂S₁₂ contains S²⁻ but all sulfur in MoS₂ is S²⁻. The edge position of S K in (NH₄)₂Mo₂S₁₂ slightly shifts to a lower energy than that of (NH₄)₂Mo₃S₁₃, suggesting a higher electron density around the sulfur atoms in (NH₄)₂Mo₂S₁₂, which may contribute to the superior HER catalytic activity.
7.3.4 XANES spectra of (NH₄)₂Mo₂S₁₂ and (NH₄)₂Mo₃S₁₃ in DMF solution at S K edges

The (NH₄)₂Mo₂S₁₂ catalysts were deposited on electrode by drop casting its DMF solution in the HER test in Chapter 4. It’s important to check if the [Mo₂S₁₂]²⁻ structure was preserved in the DMF solution. As shown in Figure 7. 9, after resolved in DMF, a new
peak at around 2480 eV appeared, which indicated that the sulfur in \([\text{Mo}_2\text{S}_{12}]^{2-}\) was oxidized. After adding NaBH4, the amount of oxidized sulfur reduced and the intensity of the peak at around 2470 increased, but the structure was still different from the original \([\text{Mo}_2\text{S}_{12}]^{2-}\). Similar oxidation has also been observed for \([\text{Mo}_3\text{S}_{13}]^{2-}\) clusters (Figure 7.10).

Figure 7.9 XANES spectra of \((\text{NH}_4)_2\text{Mo}_2\text{S}_{12}\) in DMF. The black dash line indicates the solid, the blue lines indicate the DMF solution and the red to yellow line indicate change of the DMF solution after adding NaBH4.
Figure 7. 10 XANES spectra of (NH$_4$)$_2$Mo$_3$S$_{13}$ in DMF. The black dash line indicates the solid, the blue lines indicate the DMF solution.

7. 4 Conclusion

The bulk properties of the (NH$_4$)$_2$Mo$_2$S$_{12}$ were characterized by XAS at Mo K, S K and Mo L$_2$, L$_3$ edges. The XAS results agree well with the results from other characterization techniques, such as XRD and XPS. In addition, the instability of the (NH$_4$)$_2$Mo$_2$S$_{12}$ and the (NH$_4$)$_2$Mo$_3$S$_{13}$ in DMF solution has been determined by XANES at S K edge. The result
suggests that these two catalysts have to be handled in inert atmosphere and more stable catalysts are needed for HER catalysis.

Reference


Chapter 8: Conclusion

8.1 Summary of current work

2D materials delivers new understanding of the physics and chemistry of materials. These atomic thin layers offer lots of exciting discoveries, which will break up the conventional limits of the materials. In this thesis, I have explored the rational synthesis of the layered transition metal dichalcogenides (TMDs) and their application in electronic devices for nanoscale transistors. In addition, the chemistry of transition metal chalcogenides molecules has also been explored. Through rational designing the molecules, the activity was well controlled. The work presented here involved a wide range of physical science, including the fundamental chemistry, such as the crystallization mechanism; the practical application, e.g. electronic device fabrication, and the instrumentation including synchrotron X-ray techniques.

The growth of large-scale 2D materials with high quality is difficult. The conventional top-down or bottom-up method cannot meet the requirement of the development of 2D materials. The study in Chapter 2 is the first time that the supersaturation of the precursors is well controlled to reduce the nuclei density, thus, single-crystal 2D transition metal dichalcogenides with high mobility are obtained. The van der Waals epitaxial growth mechanism has been confirmed by the triple-axis X-ray diffraction study, which clearly
presented the orientation of the 2D film with the substrate. This method has also been extended to the growth of doped 2D transition metal dichalcogenides and 2D films on the substrates that suitable for van der Waals growth.

The 2D electronics is of significant importance to overcome the conventional size limit of the electronics. In Chapter 3, the MoS$_2$ based 2D/3D heterojunctions have been fabricated, demonstrating the practical application of the 2D TMD layers. This work shows that the rational design of devices with appropriate band alignment will dramatically improve the performance of the 2D electronic devices, which paves the way to future development of the 2D electronic devices.

Through understanding the properties of the MoS$_2$, I realized that MoS$_2$ is not only a promising candidate for 2D electronics, but also an excellent catalyst to replace the expensive Pt-group catalysts for HER. Since the only the edges of MoS$_2$ are catalytically active, Mo-S clusters have been designed to expose more edge structures. The [Mo$_2$S$_{12}$]$^{2-}$ clusters has shown superior HER catalytic activities.

To understand to behavior of the Mo-S clusters, a powerful synchrotron X-ray technique, X-ray absorption spectroscopy is introduced. The XAS can help determine the short-range local environmental of a central atom in the materials, such as the oxidation state, the splitting of the orbitals, the bond distance and the coordination numbers. In Chapter 7, the XAS characterization of Mo-S clusters has been used to understand the charge distributions in the clusters. In addition, the solution sample measurement shows the instability of the catalysts, which is crucial for the further development of the Mo-S based HER catalysts.
8.2 Future work and outlook

Although the high-quality single-crystalline 2D transition metal dichalcogenides has been obtained in this thesis, due to the high temperature requirement of the synthesis, stacking different 2D materials is hardly achieved by this method. The precursor metal layers can be well controlled by the deposition techniques, such as e-beam and sputtering, however, the high temperature will cause the diffusion of the metal atoms into each other or even form alloys. It is expected that, in the future, more research will be focused on developing facial methods to synthesize the high-quality stacking 2D materials.

To understand the HER catalytic mechanism of Mo-S clusters, in-situ measurements are in demand. XAS is a promising technique with the potential for operando experiments. However, the conventional step-scan takes ~10 min for one scan, which is too slow to capture the evolution of the catalysts during the HER process. On the instrumentation side, the development of the Quick XAFS will make considerable contribution to understand the catalytic mechanism. On the chemistry side, more stable catalysts are needed.
Chapter 1


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Chapter 2


[50] Supporting Information for Epitaxial Growth of Large Area Single-Crystalline Few-Layer MoS2 with High Space Charge Room Temperature Mobility of 192 cm2V-1s-1.

Chapter 3


Chapter 4


Chapter 5


Chapter 6


Chapter 7


