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TECHNOLOGICAL
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**METAL SULFIDES FOR ELECTROCHEMICAL
ENERGY STORAGE AND CONVERSION**

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University in partial fulfilment of the requirement for
the degree of
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Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research and has not been submitted for a higher degree to any other University or Institution.

2016. 10. 27

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Abstract

Electrochemical energy storage and conversion devices are regarded as one of the most attractive technologies to overcome the crisis of fossil fuel exhaustion and the global pollution. The key to advance these technologies is to explore suitable materials with various advantages of good performance, such as high stability, low cost, and environmental friendliness. The emerging two-dimensional (2D) molybdenum sulfide (MoS_2) has shown vast potential for renewable energy storage and conversion applications, due to its intriguing physicochemical properties. Nevertheless, several issues handicap the commercial application of MoS_2 , including rapid structure degradation, low electrical conductivity, and sluggish charge transfer kinetics. Therefore, scientific research and breakthroughs are highly desirable to address these issues and satisfy the requirements for practical use.

The main aim of this thesis is to investigate MoS_2 -based composites with engineered nanostructures as prospective electrodes for energy storage and conversion devices with good performance, high stability, and excellent safety. By virtue of the scrupulous design and smart hybridization of nanoarchitectures, exceptional properties and performance could be achieved. With this in view, novel $\text{MoS}_2/\text{Ni}_3\text{S}_2$ heterostructures, flexible MoS_2 electrodes supported on different substrates and hierarchical MoS_2 hollow nanotubes have been developed and designed by facile synthetic routes. Meanwhile, the effect of different nanostructures on the electrochemical performance of energy storage and conversion devices is fundamentally investigated to provide in-depth studies on the relationship between structure and performance. The relevant studies in the thesis are divided into five parts, including $\text{Ni}_3\text{S}_2@\text{MoS}_2$ core/shell nanorod arrays on Ni foam as the supercapacitor electrode (Chapter 4), honeycomb-like MoS_2 nanoarchitectures anchored into graphene foam (GF) for enhanced lithium storage (Chapter 5), MoS_2 architectures supported on graphene foam/carbon

nanotube (GF/CNT) hybrid films: highly integrated frameworks with ideal contact for superior lithium storage (Chapter 6), MoS₂ nanosheets decorated Ni₃S₂@MoS₂ coaxial nanofibers for enhanced Na-ion storage (Chapter 7) and active sites-enriched hierarchical MoS₂ nanotubes: highly active and stable architecture for boosting hydrogen evolution and lithium storage (Chapter 8).

As the in-depth understanding of electrochemical reaction mechanisms is significant for advancing different energy storage and conversion devices, this thesis also performs the fundamental investigation of the lithium/sodium storage mechanisms, and the mechanisms of hydrogen evolution reaction (HER). The cause for enhanced performance has been also carefully explored. It is hoped that all these studies could shed more light on the fundamental understanding.

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Figure 8.8 Detailed microstructure characterization after long-term HER cycling test. XPS spectra of (a) Mo 3d peaks and (b) S 2p peaks of the MT@MS/GF. (c) Raman spectra of the MT@MS/GF. (d) Raman spectra of MoS₂ in the MT@MS/GF.

Figure 8.9 Detailed morphology characterization after long-term HER cycling test. a) SEM images of MT@MS. b) TEM image of MT@MS. c, d) HRTEM images of MT@MS, showing MoS₂ nanosheets decorating MoS₂ nanotubes and crystal planes of MT@MS.

Figure 8.10 a) The first 4 cycles CV curves of MT@MS/GF at a scan rate of 0.2 mV s⁻¹, b) the first three charge and discharge curves of MT@MS/GF at a current density of 100 mA g⁻¹, c) cycling behavior of the MT@MS/GF and MT/GF electrodes at various current densities, d) cycling behaviors of the MT@MS/GF electrode at a current density of 500 mA g⁻¹.

Figure 8.11 Cycling behaviors of the MT /GF electrode at a current density of 500 mA g⁻¹.

Abbreviations

2D	Two-dimensional
EV	Electric Vehicle
PHEV	Plug-in Hybrid Electric Vehicles
HEV	Hybrid Electric Vehicles
TMSs	Transition Metal Sulfides
LIBs	Lithium Ion Batteries
SIBs	Sodium Ion Batteries
HER	Hydrogen Evolution Reaction
CNTs	Carbon Nanotubes
GF	Graphene Foam
GF/CNT	Graphene foam/carbon nanotubes
3DGF	Three-dimensional Graphene Foam
1D	One-dimensional
0D	Zero-dimensional
3D	Three-dimensional
SC	Supercapacitor
EC	Electrochemical Capacitors
EDLC	Electrical Double Layer Capacitor
EDL	Electrical Double Layer
SSA	Specific Surface Area
SEI	Solid Electrolyte Interface
ICL	Irreversible Capacity Loss
EES	Electrical Energy Storage
rGO	Reduced Graphene Oxide
OER	Oxygen Evolution Reaction
Pt	Platinum
MoS ₂	Molybdenum Sulfides

DFT	Density Functional Theory
CVD	Chemical Vapor Deposition
RT	Room Temperature
Ni/GF	Graphene Supported on Ni Foam
TAA	Thioacetamide
Na ₂ MoO ₄	Sodium Molybdate
P123	HO(CH ₂ CH ₂ O) ₂₀ (CH ₂ CH(CH ₃)O) ₇₀ (CH ₂ CH ₂ O) ₂₀ H
NH ₂ CSNH ₂	Thiourea
PVP	Polyvinylpyrrolidone
XRD	X-Ray Diffraction
FESEM	Field Emission Scanning Electron Microscope
TEM	Transmission Electron Microscope
HRTEM	High Resolution Transmission Electron Microscope
EDX	Energy-Dispersive X-Ray Spectroscopy
XPS	X-Ray Photoelectron Spectroscopy
SAED	Selected Area Electron Diffraction
BET	Brunauer-Emmett-Teller
BJH	Barrett-Joyner-Halenda
TGA	Thermogravimetric Analysis
CV	Cyclic Voltammetry
EIS	Electrochemical Impedance Spectroscopy
AC	Alternating Current
PVDF	Polyvinylidene Fluoride
SCE	Standard Calomel Electrode
LSV	Linear Scan Voltammetry
LSV	Linear Scan Voltammetry
TOF	Turn Over Frequency
VASP	Vienna Ab-Initio Simulation Package
PAW	Projector-Augmented-Wave
GGA	Generalized Gradient Approximation

PBE	Perdew–Burke–Ernzerhof
FFT	Fast Fourier Transformation
STEM-based EDX	Scanning TEM-based Energy Dispersive Spectroscopy
EC	Ethylene Carbonate
DEC	Diethyl Carbonate
FEC	Fluoroethylene Carbonate
RHE	Reversible Hydrogen Electrode
TMD	Transition Metal Dichalcogenide
HDS	Hydrodesulfurization
HAADF–STEM	High–Angle Annular Dark–Field Scanning Transmission electron microscopy

Chapter 1

Introduction

This part mainly introduces the background, motivation, research scope, and objectives of the thesis. With growing depletion of the fossil energy and worsened environmental pollutions, there has been an unprecedented desire to search and develop renewable and clean energy sources. To advance these technologies, the key is to explore suitable active materials with various advantages of good performance, such as high stability, low cost, and environmental friendliness. The main research scope and objective of this thesis is to investigate metal sulfides and their nanocomposites as prospective electrode materials for energy storage and conversion devices with good performance, high stability, and excellent safety.

1.1 Background

Energy is unquestionably the lifeblood of human civilization and development.¹⁻
³ With the wide depletion of the fossil energy, and the rapid increase in greenhouse gas emissions and other environmental pollutions, there is an urgent need for sustainable and renewable resources. Up to now, considerable efforts have been made to look for better energy technologies of sustainable and renewable resources, including hydro, biomass, wind, solar, geothermal, biofuel, fuel cells, batteries, and supercapacitors (SCs), as alternatives to the conventional energy sources.^{4, 5} Besides, electrolysis, photoelectrochemical, and photocatalytic water-splitting techniques were explored for green and light fuel generation.⁶⁻⁸ Since many sustainable and renewable sources (wind, solar, marine and etc.) are always intermittent due to the availability of time, weather, season and location, it is highly required some storage media to store the energy during high production periods and transfer it during peak demand.

The electrochemical energy technologies are regarded as the most significant energy storage power sources for several application areas, such as transportation, stationary, and portable/micropower, due to various advantages, including pollution-free operation, high efficiency, flexible power and energy.^{9, 10} Electrochemical power sources mainly include fuel cells, batteries, SCs and photovoltaic devices. In brief, fuel cell and photovoltaic devices are electrochemical energy conversion devices, while batteries and SCs are electrochemical energy storage devices. In order to compete with today's engines based on gasoline, further research and development are essential to overcome challenges such as cost, durability, and operability problems, which hinder their application and commercialization. Especially, both high power and energy densities are highly desired in the application for mobile transport, including electric vehicles (EV), plug-in hybrid (PHEV), and hybrid electric vehicles (HEV).¹¹ The performance of the electrochemical devices inherently relies on the materials used. Consequently, the development of new materials with excellent

performance, low cost, and good safety has become the key to push these technologies commercially viable. Although considerable efforts have been made in innovative materials chemistry, further breakthroughs are still highly required to satisfy the future requirements of energy storage and conversion devices.

The emerging 2D transition metal sulfides (TMSs) have shown vast potential for renewable energy storage and conversion applications, owing to their intriguing physicochemical properties.¹²⁻¹⁴ However, the practical application of TMSs and their composites for energy storage and conversion is highly impeded by their intrinsic limitations, including low electrical conductivity and easy self-aggregation due to the excess surface free energy. Nanostructure has been convinced to be an ideal way to optimize the performance of TMSs. Although TMSs with desirable nanoarchitectures in complex metrics possess intriguing properties, achieving their practical application in energy storage and conversion still remains great challenges.

1.2 Motivation

With growing depletion of the fossil energy and worsened environmental pollutions, there has been an unprecedented desire to search and develop renewable and clean energy sources. To advance these technologies, it is the heart to explore suitable active materials with various advantages of good performance, such as high stability, low cost, and environmental friendliness.

As a typical inorganic graphene analogue, the emerging 2D MoS₂ has shown vast potential for renewable energy storage and conversion applications, due to their layered structure with weak van der Waals interaction, which can enable easy intercalation of foreign ions (H⁺, Li⁺, Na⁺) without a significant increase in volume.¹⁵ Especially, MoS₂ has been intensively investigated as one promising electrode material for lithium ion batteries (LIBs), sodium ion batteries (SIBs), SCs and HER.

So far, although a wide and distinct variety of MoS₂ and its composites with various structures have been studied and some results are encouraging, there is still no adequate research to engineering their chemical and physical properties, and thus achieve good performance for energy storage and conversion applications. Besides, electrochemical behaviors of MoS₂ materials for different applications are still not clear. Furthermore, fundamental studies are essential to demonstrate the detailed electrochemical interactions and elucidate how structure designs significantly impact the electrochemical performance. Hence, this thesis will focus on this direction to gain further understanding.

1.3 Objective and Scope of Research

The main research scope and objective of this thesis is to investigate metal sulfides and their nanocomposites as prospective electrode materials for energy storage and conversion devices with good performance, high stability, and excellent safety. The detailed goals are listed below:

1.3.1 Investigation of the correlation between the MoS₂/Ni₃S₂ heterostructure and electrochemical performance in SCs and SIBs

2D layered MoS₂ with similar structures to graphite has been reported as a potential anode material for SCs and SIBs owing to its weak van der Waals interactions, easily enabling an intercalation of foreign ions (such as H⁺, Li⁺, and Na⁺), and providing large surface area for inter-layer charge storage.^{15, 16} In addition, Mo ions possess a range of oxidation states from +2 to +6, rendering it pseudocapacitance ability, which plays an important role in enhancing electrochemical capabilities.^{17, 18} However, the further application of MoS₂ is still limited by its inherent drawbacks, such as the low electrical conductivity, easy agglomeration and significant volume change. As some study reported, the specific capacitance and sodium/lithium storage of bare MoS₂ are still very limited. The performance of electrodes relies intimately on the scrupulous design

and smart hybridization of nanoarchitectures. Some newly rising 2D MoS₂-based heterostructures such as MoS₂/graphene, MoS₂/WS₂, MoS₂/CoSe₂, MoS₂/Fe₃O₄ and MoS₂/TiO₂ have demonstrated incredible properties, which are very difficult to obtain in a single component system.¹⁹⁻²² Nevertheless, there is no systematic research about the application of MoS₂/Ni₃S₂ heterostructures for energy storage and conversion. Hence, this thesis devotes to investigate the correlation between the MoS₂/Ni₃S₂ heterostructure and its electrochemical performance in the applications of SCs and SIBs. Meanwhile, the possible growth mechanism for the formation of such unique heterostructures was proposed to shed some light on the controlled fabrication of other metal sulfides with similar morphologies. Various characterization techniques will be utilized to evaluate the composition and structural features of the as-prepared samples.

1.3.2 Study the effect of different substrates on the electrochemical properties of flexible MoS₂ electrodes for LIBs

MoS₂ has been extensively investigated for an anode material of rechargeable LIBs owing to its higher capacity (670 mAh g⁻¹ with a 4-electron transfer reaction per formula) than the commercial graphite material (372 mAh g⁻¹). However, due to the low electrical conductivity and the huge volume variation during lithiation and delithiation processes, the capacity fading and poor rate performance of MoS₂ anode are still the main challenge. To address these issues, the sp²-hybridized carbon nanomaterials (e.g. carbon nanotubes (CNTs) and graphene) are the most promising matrices to enhance the electrical conductivity and alleviate the volume change upon cycling. However, for the most of the current works, MoS₂ or MoS₂ composites are in the form of powders, and therefore conductive additives and binders are always required to coat on metallic current collector for the electrode fabrication.

Recently, an emerging new concept has been exploited to enhance the energy per footprint area by directly growing electroactive nanostructures on various

substrates, especially three-dimensional (3D) porous carbon materials as integrated electrodes for LIBs. Nevertheless, there is no systematic research about the impact of different substrates on the growth of different MoS₂ nanoarchitectures. In this thesis, one major aim is to optimize the growth system of flexible MoS₂ electrodes by comparing the lithium storage capability of different electrodes. Significantly, the theoretical calculations are provided to analyze the chemical interaction between MoS₂ and a different carbon matrix.

1.3.3 Study the impact of tubular MoS₂ nanostructures on the electrochemical properties for LIBs and HER

Tubular MoS₂ has been widely studied in various novel applications of catalysis, energy storage, lubricants, electronics, and optoelectronics. Extensive research has proved that hollow nanotubes with abundant active edge sites and high specific surface area (SSA) always exhibit excellent performance in many applications. Despite these advances in the fabrication of tubular nanostructures, it is still a considerable challenge to obtain MoS₂ nanotubes with sufficient exposed active sites, high SSA and robust stability by a facile method. In addition, there is no adequate research on the relationship between the tubular structure design and the electrochemical performance. Hence, herein, we firstly propose a novel bottom-up approach to prepare tubular MoS₂ structures using Ni₃S₂ nanowires as the precursor and self-sacrificial template. Significantly, this thesis devotes to elucidate how tubular structure can significantly impact the surface chemistry, enabling new opportunities for enhancing electrochemical properties.

1.4 Thesis Organization

Based on the research objectives, the dissertation is organized as follows.

Chapter 1 describes the introduction of the research background and motivation, identifying the scope and objectives of the research.

Chapter 2 briefly introduces the basic configuration and operation principles of LIBs, SIBs, SCs and HER. Meanwhile, the representative electrode materials for these applications are respectively reviewed.

Chapter 3 describes various experimental techniques employed in this thesis, including material characterization tools, synthesis methodologies for MoS₂ and its composites, and electrochemical measurement procedures.

Chapter 4 demonstrates a facile synthesis of core/shell Ni₃S₂@MoS₂ heterostructure and investigates the correlation between microstructure and electrochemical performance.

Chapter 5 describes a facile strategy to grow novel MoS₂ nanoarchitectures on GF and investigates the electrochemical Li storage mechanism.

Chapter 6 investigates the impact of different substrates for the growth of flexible MoS₂ electrodes and demonstrates the relationship between nanostructures and electrochemical performance.

Chapter 7 investigates the effect of Ni₃S₂-MoS₂ heterostructure on the electrochemical performance for SIBs and studies the relationship between the heterostructures and their properties.

Chapter 8 describes a self-sacrificial template strategy to obtain tubular MoS₂ structures on GF and carries out a series of fundamental studies on the flexible tubular MoS₂ electrodes, such as electrocatalytic activity studies and electrochemical Li storage mechanism.

Chapter 9 reaches the conclusion of the whole research project, together with the proposed future studies.

Chapter 2

Literature Review

This section is a brief introduction of the basic configuration and operation principles of different energy storage and conversion devices, including electrochemical capacitors (ECs), LIBs, SIBs, and HER. Meanwhile, previous works on the representative electrode materials in different electrochemical systems are reviewed. Especially, the relevant research status, the synthesis strategies, as well as the applications of MoS₂ in various energy storage and conversion devices are reviewed in this part.

2.1 Introduction

Compared to various established technologies, electrochemical energy storage and conversion devices possess a number of advantages, including environmental friendliness, high efficiency, flexible power, long cycle life, and low maintenance.^{10, 23} With the increasing crisis of fossil energy and the severe environmental pollution concerns, various high-performance electrochemical energy storage and conversion devices have been proposed as promising alternatives to replace fossil fuels. Up to now, there are several energy storage technologies that are based on electrochemical storage as indicated in **Figure 2.1**.³ Nevertheless, there still remain significant challenges to realize high stability, low-cost and large energy/power densities in energy storage and conversion devices. To advance these technologies, the key is to develop innovative materials.^{3, 24}

Figure 2.1 Comparison of discharge time and power rating for existing energy storage technologies.³

2.2 Electrochemical Energy Storage/Conversion Systems

2.2.1 ECs

ECs, named SCs, have drawn extensive interests owing to their significant advantages, including long cycling life, high power density and the compensation of the energy/power gap between fuel cells/batteries and traditional dielectric capacitors.²⁵⁻³⁰ As illustrated in a simplified Ragone plot (**Figure 2.2**) for various energy conversion and storage systems, SCs occupy an important position in terms of energy and power density.³¹

Figure 2.2 Specific power against specific energy, also called a Ragone plot, for various electrical energy storage devices. If a supercapacitor is used in an electric vehicle, the specific power shows how fast one can go, and the specific energy shows how far one can go on a single charge. Times shown are the time constants of the devices, obtained by dividing the energy density by the power.³¹

In principle, SCs can be classified into two kinds: electrical double layer capacitor (EDLC), and pseudo-capacitor, according to their charge storage mechanism.³⁰ The capacitance of EDLCs derives from the pure electrostatic

charge accumulated on the electrode/electrolyte interface without any chemical reactions, such as carbon materials (**Figure 2.3a**). The capacitance of the pseudo-capacitor, mainly arises from reversible oxidation/reduction (redox) or Faradaic redox reactions taking place on the active species, for example, transition metal oxides/sulfurs/nitrides and polymers (**Figure 2.3b**).

Figure 2.3 Schematic of (a) a parallel-plate capacitor and (b) an electrochemical supercapacitor.³²

The first model of the electrical double layer (EDL) was made by von Helmholtz in the 19th century. In this model, two opposite charge layers accumulate on the electrode/electrolyte interface. The model is exactly the same as that of two-plate conventional capacitors. Subsequently, Gouy and Chapman, and Stern and Geary modified this Helmholtz EDL model, on consideration of the effect of a diffuse layer arising from the accumulation of electrolyte ions in the electrolyte solution.^{33,34} The capacitance of the EDLC is mainly determined by the effective thickness of the double layer, the SSA of active materials, and the type of electrolyte, according to the following formula as that of the double layer capacitance:³⁵

$$C = \frac{\epsilon_r \epsilon_0}{d} A \text{ or } C/A = \frac{\epsilon_r \epsilon_0}{d} \quad (2.1)$$

where ϵ_r is the electrolyte dielectric constant, $\epsilon_0 = 8.854 \times 10^{-12} \text{ F m}^{-1}$ is the permittivity of the vacuum, d is the effective thickness of the double layer and A is the SSA of active materials. As only the surface of the active materials that is accessible to electrolyte ions can contribute to the charge storage, it is highly

required to tune surface properties, pore structure, pore size, and electrical conductivity.³⁶

The key of obtaining high capacitance of the EDLCs is to utilize the electrode materials with high SSA and good electronic conductivity.^{29, 31} Generally, graphitic carbon exhibits obvious advantages and meets all the requirements for EDLC, including good electrochemical stability, high electrical conductivity, and open porosity. Besides, other carbonaceous materials, for example templated, activated, and carbide-derived carbons, carbon fibers, CNTs³⁷, carbon onions³⁸ and nanohorns³⁹ have been studied for the electrode materials of EDLCs. Among them, activated carbons have become the most extensively used electrode materials, owing to the high SSA and low cost.

The second type of ECs is pseudo-capacitors, in which reversible redox processes take place, accompanying the transfer of the electrons of electroactive materials across the electrode/electrolyte interface, leading to a potential-dependent capacitance. The pseudo-capacitance can be represented by an approximately linear variation of capacitance with the extent of charge stored ΔQ and the corresponding change of the potential ΔV as follows⁴⁰:

$$C = \frac{\Delta Q}{\Delta V} \quad (2.2)$$

In contrast to EDLC, which stores charge electrostatically, pseudocapacitor stores charge Faradaically through the transfer of charge between the electrolyte and electrode. Unlike the redox processes in batteries, Faradaic processes in pseudo-capacitors are subject to a thermodynamic change of the potential during the charge accumulation. The ions contributing to the pseudo-capacitance are simply cling to the surface structure of the active materials by physical adsorption, without making or breaking chemical bonds. Hence, capacitive faradaic processes are much faster and have better reversibility. Redox SCs possess not only battery-like behavior with Faradaic reactions, and electrostatic capacitor-like behavior with high power and high reversibility. Metal oxides such as RuO_2 ⁴¹⁻⁴³, MnO_2 ⁴⁴⁻⁴⁸ or Fe_3O_4 ⁴⁹⁻⁵¹, and some conducting polymers (polyaniline

and polypyrrole)⁵²⁻⁵⁶, have been widely investigated as electrode materials for pseudo-capacitors. In pseudo-capacitors, fast and reversible redox or Faradaic charge transfer reactions take place on electro-active species. However, like batteries, pseudo-capacitors always suffer from the problem of poor reversibility owing to the redox reactions involving in pseudo-capacitors.

2D layered MoS₂ as one inorganic graphene analogue, are consisted of S–Mo–S units. The adjacent layers stack via weak van der Waals interactions. Especially, Mo exhibits a range of oxidation states from +2 to +6, endowing it pseudocapacitance abilities. When using as electrodes for SCs, MoS₂ can deliver a theoretical specific capacitance of around 1000 F g⁻¹. Nowadays, numerous research works report the application of MoS₂ in SCs. Ajayan *et al.* reported micro-supercapacitors based on the electrode of 2D MoS₂ films delivered a relatively high capacitance of 8 mF cm⁻² and superior cyclability.⁵⁷ Therefore, MoS₂ nanostructures hold significant promise for the application of SCs.

2.2.2 LIBs

Developing new energy technologies is critical for alleviating the growing energy crisis and escalating demand for environmental protection. Among the various existing technologies (**Figure 2.4**), rechargeable LIBs currently outperform other systems due to their prominent superiorities of high energy density, light weight, and long cycling life.^{2, 11, 58-63} LIBs have successfully dominated the commercial market of power sources for portable consumer electronic devices, from laptop computers to mobile phones and camcorders. They have also been extensively investigated as the most promising power sources for next generation EVs and HEVs.^{60, 64}

A lithium-ion device is consisted of an anode (generally graphite), a layered oxide cathode (generally the lithium metal oxide, LiCoO₂), and a porous membrane separator soaked into nonaqueous electrolyte (LiPF₆ in ethylene carbonate/diethylcarbonate), which not only enables ion transfer but also

prevents directly contact between the two electrodes (**Figure 2.5**).⁶⁵ During the charge process, Li ions deintercalate from the cathode and insert into the anode. Meanwhile, the electrons transfer from cathode to anode via the external circuit. For the discharge process, it is exactly contrary. Li ions are extracted from the anode and then intercalate back into the cathode. During charge/discharge cycling, Li ions are transported backwards and forwards between cathode and anode, which are separated by the organic electrolyte. In the meantime, the chemical energy is reversibly converted into electricity and the electrical energy is subsequently stored within LIBs. The chemical reactions can be summarized as follows:⁶¹

Figure 2.4 Comparison of different battery technologies in terms of volumetric and gravimetric energy density.²

Ideal electrode materials for LIBs not only should deliver high reversible capacities, good rate capability, long cycle life, good safety, but also should be inexpensive and environmental-friendly. Currently, as the dominant commercial anode material for LIBs, graphite possesses several advantages, including flat and low working potential, favorable cycling stability and low cost. However, a

theoretical capacity of around 372 mAh g^{-1} only can be provided by graphite anode, which is calculated based on a reversible conversion reaction of one lithium ion with six C-atoms (**Equation 2.4**). The low capacity can hardly meet the industrial requirements for high energy applications. Additionally, graphite-based LIBs usually suffer from the problem of low Coulombic efficiency, owing the formation of a passivated solid electrolyte interface (SEI) layer on the graphite surface. Such a layer can inhibit exfoliation of graphite electrodes, but also lead to the consumption of excessive charge, resulting in a low Coulombic efficiency. Moreover, even severe concern is the lithium dendrite formation during the overcharging, arising from the low lithium intercalation potential into graphite (less than 100 mV versus Li^+/Li). Furthermore, the low diffusion rates of Li ions in graphite anode (always $< 10^{-6} \text{ cm}^2 \text{ s}^{-1}$) seriously limit power density of LIBs, which is determined by the chemical diffusion coefficient of Li ions. In the last two decades, many attempts have been made to explore alternative anodes of LIBs, with the prominent performance of high reversible capacity, good rate capability, long cyclability and good safety. Up to now, there are very many materials that have been explored, especially alloys, metal oxides and metal sulfurs/nitrides.

Figure 2.5 Schematic representation of a lithium-ion battery. The negative electrode (graphite), positive electrode (LiCoO_2), separated by a nonaqueous liquid electrolyte.⁶⁵

A range of elements in groups IV and V (e.g. Si, Sn, Ge, Al, Mg and Zn) can electrochemically alloy with metal Li at a low potential (below 1 V vs. Li/Li⁺).⁶⁶⁻⁶⁸ These alloyed anodes always possess large theoretical capacities. Especially, the theoretical capacities of Sn and Si are as high as 933 and 4200 mAh g⁻¹, respectively, which are calculated corresponding to the stoichiometry of Li_{4.4}M in a reversible charge/discharge processes. Nevertheless, the large volume variation during Li ion intercalation/extraction, deadly hinders their practical utilization as anodes of LIBs, which would cause the loss of electrical contact and crack in electrodes. Up to now, several strategies have been investigated to alleviate these problems, such as the design of nanostructures, modification with carbon matrix and alloying with a second phase M.⁶⁶⁻⁷¹

Recently, various metal oxides have been widely studied as promising anodes of LIBs owing to their high reversible capacities. The reaction mechanisms involved in these oxide anodes for LIBs can be classified into the following three different types⁷²: (1) intercalation/deintercalation reaction mechanism, notably exhibited by the titanium oxides, (2) alloy/dealloy conversion reaction mechanism, and (3) the conversion (redox) reaction mechanism. Although intercalation electrode materials exhibit various advantages of low cost, environmental compatibility, and very good stability, they still suffer from limited capacity and poor electrical conductivity, which hinder their commercial use.⁷³⁻⁷⁶ Nevertheless, for electrode materials based on alloying–dealloying reaction and conversion reaction, the major drawback lies in large irreversible capacity loss (ICL) in the initial cycle and large electrode polarization due to huge volume variation during lithiation/delithiation process.^{61, 72, 77-81} These fundamental challenges make metal oxides far from commercial application.

In order to develop advanced LIBs with both high power and energy density, numerous TMSs (MS_x, M=Mo, W, Sn, Ga, Nb, and Ta) have been investigated as potential prospective anodes due to their favorable lattice structure for guest ions and high capacity.⁸²⁻⁸⁷ Similar to metal oxides, the reaction involves in most of metal sulfides for the anode of LIBs is based on the conversion reaction

mechanism, notably exhibited by TiS_2 ⁸⁶, CoS_2 ⁸⁸ and Ni_3S_2 ⁸⁹. Commonly, the intercalation/de-intercalation reaction between Li and metal sulfides can be described as follows⁹⁰:

For the process of Li intercalation, it corresponds to the reduction reaction of M^{n+} to M^0 , and also the diffusion of Li ions into the gaps of adjacent layers, accompanying a complete charge transfer. As a typical example, MoS_2 , another inorganic graphene analogue, consists of S–Mo–S units chemically bonded to form nanosheets which stack via Van der Waals interactions. The unique structure allows foreign ions intercalate into the gallery between the MoS_2 layers. As anodes of LIBs, a theoretical capacity of 670 mAh g^{-1} is provided based on the 4-electron transfer reaction. Therefore, up to now, it is being intensively studied as a high-capacity anode for LIBs. The detailed reaction mechanism of MoS_2 during the first discharge is described by the following equation, which is similar to those of metal oxides.

However, after the first cycle, the electrochemically active couple is S and Li_2S rather than MoS_2 and $(\text{Mo}+\text{Li}_2\text{S})$. The discharge process is followed by

It should be noted that the metallic Mo nanoparticles can enhance the conductivity of the $\text{Li}_2\text{S}/\text{Mo}$ or S/Mo nanocomposites. In addition, the existence of Mo can effectively alleviate the diffusion of soluble polysulfide (Li_2S_8 and Li_2S_4) into the electrolyte during the lithiation/delithiation process due to the as-formed polysulfides anchored into Mo host through sharing bonds with Li.^{91, 92}

It is demonstrated that layered crystalline MoS_2 electrodes have much higher capacity than the commercially used graphite. The vast majority of studies have indicated the electrochemical performance of MoS_2 is heavily dependent on its

structure and morphology. Although bulk MoS₂ exhibits a high specific capacity in the initial cycle, a rapid capacity fading can be always observed during the subsequent cycles at high charge/discharge rate.⁹³ In contrast, ultrathin 2D MoS₂ nanostructures can exhibit higher specific capacities and better rate performance compared to bulk materials owing the high electrolyte contact area, the decreased diffusion lengths, and then enhanced kinetics.⁹⁴⁻⁹⁷ However, 2D structured MoS₂ always suffers from easy self-aggregation due to the excess surface free energy and weak van der Waals interactions. To alleviate these obstacles, considerable efforts have been made, including constructing 3D architectures based on 2D materials, modification with conductive carbonaceous, and the novel design of heterostructures.⁹⁸⁻¹⁰⁰ Nevertheless, it should be mentioned that the capacity fading upon cycling and large polarization at high rates can still be observed in almost all cases. Therefore, continuing efforts should be made to improve MoS₂-based electrode materials for LIBs.

2.2.3 SIBs

LIBs have dominated the commercial market of energy power sources for portable electronic devices and been considered as the potential candidate to power EVs and HEVs, and to compete in an emerging market for electrical energy storage (EES). Nevertheless, the less abundant reserves of Li have pushed the researchers to search alternative battery technologies to replace LIBs. The relative abundance of lithium in the Earth's crust is limited to be 20 ppm as shown in **Figure 2.6**. Indeed, the material cost (the price of Li₂CO₃) was steeply increased in the past two decades. Compared to lithium, sodium resources are abundant in the Earth's crust. Thus, with various advantages of the large abundance and low cost of Na resources as well as suitable standard electrode potential ($E^0_{(\text{Na}^+/\text{Na})} = -2.71 \text{ V}$), rechargeable SIBs are the ideal alternative to LIBs (**Table 2.1**).¹⁰¹

Figure 2.6 Elemental abundance in the Earth's crust.¹⁰²

Table 2.1 Main characteristics of Na and Li materials. S.H.E.: Standard Hydrogen Electrode.¹⁰³

Characteristics	Na	Li
Price (for carbonates)	\$150/ton	\$5000/ton
Capacity (mAh g ⁻¹), metal	1165	3829
E ⁰ (vs. SHE) (V)	-2.7	-3.0
Cation Radius (Å)	0.98	0.69

Figure 2.7 shows the basic principle of SIBs, which is composed of positive, negative electrodes, a separator and a nonaqueous (or aqueous) Na ion electrolyte (**Figure 2.8**).⁹ The working mechanisms of SIBs are almost the same as that of LIBs, which using Na ions to replace Li ions. During charging, Na ions deintercalate from the cathode and insert into the anode, accompanying the electrons transfer from the cathode to the anode via the external circuit. For the discharge process, it is exactly contrary. Na ions are extracted from the anode and then intercalate back into the cathode. The reversible reaction between Na ions and electrode materials makes the reversible conversion of the chemical energy into electricity. Meanwhile, the electricity is stored in the SIBs.

Figure 2.7 Operating principle of a typical non-aqueous or aqueous sodium-ion battery. Sodium ions migrate back and forth in the electrolyte between the negative and positive electrodes upon discharge or charge, and electron flow counterbalances the ion flow within the electrode materials and externally through the outer electrical circuit. The potential difference between the positive and negative electrodes defines the cell voltage.⁹¹

Compared to Li metal anodes, devices based on Na metal possess lower theoretical energy densities owing to the lower specific capacity (1166 mAh g^{-1}) and higher standard reduction potential of Na (-2.71 V vs. SHE, compared to -3.04 V).¹⁰³ Generally, the battery performance is inherently dependent on the electrode materials. Therefore, the key to advance SIBs is to develop suitable electrode materials with outstanding electrochemical performance. **Figure 2.8** depicts the specific capacity and operation potential of cathodes and anodes of SIBs.¹⁰⁴ It reveals that the number of candidates proposed as positive and negative electrodes is increasing sharply during the past three years. For anodes, considerable attention has been mainly paid to carbonaceous materials. Nevertheless, the most commonly used graphite anode in LIBs possesses large irreversible loss and low capacity in SIBs.¹⁰⁵ In contrast, other carbon materials such as hard carbon and carbon blacks exhibit better reactivity with Na. Among the most studied candidates, hard-carbons with large reversible capacity (300 mAh g^{-1}) and superior cycling stability are currently identified as the most potential anodes of SIBs.¹⁰⁶⁻¹⁰⁹ It should be noted that the elaborate microstructure modification can obviously enhance the electrochemical

performance of carbon anodes. In the last few years, a number of carbonaceous materials with capacities over 300 mAh g^{-1} have been proposed, such as reduced graphene oxide (rGO),¹¹⁰ N-doped porous carbon nanosheets,¹¹¹ porous carbon nanofibers (CNFs),¹¹² hard carbon from sugar,¹¹³ and bio-derived carbon.^{114, 115} Moreover, Sb¹¹⁶⁻¹²¹ and Sn¹²²⁻¹²⁶ based materials based on Na-alloying/de-alloying mechanism have drawn much attention as promising anodes of SBs, owing to their high capacities. However, the poor cycling stability and deadly capacity fading owing to the huge volume variation upon cycling, have become the main two hindrances for the practical use. Therefore, carbonaceous and other materials are utilized to alleviate the large volume change and provide the electrical conducting networks.

Figure 2.8 Recent acceleration in the number of reported electrode materials for sodium-based batteries. Voltage versus capacity for reported positive and negative electrode materials with plausible application in Na-ion cells within the past three decades (1980–2010; left) and as studied during the past three years (2010–2013; right).¹²⁷

Recently, some layered TMSs, have drawn much attention as potential anodes of SIBs, such as MoS_2 , WS_2 and SnS_2 , due to their high capacities. MoS_2 as a layered material stacked with S–Mo–S layers can reversibly accommodate Na ions without obvious structure change. The reversible reaction in MoS_2 as anode of SIBs can be expressed by the following equations:^{128, 129}

However, owing to the low electrical conductivity and large volume variation during Na ion intercalation/deintercalation process, MoS₂ electrode materials always exhibited poor rate capability and rapid capacity fading during cycling, which significantly hinder its practical use. Nowadays, various strategies have been developed to address these issues by using nanotechnologies and carbonaceous materials as the conductive matrix.¹³⁵⁻¹³⁷ Compare to microscale or bulk MoS₂, MoS₂ nanosheets with thinner thickness and smaller lateral size can not only enhance the accessibility of Na ions, but also result in short diffusion lengths, thus rendering the material with excellent kinetics, high capacity and good rate capability.¹³⁰ Besides, dispersing MoS₂ nanostructures in conductive carbonaceous materials has been demonstrated as an effective strategy to alleviate the huge volume variation during cycling and also provide the electrical conductive network, thereby resulting in excellent electrochemical performance for SIBs. In the last few years, the decent electrochemical performance for SIBs has been demonstrated in different MoS₂-carbon hybrids, for example, MoS₂/graphene microspheres, MoS₂/CNT composites, freestanding MoS₂@carbon paper electrode, and MoS₂ nanoplates embedded in CNFs.^{20, 131-133} Similar to the current obstacles of LIBs, the capacity fading upon cycling and large polarization at high rates are still observed in almost all cases of MoS₂ anodes for SIBs. Thus, efficient strategies are highly required to improve the electrochemical performance of SIBs.

2.2.4 Catalyst for HER

Hydrogen (H₂), a clean and renewable fuel, is regarded as a potential energy carrier for future energy infrastructure. Nowadays, the main way for hydrogen manufacturing is by steam methane reforming, which is based on the reaction of water and methane to produce carbon dioxide and. hydrogen¹³⁴ However, the

large emission of greenhouse-gas during hydrogen manufacturing is neither renewable nor carbon-neutral. In contrast, electrochemical water splitting produces hydrogen with high energy conversion efficiency.

Generally, two half reactions, HER and oxygen evolution reaction (OER) are accompanying during the water splitting reaction.¹³⁴ For the HER half-reaction in acidic media, three possible reaction steps on various electrocatalysts are proposed to explain the HER process.^{135, 136} Volmer step (electrochemical hydrogen adsorption):

Subsequently, this step is followed either by Heyrovsky step (electrochemical desorption)

or Tafel step (chemical desorption)

where M refers to a metal active site and MH_{ads} donates an intermediate of adsorbed H.¹³⁷ Generally, in order to decrease the overpotential and enhance the HER efficiency, an efficient catalyst is highly required. Ideal HER electrocatalysts should provide various characteristics of high current density, a small overpotential, good stability and low cost of fabrication. Currently, platinum (Pt) and its alloys have been regarded as the state-of-the-art catalysts for HER, while high cost and the scarcity impede their wide application for electrolysis. Therefore, achieving highly efficient HER electrocatalysts with low cost and high abundance remains great challenges.

Recently, abundant and inexpensive binary metal compounds, such as metal sulfides, metal nitrides, metal borides, and metal phosphides have been investigated as alternatives of HER electrocatalysts to replace precious metal Pt. Theoretical and experimental studies have revealed that 2D layered MoS_2 -based materials are the promising HER catalysts due to the optimal affinity of H_2 on

the edges of MoS₂. According to the calculation result of density functional theory (DFT), active sites for the hydrogen adsorption are located at S–Mo–S edges in MoS₂. The [1010] Mo edges always contribute a beneficial free energy change for the adsorption of the hydrogen atom. It is similar to that observed on Pt surfaces.¹³⁸ Therefore, based on these valuable theoretical and experimental studies, three strategies are mainly proposed to boost the catalytic activity of MoS₂-based electrocatalysts: (1) increasing the number of exposed active edge sites via modifying the microstructure of MoS₂; (2) Enhancing the electrical conductivity and diffusion characteristics of MoS₂, which can be achieved by reducing the aggregation, and modifying with to conductive materials; (3) improving the inherent catalytic activity of MoS₂, which always can realize by tuning the electronic structure of the edge to enhance the bond strength of the adsorbed H.¹³⁹

2.3 The Synthesis of MoS₂ for Energy Storage and Conversion Applications

2.3.1 Various approaches leading to MoS₂

MoS₂ as a typical layered transition metal dichalcogenide (TMD) are being widely investigated for numerous fields including catalysis, energy storage devices, and electronic transistors. In MoS₂ crystals, Mo layers are sandwiched between S layers (**Figure 2.9**) via strong Mo–S covalent bonding.¹⁴⁰ However, the weak van der Waals interactions between adjacent layers easily enable MoS₂ to form bulk materials. The characteristics of MoS₂ can be easily optimized by reducing dimensions, modification with carbonaceous materials, and design of heterostructures.

In order to obtain desired characteristics, the variety of techniques have been proposed. Up to now, various chemical or physical strategies have been established to prepare MoS₂, including mechanical exfoliation¹⁴¹, electrochemical Li-intercalation, and exfoliation¹⁴², direct sonication in

solvents¹⁴³, hydrothermal reaction^{144, 145} and chemical vapor deposition (CVD)¹⁴⁶⁻¹⁴⁸.

Figure 2.9 Three-dimensional schematic representation of a typical MoS₂ structure, with the chalcogen atoms (S) in yellow and the metal atoms (Mo) in gray.¹⁴⁹

2.3.1.1 Top-down methods

The mechanical cleavage as a conventional method has been utilized to obtain atomically thin flakes consisting of tens to hundreds of layers. In a typical process, MoS₂ flakes can be peeled from the bulk materials using adhesive tape, optically identified by light interference.¹⁵⁰ Mechanical cleavage can always generate single-crystal flakes with high purity and cleanliness which can be applied for fundamental characterization and fabrication of individual devices. However, this method is not easily scalable, and flake size and thickness can not be systematically controlled.

2.3.1.2 Intercalation methods

For obtaining large quantities of exfoliated MoS₂ nanosheets, intercalation methods have been demonstrated as effective strategies. In a typical preparation, bulk MoS₂ powders were submerged in a solution of n-butyllithium for a long time (usually longer than one day) to enable the intercalation of lithium ions, then followed by exposing the intercalated material to water.^{151, 152}

Exfoliation intercalation methods can produce large-scale monolayers with submicrometer sizes, but the exfoliated material obviously exhibits different electronical and structural properties compared to the bulk material. However, such exfoliation strategy requires a long time and complicated process.

Recently, some researchers have reported chemical or electrochemical Li-intercalation strategies to prepare MoS₂ nanosheets.^{153, 154} The process is utilized in a LIB configuration composing of bulk MoS₂ cathode and metallic lithium anode. After discharge, the product of Li_xMoS₂ can be obtained based on the electrochemical reaction ($\text{MoS}_2 + x\text{Li}^+ + xe^- \rightarrow \text{Li}_x\text{MoS}_2$). Then, Li_xMoS₂ is ultrasonicated in the solvent of water or ethanol. Lithium reacts with a solution and generated H₂ gas, which exfoliates MoS₂ layers effectively. Well-dispersed MoS₂ nanosheets can be finally obtained, under agitation by sonication. Although Li intercalation by an electrochemical method has enabled the exfoliation process more controllable and faster, the high cost of Li metals and the flammability of Li compounds in ambient conditions impede the wide use of this approach. Therefore, it is still highly required to search for alternative strategies.

2.3.1.3 Chemical vapour deposition method

MoS₂ with uniform layers and in a large area is highly required for various applications such as flexible and transparent optoelectronics, as well as electronic devices. Compared to the deformed crystal structure by the violent chemical exfoliation, CVD method can efficiently grow high quality MoS₂ monolayer films on substrates (SiO₂/Si¹⁵⁵ or Au¹⁵⁶) with controllable layers.¹⁵⁷ Up to now, there are several reports employing solid precursors heated to high temperature. For example, sulphur powder and MoO₃ powders are vaporized and co-deposited onto a nearby substrate.¹⁴⁶ In another strategy, substrates are dip-coated in a solution of (NH₄)₂MoS₄ and heated in the presence of sulphur gas.¹⁵⁸ However, for these methods, the thickness of the final MoS₂ film strongly relies on the thickness or concentration of the precursor. Therefore, accurate

control of the layer number in a large area has not been realized yet. Current studies can still drive further work to grow large-area and uniform MoS₂ sheets or other than MoS₂ with controllable layer number.

2.3.1.4 Hydrothermal reaction

Hydrothermal or solvothermal synthesis is another effective bottom-up method to prepare MoS₂. Since the 1960s, the hydrothermal method has been extensively utilized to synthesize a variety of functional nanomaterials with desired morphology. Mostly, the hydrothermal process is realized by heating the reaction solution in a stainless steel autoclave sealed with Teflon liner at a defined temperature. Up to now, the hydrothermal method has achieved great success in preparation MoS₂ with different morphologies.

In a typical hydrothermal reaction, sodium molybdate (Na₂MoO₄) or ammonium molybdate tetrahydrate ((NH₄)₆Mo₇O₂₄·4H₂O) are usually used as Mo sources, and the common sulfur sources are thiourea, thioacetamide, and L-cysteine. After hydrothermal reaction in a sealed autoclave with Teflon liners, the low-quality MoS₂ nanoarchitectures with abundant active sites can be obtained. Chen et al.⁹⁸ have reported a simple process to prepare MoS₂/graphene composites via an L-cysteine-assisted hydrothermal method. Although the thickness of flakes is not monolayers, such method can produce reasonably high-quality materials with sizes from hundreds of nanometers to a few micrometers. As the performance of MoS₂ is strongly dependent on its morphology and structure, we can expect the tuning structure of MoS₂ is still a hot topic to satisfy various different requirements.

2.3.2 MoS₂ and its hybrids for Energy Storage and Conversion Applications

As the electrochemical performance of the electrode materials is heavily dependent on their morphologies and structures, designing smart architectures has been regarded as a promising way to satisfy the requirements of assigned morphologies and structures. Bearing this in mind, MoS₂ sheets have been

designed or synthesized or assembled onto, with or in several nanostructures, such as hybridization with metal oxides/hydroxides (TiO_2 ¹⁵⁹, Fe_3O_4 ¹⁹, MoO_3 ¹⁶⁰, $\text{Ni}(\text{OH})_2$ ¹⁶¹), carbonaceous materials (CNTs^{99, 162, 163}, graphene^{98, 164, 165} and 3D graphene¹⁶⁶) and other conductive polymers^{91, 97} for a wide range of applications.

2.3.2.1 Assembly of three-dimensional (3D) architectures

Extensive research has demonstrated that nanomaterials always exhibit better electrochemical performance in various applications, compared to their bulky counterparts, owing to the increased contact area, decreased diffusion lengths, and enhanced kinetics. However, owing to the excess surface free energy, MoS_2 nanosheets tend to self-aggregate, which significantly decreases the effective contact areas and affects the performance in many applications. One feasible way is to assemble 2D MoS_2 nanosheets into 3D hierarchical structures, which synergistically combines all the advantages of microstructures and nanostructures, pushing nanomaterials an important step forward into practical applications.

Recently, hierarchical structures composed of numerous nanostructured building blocks have drawn much attention due to the unique structures, which synergistically take the advantages of both micromaterials and nanomaterials.^{95, 100, 167} In these hierarchical structures, the nanostructured building blocks enhances the kinetics of Li-ion storage due to the reduced diffusion paths. Meanwhile, the primary architecture at the micrometer scale effectively avoids aggregation of the active nanomaterials and facilitates the transport of electrons and ions. Wang and co-workers developed a solvothermal method to synthesize 3D tubular architectures, which are built with single-layered MoS_2 nanosheets.¹⁰⁰ The 3D assembled tubes deliver superior electrochemical properties as anodes for LIBs, and also possess high activity and stability for thiophene hydrodesulfurization. The excellent performance can be ascribed to the hollow tubular architecture constructed hierarchically by 2D nanosheets, which can

facilitate the reversible transport and lithium storage, as well as expose more catalytically active sites for reactions.

2.3.2.2 Hybridization of MoS₂

MoS₂ has emerged as a promising candidate for LIBs and SIBs due to its sandwich-like layered structure, enabling the easy intercalation and exfoliation of lithium ions and sodium ions. However, low intrinsic electric conductivity and huge volume changes during the lithium/sodium insertion and extraction process, result in dramatic pulverization and loss of electrical contact in the electrode, thus resulting in poor cyclability and sluggish dynamic. It has been identified that carbonaceous materials are a suitable matrix to alleviate the volume variation and avoid the aggregation of nanostructured MoS₂ during cycling. Moreover, it can greatly enhance the electrical conductivity of MoS₂ electrode to improve the electrochemical kinetics of cells. On the other hand, MoS₂-based electrocatalysts are being intensively studied as prospective alternatives to Pt for HER. Increasing the number of exposed active sites on the edges and enhancing the electrical conduction by employing appropriate conductive substrates have been currently identified as two efficient strategies to enhance the electrocatalytic efficiency of MoS₂.

Moreover, amorphous carbon and carbon fibers/tubes have also been widely investigated as templates or matrices for the growth of or hybridization with MoS₂ nanosheets.⁹⁵ Besides, the synthesis of MoS₂ nanosheets on TiO₂ nanobelts/tubes¹⁶⁸, MoC nanoparticles¹⁶⁹, and Co₉S₈ nanoparticles¹⁷⁰, has also been achieved via hydro/solvothermal methods. The hybrid structures have been demonstrated excellent electrochemical performances as electrodes for LIBs, and HER.

2.3.2.3 Free-standing MoS₂-based electrodes

The concept of flexible electronics can be dated back to thin film transistors using polymeric and molecular organic materials.¹⁷¹ Compared to the conventional inorganic electronics, organic transistors possess lower cost and simpler

packaging, as well as better compatibility with flexible substrates, which render devices with high flexibility. Recently, with the high demand of flexible electronic devices, such as rollup displays, e-paper, wearable electronics, there are an urgent need to develop high-performance flexible energy storage devices.¹⁷²⁻¹⁷⁴

In general, structural designs and developing novel elastic materials are main strategies to achieving flexible devices. Compared to other brittle materials, graphene and CNTs have significantly better mechanical properties in building flexible devices, and they have shown their significance either as intrinsic bendable materials or as a component in stretchable or compressible devices.^{133, 175-177} With a similar structure to graphene, 2D MoS₂ possesses various advantages of ultrathin structure and flexibility, which is being widely studied as a potential prospective electrode material for prospective flexible energy storage devices. Up to now, there are variety studies on the development of flexible conductive backbones for loading MoS₂ nanoparticles, such as three-dimensional graphene foam (3DGF), carbon cloth and CNT foam.^{133, 177}

2.4 Summary

The basic principles, working mechanism of different devices (capacitors, SCs, LIBs, SIBs and HER), and retrospect previous works on the synthesis of MoS₂ and their applications in energy storage and conversion devices are summarized in this part. The detailed literature survey demonstrates that the emerging MoS₂ has shown vast potential for the applications of electrochemical energy storage and conversion. By virtue of the scrupulous nanoarchitecture design and smart hybridization of bespoke active materials, exceptional properties and performance could be obtained. Especially, MoS₂ and its composites provide more possibility and feasibility to tailor the electrochemical performance and stability by rational design and hybridization. Nevertheless, facile and controllable synthesis of MoS₂ and its composites with purposefully designed nanoarchitectures still remains great challenges. Meanwhile, a correlation

between the structure/chemistry and their properties is not yet fully understood. Therefore, this thesis aims to develop MoS₂-based composites with sophisticated nanostructures as advanced electrodes for energy storage and conversion devices with good performance, high stability and excellent safety. To gain deep understanding the effect of morphology modification and structure design, the electrochemical performance of as-prepared different nanostructures would be investigated in depth. The relevant electrochemical mechanism in various devices is established by detailed study.

Chapter 3

Experimental Methodology

This section is a general overview of materials synthesis procedures, structural characterization, and electrochemical characterization methodologies employed in this thesis. We present the materials synthesis procedures with schematic illustration in detail, which are consisted of five parts, including Growth of 3D carbon substrates (3.1), Synthesis of $\text{Ni}_3\text{S}_2@\text{MoS}_2$ core/shell nanorod arrays on Ni foam (3.2.1), Self-assembly of honeycomb-like MoS_2 nanoarchitectures@GF (3.2.2), Self-assembly of nanoworm-like MoS_2 architectures@GF/CNT (3.2.3), Synthesis of MoS_2 Nanosheets Decorated $\text{Ni}_3\text{S}_2@\text{MoS}_2$ Coaxial Nanofibers on Ni/GF (3.2.4), and Fabrication of hierarchical MoS_2 nanotubes on GF (3.2.5). For the materials structural characterization (3.3) and the electrochemical characterization (3.4), the relevant principles and measurement methods are also given in details.

3.1 Growth of 3DGF and GF/CNT Hybrid Films

The growth of 3DGF was grown by CVD using Ni foam as the template, as previously reported.¹⁷⁸ In a typical process, Ni foams with a size of 8×8 cm are put into the tube furnace (First Nano's Easy Tube 3000 System). Then, the temperature is increased to 1000 °C in H₂/Ar (200 sccm/500 sccm) atmosphere and kept at 1000 °C for 5 min to eliminate the oxide layer on Ni foam. Subsequently, a trace of CH₄ flow in at ambient pressure. The flow rates of Ar, H₂, and CH₄, are 800, 100, and 50 sccm, respectively. After two mins, the temperature was rapidly decreased to room temperature (RT) at a rate of 100 °C min⁻¹ in H₂/Ar (200 sccm/500 sccm) atmosphere. Then, we can obtain graphene supported on Ni foam (Ni/GF). Freestanding 3DGF was obtained via etching of nickel template in a mixture solution of 1M FeCl₃ and 0.5 M HCl for one day.

For the growth of GF/CNT films, the above mentioned GF was used as the substrate as described in the literature.¹⁷⁹ The typical areal mass of GF in this study is about 0.4-0.6 mg cm⁻². The NiCo catalyst was deposited on GF through a hydrothermal reaction. Briefly, 0.1 mmol of Ni(NO₃)₂·6H₂O and 0.2 mmol of Co(NO₃)₂·6H₂O were dissolved in 40 ml of deionized (DI) water to form a clear pink solution. After that, 1.2 mmol of urea was added to the obtained solution. Then, the obtained solution was transferred into a steel autoclave sealed with Teflon liner. A piece of GF was fixed on one piece of a glass slide by Kapoton tape and immersed into the reaction solution. The hydrothermal reaction was conducted at 120 °C for 2 h, after sealing the autoclave. The GF/NiCo precursor was then annealed in air at 350 °C for 1 min and employed directly as the catalyst-loaded substrate for the growth of CNTs at 750 °C in a mixture of C₂H₄, H₂ and Ar with flow rates of 20, 40 and 100 sccm, respectively. H₂ was introduced prior to the growth process in order to activate the catalyst effectively. In order to remove NiCo precursor, the obtained GF/CNT were hydrothermally treated in 35wt% HNO₃ solution at 90 °C for 10 h, followed by washing with DI water until neutral pH, and drying at 60°C in an electric oven. A typical areal mass of

GF/CNT in this study is about $0.6\text{--}0.8\text{ mg cm}^{-2}$.

3.2 Synthesis of MoS₂ and Its Composites

3.2.1 Synthesis of Ni₃S₂@MoS₂ core/shell nanorod arrays on Ni foam

Ni₃S₂@MoS₂ nanorod arrays were synthesized using a facile one-step hydrothermal process. In a typical experiment, some amount of thioacetamide (TAA, C₂H₅NS), 45 mg of Na₂MoO₄ and 0.1 g of P123 (a triblock copolymer, HO(CH₂CH₂O)₂₀(CH₂CH(CH₃)O)₇₀(CH₂CH₂O)₂₀H) were mixed in 30 mL of distilled water. Then, this resulting mixed solution was transferred into a steel autoclave sealed with Teflon liner. A piece of Ni foam with an area of 8 cm² was immersed into the reaction solution. The Ni foam was first treated with a 5% HCl solution to get rid of the oxide layer on the surface before reaction. The hydrothermal reaction was conducted at 200 °C for 24 h, after sealing the autoclave. When the temperature was cooled down to room temperature, we can obtain the samples after rinsed with DI water for several times and then dried in an electric oven at 60 °C for 12 h. The schematic illustration of the synthesis of core/shell Ni₃S₂@MoS₂ nanoarrays on Ni foam is showed in **Figure 3.1**. For the comparison, the samples were prepared with 30, 45, 60 and 90 mg of TAA, which were labelled as NM-1, NM-2, NM-3 and NM-4, respectively. The achieved samples were thermally decomposed in a tube furnace at 400 °C for 2 h under H₂/Ar (5:95 v/v) atmosphere with a heating rate of 10 °C min⁻¹. Besides, we also prepared the sample with 60 mg of TAA but without adding Na₂MoO₄ for comparison (labelled as NM-0).

Figure 3.1 Schematic illustration of the formation of core/shell Ni₃S₂@MoS₂ nanoarrays by a facile one-step process.

3.2.2 Self-assembly of honeycomb-like MoS₂ nanoarchitectures@GF

Hierarchical MoS₂ nanoarchitectures anchored into 3DGF are prepared by a P123-assisted hydrothermal method. Sodium molybdate, thiourea and P123 are selected as starting materials. In a typical experiment, thiourea (45 mg, NH₂CSNH₂), Na₂MoO₄ (22.5 mg) and P123 (0.2g) are mixed in distilled water (30 mL). Then, the obtained mixed solution is transferred into a Teflon-lined stainless steel autoclave. A piece of GF with an area of 8 cm² is immersed into the reaction solution. The hydrothermal reaction is conducted at 200 °C for 24 h, after sealing the autoclave. When the temperature is cooled down to room temperature, we can obtain the samples after rinsed with DI water for several times and then dried in an electric oven at 60 °C for 12 h. The achieved samples are thermally decomposed in a tube furnace at 400 °C for 2 h under H₂/Ar (5:95 v/v) atmosphere with a heating rate of 10 °C min⁻¹. The fabrication process for honeycomb-like MoS₂ nanoarchitectures@GF is depicted in **Figure 3.2**. The weight of MoS₂ supported on GF can be obtained by weighting the obtained sample before and after the reaction. For the comparison, MoS₂ hollow spheres are synthesized via the same process but without the substrate of GF.

Figure 3.2 Schematics of the fabrication of the honeycomb-like MoS₂ nanoarchitectures@GF.

3.2.3 Self-assembly of nanoworm-like MoS₂ architectures@GF/CNT

Hierarchical MoS₂ architectures anchored into GF/CNTs are prepared by a P123-assisted solution-phase method, in which sodium molybdate, thioacetamide and P123 are used as starting materials (**Figure 3.3**). In a typical experiment, the mixed solution is prepared by dissolving 80 mg of TAA, 40 mg of Na₂MoO₄ and

0.2 g of P123 in 30 mL of distilled water. Then, this resulting solution is transferred into a stainless steel autoclave sealed with Teflon liner. One piece of GF/CNTs films with an area of 8 cm² is fixed on one piece of a glass slide by Kapoton tape and immersed into the above solution. The hydrothermal reaction is conducted at 200 °C for 24 h, after the autoclave is then sealed. When the temperature is cooled down to room temperature, we can obtain the samples after rinsed with DI water for several times and then dried at 60°C in an electric oven. The achieved samples are thermally decomposed in a tube furnace at 400 °C for 2 h under H₂/Ar (5:95 v/v) atmosphere with a heating rate of 10 °C min⁻¹. The weight of MoS₂ in the 3D architectures is calculated by weighting the obtained sample before and after the reaction. The obtained nanoworm-like MoS₂ architectures anchored into GF/CNTs is denoted as MoS₂@GF/CNT. For the comparison, MoS₂ grown on GF is prepared by the same process and denoted as MoS₂@GF. Before the hydrothermal reaction, the GF/CNT films are treated by oxygen plasma with a constant oxygen flow maintained at 80 sccm for 100 seconds.

Figure 3.3 Schematics of the fabrication of MoS₂@GF/CNT electrode.

3.2.4 Synthesis of MoS₂ Nanosheets Decorated Ni₃S₂@MoS₂ Coaxial Nanofibers on Ni/GF

MoS₂/Ni₃S₂@MoS₂ nanofibers were prepared using a facile one-step hydrothermal process (**Figure 3.4**), using Na₂MoO₄, thiourea and PVP as starting

materials. In a typical experiment, 150 mg of thiourea, 75 mg of Na_2MoO_4 and 0.2 g of Polyvinylpyrrolidone (PVP) were dissolving in 30 mL of distilled water. Then, this resulting solution was transferred into a steel autoclave sealed with Teflon liner. A piece of Ni/GF with an area of 8 cm^2 was immersed into the reaction solution. The hydrothermal reaction was conducted at $200\text{ }^\circ\text{C}$ for 12 h after the autoclave was sealed. When the temperature was cooled down to room temperature, the samples were rinsed with DI water for several times and then dried in an electric oven at $60\text{ }^\circ\text{C}$ for 12 h. The achieved samples were thermally decomposed in a tube furnace at $400\text{ }^\circ\text{C}$ for 2 h under H_2/Ar (5:95 v/v) atmosphere with a heating rate of $10\text{ }^\circ\text{C min}^{-1}$. For the comparison, the samples were prepared with the same reactant concentration at $200\text{ }^\circ\text{C}$ for different reaction time.

Figure 3.4 Schematic illustration of the synthesis process of the $\text{MoS}_2/\text{Ni}_3\text{S}_2@\text{MoS}_2$ heterostructure.

3.2.5 Fabrication of hierarchical MoS_2 nanotubes on GF

Hierarchical MoS_2 nanotubes on flexible 3DGF are firstly produced by a bottom-up approach using Ni_3S_2 nanowires as the precursor and self-sacrificial template. We employed $\text{MoS}_2/\text{Ni}_3\text{S}_2@\text{MoS}_2$ nanofibers on Ni/GF as the precursor, which were prepared using a facile one-step hydrothermal process.¹⁸⁰ In a typical experiment for the synthesis of $\text{MoS}_2/\text{Ni}_3\text{S}_2@\text{MoS}_2$ nanofibers on Ni/GF, 150 mg of thiourea, 75 mg of Na_2MoO_4 and 0.2 g of PVP were dissolved in 30 mL of distilled water. Then, this resulting solution was transferred into a steel autoclave

sealed with Teflon liner. A piece of Ni/GF with an area of 8 cm² was immersed into the reaction solution. The hydrothermal reaction was conducted at 200 °C for 12 h, after autoclave was sealed. When the temperature was cooled down to room temperature, we can obtain the sample after rinsed with DI water for several times and then dried in an electric oven at 60 °C for 12 h. The achieved samples were thermally decomposed in a tube furnace at 400 °C for 2 h under H₂/Ar (5:95 v/v) atmosphere with a heating rate of 10 °C min⁻¹. For the comparison, the samples were prepared with the same reactant concentration at 200 °C for 8 h to prepare Ni₃S₂@MoS₂ nanofibers on GF.

Figure 3.5 Illustration of the synthesis process of hierarchical MT@MS/GF.

The obtained Ni₃S₂–MoS₂ hybrid nanofibers supported on Ni/GF were immersed in a mixed solution of FeCl₃ (1M) and HCl (0.5M) for 48 h. Meanwhile, Ni₃S₂ can be oxidized to NiS₂. In order to remove the residual NiS₂, the achieved samples were hydrothermally treated in 5M HCl solution at 90 °C for 4 h, followed by washing with DI water until neutral pH, and drying at 60°C in an electric oven. Then, we can obtain MoS₂ hollow nanotubes decorated with MoS₂ nanosheets on 3DGF (MT@MS/GF). The synthesis strategy of hierarchical MT@MS/GF is schematically depicted in **Figure 3.5**. After hydrothermal treatment, MoS₂/Ni₃S₂@MoS₂ nanofibers supported on Ni/GF transform into MoS₂ hollow nanotubes decorated with MoS₂ nanosheets on 3DGF, which is donated as MT@MS/GF. In the meanwhile, Ni₃S₂@MoS₂ nanofibers supported on Ni/GF transform into tubular MoS₂ nanostructures on 3DGF, which is donated as MT/G. The weight of MoS₂ in the 3D architectures is calculated by weighting

3DGF and the final hierarchical composites after hydrothermal treatment.

3.3 Materials Characterizations

3.3.1 Powder X-ray diffraction (XRD)

The crystalline components of the obtained powder samples are determined using a Shimadzu X-ray diffractometer (Cu-K α) with step scanning (40 kV, 0.5s dwell time, 0.01°) over a 2 θ range between 5 and 85°.

3.3.2 Thin film X-ray diffraction (XRD)

The crystalline structures of flexible electrodes are characterized through a thin film XRD (Shimadzu, Cu-K α radiation, with step scanning over a 2 θ range between 5 and 85°).

3.3.3 Field emission scanning electron microscope (FESEM)

Field emission scanning electron microscopy (JSM-7600F, JEOL Ltd, Tokyo, Japan) is employed to investigate the morphologies of the as-prepared samples at an acceleration voltage of 5 kV and working distance of around 7 cm. Before taking the images, the sample should be fixed onto the stainless steel holder using carbon tapes. Before capturing the images, the samples are usually coated with around 10–15 nm of Pt using a sputtering coater (JEOL JFC-1600) to avoid the charging effect.

3.3.4 Transmission electron microscope (TEM)

TEM images are taken using a JOEL JEM 2100F microscope at an acceleration voltage of 200 kV. Various morphological and crystallographic information, including crystal sizes, the orientation of nanocrystals, and the morphology of superstructures can be identified from the TEM images and diffraction pattern. Qualitative and quantitative measurements of the concentration and elemental

compositions can be conducted with the aid of the characteristic X-ray spectra through the energy dispersive X-ray attachment.

3.3.5 Energy dispersive X-ray spectroscopy (EDX)

EDX is employed to qualitatively or semi-quantitatively determine the composition of samples, which is always affected by various factors, such as the density and the mount of the measured sample, as well as the energies of the used X-ray. In addition, the element distribution can also be obtained by using elemental mapping. Elemental composition of the samples is investigated using EDX attachment of FESEM, while elemental mapping is conducted using the EDX equipped on TEM. Usually, the working distance for using EDX attached on FESEM is 15 cm, and the accelerating voltage is 15 kV to avoid charging of sample and gain appropriate spectrum.

3.3.6 X-ray photoelectron spectroscopy (XPS)

XPS as a surface-sensitive and semi-quantitative spectroscopic technique is always used to investigate several important information of elements, including the chemical state, the electronic state, and elemental composition. The XPS spectrum is obtained by irradiating the sample using a beam of X-rays. A variety of information on the material surface can be obtained, by analyzing the number of electrons which escape from the top surface (around 10 nm) and measuring their kinetic energy. XPS can also be employed to determine the valences of metal ions even within various compounds. As the characteristic binding energy peaks of ions inherently rely on their crystal lattice coordination and oxidation state, XPS has been widely used to analyze various materials for energy-related applications. In our thesis, the measurement of XPS is performed on a Kratos AXIS Ultra spectrometer with the monochromatic Al K α X-ray. Survey scans are measured from 0 to 1200 eV, which is calibrated by referring to adventitious carbon at 284.8 eV.

3.3.7 Raman spectroscopy

Raman spectroscopy is a technology based on the inelastic scattering of monochromatic light from a material.¹⁸¹ It is always employed to investigate vibrational, rotational, and molecular bond in materials. Herein, Raman spectroscopy is recorded by Renishaw Raman Microscopy with 2.33 eV (532 nm) excitation laser. Before the measurement, the sample should be completely compressed into a flat film on a Si/SiO₂ wafer.

3.3.8 Nitrogen adsorption/desorption isotherm

Surface area analysis is conducted by applying N₂ adsorption on Micromeritics, ASAP 2020 at 77 K via the Brunauer–Emmett–Teller (BET) theory. Before the measurement, the as-prepared samples are degassed at 393 K under nitrogen flow for 2–4 h. A Barrett-Joyner-Halenda (BJH) analysis is then conducted to determine the pore size distributions and the SSA.

3.3.9 Thermogravimetric analysis (TGA)

TGA is a very useful tool to identify the mass gain or loss owing to oxidation, decomposition, or loss of volatiles. It provides useful information about the organic and inorganic content of the sample, and predicts the material structure. In our thesis, TGA is used to determine weight change on TA instrument Q500 apparatus. In the measurement, the samples are heated to the target temperature at a ramping rate of 5 °C min⁻¹ in N₂ atmosphere.

3.4 Electrochemical Characterization

3.4.1 Cyclic voltammetry (CV)

CV tests are conducted on a CHI 760D electrochemical workstation at a constant scanning rate in a certain voltage range. Scanning rates are determined by

different systems, types of electrode materials and the study purposes. Herein, the cathodic peaks are corresponding to the reduction reaction, while the anodic peaks represent the oxidation reaction.

3.4.2 Electrochemical impedance spectroscopy (EIS)

EIS is employed to investigate the dynamics of an electrochemical process through small voltage or current perturbation.¹⁸² In a typical measurement, an alternating current (AC) potential is applied to an electrochemical cell. In the meanwhile, the current is surveyed in a wide frequency range. By building appropriate circuit model and fitting it to the EIS results, many information like the solvent resistance, charge transfer resistance and capacitance can be extracted and further analyzed.

Herein, EIS is carried out in equilibrated coin cells or setups before cycling and cycled electrodes at a different voltage, which are equilibrated at least for 2-3 h. In a typical measurement, EIS is measured by using 10 mV bias voltage from the frequency range between a 100 kHz and 0.1 Hz at room temperature. The data are recorded as the Nyquist plots $-Z''$ vs. Z' , which can be evaluated by utilizing Zview software.

3.4.3 Supercapacitor measurements based on three-electrode setups

An obtained binder-free electrode is directly used as the working electrode. A 760D electrochemical workstation is used to test electrochemical performance via a three-electrode setup in 2M KOH aqueous solution within the potential window of approximately -0.2 to 0.6 V. Standard calomel electrode (SCE) and a Pt foil are utilized as the reference electrode and counter electrode, respectively. The galvanostatic charge/discharge measurements are also conducted on an electrochemical workstation. The specific capacitance can be obtained from CV curves and discharge curves, which are described in section 3.4.5.

3.4.4 Lithium ion coin cell fabrication and electrochemical measurements

To test the lithium storage performance of the synthesized materials, CR 2016 coin cells are made using Celgard 2400 as the separator and 1M LiPF₆ in ethylene carbonate-diethylene carbonate (EC:DEC=1:1) as the electrolyte. The metallic lithium is used as the reference and counter electrode. The coin cells are assembled inside an argon-filled glovebox with oxygen and water contents below 1 and 0.1 ppm, respectively. The obtained flexible or binder-free electrode is directly employed as the working electrode, and then assembly into a coin cell without binders or carbonaceous materials. For the powder sample, after mixing the powders with the binder of polyvinylidene fluoride (PVDF) and conductive carbon black with a weight ratio of 8:1:1, we can obtain homogenous black slurries, which are subsequently coated on copper foil. After drying overnight in a vacuum oven at 60 °C, we can obtain the as-prepared electrodes. Galvanostatic charging and discharging measurements are conducted on a battery tester (NEWARE) at different current rates. CV curves are measured using a CHI 760D electrochemical workstation from 10 mV to 3 V at a scan rate of 0.5 mV s⁻¹. EIS is also measured with an electrochemical workstation over a frequency range from 10⁶ Hz to 100 mHz at open circuit potential after two galvanostatic charging and discharging cycles at 100 mA g⁻¹.

3.4.5 Sodium ion coin cell fabrication and electrochemical measurements

To measure the sodium storage performance of the synthesized materials, CR 2032 coin cells are made using glass fiber as the separator and 1M NaPF₆ in ethylene carbonate (EC)-diethyl carbonate (DEC)-fluoroethylene carbonate (FEC) (1:1:0.03 in volume) as the electrolyte. The assembling of coin cells is conducted inside an Ar-filled glovebox with O₂ and H₂O contents below 1 and 0.1 ppm. Galvanostatic charging and discharging tests are conducted using a NEWARE battery tester at different current rates. CV curves are performed using an electrochemical workstation (CHI 760D, Chenhua, Shanghai) from 10 mV to

3 V at a scanning rate of 0.5 mV s^{-1} . EIS is also measured with an electrochemical workstation over a frequency range from 10^6 Hz to 100 mHz at open circuit potential after two galvanostatic charging and discharging cycles at 100 mA g^{-1} .

3.4.6 Electrochemical HER tests

The obtained flexible electrodes are directly employed as working electrodes for HER performance evaluation. The electrochemical HER tests are performed in a $0.5\text{M H}_2\text{SO}_4$ electrolyte with saturated calomel electrode (SCE) and Pt foil as reference and counter electrodes, respectively, within a three electrode set-up. Linear scan voltammetry (LSV) is conducted in $0.5\text{M H}_2\text{SO}_4$ with a scan rate of 5 mV s^{-1} . Tafel plots are measured from the polarization curves to evaluate the HER kinetics of catalysts, which are plotted with the relationship between overpotential (η) and log current ($\log j$). Tafel slope (b) can be achieved by fitting the linear portion of the Tafel plots, according to Tafel equation ($\eta = b \log(j) + a$).¹⁸³ It should be mentioned that all data were reported without iR compensation. The used reference electrode is SCE in all measurements. The potentials reported in the thesis are vs. the reversible hydrogen electrode (RHE) through RHE calibration, which was typically carried out in a hydrogen-saturated electrolyte using the working electrode of a Pt foil. CV is measured at a scan rate of 5 mV s^{-1} . In $0.5\text{M H}_2\text{SO}_4$ solution, $E_{\text{RHE}} = E_{\text{SCE}} + 0.28 \text{ V}$. The long-term stability tests are performed by continuous LSV scans from 0.08 to 0.88 V (vs. RHE, in $0.5\text{M H}_2\text{SO}_4$) at a scan rate of 5 mV s^{-1} .

3.4.7 Calculations about the capacitance

The specific capacitance of SCs can be calculated from the CV curves and the discharge curves.¹⁸⁴

The calculation based on the CV curves is according to the following equation:

$$C = \frac{Q}{m\Delta V} \quad (3.1)$$

where C , m , Q and ΔV represent the specific capacitance ($F\ g^{-1}$), the weight of active materials (g), the average charge during one cycle (C), and the potential range (V), respectively.

Also, based on the galvanostatic discharge curves, we can also calculate the specific capacitance based on the following equation:

$$C = \frac{I\Delta t}{m\Delta V} \quad (3.2)$$

where I , Δt , ΔV and m are the discharge time (s), the discharge current (A), the potential range (V), and mass of the active materials (g), respectively.

The areal capacitance could also be obtained based on the galvanostatic discharge curves based on the following equation:

$$C = \frac{I\Delta t}{S\Delta V} \quad (3.3)$$

where Δt , I , ΔV and S are the discharge time (s), the discharge current (A), the potential range (V), and the area of the active electrodes (cm^2), respectively.

3.4.8 Calculation about the mode of transport

According to the anodic and cathodic peak current (i_p) at different scan rates (ν), we can quantitatively determine the mode of transport processes by analyzing the relationship between i_p and ν , such as diffusion-controlled battery-behavior mode or surface adsorption-controlled supercapacitive mode.

For the former, a diffusion-controlled reaction, i_p is proportional to $\nu^{1/2}$, according to **Equation 3.4**,

$$i_p = 2.69 \times 10^5 n^{3/2} A D^{1/2} \nu^{1/2} C^* \quad (3.4)$$

where i_p , n , A , D , ν , and C^* represent the peak current (A), the number of electrons transferred, the area of the electrode (cm^2), the diffusion coefficient ($cm^2\ s^{-1}$), the scan rate ($V\ s^{-1}$) and the bulk concentration of analyte ($mol\ cm^{-3}$), respectively.

For the latter, an adsorption-controlled reaction, i_p is proportional to v according to **Equation 3.5**,

$$i_p = (n^2 F^2 / 4RT) v A G^* \quad (3.5)$$

where i_p , n , F , R , T , v , A and G^* represent peak current (A), number of electrons, Faraday's constant, gas constant ($\text{J mol}^{-1} \text{K}^{-1}$), scan rate (V s^{-1}), area of electrode (cm^2), molar amount of analyte adsorbed on the electrode (mol cm^{-2}), respectively.

3.4.9 The calculation of catalytic parameters

All HER parameters described below were obtained from the measurements under the same conditions, i.e., the flexible electrode directly tested in 0.5 M H_2SO_4 solution.

(1) Calculation of active sites

The absolute components of voltammetric charges which include both the cathodic and anodic scans can be attained from the CV curves. The total absolute charge is then divided by two, assuming a one electron redox process. Later, this value is further divided by Faraday constant to get the number of active sites (in moles) of the electrodes.

(2) Exchange current density and Tafel slope

For HER with an acid electrolyte, the rate of hydrogen evolution is characterized using the current through the three-electrode circuit. The current-overpotential equation can be described by Butler-Volmer Equation:

$$i = i_0 [C_0(0,t)/C_0^* e^{-\alpha n f \eta} - C_R(0,t)/C_R^* e^{(1-\alpha) n f \eta}] \quad (3.6)$$

where C_R and C_0 are the concentrations of the participants, i_0 , α and η are the exchange current, the asymmetry coefficient, and the overpotential, respectively, and f stands for $f=F/RT$. When the overpotential is as much as negative, Tafel equation is simplified as:

$$i = i_0 e^{-\alpha n f \eta} \quad (3.7)$$

Then, Tafel slope ($1/\alpha n f$) and exchange current (i_0) can be achieved by fitting the linear portion of the Tafel curves, according to the Tafel equation ($\eta = b \log(j) + a$). As two parameters of catalysts for HER, exchange current should be as large as possible, while Tafel slope should be as small as possible.

(3) TOFs were measured at $\eta = 300$ mV

The turn over frequency (TOF) which is related to the active site number can be calculated using the equation:

$$\text{TOF} = \frac{I}{nF} \frac{1}{2} \quad (3.8)$$

Where, I is the current in Amperes during the linear scan measurement, F is Faraday constant (C/mol), and n is the number of active sites (mol). The factor $\frac{1}{2}$ represents that 2 electrons are required to form one hydrogen molecule from two protons ($2\text{H}^+ + 2\text{e}^- = \text{H}_2$).

3.4.10 First-principle theoretical calculations

Theoretical calculations are carried out based on first-principle DFT using the Vienna Ab-Initio Simulation Package (VASP). In our calculations, projector-augmented-wave (PAW) potentials are used to account for the electron-ion interactions, while electron exchange–correlation interactions are treated using a generalized gradient approximation (GGA) in the Perdew–Burke–Ernzerhof (PBE) version. The stabilities of the mixed system are manually modeled by absorption of MoS_2 clusters onto graphene and CNT. The optimization of the plane wave codes, volume, and cell generally affects the calculations of Pulay stress, leading to incorrect calculations of the diagonal components of the stress tensor. Therefore, we need high cut-off energy for the plane wave basis sets to obtain a reliable stress tensor. Here, 480 eV of cut-off energy is taken for our calculations.

Chapter 4

Ni₃S₂@MoS₂ Core/Shell Nanorod Arrays on Ni Foam for High-Performance Electrochemical Supercapacitor

As a typical metal sulfide, MoS₂ with the layered structure and weak van der Waals interaction enable the easy intercalation of foreign ions (H⁺, Li⁺), providing large surface area for inter-layer charge storage. In addition, the transition metal Mo ions possess a range of oxidation states from +2 to +6, endowing it pseudocapacitance abilities, which plays a critical role to improve electrochemical capabilities. However, the specific capacitance of MoS₂ is still very limited in alone for energy storage applications. Here, novel Ni₃S₂@MoS₂ core/shell hierarchical nanostructures are directly grown on Ni foam by a facile but powerful one-step solution method. On the basis of control experiments for Ni₃S₂@MoS₂ arrays with various morphologies, a plausible growth mechanism is proposed which involves self-assembly and oriented attachment of nanocrystalline. The hierarchical Ni₃S₂@MoS₂ core/shell nanorods exhibit evidently higher specific capacitance than the bare Ni₃S₂ sample, as well as improved rate capability and cycling ability.

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4.1 Introduction

With the escalating energy crisis and ever-growing demand for environmental protection, there is a huge surge in developing efficient and scalable strategies for synthesizing one-dimensional (1D) heterostructured nanomaterials due to their high versatility and applicability as essential components in nanoscale catalysis, chemical sensing, and energy conversion storage devices.¹⁸⁶⁻¹⁸⁸ Often, it is demonstrated that the rational synthesis of core/shell heterostructures is very facile and effective to modify the properties of materials because of the synergetic effect. Desired properties and multifunctionality can be achieved by fine-tuning their compositions, shapes, and controlled alignments of the primary nanobuilding blocks. To date, various core/shell heterostructures including metal/metal oxide, metal/metal, metal oxide/metal oxide, and metal oxide/conductive polymer have been extensively studied in the design of high-energy-density pseudocapacitor electrodes.^{184, 189-200} Pseudocapacitor electrodes based on metal oxides are often confronted with a compromised rate capability and reversibility, which rely on the Faradic redox reaction. Recently, metal sulfides, another kind of promising active materials, have drawn increasing attention owing to their good performance in energy storage applications including SCs. However, studies on core/shell nanostructured metal sulfides have hardly been reported thus far.

TMSs (MS_x, M=Mo, Ti, Ni, Sn) have wide applications because of their unique properties. As a typical example, MoS₂ has been extensively investigated in the field of energy harvesting, optoelectronics and heterogeneous catalysis owing to its attractive physical and chemical properties. MoS₂ has a similar structure to that of graphene, which is composed of three atom layers (S-Mo-S) stacked together through van der Waals interactions. The layered structure and weak van der Waals interaction enable the easy intercalation of foreign ions (H⁺, Li⁺), providing large surface area for inter-layer charge storage.^{96, 201} In addition, the transition metal Mo ions show a range of oxidation states from +2 to +6,

rendering it pseudocapacitance abilities, which plays an important role in enhancing electrochemical capabilities. Soon and Loh et al. reported that MoS₂ could also be used as an electrode material for capacitor due to their sheet-like morphology, which provides large surface area for double-layer charge storage.¹⁷ However, the specific capacitance of MoS₂ is still very limited in alone for energy storage applications.^{17, 202, 203} Ma et al. reported MoS₂ can only exhibit a low specific capacitance of 235 F g⁻¹ at 1 A g⁻¹.²⁰⁴ Huang et al. synthesized layered MoS₂-graphene 3D sphere-like composite, which delivered a specific capacitance of 243 F g⁻¹ at 1 A g⁻¹.²⁰⁵

As another TMS, Ni₃S₂ has been investigated comprehensively for energy storage applications, especially as the electrode of SCs with high specific capacitance. Single crystalline Ni₃S₂ is a good metallic conductor with an RT resistivity of around $1.8 \times 10^{-5} \Omega \text{ cm}$, resulting in the fast transportation of electrons.²⁰⁶ Recent studies have revealed that the electrochemical performances of Ni₃S₂ can be remarkably improved by combining Ni₃S₂ with other metal oxides (Ni(OH)₂) or conductive materials (CNT) to form hybrid heterostructures when used as supercapacitor electrodes.^{207, 208} However, these strategies always rely on complex matrix such as 3D graphene which is grown using a complicated CVD method.²⁰⁷ Hence, the fabrication cost will restrict the composite's potential development. Moreover, core/shell hierarchical nanostructures are often fabricated by a multi-step transformation route.²⁰⁸ Up to date, there still lack simple and high-efficiency methods to synthesize core/shell metal sulfide arrays with precise structure control. Therefore, it is highly desirable to synthesize core/shell metal sulfide arrays with suitable morphologies and tunable functions while maintaining a low fabrication cost.

Herein, we present a facile but powerful one-step solution method to produce core/shell Ni₃S₂@MoS₂ nanoarrays directly on Ni foam. The obtained novel core/shell hierarchical nanostructures have the following three major merits: (1) highly porous 1D core/shell Ni₃S₂@MoS₂ nanoarrays are directly grown on Ni foam by a facile hydrothermal reaction ; (2) in the designed core/shell

Ni₃S₂@MoS₂ heterostructures, a highly conductive 1D core material (Ni₃S₂, a good metallic conductor), renders the quick transport of electrons along Ni₃S₂ nanorods to Ni foam; (3) the void space between neighbouring MoS₂ nanosheets in heterostructures can serve as an "ion reservoir" to facilitate the transportation of electrolyte ions, and can also buffer the volume change during charge/discharge process to protect the core materials. Owing to this design, compared to the electrodes with a sole component, the hierarchical core/shell Ni₃S₂@MoS₂ electrode has robust hierarchical porosity for electrochemical reaction, fast ion and electron transport, and improved cyclic retention. Such a unique core/shell nanostructure will have potential applications in SCs, LIBs, electrochemical or photocatalysis devices and energy conversion storage.

4.2 Results and Discussions

Hierarchical Ni₃S₂@MoS₂ core/shell heterostructured nanoarrays are fabricated by a facile one-step hydrothermal method as illustrated in Section 3.1.1. During the reaction, the active species (S ions) are derived from thioacetamide (TAA) according to **Equation 4.1**. The derived S ions react with Ni foam to produce Ni₃S₂ particles (**Equation 4.2**), and with MoO₄²⁻ ions to produce MoS₂ nanosheets (**Equation 4.3**). Ni₃S₂ nanoparticles convert into Ni₃S₂ nanorods via an oriented attachment process, which subsequently acting as the backbone to guide the MoS₂ nanosheets preferential deposition. Ni foam acts a dual role during the hydrothermal reaction. It is the backbone for loading nanostructured arrays, as well as it is the nickel source of Ni₃S₂.

Figure 4.1 (a) SEM image of Ni₃S₂@MoS₂ nanorod arrays obtained from 1.5 g L⁻¹ of thioacetamide. (b) The magnified SEM images of (a). (c) XRD pattern Ni₃S₂@MoS₂ nanorod arrays (inset: the full XRD pattern). and (d) Nitrogen adsorption-desorption isotherms and pore-size distribution curves (inset) of the heterostructures.

FESEM images of a typical Ni₃S₂@MoS₂ nanorod arrays show that Ni foam is covered by Ni₃S₂ nanorods with a length of 1-5 μm and a diameter of 100-200 nm, which grow densely and almost vertically on Ni foam (**Figure 4.1a** and **b**). The obtained Ni₃S₂@MoS₂ nanorods are well aligned on Ni foam. **Figure 4.1b** shows a close SEM image, demonstrating the uniform coverage of MoS₂ nanosheets on Ni₃S₂ nanorods. The MoS₂ nanosheets are interconnected with each other and almost coat the full Ni₃S₂ core. The robust mechanical adhesion of the heterostructure is confirmed by an ultrasonication test which shows no material loss occurred after ultrasonication in solution for several minutes. The XRD patterns of the as-prepared Ni₃S₂@MoS₂ nanorod arrays are shown in **Figure 4.1c**. The three strong peaks at $2\theta=44.7$, 52.1 and 76.6° arise from Ni foam. The diffraction peaks at $2\theta=22$, 31.3 , 37.9 , 44.4 , 49.9 , 50.2 , 55.5 and 73.3°

are attributed to the (101), (110), (003), (202), (113), (211), (122) and (214) planes of Ni₃S₂ (JCPDS no. 44-1418). The detected peaks at $2\theta=32.3, 35.9, 40.2, 58.7, 62.5$ and 82.2° are corresponding to the (101), (012), (015), (110), (113) and (208) planes of the hexagonal phase MoS₂ ($a=b=0.316$ nm, $c=1.230$ nm, JCPDS card no. 37-1492). The absence of the MoS₂ basal peak ($\sim 14.5^\circ$) indicates that MoS₂ nanosheets coated on Ni₃S₂ nanorods may be very thin only with few layers, which are not easily observed by XRD. Furthermore, due to the porous sheet shell, the heterostructured Ni₃S₂@MoS₂ nanorod arrays also exhibit a high BET SSA of $197.1 \text{ m}^2 \text{ g}^{-1}$ with a pore volume of $0.56 \text{ m}^3 \text{ g}^{-1}$, as shown in **Figure 4.1d**, which is very beneficial for the transport and diffusion of electrolyte ions during the charging and discharging processes of SC.

Figure 4.2 (a) TEM image of Ni₃S₂@MoS₂ nanorod arrays. (b and c) HRTEM images of Ni₃S₂ nanorods and MoS₂ nanosheets from the square areas nanosheets from the white square areas highlighted in (a) (inset: the SAED pattern). (d) EDX spectrum.

Figure 4.3 SEM images of nanostructured Ni₃S₂@MoS₂ arrays obtained from the different concentration of TAA: (a) 1 g L⁻¹, (b) 1.5 g L⁻¹, (c) 2 g L⁻¹, and (d) 3 g L⁻¹.

The structure and morphology evolution of Ni₃S₂@MoS₂ nanorod arrays were further investigated using TEM. A typical TEM image of an individual Ni₃S₂ nanorod covered by thin MoS₂ nanosheets is shown in **Figure 4.2a**. MoS₂ nanosheets of ~10 nm thickness are grown tightly on Ni₃S₂ nanorods after a facile hydrothermal process. The HRTEM image obtained from the white square area (labelled B in **Figure 4.2a**), exhibiting a lattice of 0.28 nm in the backbone area of the Ni₃S₂ nanorod (see **Figure 4.2b**), which corresponds to the (110) interplanar spacing of Ni₃S₂ (hexagonal, a=b=0.574 nm, c=0.714 nm). As shown in **Figure 4.2c**, the lattice in the inner square area (labelled C in **Figure 4.2a**) and the inset FTT pattern corresponds the nature of MoS₂. The EDX results also confirm the composition of Ni₃S₂@MoS₂ arrays (**Figure 4.2d**). The thickness of MoS₂ shell and the length of Ni₃S₂ nanorod can be optimized by tuning the reaction time and the concentration of sulfur source. This enables us to optimize the electrochemical performance of the nanorod arrays and to study the correlation between the structure and electrochemical performance.

Figure 4.4 XRD patterns of the products obtained from the different concentration of sulphur source: (a) 1 g L⁻¹, (b) 1.5 g L⁻¹, (c) 2 g L⁻¹, and (d) 3 g L⁻¹.

Figure 4.3a-d shows the SEM images of the obtained Ni₃S₂@MoS₂ nanorod arrays prepared with the different concentration of the sulfur source. All samples can be indexed to the mixture of Ni₃S₂ and MoS₂ (**Figure 4.4**). For the sample NM-1 prepared from a low concentration (1 g L⁻¹) of TAA, Ni₃S₂ nanorods shows diameters of 200-400 nm, with no MoS₂ nanosheets in the tip of the nanorods (**Figure 4.3a**). With increasing the concentration of TAA to 1.5 and 2 g L⁻¹, Ni₃S₂ nanorods become thicker and the coverage of MoS₂ nanosheets increases, finally uniformly covering Ni₃S₂ nanorods (**Figure 4.3c**). Ni foam is fully coated by Ni₃S₂@MoS₂ arrays with a diameter of 100-300 nm in large scale. With increasing the concentration of TAA to 3 g L⁻¹, the morphology of the sample NM-4 is very different from those of the above three samples. Hollow tubes with diameters from 500 nm to 2 μm can be observed in **Figure 4.3d**. Under hollow tubes, some nanorods still can be observed particularly in the square area highlighted in **Figure 4.3d**. SEM images of the sample NM-4 at different magnifications show that Ni foam is uniformly covered by massive hollow tubes

in a large scale (see **Figure 4.5**). The EDX can confirm that the hollow tubes are composed of MoS₂ (see **Figure 4.5d**).

Figure 4.5 (a), (b), (c) SEM images of nanostructured Ni₃S₂@MoS₂ arrays obtained from 3 g L⁻¹ of TAA at different magnification. (d) magnified SEM image of selected red circular area. (e) magnified SEM image of selected blue circular area. (f) EDX spectrum of Ni₃S₂@MoS₂ electrodes in the selected red circular area (d).

The corresponding schematic illustration for the formation of the above four samples is proposed in **Figure 4.6**. Based on the observations described above, a growth mechanism for the core/shell heterostructures can be proposed as follows: (1) P123 as a polymer surfactant can link with nickel ions and MoO₄²⁻ ions to

form micelles in aqueous solutions in the hydrothermal reaction system, then facilitate the following oriented growth of Ni₃S₂ nanorods and MoS₂ nanosheets; (2) The growth mechanism of Ni₃S₂ nanorods may be attributed to "oriented growth", which involves an oriented aggregation process, that primary nanostructured building blocks are organized to share an identical crystallographic orientation and join at the plane interfaces to form single-crystalline architectures^{209, 210}; (3) The growth mechanism of shell structure is probably attributed to the "oriented attachment" and "self-assembly" processes, which involve a self-organization of adjacent particles, then followed by assembling of these particles on a planar interface.^{209, 211, 212} The above hypothesis is supported by inspecting the morphologies at different growth stages by controlling the time (**Figure 4.7**). At the early stage (reaction for 6 h), only MoS₂ nanosheets can be observed on Ni foam, with a few nanoparticles (dotted circles) starting to grow out of Ni foam. As the reaction time increases, these nanoparticles self-assemble to form nanorods, which act as the backbone to guide the MoS₂ nanosheets preferential deposition. Finally, after reaction for 24 h, we can obtain the interesting core/shell heterostructured nanorods. It is noteworthy that the thickness of MoS₂ shell can be easily increased by prolonging the reaction time.

Figure 4.6 Schematic illustration of the formation of the obtained samples from the different concentration of TAA.

Figure 4.8a shows the CV curves of the obtained Ni₃S₂@MoS₂ nanorod arrays prepared with the different concentration of the sulfur source. All the CV curves show a pair of redox peaks, which are distinguishable from those of EDLCs, proving the presence of a reversible Faradic reaction and pseudocapacitive behavior.²⁰³ The specific capacitances of the samples NM-1, NM-2, NM-3 and NM-4 calculated from CV curves at 5 mV s⁻¹ are 453, 789, 1165 and 564 F g⁻¹, respectively. Herein, for Ni₃S₂@MoS₂ nanowire arrays, the total mass of the active materials should include the mass of MoS₂ and the mass of Ni₃S₂.

Figure 4.7 SEM images of nanostructured Ni₃S₂@MoS₂ arrays obtained after hydrothermal reaction for different times, showing the morphology evolution of the core/shell nanowires: (a) 6 h, (b) 12 h, (c) 18 h, and (d) 24 h.

As the Ni₃S₂@MoS₂ nanowire arrays were synthesized in one step, it is very difficult to calculate the real mass ratio of MoS₂ and Ni₃S₂ in the composite electrodes. The calculation is described as following: the weight increment (x mg) of Ni foam can be directly weighted after the synthesis of Ni₃S₂@MoS₂ nanowire arrays on Ni foam. If assuming the composite is pure Ni₃S₂, $m = x \text{ mg} \times (M_{\text{Ni}_3\text{S}_2} / 2M_{\text{S}}) = x \text{ mg} \times (240.2 / 64) = 3.75x \text{ mg}$, where M is the molecular weight or atomic weight. If assuming the composite is pure MoS₂, $m = x \text{ mg}$. Therefore,

based on the equations (S1) and (S2), the capacitance of composite electrodes calculated by Ni₃S₂ is less than that calculated by MoS₂. In our paper, we use the lower capacitance values based on Ni₃S₂. Therefore, the actual capacitance value of Ni₃S₂@MoS₂ nanowire arrays is higher than the presented value in the paper.

The sample NM-3 shows the most specific capacitance, which is composed of Ni₃S₂ nanorods uniformly coated with 3D nanosheet networks with a very high SSA (197.1 m² g⁻¹) and pore volume (0.56 m³ g⁻¹). It can be comparable to those of other reported Ni₃S₂-based composite supercapacitive materials, such as the hybrid CNT/Ni₃S₂ (586 F g⁻¹ at 1 mV s⁻¹).²⁰⁸ On the basis of the above-proposed growth mechanism and the verification of morphology, we can predict that the Ni₃S₂ content in Ni₃S₂@MoS₂ nanorods decreases with the concentration of the sulfur source. Therefore, the content of Ni₃S₂ in the sample NM-1 is the highest among above four samples. It is noteworthy that the pseudocapacitive Faradic charging for MoS₂ is only obvious at very low scan rates, such as 1 mV s⁻¹.¹⁷ Normally, MoS₂ always shows a low capacitance compared to Ni₃S₂. However, the high-Ni₃S₂-content NM-1 sample exhibits relatively the lowest capacitance of 453 F g⁻¹. The CV curves of the sample NM-3 at different scan rates are displayed in **Figure 4.8b**. With the increased scan rates, the current response increases accordingly and the shapes of CV curves are retained, proving its good rate capability. According to the CV curves, for the sample NM-3, the specific capacitance increases from 514 to 1165 F g⁻¹ with increasing the scan rate from 5 to 20 mV s⁻¹. **Figure 4.8c** displays the charge/discharge curves of the sample NM-3 at different current densities. **Figure 4.8d** illustrates the correlation of specific capacitance and current density. The sample NM-3 delivers the highest specific capacitance of 848 F g⁻¹ at 5 A g⁻¹. This result is comparable to or better than those of previous Ni₃S₂-based nanocomposite electrodes. For example, the hybrid CNT/Ni₃S₂ exhibits a specific capacitance of 514 F g⁻¹ at 4 A g⁻¹²⁰⁸, 717 F g⁻¹ can be reached in Ni₃S₂ flaky at 2 A g⁻¹¹²¹³ and Ni₃S₂/MWCNT-NC can deliver a specific capacitance of 800 F g⁻¹ at 3.2 A g⁻¹¹²¹⁴. Nevertheless, herein, at a high current density of 20 A g⁻¹, the sample NM-3 still exhibits a high

specific capacitance of 395 F g⁻¹. The rate performance is nearly comparable to that of Ni₃S₂@Ni(OH)₂/3DGN (398 F g⁻¹ at 19.8 F g⁻¹).²⁰⁷ The cycling stability of the electrode materials is another critical factor for practical applications. **Figure 4.8e** shows the cycling performance of Ni₃S₂@MoS₂ hybrids prepared with 2 g L⁻¹ of TAA at 8 A g⁻¹. Especially, the electrode materials can still maintain the specific capacitance of 720 A g⁻¹ (91% of the initial capacitance) after 2000 cycles. The last ten charge/discharge curves (**Figure 4.8f**) is nearly unchanged, indicating its excellent cyclability.

Figure 4.8 (a) Cyclic voltammograms of Ni₃S₂@MoS₂ array electrodes within the potential range of -0.2 V to 0.6 V at a constant scan rate of 5 mV s⁻¹. (b) Cyclic

voltammograms of the sample NM-3 at different scan rates of 5, 10, 15 and 20 mV s⁻¹. (c) Discharge curves of the sample NM-3 at various current densities. (d) Specific capacitances of the sample NM-3 at different current densities. (e) Cycling performances of the sample NM-3 at a current density of 6 A g⁻¹. (f) The last 10 charge/discharge curves of the sample NM-3 at a current density of 6 A g⁻¹.

To in-depth investigate the effect of the Ni₃S₂ content on the electrochemical performance of the hybrid electrode, **Figure 4.9a** and **b** displays the specific capacitances at different current densities and cycling performance of all the hybrid electrodes. Similar results as that of CV tests can be obtained from charge/discharge tests. The sample NM-3 shows the highest specific capacitance. The NM-1 sample composed of bare Ni₃S₂ nanorods with low-density MoS₂ nanosheets shows the lowest specific capacitance (453 F g⁻¹). Except for the sample NM-4, the samples with lower Ni₃S₂ content can show higher specific capacitance. It is noteworthy that the pseudocapacitive Faradic charging for MoS₂ is only obvious at very low scan rates, such as 1 mV s⁻¹.¹⁷ Normally, MoS₂ always showed a low capacitance compared to Ni₃S₂.^{202, 204} Therefore, the low specific capacitance of the sample NM-4 may be attributed to its low content of Ni₃S₂, which can be verified from its morphology. In the contrast, compared with the sample NM-1 with a high content of Ni₃S₂, the excellent electrochemical performance of obtained Ni₃S₂@MoS₂ nanowire arrays (NM-2 and NM-3) is mainly due to the synergetic effect and the novel structure.

Figure 4.9 (a) Specific capacitances of the products obtained from different concentration of sulphur source at different current densities. (b) Cycling performances at a current density of 6 A g⁻¹.

After long-term cycling, the electrolyte remains transparent (no changes are visible) and the Ni₃S₂@MoS₂ core-shell nanorods are overall preserved with little change as shown in **Figure 4.10**. **Table 4.1** summarizes the reported electrochemical performance of nickel sulfide applied as a supercapacitor electrode material.^{207, 208, 213, 214} We can see Ni₃S₂@MoS₂ hybrids exhibit comparable performance to or even better performance, compared to the other Ni₃S₂ supercapacitor electrodes.

Figure 4.10 (a) Photos of Ni₃S₂@MoS₂ nanowire arrays on Ni foam (the sample NM-3) before cycle (left) and after cycle (right). (b) XRD patterns of Ni₃S₂@MoS₂ nanowire arrays after cycle. (c) and (d) SEM images with different magnifications of Ni₃S₂@MoS₂ nanowire arrays after cycle.

The above results reveal Ni₃S₂@MoS₂ core/shell nanorods exhibit high specific capacitance, excellent rate capability and remarkable cycling performance used as high-performance electrochemical pseudocapacitors. Such excellent electrochemical performance can be attributed to the following factors. First, the void space between neighbouring MoS₂ nanosheets in heterostructures effectively creates a spatial confinement to the electrolyte between the Ni₃S₂ core and the MoS₂ shell. Within this open space, a close contact between active materials and electrolyte can be ensured allowing for an easy electrolyte diffusion and a rapid ion transport (**Figure 4.11**). The curve of $\log i_p$ versus $\log v$ is shown

in **Figure 4.12**. This graph has a slope of 0.48, approximate to 0.5. Therefore, we can conclude the process is diffusion-controlled. The open space in the hierarchical structure can serve as an "ion and electrolyte reservoir" to facilitate the transportation of electrolyte ions, and can also buffer the volume change during charge/discharge process to protect the core materials. According to the anodic and cathodic peak current, we can determine the charge/discharge process of Ni₃S₂@MoS₂ hybrids is diffusion-controlled (**Figure 4.12**, for detailed calculations, see the Section 3.4.8). This may explain the improved rate capability of Ni₃S₂@MoS₂ core-shell nanorods, compared to that of pristine Ni₃S₂ samples. Second, especially, the SSA of the hybrids is significantly improved due to the uniform hierarchical nanostructure. It is reported that a conformal coating of shell material can increase the surface area several times. The high SSA can provide considerable electric double-layer capacitors. Third, it is reported that Ni₃S₂ has a heazlewoodite structure with short metal-metal distances in an approximately body-centred cubic sulphur lattice, which results in its good electrical properties and endows the quick transport of electrons along Ni₃S₂ nanorods.²⁰⁶ Due to the uniform connection between MoS₂ shell with Ni₃S₂ core, the physical charge on Ni₃S₂ core can be transported eventually to MoS₂ shell. All the above results can demonstrate the as-prepared hybrids are very stable as active electrode materials.

Figure 4.11 Schematic illustration showing the charge storage advantage of Ni₃S₂@MoS₂ core/shell nanorods. (a) The electrolyte can easily diffuse into the Ni₃S₂@MoS₂ heterostructures from the open spaces between neighboring nanosheets. (b) The porous structure can ensure that the heterostructures closely

contact with the electrolyte, and that electrons and electrolyte ions can easily diffuse in between.

Table 4.1 The electrochemical performances of some reported hybrid nanostructures based on nickel sulfide.

Hybrid Nanomaterials	Maximum capacitance (F g ⁻¹) at given current density (A g ⁻¹)	Capacitance retention after long-time cycling
CNT@Ni ₃ S ₂ ²⁰⁵	514 (4)	88 % (5.3 A g ⁻¹ , 1500)
Ni ₃ S ₂ @Ni(OH) ₂ /3DGN ²⁰⁷	1037.5 (5.1)	99.1% (5.9 A g ⁻¹ , 2000)
Ni ₃ S ₂ flaky ²¹³	717 (2)	91% (4 A g ⁻¹ , 1000)
Ni ₃ S ₂ @MWCNT ²⁰⁸	800 (3.2)	90% (4 A g ⁻¹ , 1000)
Ni ₃ S ₂ @MoS ₂ (Our work)	848 (5)	91% (8 A g ⁻¹ , 2000)

Figure 4.12 The relationship between $\text{Log } i_p$ and $\text{Log } v$ and the fitting line obtained from the the cyclic voltammograms of Ni₃S₂@MoS₂ array electrodes at different scan rates.

4.3 Conclusions

In conclusion, a scalable and one-step hydrothermal method has been proposed to synthesize Ni₃S₂@MoS₂ core/shell nanoarrays on Ni foam. On the basis of

control experiments for Ni₃S₂@MoS₂ arrays with various morphologies, a plausible growth mechanism is proposed which involves self-assembly and oriented attachment of nanocrystalline. The hierarchical Ni₃S₂@MoS₂ core/shell nanorods exhibit evidently higher specific capacitance than the bare Ni₃S₂ sample, as well as improved rate capability and cycling ability. The specific capacitance of the hybrid Ni₃S₂@MoS₂ nanorods reaches as high as 848 F g⁻¹ at 5 A g⁻¹, which is about twice that of the pristine Ni₃S₂ (425 F g⁻¹). Even at 20 A g⁻¹, a specific capacitance as high as 395 F g⁻¹ can be obtained, about 46.6% capacity retention. The increment of performance is mainly due to the porous structure of the hybrid Ni₃S₂@MoS₂ nanorods. Furthermore, a novel design with a conductive 1D core material renders the fast electron transportation between Ni₃S₂ nanorods and Ni foam. Importantly, the present study can also be adopted in the synthesis of other Ni₃S₂ based hybrid metal sulfides. The obtained hybrids can provide great potentials in large-scale energy storage device applications.

Chapter 5

Honeycomb-like MoS₂ Nanoarchitectures Anchored into Graphene Foam for Enhanced Lithium-Ion Storage

In Chapter 5, honeycomb-like MoS₂ nanoarchitectures anchored into 3DGF are successfully fabricated as a high-performance anode electrode for enhanced Li-ion storage. The unique 3D interpenetrating honeycomb-like structure is the key to the high performance, which can effectively inhibit the aggregation of exfoliated MoS₂ nanosheets and mechanical failure of the active materials, and then enhance the performance and stability of active materials. More importantly, the obtained honeycomb-like MoS₂ nanoarchitectures possess a high surface area usable for electrolyte/electrode interfaces, and the ultrathin nature of adjacent MoS₂ walls can effectively reduce the diffusion length of both electrons and ions. With these merits, honeycomb-like MoS₂ architectures@3DGF exhibits the high reversible capacity, superior high-rate capability and excellent cycling stability.

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5.1 Introduction

Rechargeable LIBs have attracted great attention in many fundamental applications due to their high energy density and design flexibility.^{2, 58, 60, 215, 216} They have been considered as one of the most promising next generation power sources for EVs, which always require operating under much higher current condition than mobile devices. Unfortunately, the practical applications of LIBs for EVs are largely hindered due to a high level of polarization for bulk electrode materials and degradation of electrochemical properties at a high current rate during charge/discharge process. Extensive research has proved that nanomaterials can achieve higher specific capacity and better rate performance compared with bulk materials due to the decreased diffusion lengths, enhanced kinetics, and high electrolyte contact area.^{11, 61, 217-221} However, owing to the excess surface free energy, nanostructured materials always tend to self-aggregation, which reduces the effective area of electrode/electrolyte interface. Therefore, it is crucial to retain the large contact area to fully fulfil the advantages of active nanomaterials. Recently, constructing 3D architectures based on 2D materials has been proved to be an effective approach to solve this problem. In such structures, lithium ion intercalation/extraction in the nanoscale dimension of building blocks is much faster than that in bulk materials while the primary 3D architecture (usually at the micrometer scale) can effectively avoid the aggregation of active nanomaterials and provide more active sites for lithium ion intercalation/extraction. To further increase the conductivity and reduce the diffusion length, 3D architectures have been constructed with various conductive backbone, for example, a variety of carbonaceous materials such as porous carbons, CNTs, graphene, and conductive polymers.^{94, 202, 222-224} Especially, graphene is the most promising matrix due to the high electrical conductivity, good flexibility, and high chemical stability.

As a typical layered TMS, MoS₂ has a similar structure to that of graphene, which is composed of three atom layers (S-Mo-S) stacked together through van der

Waals interactions.⁹⁶ The layered structure and weak van der Waals interaction enable the easy intercalation of lithium ions without a significant increase in volume. MoS₂ as anode materials for rechargeable LIBs can deliver a higher capacity (~670 mAh g⁻¹ with 4-electron transfer reaction per formula) than the commercial graphite material (372 mAh g⁻¹). However, the capacity fading and poor rate performance of MoS₂ anode are still the main challenges. To address these issues, various strategies have been developed to enhance the electrochemical performance of MoS₂ or MoS₂ composites by using nanotechnologies^{94, 100, 225} and carbonaceous materials as the conductive matrix.⁹⁶⁻⁹⁸ Especially, graphene is the most promising matrix due to the high electrical conductivity, good flexibility, and high chemical stability. In these systems, the decent electrochemical performance has been demonstrated. However, in all these works, MoS₂ or MoS₂ composites are in the form of powders and need to be mixed with conductive additives (such as carbon black) and polymer binders to obtain homogeneous slurries, and finally coated on current collectors (Cu foil). The extra conductive additives, polymer binders and metallic current collectors not only decrease the energy and power density of full batteries but also affect the rate and cycling performance.

Recently, a new electrode design strategy has been employed to fabricate integrated, binder-free and lightweight LIB electrodes by direct coating, growing and depositing active materials on self-supported 3D porous carbon materials. Especially, 3DGF has been regarded as an excellent backbone for loading MoS₂ nanoparticles and a highly conductive matrix for them.¹⁷⁸ Since 3DGF can provide pathways for highly efficient electronic transport and lithium ion exchange during the charge/discharge cycles, it can act as the current collector without conductive additives. However, the electrochemical performance of this system is significantly determined by the morphology of active materials and intimate contact between active materials and GF. Thus, the achievement of robust 3D graphene-backboned MoS₂ architectures with superior electrochemical performances remains a big challenge.

In this paper, we developed a facile strategy to grow honeycomb-like MoS₂ nanoarchitectures anchored into 3DGF by a facile P123-assisted solution-phase method. The obtained sample, honeycomb-like MoS₂ anchored into 3DGF is denoted as HC-MoS₂@GF, in which ultrathin MoS₂ nanosheets with a thickness of ~3 nm build honeycomb-like blocks of 3D architectures. Such a unique structure has the following characteristics: First, the 3DGF grown by CVD has a relatively high electrical conductivity (around 1000 S m⁻¹) that can ensure fast electron and ion transportation. With this design, 3DGF acts as both a lightweight scaffold for the growth of 3D honeycomb-like MoS₂ architecture and an efficient current collector. Therefore, the direct contact and interconnection between the 3DGF and active materials provide a superior charge transport between the current collector and electrode materials and also an excellent ion transport from the electrolyte to the active material surface. Second, the obtained honeycomb-like MoS₂ nanoarchitectures are homogenously anchored into the skeleton of 3DGF with a close and robust physical contact. To our best knowledge, it is the first time to report such a new type of MoS₂ nanosheets with a novel 3D honeycomb-like structure, especially obtained directly on 3DGF. More importantly, MoS₂ nanosheets self-assembly into honeycomb-like nanoarchitectures, which can effectively inhibit the aggregation of exfoliated MoS₂ nanosheets and mechanical failure of the active materials, and then enhance the stability of active materials. Meanwhile, the obtained honeycomb-like MoS₂ nanoarchitectures possess a high surface area usable for electrolyte/electrode interfaces, and the ultrathin nature of adjacent MoS₂ walls can effectively reduce the diffusion length of both electrons and ions. With these merits, our HC-MoS₂@GF exhibits high reversible capacity, superior high-rate capability, and excellent cycling stability.

5.2 Results and Discussions

The fabrication process for HC-MoS₂@GF is depicted in **Section 3.1.2**. The growth of honeycomb-like MoS₂ nanoarchitectures *in-situ* onto 3DGF was

obtained by a hydrothermal reaction between Na₂MoO₄ and thiourea with the help of the surfactant P123 at 200 °C for 24 h. The honeycomb-like MoS₂ nanoarchitectures are anchored into the skeleton of GF by spontaneous self-assembly of MoS₂ nanosheets. The weight of MoS₂ in the 3D architectures is calculated by weighting 3DGF before and after the reaction. Notably, the weight fractions of MoS₂ in the as-prepared 3D architectures is facilely controlled by adjusting the concentration of the reactants (Na₂MoO₄ and thiourea) using 3DGF with nearly the same area. More details of the synthesis procedure are given in the **Section 3.1.2**.

Figure 5.1 a-c) Typical FESEM images at different magnifications; d) and e) the crystal structures of MoS₂ with (001) and (110) crystal planes; f) XRD patterns of GF and HC-MoS₂@GF.

The morphology and phase of the as-prepared HC-MoS₂@GF were systematically investigated by FESEM and XRD. **Figure 5.1a-c** shows the typical morphology of HC-MoS₂@GF at different magnifications. As can be seen, the highly interconnected and porous 3D honeycomb-like architectures built from numerous nanosheets are uniformly distributed on 3DGF, which are similar to those reported for 3D graphene networks²²⁶ and aerogels²²⁷. Further investigations show that the building block nanosheets have lateral sizes of ~100 nm, they are randomly connected with the adjacent nanosheets to self-assemble into continuous and interconnected 3D honeycomb-like architectures. This internal cross-linked structure would effectively prevent both the lamellar aggregation and mechanical failure (leading to the disconnection of active materials from the current collector) after repeated charge/discharge processes, and hence can efficiently maintain the long-standing existence of nanosheets and good electrical contact. The pore size from 50 nm to several hundred nm could be identified in the architectures; the pore structure is derived from the assembly process. The highly porous structure allows for easy diffusion of electrolyte, ensuring MoS₂ nanosheets in high contact with the electrolyte and also facilitating fast transportation of lithium ions and electrons, resulting in an excellent electrochemical performance. No material loss was observed after ultrasonication of the sample in solution for several minutes, indicating a robust mechanical adhesion of HC-MoS₂@GF electrode, which is very promising for improving the electrochemical performance.

Figure 5.1d-e schematically illustrates the crystal structures of MoS₂ nanosheets with (001) and (110) crystal planes, respectively. **Figure 5.1f** shows the XRD patterns of the bare GF and HC-MoS₂@GF. The as-grown GF displays two typical diffraction peaks at 26.5 ° and 54.6 °, corresponding to the (002) and (004) reflections of graphitic carbon, respectively (JCPDS card no. 75-1621). The highly crystalline structure of GF is favourable for the electron transfer and ion diffusion. By comparison, the detected peaks at $2\theta=14.1, 32.3, 39.4$ and 58.7° in the pattern of HC-MoS₂@GF composites can be assigned to the (002), (100),

(103) and (110) planes in the hexagonal phase MoS₂ ($a=b=0.316$ nm, $c=1.230$ nm, JCPDS card no. 37-1492).

Figure 5.2 a) TEM images of HC-MoS₂@GF; b) HRTEM image of honeycomb-structured MoS₂ nanosheet layers and its orientation along [002] direction as the inset FFT pattern demonstrated; (c) HRTEM image of honeycomb-structured MoS₂ nanosheet plane; (d) SAED pattern.

The structure of HC-MoS₂@GF composites was further studied by TEM. The HC-MoS₂@GF composites were sonicated in ethanol for 30 min, which was then dropped onto a TEM grid and dried at ambient conditions. The honeycomb-like structures were collapsed due to the ultrasonication effect. A typical TEM image in **Figure 5.2a** shows the intrinsic wrinkles or corrugations of cell sheets. A representative high-resolution TEM (HRTEM) image in **Figure 5.2b**, illustrates the layered crystal lattice structure. We can observe that most of the building

blocks in hierarchical nanostructures are 3~5 layers of MoS₂. Typical lamellar structure with an interlayer spacing of 0.64 nm can be observed from the HRTEM image (**Figure 5.2b**); this spacing is slightly larger than the layer-to-layer spacing of 6.1 Å in bulk MoS₂. The fast Fourier transformation (FFT) pattern in the inner square area as the inset of **Figure 5.2b** reveals the orientation of layers along the [002] direction. Interplanar spacing of 0.27 nm can be observed in **Figure 5.2c**, which is consistent with the d spacing of (100) planes of hexagonal MoS₂. The selected area electron diffraction (SAED) pattern in **Figure 5.2d**, clearly demonstrates a polycrystalline structure of MoS₂.

Figure 5.3 (a) Raman spectra of HC-MoS₂@GF and GF, respectively (the insert magnified Raman spectrum of HC-MoS₂@GF showing the typical Raman signature of MoS₂); XPS spectra of (b) Mo 3d and S 2s peaks, and (c) S 2p peaks of HC-MoS₂@GF; d) N₂ adsorption/desorption isotherms, and the insert corresponding pore size distribution of HC-MoS₂@GF composites.

GF and HC-MoS₂@GF were further examined by Raman spectroscopy. Raman spectra in **Figure 5.3a** indicates three characteristic peaks of graphene, observed

at 1350, 1580, and 2720 cm⁻¹ and corresponding to the D, G, and 2D bands, respectively. Here, the Raman intensity of the G band is much higher than the 2D band, which is very consistent with the multilayer properties of GF. Thus, this makes GF rigid to serve as the scaffold for battery electrodes. The HC-MoS₂@GF composites have two obvious peaks at 383 cm⁻¹ and 405 cm⁻¹, which corresponding to E_{2g}¹ and A_g¹ Raman modes of MoS₂, respectively. The X-ray photoelectron spectroscopy (XPS) was used to investigate the chemical states of Mo and S in the products as shown in **Figure 5.3b, c**. The binding energies of Mo 3d_{3/2} and Mo 3d_{5/2} peaks are located at 232.5 and 229.3 eV, respectively, which are a characteristic of Mo⁴⁺ in MoS₂. The binding energies at 162 and 163.2 eV in S 2p spectra are attributed to the S²⁻ of MoS₂.^{228, 229}

Full nitrogen sorption isotherms of the HC-MoS₂@GF composites were measured to obtain the information on the pore size distribution and SSA. As shown in **Figure 5.3d**, a type-IV isotherm with a type-H3 hysteresis loop in the relative pressure range of 0.45-1.0 P/P₀ indicates the presence of mesoporous structure. Accordingly, the SSA is calculated to be 182 m² g⁻¹ via the Brunauer-Emmett-Teller (BET) method. The pore size distribution derived from the BJH method is given in the inset of **Figure 5.3d**. The sharp peak at 37.9 nm is attributed to mesoporous channels in HC-MoS₂@GF architectures. Besides, the sharp peak at 122.8 nm corresponds to macropores. Such a high SSA of HC-MoS₂@GF with massive mesopores and macropores could be desirable for energy storage application or other applications. These mesopores and macropores in the 3D honeycomb-like architectures can serve as an "ion and electrolyte reservoir" to facilitate the transportation of electrolyte ions, and can also buffer the volume change during charge/discharge process to protect the active materials.

Concerning the growth mechanism of the honeycomb-like MoS₂ architectures, GF and P123 may play crucial roles during the formation process in our study. Based on the experimental condition, a plausible mechanism of the formation process is proposed, which can be divided into two stages, (i) the hydrolysis of

NH₂CSNH₂ and (ii) the processes of crystallization. First, thiourea reacts with H₂O to produce NH₃, H₂S and CO₂. The detailed reaction equation is described as follows.^{230, 231}

During the reaction, the growth of MoS₂ sheets is found to be favorably selective on GF, with little free particle growth in solution. Obviously, GF provides a novel substrate for the nucleation and subsequent growth of MoS₂ crystals. The selective growth of MoS₂ on GF was attributed to the interactions between functional groups of GF and MoO₄²⁻ precursors with the help of surfactant P123. The amphiphilic P123 triblock copolymer can bond with the functional groups of GF, which were created after plasma treatment.^{232, 233} Meanwhile, the charged functional groups of GF could help to adsorb metal ions (MoO₄²⁻) and anchor them on GF surface, causing the enhanced interfacial adhesion between the active materials and GF substrate. When the reaction occurred, the MoO₄²⁻ precursors were absorbed on the surface of graphene and then reacted with H₂S to in situ form MoS₂ nucleus. The possible reaction on the surface of GF may be expressed as follows.

The freshly-formed nuclei are unstable due to their high surface energy and tended to aggregate to minimize interfacial energy. The P123 triblock copolymer plays a pivotal role as a structure directing agent, promoting the formed agglomerates to grow sideways and assembly into thin-layered nanosheets. As the reaction went on, P123 also acts as a “connector”, causing the well-fined nanosheets self-assembly into honeycomb-like architectures for removing surface energy associated with unsatisfied bonds. The verification of detailed mechanism for the formation of honeycomb-like structures will require more carefully designed experiments and it is beyond the scope of this work.

Figure 5.4 FESEM images (a and b) of MoS₂ hollow spheres grown in solution without GF substrate.

In strong contrast, in the absence of GF, the exact same synthesis process produced MoS₂ hollow spheres (HS-MoS₂) of about 1.5 μm in diameter (**Figure 5.4a**). **Figure 5.4b** reveals MoS₂ hollow spheres are constructed by interconnected thin nanosheets. The thickness of the hierarchical wall is about 200 nm, which is several ten folds thicker than the wall of HC-MoS₂ (see **Figure 5.1c**). The obvious morphological difference highlights the important role of GF substrate as a novel support material in mediating the growth of nanomaterials. The electrochemical properties of HC-MoS₂ were further evaluated. HC-MoS₂@GF was directly used as the electrode of half-cells for tests without conducting carbon, polymer binder and the current collector. However, as a control experiment for comparison, two different electrodes with MoS₂ hollow spheres were also prepared and evaluated, in which hollow MoS₂ sphere powders were mixed with the conductive carbon black and PVDF binder in a weight ratio of approximately 8:1:1, and the slurries were coated on GF and Cu foil, respectively. They are denoted as HS-MoS₂@GF and HS-MoS₂, respectively. The CV curves of HC-MoS₂@GF during the first 4 cycles are presented in **Figure 5.5a**. Two reduction peaks at 0.9 V and 0.4 V and two oxidation peaks at 1.8V and 2.3 V can be observed during the first cycle. The reduction peak at 0.9 V can be attributed to Li insertion into the interlayers of MoS₂, accompanied by phase transformation from 2H to 1T structures of Li_xMoS₂. The second obvious reduction peak at 0.4 V can be ascribed to the reduction of Li_xMoS₂ to Mo metal

and Li₂S via a conversion reaction, and then the formation of a gel-like polymeric layer resulting from electrochemically driven electrolyte degradation. The oxidation peak at 1.8 V can be attributed to partial oxidation of Mo to form MoS₂ due to the defect sites leading to the formation of MoS₂. During the subsequent cycles, the reversible reaction based on the equation: $\text{MoS}_2 + 4\text{Li} \rightarrow \text{Mo} + 2\text{Li}_2\text{S}$, is accompanied by the redox of Mo nanoparticles and the reversible growth of the gel-like layer.^{97, 162, 234} During subsequent discharge cycles, a strong peak observed at 0.4 V disappears while two new peaks are repeatedly observed at 1.8 V and 1.1 V, which is in agreement with other results in the literature.^[23, 24] The shape of CV curve and the oxidation/reduction peaks can still retain indicating the good stability of the electrochemical process after several cycles. **Figure 5.5b** displays the representative charge/discharge profiles of the HC-MoS₂@GF at a current density of 100 mA g⁻¹. In agreement with the CV curves, two voltage plateaus at around 1.1-1.4 V and 0.6 V can be observed in the discharge process of the first cycle. The small plateau at ~1.2 V during the first discharge reflects the formation of the SEI film and contributes to the irreversible capacity thus lowering the efficiency in the first cycle. The second potential plateau at ~0.6 V corresponds to the conversion of MoS₂ to metallic Mo and Li₂S. The HC-MoS₂@GF electrode delivered the initial discharge and charge capacities of 1158 and 1397 mAh g⁻¹, respectively, giving a Coulombic efficiency of 82.9%. Such a high initial lithium storage capacity might be attributed to the unique 3D graphene-backboned honeycomb-like MoS₂ architectures. The ICL of around 200 mAh g⁻¹ is mainly due to the electrolyte decomposition and SEI formation in the first discharge process, which is inevitable. The Coulombic efficiency rapidly reaches more than 99% after the second cycle. The second and third discharge profiles are almost coincided with each other, showing an excellent cycling performance. The potential plateaus at 1.8 V and 1.1 V (**Figure 5.5b**) are also in agreement with the two peaks of the CV curves in **Figure 5.5a**. Even after 40 cycles, both the discharge and charge capacities of the HC-MoS₂@GF electrode are stable at about 1100 mAh g⁻¹, delivering nearly 99% capacity

retention, as shown in **Figure 5.5c**. These results are in stark contrast to those of HS-MoS₂ electrodes (HS-MoS₂@GF and HS-MoS₂), which show continuous and progressive capacity decay under the same testing conditions. After 50 cycles, HS-MoS₂@GF and HS-MoS₂ electrodes only deliver a capacity of 820 mAh g⁻¹ and 600 mAh g⁻¹, respectively. Moreover, the HC-MoS₂@GF electrode exhibits excellent rate performance. As shown in **Figure 5.5d**, even cycled at a high current of 5000 mA g⁻¹, the specific capacities of ~800 mAh g⁻¹ can be maintained. Remarkably, these values are much higher than those of other two samples, 400 mAh g⁻¹ (HS-MoS₂@GF) and 200 mAh g⁻¹ (HS-MoS₂). Moreover, after deep cycling at 5000 mA g⁻¹, the specific capacity is recovered to the same levels as the previous measurement when the testing current is returned back to 100 mA g⁻¹. A complete comparison of electrochemical properties of MoS₂ and hybrid composites, summarized in **Table 5.1**, shows that HC-MoS₂@GF possesses excellent electrochemical properties, including high initial Coulombic efficiency, high specific capacity, high rate performance and stable cyclability, much better than those of HS-MoS₂@GF, HS-MoS₂ and various MoS₂-based electrodes reported in the literature. Owing to the good electrical contact between GF and MoS₂ hollow spheres, HS-MoS₂@GF exhibits more excellent cycling response to different current rates, compare with that of HS-MoS₂.

To gain insight into the reason that the unique 3D graphene-backboned honeycomb-like MoS₂ architectures possesses such excellent electrochemical performances for lithium storage, we performed EIS for these three electrodes as shown in **Figure 5.5f**. Obviously, the diameter of the semicircle for HC-MoS₂@GF in the high-medium frequency region is the smallest one compared with those of HS-MoS₂@GF and HS-MoS₂, which indicates that HC-MoS₂@GF possess the lowest contact and charge-transfer resistances. The kinetic differences of these MoS₂ electrodes were further investigated using the common R-C equivalent circuit. The high-frequency semicircle in **Figure 5.5f** could be attributed to resistance R_{sf} and CPE1 of the SEI film, the medium frequency semicircle to the charge transfer resistance of the electrode reaction R_{ct} and CPE2

of the electrode-electrolyte interface, and the inclined line in the low-frequency region to lithium ion diffusion processes. The R_{sf} and R_{ct} can be obtained by fitting data according to the equivalent circuit model in **Figure 5.5f**. The R_{sf} and R_{ct} of HC-MoS₂@GF electrode are 3.89 and 10.37 Ω , respectively, which are much lower than those of HS-MoS₂@GF (R_{sf} =10 and R_{ct} =30 Ω) and HS-MoS₂ (R_{sf} =15 and R_{ct} =80 Ω). For the three samples, the solution resistances are almost the same owing to the same electrolyte testing system. In contrast, the charge transfer resistance of HC-MoS₂@GF is the lowest, which is much lower than those of HS-MoS₂@GF and HS-MoS₂, clearly demonstrating the highest electrochemical activity of HC-MoS₂@GF for energy storage. This result clearly validates that our 3D graphene-backed honeycomb-like MoS₂ architecture can not only ensure a high conductivity of the overall electrode but also largely enhance the electrochemical activity of MoS₂ anode materials during the cycle processes. It should attribute to its high surface area, massive porous hierarchical structure, highly conductive substrates directly as a current collector, and 3D interpenetrating structure as we expected.

Figure 5.5 a) The first 4 cycles CV curves of HC-MoS₂@GF at a scan rate of 0.2 mV s⁻¹, b) the first three charge and discharge curves of HC-MoS₂@GF at a current density of 100 mA h g⁻¹, c) cycling behaviors of the HC-MoS₂@GF, HS-MoS₂@GF and HS-MoS₂ electrodes at a current density of 200 mA h g⁻¹, d) cycling behavior of the HC-MoS₂@GF,

HS-MoS₂@GF and HS-MoS₂ electrodes at various current densities, e) schematic illustration of the additional active edge sites at the intersection of adjacent MoS₂ nanosheets and the fast transportation of electron in HC-MoS₂@GF, f) Nyquist plots of the HC-MoS₂@GF, HS-MoS₂@GF and HS-MoS₂ electrodes obtained by applying a sine wave with amplitude of 5 mV over the frequency range from 200 KHz to 0.01 Hz; the smallest circle diameter indicates the lowest of resistance in HC-MoS₂@GF electrode (magnified figure at the high frequency and the equivalent circuit model of the studied system, inset).

Table 5.1 The comparison of electrochemical performances for the three electrodes, HC-MoS₂@GF, HS-MoS₂@GF, and HS-MoS₂.

Electrode description	1st Specific capacity (mAh g ⁻¹)	1st Coulombic efficiency	Cycling stability (%)	Rate performance
HC-MoS ₂ @GF	1397 mAh g ⁻¹ at 100 mA g ⁻¹	82.9%	85.8 % after 60 cycles at 200 mA g ⁻¹	1172, 1095, 1007, 966 and 800 mAh g ⁻¹ at 200, 500, 1000, 2000 and 5000 mA g ⁻¹
HS-MoS ₂ @GF	1331 mAh g ⁻¹ at 100 mA g ⁻¹	78.5%	68.8 % after 60 cycles at 200 mA g ⁻¹	939, 828, 702, 586 and 442 mAh g ⁻¹ at 200, 500, 1000, 2000 and 5000 mA g ⁻¹
HS-MoS ₂	1302 mAh g ⁻¹ at 100 mA g ⁻¹	78.8%	51.5 % after 60 cycles at 200 mA g ⁻¹	843, 663, 532, 412 and 246 mAh g ⁻¹ at 200, 500, 1000, 2000 and 5000 mA g ⁻¹

The theoretical capacity of MoS₂ is only ~670 mAh g⁻¹ based on the conversion reaction (4 mol lithium ion can be reacted with 1 mol MoS₂). Here, the enhanced lithium ion storage properties and improvement of the high rate performance for HC-MoS₂@GF can be mainly attributed to the following reasons: First, the obtained honeycomb-like MoS₂ nanoarchitectures are homogenously anchored into the skeleton of GF with a close and robust physical contact. With this design, the substrate of highly electrical conductive GF as a current collector can ensure

fast electron and ion transportation for the unique honeycomb-like MoS₂ architecture. The direct contact and interconnection between GF and active materials not only provide the excellent ion transport from the electrolyte to the active material on GF but also from MoS₂ to the current collector (GF). Moreover, MoS₂ nanosheets assembly into honeycomb-like nanoarchitectures, which possess a high SSA of 182 m² g⁻¹ with massive mesopores and macropores. This can greatly enhance the electrolyte/electrode contact. The unique structure also holds the electrode integration and hence mitigates the aggregation and mechanical failure of the active materials after repeated lithiation/delithiation. In addition, the ultrathin nature of adjacent MoS₂ walls can effectively reduce the diffusion length of both electrons and ions. Besides, as shown in **Figure 5.5e**, there are numerous crossing points in the structure of honeycomb-like MoS₂ nanoarchitectures, indicating massive defect sites. It is speculated that those dislocations, vacancies, and distortions in the intersection of adjacent MoS₂ nanosheets can provide massive active sites for lithium ions and would be extended gradually, thereby facilitating more intercalation of lithium ions. Therefore, the unique honeycomb-like MoS₂ nanoarchitectures@GF exhibits exceptional high capacity, superior cyclic stability and high-rate capability which could be further explored for other energy storage/conversion applications. The typical mass loading of honeycomb-like MoS₂ nanoarchitectures grown on 3DGF is estimated to be 0.8~1.1 mg cm⁻². Higher energy density can be achieved by stacking such GF-supported active material electrodes to form a multilayer film, which can push such a promising electrode an important step forward into practical applications.

5.3 Conclusions

In summary, we have rationally designed a facile P123-assisted route to synthesize 3D honeycomb-like MoS₂ nanoarchitectures anchored into 3DGF. The as-obtained 3DGF provides a novel substrate for the nucleation and subsequent growth of honeycomb-like MoS₂ nanoarchitectures, in which the

hierarchical MoS₂ nanoarchitectures are well-defined by self-assembly of ultrathin nanosheets. This unique 3D honeycomb-like MoS₂ nanoarchitectures@GF exhibits greatly improved lithium ion storage capability owing to its high surface area, massive porous hierarchical structure, highly conductive substrates directly as current collector, and 3D interpenetrating structure. The 3D honeycomb-like structure of HC-MoS₂@GF displays a high discharge capacity of 1235.3 mAh g⁻¹ at a current density of 200 mA g⁻¹, retaining 85.8% of the initial reversible capacity after 60 cycles. These results clearly demonstrate the advantage of HC-MoS₂@GF. We believe that our 3D honeycomb-like MoS₂ nanoarchitectures@GF is very promising for further broad applications such as sensors, catalysis, and supercapacitors.

Chapter 6

MoS₂ Architectures Supported on Graphene Foam/Carbon Nanotube Hybrid Films for Lithium Ion Battery

In Chapter 6, light-weight, free-standing MoS₂ nanoarchitectures based anode electrodes have been successfully synthesized by growing 3D worm-like MoS₂ nanoarchitectures directly on graphene foam/carbon nanotube (GF/CNT) hybrid films. Herein the sp²-hybridized GF/CNT film provides a novel robust framework for the nucleation and subsequent massive growth of worm-like MoS₂ nanoarchitectures per unit area, while acts as an efficient current collector for binder-free electrodes. By comparison with samples grown on GF, it is demonstrated that this unique hierarchical MoS₂ electrode supported on GF/CNT may contribute the improved lithium-ion storage capability and cyclability due to the robust electrical contact, fast transportation of electrolyte ions, 3D interpenetrating structure and the strong bonding energy between active materials with CNT.

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6.1 Introduction

Ever-growing demand for LIBs with ultrafast charging and discharging rates has captivated the attention of many investigators in various applications such as portable electronic devices and electrical vehicles applications.^{2, 11, 62, 63} In particular, LIBs with high reversible capacity, stable cycle performance, capacitor-like rate performance and high energy density, highly desirable for next generation power sources of EVs, are known to be largely hindered by the lack of suitable electrode materials. Up to now, various electrochemically active materials made of carbonaceous material, metal oxides and metal sulfide have been developed for lithium storage. Especially, layered MoS₂ has been extensively investigated for anode materials of rechargeable LIBs because it can deliver a higher capacity (~670 mAh g⁻¹ with 4-electron transfer reaction per formula) than the commercial graphite material (372 mAh g⁻¹).^{15, 236, 237} Unfortunately, a large specific volume change commonly occurs during the cycling processes, resulting in the aggregation of active materials. Thus, the capacity fading and poor rate performance of MoS₂ anode are still the main challenges.

To address these above issues, various strategies have been developed to enhance the electrochemical performance of MoS₂ or MoS₂ composites by using nanotechnologies⁹⁴, heterostructures²³⁸⁻²⁴⁰, and carbon materials as the conductive matrix.^{131, 241} Especially, the sp²-hybridized carbon nanomaterials (e.g. 1D CNTs and 2D graphene) are the most promising matrix due to superior mechanical strength, electrical conductivity, and extraordinary adaptability to different interfacial processes.^{179, 242, 243} In these systems, decent electrochemical performance has been demonstrated. Excellent cycling performance has been achieved by embedding single-layered ultrasmall MoS₂ nanoplates in electrospun CNFs.¹³¹ Ultrathin MoS₂ nanosheets grown on N-doped graphene sheets have been reported to deliver excellent cyclic stability and high-rate capability.⁹⁶

However, in all these works, MoS₂ or MoS₂ composites are in the form of powders and therefore conductive additives and binders are always required.

Recently, an emerging new concept has been exploited to enhance the energy per foot-print area by directly growing electroactive nanostructures on various substrates, especially 3D porous carbon materials as integrated electrodes for LIBs. Superior electrochemical performance has been achieved by constructing 3D porous interconnected nanocomposites with zero-dimensional (0D) MoS₂, 1D CNTs, and 2D graphene on stainless steel or Ni foam. However, the typical loading mass was only around 0.5 mg cm⁻². 3DGF and carbon nanotube (CNT) film have been regarded as excellent backbones for loading MoS₂ nanoparticles due to their lightweight and high conductivity.²⁴³⁻²⁴⁵ However, CNTs prefer to form bundles and graphene sheets tend to agglomerate and clump together, leading to their limited external accessible surface area for ions and electrolyte. GF is usually brittle and can hardly support massive active materials. Compared with their single components, graphene/CNT hybrid films have shown improved physical and chemical properties, including enhanced electrical conductivity and mechanical flexibility, due to the synergistic effects.²⁴⁶⁻²⁵⁰ Moreover, graphene/CNT hybrid films provide increased active surface area for the growth of active materials, leading to the increased areal loading but without aggregation and sacrificing a good electrical contact between the graphene and CNTs.^{179, 242} Nonetheless, there is no report on the integrated MoS₂ architectures directly supported on flexible graphene/CNT hybrid films.

In this paper, we present an alternative route to construct few-layer MoS₂ hierarchical architectures on hybrid films consisting of 1D CNTs supported on 3D GF, which is denoted as GF/CNT. The obtained samples, 3D hierarchical MoS₂ architectures supported on GF/CNT substrates are denoted as MoS₂@GF/CNT. This rational design has the following merits: First, GF/CNT acts as both a lightweight scaffold for the growth of 3D MoS₂ architectures and an efficient current collector, which provides fast pathways for electron transportation. Second, the nanoworm-like architectures built from

interconnected nanosheets effectively inhibit the aggregation of MoS₂ architectures, while the ion reservoir induced by the void space between sheet-like subunits facilitates the transportation of electrolyte ions, and accommodates the volume change during charge/discharge process. Moreover, the ultrathin nature of MoS₂ nanosheets can effectively reduce the diffusion length of both electrons and ions. Third, the strong adsorption effects between MoS₂ and CNT can provide an energetically favored process for boosting the vast growth of MoS₂ nanosheets onto CNT and immobilizing them, in favor for an increased areal loading but without aggregation, which can be verified through first-principle *ab initio* calculations and experimental results. The flexible MoS₂@GF/CNT electrode gives a higher mass loading of $\sim 3 \text{ mg cm}^{-2}$, compared to that of MoS₂@GF electrode prepared with the same condition. Higher areal mass loading of battery electrode materials is preferred which can reduce the number of manufacturing steps for achieving the same total energy and also lower the separator cost. With these merits, our MoS₂@GF/CNT electrode exhibits high reversible capacity, superior high-rate capability and excellent cycling stability.

6.2 Results and Discussions

The fabrication process of the MoS₂@GF/CNT electrode is depicted in **Section 3.1.3**. The catalyst-assisted CVD-derived GF/CNT is directly employed as 3D light-weight frameworks for the growth of hierarchical MoS₂ architectures, which are achieved by a hydrothermal reaction between Na₂MoO₄ and TAA with the help of the surfactant P123. The 3D MoS₂ architectures are anchored into the skeleton of GF/CNT films by spontaneous self-assembly of MoS₂ nanosheets. The mass of MoS₂ in the 3D architectures is calculated by weighting the obtained sample before and after the reaction. It should be noted that the as-prepared MoS₂@GF/CNT was directly employed as the electrode of half-cells for tests without conducting carbon, polymer binder and current collector. **Figure 6.1** shows the morphology and microstructure of GF and GF/CNT. The weight fractions of MoS₂ in the obtained electrodes can be rationally controlled by

adjusting the concentration of the reactants (Na₂MoO₄ and TAA) using the GF/CNT films with nearly the same area (**Figure 6.2**). We can clearly see the loading of MoS₂ nanosheets on GF/CNT films increasing with the concentration of the reactants.

Figure 6.1 SEM images of GF (a), (b) and (c), and TEM image of GF (d). SEM of the CNT-GF (e), (f), (g) and (h) TEM of the CNTs. Inset in (h) shows the FFT pattern taken from the marked area.

Figure 6.2 SEM images of samples prepared with different concentration of reactants: (a) and (b) the MoS₂@GF/CNTs sample prepared with 1.33 mg ml⁻¹ of TAA and 0.67

mg ml⁻¹ of sodium molybdate. (c) and (d) the MoS₂@GF/CNTs sample prepared with 2 mg ml⁻¹ of TAA and 1 mg ml⁻¹ of sodium molybdate.

Figure 6.3 (a-c) Top-view FESEM images of self-supported MoS₂@GF/CNT electrodes. (d-e) Cross-sectional images of MoS₂@GF/CNT branch. (f-g) Typical FESEM images at high magnification. (h) and (i) XRD pattern and Raman spectra of MoS₂@GF/CNT and GF/CNT composites.

The morphology and phase of the as-prepared MoS₂@GF/CNT were systematically investigated by FESEM and XRD. The obtained sample can be bent or fold without any protective case and will neither break, nor will the nanosheet layer peel off during repeated bending or folding. Hence, MoS₂@GF/CNT can be directly employed as a freestanding electrode without the need of conventional binders, conductive additives, and metallic current collectors. **Figures 6.3a and b** show the 3D network morphology with branches of 60–100 μm and macropores of 150–500 μm. The further well-defined interconnected network structure is shown in **Figure 6.3c**, where the GF is uniformly covered with a layer of MoS₂@CNT nanoworm-like architectures. In

addition, the corresponding cross-sectional images reveal that MoS₂@CNT architectures are grown on the outer and inner surfaces of GF backbones as shown in **Figures 6.3d-e**. From SEM images at high magnification (**Figure 6.3f**), we can clearly see the highly interconnected and porous 3D nanoworm-like architectures built from numerous ultra-thin MoS₂ nanosheets branching uniformly on CNT surface. Further investigations show that the building block nanosheets with lateral sizes of ~100 nm are randomly continuous and interconnected with each other, forming a highly porous nanonoworm-like morphology (**Figure 6.3g**). We consider that this internal cross-linked structure would effectively restrain both lamellar aggregation and mechanical failure (leading to the disconnection of active materials from the current collector) after repeated charge/discharge processes, and hence can efficiently maintain the long-standing existence of nanosheets and good electrical contact. Besides, the interconnected nanosheets form a large number of voids between each other, with sizes from 50 nm to several hundred nm, which are possibly derived from the self-assembly process. These internal voids between sheet-like subunits serve as an “ion reservoir” to allow for an easy diffusion of electrolyte ions, while accommodating the volume change during lithiation/delithiation.

During the reaction, the growth of MoS₂ sheets is found to be favorably selective on GF/CNT, with little free particle growth in solution. Obviously, GF/CNT provides a novel substrate for the nucleation and subsequent growth of MoS₂ crystals. The selective growth of MoS₂ on GF was attributed to the interactions between functional groups of GF/CNT and MoO₄²⁻ precursors with the help of surfactant P123. The amphiphilic P123 triblock copolymer can bond with the functional groups of GF/CNT, which was created after plasma treatment. The possible reaction on the surface of GF/CNT may be expressed as follows:

The XRD patterns of the bare GF/CNT and MoS₂@GF/CNT composites are displayed in **Figure 6.3h**. The as-grown GF/CNT substrates show a typical diffraction peak at 26.5 °, corresponding to the (002) reflection of graphitic carbon, respectively (JCPDS card no. 75-1621). The highly crystalline structure of GF/CNT is very favorable for the electron transfer and ion diffusion. By comparison, the detected peaks at $2\theta=14.1, 32.3, 39.4$ and 58.7° in the pattern of MoS₂@GF/CNT composites can be assigned to the (002), (100), (103) and (110) planes in the hexagonal phase MoS₂ ($a=b=0.316$ nm, $c=1.230$ nm, JCPDS card no. 37-1492). Raman spectroscopy was employed to further investigate the structures of the bare GF/CNT and MoS₂@GF/CNT composites (**Figure 6.3i**). The two characteristic peaks at 1580 and 2720 cm⁻¹ correspond to the G and 2D bands, respectively. The 2D/G intensity ratio as well as the absence of the D peak at 1350 cm⁻¹ in the spectrum of GF suggests the high quality of GF/CNT before MoS₂ growth. In comparison, the appearance of the D band at 1350 cm⁻¹ after MoS₂ growth is an indication of the presence of sp³ bonding which in turn shows a strong coupling between the MoS₂ and the GF/CNT scaffold. The MoS₂@GF/CNT composites have two obvious peaks at 383 cm⁻¹ and 405 cm⁻¹, which correspond to E_{2g}¹ and A_g¹ Raman modes of MoS₂, respectively.

The detailed microstructure of MoS₂@GF/CNT electrodes was further studied by TEM and high-resolution TEM (HRTEM). The MoS₂@GF/CNT composites were sonicated in ethanol for 30 min, which were then dropped onto a TEM grid and dried at ambient conditions. **Figures 6.4a** and **b** show the typical TEM images of MoS₂ branch anchored into CNTs. Most of the building blocks in hierarchical nanostructures are 3~5 layers of MoS₂ as displayed in **Figure 6.4c**. Typical lamellar structure with a different interlayer spacing of 0.67 and 0.69 nm can be observed from the HRTEM image (**Figure 6.4d**). The inset FFT pattern in the inner square area reveals the orientation of layers along the [002] direction of CNTs (**Figure 6.4d**). Interplanar spacing of 0.35 nm can also be observed, which is in good consistency with the d spacing of (002) planes of CNTs. To further reveal the elemental distribution in individual single hybrid nanotube of

MoS₂@GF/CNT, scanning TEM-based energy dispersive spectroscopy (STEM-based EDX) was used to obtain line scans and mapping analysis, shown in **Figures 6.4e-i**, unambiguously demonstrating CNT-core/MoS₂-branch hierarchical structure. EDX spectrum is consistent with the mapping result shown in **Figure 6.4j**.

Figure 6.4 (a) and (b) Low-magnification TEM image of MoS₂ architectures@GF/CNT foam. (c) and (d) HRTEM images of MoS₂ nanosheets anchored into CNTs. Inset in

Figure (d) shows the FFT pattern taken from the marked area. (e-h) Dark field TEM image of MoS₂ nanosheets@GF/CNT and corresponding elemental mapping images of C, Mo and S. (i) and (j) HR-EDX line profile across MoS₂ nanosheets@GF/CNT with an individual ~80 nm diameter and corresponding EDX spectrum.

Figure 6.5 XPS spectra of a) Mo 3d and S 2s peaks, and b) S 2p peaks. c) N₂ adsorption/desorption isotherms, and d) corresponding pore size distribution of MoS₂ architectures@GF/CNT.

XPS was used to investigate the chemical states of Mo and S in MoS₂@GF/CNT composites as shown in **Figures 6.5a** and **b**. The peaks of Mo 3d_{3/2} and Mo 3d_{5/2} are located at binding energies of 232.5 and 229.3 eV, respectively, which are the characteristic peaks of Mo⁴⁺ in MoS₂. The S 2p peaks at 162 and 163.2 eV are attributed to S²⁻ of MoS₂.²²² Full nitrogen adsorption/desorption isotherms of MoS₂@GF/CNT composites were measured to obtain the information of the pore size distribution and SSA. As shown in **Figure 6.5c**, a type-IV isotherm with a type-H3 hysteresis loop in the relative pressure range of 0.45-1.0 P/P₀ indicates the presence of the mesoporous structure. Accordingly, the SSA is calculated to be 168 m² g⁻¹ via the BET method. The pore size distribution derived from the

BJH method is given in the inset of **Figure 6.5d**. The sharp peak at 34.1 nm is attributed to mesoporous channels in MoS₂@GF/CNT architectures. Besides, the sharp peak at 124.8 nm corresponds to macropores. Such a high SSA of MoS₂@GF/CNT composites with massive mesopores and macropores could be desirable for energy storage application or other applications. These mesopores and macropores in the 3D MoS₂@GF/CNT architectures can serve as an "ion and electrolyte reservoir" to facilitate the transportation of electrolyte ions, and can also buffer the volume change to prevent mechanical failure for superior stability and cyclability.

Figure 6.6 FESEM images (a and b) of MoS₂ blanket-like architectures grown on GF substrate (fine structures in the inset of Figure a). (c) TEM images of MoS₂@GF. The insets show a SAED pattern. (d) HRTEM images of MoS₂@GF. The inserted HRTEM image with d-space of 0.66 nm is enlarged regions of the dashed circles.

In strong contrast, highly interconnected blanket-like architectures built from numerous MoS₂ nanosheets are uniformly distributed on GF, in the absence of

CNTs (**Figure 6.6a** and **b**). The inset of **Figure 6.6a** reveals the 3D network morphology of MoS₂@GF with branches of 60–100 μm . Further investigations show that the building nanosheets have lateral sizes of ~ 100 nm, and they are randomly connected with the adjacent nanosheets to self-assemble into continuous and porous blanket-like architectures on GF, which shows a SSA of $28.9\text{ m}^2\text{ g}^{-1}$ as in **Figure 6.7**. A typical TEM image in **Figure 6.6c** shows the intrinsic wrinkles or corrugations of MoS₂ nanosheets distributed on GF. The SAED pattern in the inset of **Figure 6.6c**, clearly demonstrates a polycrystalline structure of MoS₂. Typical lamellar structure with an interlayer spacing of 0.66 nm can be observed from the HRTEM image (**Figure 6.6d**). The typical layer number of MoS₂ sheets is 3–5. The typical mass loading of MoS₂ nanosheets on GF prepared with the same synthesis process is only $\sim 0.5\text{--}0.8\text{ mg cm}^{-2}$. In contrast, the typical mass loading of nanoworm-like MoS₂ architectures grown on GF/CNT is estimated to be $\sim 3\text{ mg cm}^{-2}$. The obvious morphological difference and areal loading of active materials highlight the important role of GF/CNT films as a novel framework in mediating the growth of nanomaterials.

Figure 6.7 N₂ adsorption/desorption isotherms, and the insert corresponding pore size distribution of MoS₂@GF composites prepared with 2.67 mg ml^{-1} of Na₂MoO₄ and 1.33 mg ml^{-1} of TAA.

The electrochemical properties of MoS₂@GF/CNT were further evaluated. MoS₂@GF/CNT was directly used as the electrode of half-cells for tests without conducting carbon, polymer binder and the current collector. As a control experiment for comparison, MoS₂@GF electrode was also employed as the testing electrode. The CV curves of MoS₂@GF/CNT during the first 4 cycles are presented in **Figure 6.8a**. During the first cycle, there are two reduction peaks located at 0.4 and 0.9 V and two oxidation peaks located at 1.8 and 2.3 V. The reduction peak at 0.9 V can be attributed to Li insertion into the interlayers of MoS₂, accompanied by phase transformation from 2H to 1T structures of Li_xMoS₂. The second obvious reduction peak at 0.4 V corresponds to the reduction of Li_xMoS₂ to Mo metal and Li₂S, which is based on the following conversion reaction:^{186, 251-263}

The oxidation peak at 1.8 V can be ascribed to partial oxidation of Mo to form MoS₂ due to the defect sites. The following distinct peak located at 2.3 V is associated with the oxidation of Li₂S to S. After the first cycle, the electrode is mainly composed of Mo and S instead of the initial MoS₂. The dominant reduction peak at 1.8 V is well known in lithium-sulfur batteries and is attributed to the formation of Li₂S, and the smaller peak at 1.1 V can be the conversion of residual S₈²⁻ to Li₂S.^{97, 234} Accordingly, the oxidation peak at 2.3 V is related to the oxidation of Li₂S to S. The shape of CV curve and the oxidation/reduction peaks can still retain, indicating the good stability of the electrochemical process after several cycles.

Figure 6.8b displays the representative charge/discharge profiles of MoS₂@GF/CNT at a current density of 100 mA g⁻¹. In agreement with the CV curves, two potential plateaus at around 1.1–1.4 V and 0.6 V can be observed during the first discharge (lithiation) process. The former was attributed to the Li insertion reaction that led to the formation of Li_xMoS₂, whereas the latter at 0.6 V was related to a conversion reaction of MoS₂ to Mo particles. The

MoS₂@GF/CNT electrode delivers initial discharge and charge capacities of 1568 and 1252 mAh g⁻¹, respectively, giving a Coulombic efficiency of 79.8%. However, the bare GF/CNT electrode can only deliver initial discharge and charge capacities of 592 and 294 mAh g⁻¹, respectively (**Figure 6.9a** and **b**), which is almost the similar level as that of GF electrode (see **Figure 6.9c** and **d**). Such high initial lithium storage may be attributed to the unique 3D graphene-backboned nanoworm-like MoS₂@CNT architectures. The ICL of around 300 mAh g⁻¹ is mainly due to the irreversible process such as the formation of the SEI layer, the electrolyte decomposition and reduction of oxygen-containing groups. The Coulombic efficiency rapidly reaches more than 99% after the second cycle. The second and third discharge profiles are almost coinciding with each other, exhibiting excellent cycling performance. The potential plateaus at 1.8 V and 1.1 V (**Figure 6.8b**) are also in agreement with the two peaks of the CV curves in **Figure 6.8a**. The cycling performance is also outstanding: even after 120 cycles, both the discharge and charge capacities of the MoS₂@GF/CNT electrode are stable at about 1112 mAh g⁻¹ at the current density of 200 mA g⁻¹, delivering nearly 81.3% capacity retention (**Figure 6.8c**). In contrast, the MoS₂@GF electrode shows continuous and progressive capacity decay under the same testing conditions. After 120 cycles, MoS₂@GF electrode only delivers a capacity of 766 mAh g⁻¹. The excellent rate retention of MoS₂@GF/CNT is shown in **Figure 6.8d**. The specific capacities of 1064 and 1006 mAh g⁻¹ can be maintained at high rates of 1 and 2 A g⁻¹, respectively. Even cycled at a high current of 5 A g⁻¹, the specific capacities of 823 mAh g⁻¹ can be maintained. Remarkably, these values are much higher than that of MoS₂@GF (565 mAh g⁻¹). Moreover, after deep cycling at 5 A g⁻¹, the specific capacity is recovered to the same levels as the previous measurement when the current is returned back to 100 mA g⁻¹. Even after 120 cycles at a high current density of 1 A g⁻¹, the discharge capacity can be stabilized at 936.3 mAh g⁻¹ as shown in **Figure 6.10c**. Indeed, the TEM image of the MoS₂@GF/CNT electrode after cycling shows that the clusters of active material are still anchored on CNT (shown in **Figure 6.10d**).

A complete comparison of electrochemical properties of these two samples, summarized in **Table 6.1**, shows that MoS₂@GF/CNT possesses excellent electrochemical properties, including high initial Coulombic efficiency, high specific capacity, high rate performance and stable cyclability.

Figure 6.8 Electrochemical characterization of the MoS₂@GF/CNT electrode as the cathode of LIBs: (a) The first 4 cycles CV curves at a scan rate of 0.2 mV s⁻¹, b) the first three charge and discharge curves at a current density of 100 mAh g⁻¹, c) cycling behaviors at a current density of 200 mAh g⁻¹, d) cycling behavior at various current densities, e) Nyquist plots over the frequency range from 200 KHz to 0.01 Hz. (the equivalent circuit model of the studied system, inset), f) Schematic illustration of convenient electrolyte ions diffusion and fast transportation of electron in MoS₂ architectures@GF/CNT electrode.

To gain better insight into the reason of the unique 3D graphene-backboned nanoworm-like MoS₂@CNT architectures for boosting lithium storage, we performed EIS for both electrodes as shown in **Figure 6.8e**. Obviously, the diameter of the semicircle for the MoS₂@GF/CNT in the high-medium frequency region is smaller than that of MoS₂@GF, which indicates that MoS₂@GF/CNT possesses the lower contact and charge-transfer resistances. The kinetic differences of both MoS₂ electrodes were further investigated using the R–C equivalent circuit. The high and medium frequency semicircle in **Figure 6.8e**

could be attributed to the resistance R_{sf} and CPE1 of the SEI film, the medium frequency semicircle to the charge transfer resistance of the electrode reaction R_{ct} and CPE2 of the electrode-electrolyte interface, and the inclined line in the low-frequency region to lithium-ion diffusion processes. R_{sf} and R_{ct} can be obtained by fitting data according to the equivalent circuit model in **Figure 6e**. R_{sf} and R_{ct} of MoS₂@GF/CNT electrode are 4.32 and 12.35 Ω , respectively, which are much lower than those of MoS₂@GF (R_{sf} =8.75 and R_{ct} =28.64 Ω). For both samples, the solution resistances are almost the same due to the same electrolyte testing system. In contrast, the charge transfer resistance of MoS₂@GF/CNT is much lower than that of MoS₂@GF, clearly demonstrating a better electrochemical activity of MoS₂@GF/CNT for lithium-ion storage. This result clearly validates that nanoworm-like MoS₂ architectures based on GF/CNT hybrid films not only ensure a high electrical conductivity of the overall electrode, but also remarkably enhance the electrochemical activity of MoS₂ anode during the cycle processes.

Figure 6.9 (a) Charge and discharge curves and (b) cycling behavior of pure GF at a current density of 200 mAh g⁻¹. (c) Charge and discharge curves and (d) cycling behavior of pure GF/CNT at a current density of 200 mAh g⁻¹.

Figure 6.10 Charge and discharge curves of (a) MoS₂@GF/CNT and (b) MoS₂@GF at different C-rates. (c) Cycling behaviors of MoS₂@GNF at current densities of 1000, 2000 and 5000 mAh g⁻¹.

Therefore, it is not difficult to understand the reason for the enhanced lithium ion storage and improved high rate performance of MoS₂@GF/CNT, which has the several well-known characteristics: (a) The unique nanoworm-like MoS₂ architectures are homogenously anchored into the skeleton of GF/CNT with a close and robust physical contact, which provides fast electronic conduction channels and ensures the individual MoS₂ nanosheets electrically connected during charge/discharge cycles. (b) The large internal void between sheet-like subunits serves as an “ion reservoir” to allow for an easy diffusion of electrolyte ions and high contact between MoS₂ nanosheets and electrolyte, while also accommodating the volume change during lithiation/delithiation. Hence, this 3D interpenetrating structure not only provides an excellent ion transport from the electrolyte to active materials on GF/CNT, but also from active materials to the current collector, as shown in **Figure 6.8e**.

Table 6.1 The comparison of electrochemical performances for two electrodes, MoS₂@GF/CNTs, and MoS₂@GF.

Electrode description	1st Specific capacity (mAh g ⁻¹)	1st Coulombic efficiency (%)	Cycling stability (%)	Rate performance
MoS ₂ @GF/CNTs	1568 mAh g ⁻¹ at 100 mA g ⁻¹	79.8%	1125 mAh g ⁻¹ after 80 cycles at 200 mA g ⁻¹	984, 927 and 820 mAh g ⁻¹ at 1000, 2000 and 5000 mA g ⁻¹
MoS ₂ @GF	1502 mAh g ⁻¹ at 100 mA g ⁻¹	65.2%	798 mAh g ⁻¹ after 80 cycles at 200 mA g ⁻¹	713, 664 and 565 mAh g ⁻¹ at 1000, 2000 and 5000 mA g ⁻¹

Figure 6.11 Cross-section illustration of MoS₂ cluster bonding with (a) graphene and (b) CNT.

In addition to the above two significant merits for boosting LIB performance, the most striking feature of our MoS₂@GF/CNT architectures is that GF/CNTs films provide an ideal interface for boosting vast MoS₂ growth (with a loading of 3 mg cm⁻²) and fast electronic conduction transportation for active materials (lower resistance). In order to better understand the interesting CNT and graphene interfaces on immobilizing MoS₂, we performed first-principle DFT using Vienna Ab-initio Simulation Package (VASP) to explore the adsorption energy

of MoS₂ on the surface of graphene and CNT. For the molecule-surface interaction, we calculate the adsorption energy based on the equation: $E_{ab} = (E_{total} - E_G - E_{MoS_2-C})/n$, where E_{total} , E_G and E_{MoS_2-C} denote the total energies of the calculated system, graphene nanosheet (CNT) and MoS₂, respectively, and n is the number of MoS₂ units. For the calculation, the same numbers of MoS₂ and C atoms are used in the calculated models, where contains 20 MoS₂ units and 216 carbon atoms. The cross-section illustration of MoS₂ bonding with graphene and CNT is shown in **Figure 6.11**. Here, we calculated adsorption energies of MoS₂ on the surfaces of CNTs with the various chiral indices ((10, 10), (12, 12), (15, 15), (18, 18) and (25, 25)). The calculated adsorption energies of MoS₂ at various active sites of graphene and CNT with different diameters are listed in **Table 6.2**. The results indicate the CNTs have stronger adsorption energy with MoS₂ compared to graphene. Based on the fitted function relationship between the adsorption energies and diameters of CNT (**Figure 6.12**), it is found that the CNTs with smaller diameters have stronger adsorption energy with MoS₂. In our study, the typical diameters of CNTs vary between 20 and 80nm, and the calculated adsorption energies of MoS₂ on CNTs are nearly close to -18.98 meV, which is stronger than that on graphene (-18.7 meV). Obviously, it is found that MoS₂ preferentially adsorbs on CNT rather than graphene, demonstrating an evident synergistic effect in the MoS₂@GF/CNT electrode. Actually, the experimental results (the higher areal loading of MoS₂ on GF/CNT) can also support our calculation results. The Raman result of the appearance of the D band at 1350 cm⁻¹ after MoS₂ growth on GF/CNT verifies the presence of sp³ bonding indicating a strong coupling between the MoS₂ and the GF/CNT scaffold. Also, we compare the Raman spectra of E_{2g}¹ and A_{1g} modes of MoS₂@GF/CNT (**Figure 6.13**). Blue shifting of 3~5 cm⁻¹ for A_{1g} and E_{2g}¹ modes can be observed in the sample of MoS₂@GF/CNT, which also verifies the strong coupling between MoS₂ and CNT (or GF), resulting in the structure changes of MoS₂ nanosheets. Blue shifting is mainly due to the change of the force constant resulted from the change of the interlayer Van der Waals force in MoS₂ layers

(for A_{1g} mode) and the structure changes or long-range Coulombic interlayer interactions (for E_{2g}¹ mode).²⁵¹ Herein, GF/CNTs provide an ideal interface with the strong adsorption effects for vast growth of MoS₂ nanosheets without aggregation, which effectively enhance the stability of active materials. Therefore, a close and robust conductive contact between MoS₂ and CNTs, and the strong coupling between graphene and CNTs render the intact wire-up framework during the repeated charge and discharge processes, resulting in the maximization of synergistic interaction.

Figure 6.12 The relationship between the adsorption energies and diameters of CNTs.

Figure 6.13 The Raman spectra of E_{2g}¹ and A_{1g} modes of (a) the MoS₂@GF taken at different five points and MoS₂ nanosheets.(b) the MoS₂@GF/CNT taken at five different points and MoS₂ nanosheets.

Table 6.2 Calculated adsorption energies of MoS₂ cluster at various active sites of Graphene and CNT with different diameters. For all calculated models, one unit contains 20 MoS₂ units and 216 carbon atoms.

Sample		Active site	Diameter (nm)	Adsorption energy E _{ab} (meV)
CNT with different diameters	(10, 10)	T	1.3597	-24.2
	(12, 12)	T	1.6272	-22.9
	(15, 15)	T	2.0328	-21.2
	(18, 18)	T	2.44	-20.1
	(25, 25)	T	3.38	-19.1
Graphene		H	–	-18.7

6.3 Conclusions

In summary, we have designed and successfully fabricated nanoworm-like MoS₂ architectures@GF/CNT as self-supported, binder-free anode electrodes. The rational sp²-hybridized 3D GF/CNT provides a novel substrate for the nucleation and massive growth of nanoworm-like MoS₂ architectures, which are well-defined by self-assembly of ultrathin nanosheets. Also, the highly integrated frameworks can provide an ideal conductive contact between MoS₂ and CNT, resulting in the maximization of synergistic interaction. Such unique MoS₂@GF/CNT architectures with robust interface synergistic effect make it as a new class of anode materials for developing LIBs with very high energy and power densities as well as extremely high cyclability. High discharge capacities of 1368 mAh g⁻¹ and 823 mAh g⁻¹ at current densities of 200 mA g⁻¹ and 5 A g⁻¹ are achieved, which can retain 81.3% of the initial reversible capacity after 120 cycles. These results clearly demonstrate the strong synergistic effect of

MoS₂@GF/CNT. The DFT calculations reveal the existence of the strong absorption energy between MoS₂ and CNT, which can provide energetically favored processes for boosting the vast growth of MoS₂ nanosheets onto CNT and maintaining the electrode integration during the repeated charge and discharge processes. The technique demonstrated here can be easily used with other batteries chemistry with higher energy density and power density. This work also offers a facile and ingenious design concept to combine the sp²-hybridized GF/CNT films with nanostructured materials, which can be readily generalized to other materials, to build multifunctional flexible electrodes for a large spectrum of device applications.

Chapter 7

MoS₂ Nanosheets Decorated Ni₃S₂@MoS₂ Coaxial Nanofibers for Enhanced Sodium-Ion Storage

The performance of SIBs is inherently determined by the properties of electrode materials. The high performance of electrode materials relies largely on the scrupulous design of nano-architectures and smart hybridization of bespoke active materials. It is fundamentally important for establishing a relationship between the structure and the electrochemical performance. Herein, we developed a novel synergistic Ni₃S₂-MoS₂ core-shell nanofiber superstructure on 3D Ni/GF by a PVP-assisted solution reaction. Such core-shell nanofibers possess the homogeneous heterointerface with porous configuration, rendering the maximization of synergistic interaction. This unique structure results in very high specific capacity and rate capability as well as extremely long-term cycle stability when used as anode electrode of SIBs. The strategy proposed in this part can be extended to the synthesis of other hybrid superstructures for energy storage devices.

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7.1 Introduction

LIBs have been intensively employed in portable electronic devices and are anticipated to power EVs. The idea of SIBs as alternative technologies of LIBs was initially pushed by the cost considerations.^{9, 252, 253} Nowadays, SIBs have drawn much attention with their prominent advantages of the low cost, the abundant Na reserves, and negative redox potential (−2.71 V vs SHE). Nevertheless, due to the larger radius of Na⁺ than Li⁺, it is a challenge to search suitable anodes to host Na⁺ with high capacity and long-term cycle stability, which handicaps the practical utilization of SIBs. Graphite as the conventional anode of LIBs, has been proved to be not appropriate to host Na⁺ due to the lack of the formation of staged intercalation compounds between Na and graphite. Although some achievements have been made using hard carbon as anode materials, the rate capability and cycling stability are not satisfactory.^{109, 111, 114}

2D layered metal sulfides with similar structures to graphite, such as MoS₂, WS₂, SnS and SnS₂, have been widely investigated as promising anodes for SIBs, due to their open framework facilitating the insertion of Na⁺ reversibly with acceptable mobility.^{222, 254, 255} In particular, graphene-like MoS₂ has a large interlayer spacing along c-axis to accommodate foreign ions. Therefore, it is an ideal candidate as high-capacity anode materials for LIBs and SIBs. Unfortunately, MoS₂ is impeded by its inherent limitations. Usually, the excess surface free energy and weak van der Waals interactions drive it to restack for minimizing the surface energy.^{243, 256, 257} Besides, the mechanical stress deriving from the huge volume variation during sodiation/desodiation, results in the aggregation of active materials, finally causing capacity loss and cycling decay.

The enhanced electrochemical performance is not only determined by the intrinsic characteristics of electrode materials, but also the scrupulously designed nanostructures and smart hybridization of bespoke active materials.^{18, 19, 27, 30-35} Some newly rising 2D MoS₂-based heterostructures such as MoS₂/graphene, MoS₂/WS₂, MoS₂/CoSe₂, MoS₂/Fe₃O₄ and MoS₂/TiO₂ have demonstrated

incredible properties, which are very difficult to achieve in a single system.¹⁹⁻²² Despite these strategies can combine different components in a hierarchical structure with an increased active surface area, these designed heterostructures usually suffer from inhomogeneous interface/chemical distributions, a brittle contact on the heterointerfaces and significant mechanical failure during charge/discharge cycling. A key challenge in this direction is to build up a smart architecture, in which structural features and electroactivities of every component are fully manifested; the heterointerfaces are homogeneously wrapped up with every individual component, providing large interfacial areas; an increased active surface area for fast ion/electron transportation is guaranteed. To date, few studies have reported hierarchical heterostructures for SIBs with excellent high-rate and cycle performances. To overcome these shortcomings, our hypothesis is to develop heterostructures, which provides (i) homogeneous heterointerfaces for large interfacial areas and the maximized synergetic effect; (ii) direct and rapid ion/electron transport pathways and (iii) adequate electrode-electrolyte contact and short sodium ion diffusion distance comparing with other nanostructures.

Herein, to well circumvent these issues on heterostructures for SIBs, we firstly report a fabrication of a new kind of synergistic Ni₃S₂-MoS₂ hybrid nanofiber architectures, via one-step PVP-assisted hydrothermal process. In the hybrid architectures, elongated Ni₃S₂ nanofibers are wrapped up by MoS₂ nanobelts to form core-shell Ni₃S₂-MoS₂ nanofibers with a homogenous heterointerface, which are further uniformly decorated with few-layer MoS₂ nanosheets. The obtained hybrids manifest highly porous hierarchical structure with a homogeneous atomic heterointerface, which is denoted as MoS₂/Ni₃S₂@MoS₂. As a proof-of-concept, SIBs based on MoS₂/Ni₃S₂@MoS₂ hybrid nanofiber architectures, exhibit high-rate capacity and ultralong-cycling life. The correlation between the heterostructure and electrochemical performance is well discussed in this paper, providing fundamental understanding on the rational design of heterostructures as high-performance anodes for SIBs. This protocol to synthesize heterostructures with an ideal heterostructure can be applied to other

systems, providing a new strategy to develop advanced hybrid superstructures for energy storage devices.

For MoS₂/Ni₃S₂@MoS₂ nanofibers, the total mass of the active materials includes the mass of MoS₂ and Ni₃S₂. The mass of Ni₃S₂ and MoS₂ can be exactly calculated by a FeCl₃ etching method. In a typical experiment, the obtained MoS₂/Ni₃S₂@MoS₂ electrode was immersed in a mixed solution of FeCl₃ (1M) and HCl (0.5M) for 48 h. Then, the Ni foam can be removed according to the reaction: $\text{Ni} + 2\text{FeCl}_3 \rightarrow \text{NiCl}_2 + 2\text{FeCl}_2$. Meanwhile, the Ni₃S₂ can be oxidized to NiS₂ according to the reaction: $\text{Ni}_3\text{S}_2 + 4\text{FeCl}_3 \rightarrow \text{NiS}_2 + 4\text{FeCl}_2 + 2\text{NiCl}_2$, which can also be demonstrated by the XRD patterns and TEM images of the electrode after etched in a solution of FeCl₃. Therefore, the calculation of Ni₃S₂ and MoS₂ is described as following: A circular electrode (MoS₂/Ni₃S₂@MoS₂ nanofibers supported on Ni/GF) with a diameter of 12 mm was immersed in a solution of 1M FeCl₃ and 0.5 M HCl for 48 h. The weight decrement (x mg) can be directly calculated by weighting the electrode before and after etched, which includes the residual Ni foam and the loss of the element Ni from Ni₃S₂ to NiS₂ ($0.488 \cdot m(\text{Ni}_3\text{S}_2)$). Another circular Ni/GF disk with the same size was immersed in a mixed solution of 1M FeCl₃ and 0.5M HCl for 48 h. The weight of Ni foam (y mg) can be directly calculated by weighting the obtained sample before and after reaction etched in a solution of FeCl₃, which is equal to the element Ni in the electrode (MoS₂/Ni₃S₂@MoS₂ nanofibers supported on Ni/GF), including the residual Ni foam and the element Ni in Ni₃S₂ ($0.732 \cdot m(\text{Ni}_3\text{S}_2)$). Then, the mass of Ni₃S₂, $m = (y - x) \text{ mg} \times M_{\text{Ni}_3\text{S}_2} / M_{\text{Ni}} = (y - x) \text{ mg} \times (240 / 58.8) = 4.08 \cdot (y - x) \text{ mg}$, where M is the molecular weight or atomic weight. The mass of MoS₂ can be calculated by divided the mass of Ni/GF and Ni₃S₂ from the mass of MoS₂/Ni₃S₂@MoS₂ nanofibers. In order to get an accurate data, we always calculated the weight of MoS₂ and Ni₃S₂ based on at least five sets of data.

7.2 Results and Discussions

The typical fabrication process of MoS₂/Ni₃S₂@MoS₂ is schematically depicted in **Section 3.1.4**. 3DGF synthesized on the Ni foam skeleton by CVD is directly employed as a conductive framework for the growth of hierarchical MoS₂/Ni₃S₂@MoS₂ coaxial nanofiber architectures, which is obtained by a PVP-assisted hydrothermal reaction between Na₂MoO₄ and thiourea at 200 °C for 12 h. The mass of Ni₃S₂ and MoS₂ can be exactly calculated by a FeCl₃ etching method, according to the reaction: $\text{Ni}_3\text{S}_2 + 4\text{FeCl}_3 \rightarrow \text{NiS}_2 + 4\text{FeCl}_2 + 2\text{NiCl}_2$, which can also be demonstrated by the XRD patterns and TEM images of the electrode after etched in a solution of FeCl₃ (**Figure 7.1**). The weight fractions of MoS₂ and Ni₃S₂ in the as-prepared 3D architectures is facilely controlled by adjusting the concentration of the reactants (Na₂MoO₄ and thiourea) using Ni/GF with nearly the same area.

Figure 7.1 (a) XRD patterns, (b) and (c) SEM images, and (d)-(f) TEM images of Ni₃S₂@MoS₂ electrode after etched in a FeCl₃ solution.

The morphology of the obtained MoS₂/Ni₃S₂@MoS₂ was comprehensively investigated by FESEM. As showed in **Figure 7.2a** and its inset, the whole surface of Ni/GF substrate is uniformly covered with a layer of 3D porous

network-like nanofiber architectures. The further well-defined interconnected network structure is shown in **Figure 7.2b**. The building nanofibers with high aspect ratios form 3D robust cross-link network architectures. There are a large number of voids with sizes from 50 nm to hundreds nm formed between the interconnected nanofibers due to the self-assembly process. These internal voids between nanofibers serve as an “ion reservoir” to allow for high contact between the electrolyte and active materials, facilitating a fast transportation of Na ions and electrons. Further investigations show these nanofibers are randomly covered with numerous few-layer nanosheets and form a highly porous “stacking card” structure (**Figure 7.2c**). These internal pores between sheet-like subunits effectively accommodate the huge volume variation during sodiation/desodiation, and also provide an enough spare space for a sufficient contact with the electrolyte.

Figure 7.2 Synthesis process and morphology characterization. (a), (b) and (c) SEM images, (d) TEM images, (e) and (f) HRTEM images in different areas of (d) (inset of (e) showing the corresponding FFT pattern), (g) TEM-EDX mapping, and (h) HR-EDX

line profile of the MoS₂/Ni₃S₂@MoS₂ heterostructure.

Figure 7.3 Detailed microstructure characterization. (a) XRD patterns, (b) Raman spectra of the MoS₂/Ni₃S₂@MoS₂ and the pure Ni/GF. XPS spectra of (c) C 1s, (d) Ni 2p, (e) Mo 3d and S 2s peaks, and (f) S 2p peaks of MoS₂/Ni₃S₂@MoS₂.

We further investigate the microstructure of MoS₂/Ni₃S₂@MoS₂ heterostructures by TEM and HRTEM. In good accordance with the above SEM results, the as-synthesized sample shows an obvious core-shell structure, in which a large amount of ultra-small few-layer MoS₂ nanosheets decorate elongated Ni₃S₂@MoS₂ core-shell coaxial nanofibers (**Figure 7.2d**). HRTEM image (**Figure 7.2e**) confirm the presence of crystalline Ni₃S₂ with a characteristic plane of (110) (ca. 0.28 nm interspacing) in the backbone (labeled e in **Figure 7.2d**). In contrast, the shell (labeled f in **Figure 7.2d**) corresponds to the nature of MoS₂ with a characteristic plane of (002) (ca. 0.64 nm interspacing) as shown in **Figure 7.2f**. Also, the decorated nanosheet with lateral dimensions of 8 nm (**Figure 7.2d**) exhibits a (100) characteristic plane of MoS₂ (ca. 0.27 nm interspacing). The crystalline nature of Ni₃S₂ nanofibers is further evidenced by the FFT pattern in the inset of **Figure 7.2e**, which clearly displays the characteristic spots of (012) plane. We further investigate the elemental distribution of MoS₂/Ni₃S₂@MoS₂ heterostructures, as shown in **Figure 7.2g** and **h**. Obviously, Ni signals were found in the backbone region, whereas Mo and S signals were observed in the

shell and core regions, confirming the core-shell hierarchical structure. The HR-EDX line profile (**Figure 7.2h**) can also verify the core-shell structure of the MoS₂/Ni₃S₂@MoS₂ nanofibers.

Figure 7.4 (a) Schematic illustration of the synthesis process of Ni₃S₂-MoS₂ heterostructures with different interfaces and (b–g) the corresponding TEM images. TEM images of (b) and (c) MoS₂/Ni₃S₂@MoS₂ obtained at 5 h; (d) and (e) porous-structured Ni₃S₂/MoS₂ obtained at 8 h; (f) and (g) homogeneous Ni₃S₂@MoS₂ obtained at 12 h.

The crystallographic structure of the MoS₂/Ni₃S₂@MoS₂ electrode was further analyzed by XRD (**Figure 7.3a**). All the identified peaks are well corresponding to Ni₃S₂ (JCPDS no. 44-1418) and hexagonal MoS₂ (a=b=0.316 nm, c=1.230 nm, JCPDS card no. 37-1492). The three strong peaks at 2 θ =44.7, 52.1 and 76.6 arise from the Ni/GF substrate. Ni/GF and MoS₂/Ni₃S₂@MoS₂ were examined by

Raman spectroscopy. Raman spectra of Ni/GF in **Figure 7.3b** indicate three characteristic peaks of graphene observed at 1350, 1580, and 2720 cm⁻¹, corresponding to the D, G and 2D bands, respectively. Here, the Raman intensity of the G band is much higher than that of the 2D band, which is very consistent with the multilayer properties of GF. The MoS₂/Ni₃S₂@MoS₂ composites have two obvious peaks at 383 and 405 cm⁻¹, corresponding to E_{2g}¹ and A_g¹ Raman modes of MoS₂, respectively. The peaks at 223 and 601 cm⁻¹ are probably related with those of Ni₃S₂.⁴³ The composition of MoS₂/Ni₃S₂@MoS₂ hybrid electrode was further studied by XPS (**Figure 7.3c, d, e and f**). The intense C 1s peak is associated with the Ni/GF substrate (**Figure 7.3c**). **Figure 7.3d** shows broaden peaks with binding energies of around 875 and 854 eV for Ni 2p_{1/2} and Ni 2p_{3/2}, indicating the Ni⁺ and Ni²⁺ oxidation states in Ni₃S₂, and the other two satellite peaks at 860.9 and 879.7 eV corresponding to shakeup type peaks of Ni. The binding energies of Mo 3d_{3/2} and Mo 3d_{5/2} peaks at 232.5 and 229.3 eV are the characteristic of Mo⁴⁺ in MoS₂. The binding energies at 162 and 163.2 eV in S 2p spectra are attributed to the S²⁻ states in MoS₂ and Ni₃S₂.^{228, 258}

Figure 7.5 (a) XRD patterns and (b) Raman spectra of MoS₂/Ni₃S₂ and Ni₃S₂@MoS₂. FESEM images of (c) MoS₂/Ni₃S₂ and (d) Ni₃S₂@MoS₂.

The morphology of MoS₂/Ni₃S₂ hybrid nanofibers can be optimized by changing the reaction time. This enables us to study the correlation between the structure and electrochemical performance. **Figure 7.4** schematically illustrates the evolution of the MoS₂/Ni₃S₂ hybrid nanofibers prepared at different reaction time. All the samples can be indexed to the composites of Ni₃S₂ and MoS₂, from the XRD patterns and Raman spectra (**Figure 7.5a** and **b**). The corresponding SEM images clearly show their morphologies (**Figure 7.5c** and **d**). At the reaction time of 5 h, the porous nanofibers can be obtained, and denoted as Ni₃S₂/MoS₂. TEM and HRTEM images show MoS₂ nanosheets with a lateral dimension of 5 nm randomly decorate Ni₃S₂ nanofibers and form a porous shell (**Figure 7.4b–c**). At the reaction time of 8 h, interestingly, the porous MoS₂ shell evolves into belt-like nanostructures (**Figure 7.4d–e**), which wrapping Ni₃S₂ nanofibers to form core-shell nanofibers with a homogeneous atomic heterointerface. The thickness of MoS₂ nanobelt shell of 5~8 layers is ca. 8~10 nm. This obtained sample is denoted as Ni₃S₂@MoS₂. As the reaction time increases to 12 h, surprisingly, the homogeneous MoS₂ nanobelt shell partly evolves into a large amount of few-layer MoS₂ nanosheets, which randomly decorate core/shell Ni₃S₂@MoS₂ nanofibers, forming a highly porous “stacking card” structure. Obviously, it shows a different architecture from the two other Ni₃S₂-MoS₂ heterostructures. Compared to Ni₃S₂/MoS₂ just with porous hierarchical structure and Ni₃S₂@MoS₂ only with a homogeneous atomic heterointerface, the obtained MoS₂/Ni₃S₂@MoS₂ hybrids manifest highly porous hierarchical structure with a homogeneous atomic heterointerface. The key factor, which leading to the formation of MoS₂/Ni₃S₂@MoS₂ nanofibers, is the templating effect of the PVP surfactant. According to the previous report, the individual PVP polymer chains may interact with each other through the H-bonding and hydrophobic interaction, and then self-assemble into polymer fibers.²⁵⁹ Therefore, it can act as a template to control the morphology. Based on the aforementioned time-dependent reaction

products, it can be derived that the formation of MoS₂/Ni₃S₂@MoS₂ coaxial nanofibers includes three key steps as schematically illustrated in **Figure 7.4a**: (1) the growth of separated MoS₂ nanosheets on Ni₃S₂ nanofibers; (2) the transformation of separated MoS₂ nanosheets into continuous nanobelts; (3) finally the etching of top-layer MoS₂ into ultra-small nanosheets, which uniformly decorating the coaxial Ni₃S₂@MoS₂ nanofibers.

Figure 7.6 Electrochemical and SIB performance. (a) CV curves at and (b) Charge and discharge curves of the MoS₂/Ni₃S₂@MoS₂ electrode at a current density of 100 mAh g⁻¹ for the first five cycles. (c) The capacity retention of three different electrodes at different current densities. (d) Cycling behaviors of three different electrodes at a current density of 200 mAh g⁻¹. (e) Nyquist plots of three different electrodes at full-discharged state after different cycles. The resistance is simulated using the equivalent circuit model (inset in e). (f) Cycling behaviors at 2 and 5 A g⁻¹, and Rct of the MoS₂/Ni₃S₂@MoS₂ electrode during 400 cycles at 2 A g⁻¹.

It is suggested that materials suitable for SIBs have tailored nanoarchitectures with the more open framework and layered structure in order to accommodate larger volume changes compared to LIBs with smaller ion radius of charge carrier. In order to explore the potential of our Ni₃S₂-MoS₂ composites for sodium-ion storage and study the relationship between the structure and electrochemical performance, the sodium storage performance of the above three MoS₂/Ni₃S₂ heterostructures with different heterointerfaces was thoroughly evaluated. We

found that the MoS₂/Ni₃S₂@MoS₂ electrode exhibited the best specific capacity among the three samples at various current densities. The electrochemical properties were firstly investigated by the CV measurement. The CV curves of the MoS₂/Ni₃S₂@MoS₂ electrode in the first five cycles at a scan rate of 0.1 mV s⁻¹, are displayed in **Figure 7.6a**. In the first scan, there are two cathodic peaks at 0.56 and 1.04 V, respectively. The very weak peak at 1.04 V is corresponding to the insertion of Na⁺ into MoS₂ ($\text{MoS}_2 + x\text{Na} \rightarrow \text{Na}_x\text{MoS}_2$, $x < 2$).^{129, 260-263} The strong peak at 0.56 V corresponds to the insertion of Na⁺ into Ni₃S₂ ($4\text{Na}^+ + 4\text{e}^- + \text{Ni}_3\text{S}_2 \rightarrow 3\text{Ni} + 2\text{Na}_2\text{S}$) and the further insertion of Na⁺ into Na_xMoS₂ ($\text{Na}_x\text{MoS}_2 + (4-x)\text{Na} \rightarrow \text{Mo} + 2\text{Na}_2\text{S}$).^{254, 264} The characteristic peak corresponding to the formation of SEI layer is probably in the overlapped region of the broad peak below 0.56 V.¹³⁰ In the first cycle, there are three oxidation peaks, located at 0.73, 1.38 and 1.67 V. The small peak at 0.73 V corresponds to the extraction of Na⁺, and the peak at 1.38 V is ascribed to the decomposition of SEI films on the active material surface. The strong peak at 1.67 V is associated with the desodiation of the Ni₃S₂ phase ($2\text{Na}_2\text{S} + 3\text{Ni} \rightarrow 4\text{Na}^+ + 4\text{e}^- + \text{Ni}_3\text{S}_2$), and the oxidation of Mo to MoS₂. Except for the first cycle, the charge/discharge curves coincide with each other, indicating its high reversibility and cycling stability. We noted that the active materials after the initial cycle were consisted of Mo, Na_xS (instead of the initial MoS₂) and Ni₃S₂ according to the reaction mechanisms of sodiation and desodiation in MoS₂ and Ni₃S₂.²⁶⁰

Figure 7.6b displays the representative charge/discharge curves of the MoS₂/Ni₃S₂@MoS₂ sample at a current density of 100 mA g⁻¹. In agreement with the CV curves, there are flat potential plateaus at around 0.76 and 1.56 V during the first discharge (sodiation) and charge (desodiation) processes, respectively. After the first cycle, the potential of discharge plateau increases and subsequently stays at 1.2 V, indicating the improved internal resistance of the cell. Meanwhile, the charge curves are almost overlapped with each other, exhibiting excellent cycling performance. The MoS₂/Ni₃S₂@MoS₂ electrode delivers initial discharge and charge capacities of 707 and 593 mAh g⁻¹, giving a Coulombic efficiency of

83.8%. Subsequently, the Coulombic efficiency of over 97% can be maintained with a high reversible capacity of 602 mAh g⁻¹. However, the bare Ni/GF electrode can only deliver initial discharge and charge capacities of 33.6 and 2 mAh g⁻¹, and almost deliver no capacities anymore after the first cycle (**Figure 7.7**). In contrast, the two other Ni₃S₂-MoS₂ electrodes (Ni₃S₂/MoS₂ and Ni₃S₂@MoS₂) deliver lower capacities at 100 mA g⁻¹, which are 530 and 442 mA g⁻¹, respectively. The superior sodium storage of the MoS₂/Ni₃S₂@MoS₂ electrode is probably related to its unique structure with homogeneous atomic heterointerface and porous hierarchical structure. The rate capability of the MoS₂/Ni₃S₂@MoS₂ electrode was also investigated, as displayed in **Figure 7.6c**. The specific capacities of 638, 568, 519, 463, 412, 356 and 283 mAh g⁻¹ can be achieved at current densities of 100, 200, 500, 1000, 2000, 3000 and 5000 mA g⁻¹, respectively. After ten cycles at 5 A g⁻¹, a stable capacity is maintained at 572 mAh g⁻¹ when recovered back to 100 mA g⁻¹. In contrast, the Ni₃S₂/MoS₂ and Ni₃S₂@MoS₂ electrodes deliver lower capacities of 430 and 342 mA g⁻¹ at 200 mA g⁻¹, and exhibit poorer rate capability (137 and 49 mAh g⁻¹ for the Ni₃S₂/MoS₂ and Ni₃S₂@MoS₂ electrodes at 5 A g⁻¹, respectively).

Figure 7.7 (a) Charge and discharge curves and (b) cycling behavior of pure GF as anode of SIBs at a current density of 200 mAh g⁻¹.

The cycling performance of the MoS₂/Ni₃S₂@MoS₂ electrode is also outstanding even after 100 cycles. Both the discharge and charge capacities are stable at about 483 mAh g⁻¹ (at a current density of 200 mA g⁻¹), retaining nearly 82.6% capacity

(**Figure 7.6d**). In contrast, the Ni₃S₂/MoS₂ and Ni₃S₂@MoS₂ electrodes show continuous and progressive capacity decay under the same testing conditions. After 100 cycles, the Ni₃S₂/MoS₂ and Ni₃S₂@MoS₂ electrodes only delivers capacities of 277 and 199 mAh g⁻¹, with nearly 60.7% and 50.4% capacity retention, respectively. To gain better insight into the reason why the unique structure of MoS₂/Ni₃S₂@MoS₂, few-layer MoS₂ nanosheets decorated coaxial core/shell Ni₃S₂@MoS₂ nanofibers can boost sodium storage, we performed EIS for the three electrodes. As shown in **Figure 7.6e**, in the high-frequency region, the intercept of the semicircle for the MoS₂/Ni₃S₂@MoS₂ electrode almost coincides with those of the Ni₃S₂/MoS₂ and Ni₃S₂@MoS₂ electrodes, while its diameter of the semicircle is obviously much smaller compared to those of the other two, indicating the lowest charge-transfer resistances and interfacial contact. R-C equivalent circuit was employed to further distinguish the kinetic differences between the three electrodes. The resistance parameters can be obtained by fitting data according to the equivalent circuit model in **Figure 7.6e**. Compared to Ni₃S₂/MoS₂ ($R_{sf}=11.5$ and $R_{ct}=215\ \Omega$) and Ni₃S₂@MoS₂ ($R_{sf}=23.8$ and $R_{ct}=274\ \Omega$), the MoS₂/Ni₃S₂@MoS₂ electrode delivers much lower SEI film resistance (R_{sf}) and charge transfer resistance (R_{ct}) (7.6 and 88 Ω), respectively, which are much lower than those of. Additionally, the slope of Warburg impedance in the low-frequency region for the MoS₂/Ni₃S₂@MoS₂ electrode (**Figure 7.6e**) is much larger than those of the other two, clearly demonstrating its high ion mobility as well as an excellent electrochemical activity for sodium storage. This result clearly validates that our few-layer MoS₂ nanosheets decorated core/shell Ni₃S₂@MoS₂ coaxial nanofibers can ensure an enhanced electrochemical activity of the active materials during the cycle processes, which can be ascribed to the synergistic contribution of the homogenous atomic heterointerface and the “stacking card” structure derived from the assembly of MoS₂ nanosheets. Most importantly, after the first cycle, the hierarchical MoS₂ shell composed of few-layer MoS₂ nanosheets decorating MoS₂ nanobelts transforms into metallic Mo and sulfur, which homogeneously wrapping

elongated Ni₃S₂ nanofibers with close contact and forming a robust buffering matrix for accommodating the huge volume expansion during sodiation/desodiation. Meanwhile, the metallic Mo clusters act as “pin conductor”, greatly enhancing the electrical conductivity of the overall electrode. In addition, sulfur is regarded as a “polysulfide reservoir”, which can greatly boost sodium-ion capture/storage and then facilitate the diffusion of sodium ions from the shell to the internal part, hence improving the electrochemical activity.

Figure 7.8 Nyquist plots of MoS₂/Ni₃S₂@MoS₂ electrode during 400 charge/discharge cycle at different cycles. The resistance is simulated using the inset of the equivalent circuit model.

Due to the excellent electron/ion transport kinetics, the MoS₂/Ni₃S₂@MoS₂ electrode also exhibits excellent long-term cyclability as displayed in **Figure 7.6f**. Even after 400 cycles, both discharge and charge capacities of the MoS₂/Ni₃S₂@MoS₂ electrode at a 2 A g⁻¹ are stable at about 299 mAh g⁻¹, revealing an average capacity fade of 0.074% per cycle. To gain further insight into the resistance change upon sodium ion insertion/extraction cycles, the EIS is measured to monitor the cell resistance during the first to 400th cycles. The Nyquist plots at various cycles are shown in **Figure 7.8**. The charge transfer resistance R_{ct} value decreases steeply in the first 100 cycles, and then increases

slightly between 100 and 400 cycles. The reason can be proposed that the electrolyte gradually penetrated through the nanofibers to activate the heterostructures after the initial few cycles, thereby improving the sodium-ion mobility and cycle life. The subsequent mild increase of R_{ct} between 200 and 400 cycles perfectly illustrates the good cycling behavior of the electrode. To demonstrate the high-power application potential of the MoS₂/Ni₃S₂@MoS₂ electrode, we tested the long-term ultrafast charge/discharge cycling. **Figure 7.6f** shows that the specific capacity can be stabilized at 207 mAh g⁻¹, even after 400 cycles at a 5C, with a capacity fading of 0.068% per cycle. This result highlights the capability of the MoS₂/Ni₃S₂@MoS₂ electrode to meet the requirements of both long cycle lifetime and good rate capability, which are important merits for SIBs.

Figure 7.9 (a) XRD patterns, (b) and (c) SEM images, (d)-(g) TEM images of MoS₂/Ni₃S₂@MoS₂ electrode as the anode of SIBs after 400 cycles at 2 A g⁻¹.

Indeed, the morphology and phase change of the MoS₂/Ni₃S₂@MoS₂ electrode after long-term cycling was investigated using XRD, SEM, and TEM. The XRD patterns of the full charged electrode show diffraction peaks of Ni, Mo, and Ni₃S₂ (**Figure 7.9a**). This result demonstrates the active materials after cycling are mainly composed of Mo, Na_xS (in amorphous phase) and Ni₃S₂, which is

consistent with the electrochemical reaction mechanisms of sodium-ion intercalation and extraction in MoS₂ and Ni₃S₂. It can be understandable that Ni peaks are from the Ni/GF substrate. According to the previous report,²⁵⁹ the large volume variation during sodiation/desodiation is undesirable to the structural stability, and deadly decay the cycle life of batteries. **Figure 7.9b-d** show the morphologies of the MoS₂/Ni₃S₂@MoS₂ electrode after 400 charge/discharge cycles at 2 A g⁻¹. Compared with the original morphology, the MoS₂/Ni₃S₂@MoS₂ electrode still sustains the nanofiber-like structure with little structural deformation, demonstrating the unique hybrid nanofiber superstructure can well accommodate the volume variation and aggregation of nanoparticles upon cycling. In comparison, Ni₃S₂/MoS₂ without a homogeneous atomic heterointerface as the anode of SIBs after long-term cycles, exhibits the distorted morphology composed of expanded fibers with serious agglomerations (**Figure 7.10**). This result can positively corroborate the effective role of the atomic heterointerface as a protecting layer to alleviate the distortion of nanofibers. HRTEM image in **Figure 7.9f** shows the lattice fringe with d-space of 0.2 nm in the yellow square region (labeled f in **Figure 7.9e**), which is in agreement with (110) plane of Mo. HRTEM image in **Figure 7.9g** also confirms a characteristic plane of (110) (ca. 0.28 nm interspacing) of the crystalline Ni₃S₂ (labeled g in **Figure 7.9e**).

Figure 7.10 SEM images of MoS₂/Ni₃S₂ electrode as the anode of SIBs after long-term cycles.

In this work, the MoS₂/Ni₃S₂@MoS₂ electrode exhibits excellent rate (283 mAh g⁻¹ at 5 A g⁻¹) and long cycle life (over 400 cycles) at high current densities of 2 and 5 A g⁻¹, demonstrating its great potential as anode materials for SIB applications. This performance is superior to most of the previous MoS₂ and Ni₃S₂ for SIBs.⁵¹⁻⁵⁹ Especially, a very high loading of active materials has been achieved in this work, which is 8~10 mg cm⁻² for MoS₂/Ni₃S₂@MoS₂, highly exceeding a typical loading of active materials in literature (below 1 mg cm⁻²). Therefore, higher areal energy density can be obtained in our designs, which is crucial for the practical application of SIBs. The uniquely designed electrode allows us to push the rate tolerance capability in sodium-ion storage. It is not difficult to understand that the MoS₂/Ni₃S₂@MoS₂ electrode possesses several superior characteristics leading to the high performance for SIBs: **(a)** For the MoS₂/Ni₃S₂@MoS₂ hybrids, this unique MoS₂ shell (few-layer MoS₂ nanosheets self-decorating MoS₂ nanobelts) is proposed to serve as a protecting layer to alleviate the distortion of Ni₃S₂ nanofiber, which is often caused by the harsh and frequent phase variation during cycling. Especially, after the first cycle, the derived active materials of metallic Mo and Na_xS separately acting as “pin conductor” and “polysulfide reservoir” can greatly increase the electrical conductivity of the overall electrode, significantly boost the sodium-ion capture/storage and then facilitate the diffusion of sodium-ion from the shell to the internal part, hence improving the electrochemical activity. Besides, Ni₃S₂ nanofibers can well confine MoS₂ shell onto it due to the maximized interface contact/interaction, thus preventing its agglomeration and restacking. **(b)** More importantly, this unique MoS₂ shell benefiting from the nano-size effect and hierarchical structure, serve as an “ion reservoir” to facilitate the transportation of electrolyte ions and provide large reversible capacity. Also, the exposed nanosheet edges as nanosized active sites can facilitate the fast sodium-ion intercalation into the layered structure, thus enhancing the electrochemical kinetics, as shown in **Figure 7.11**. **(c)** The elongated Ni₃S₂@MoS₂ coaxial nanofibers with high aspect ratio can facilitate rapid ion/electron transportation

at high rates due to the shortened Na⁺ diffusion pathway. **(d)** The directly grown nanofibers anchored into the skeleton of Ni/GF substrate can ensure robust mechanical support and provide an electrical network to the current collector, avoiding adding polymer binders and conducting additives, which can simplify the electrode fabrication process and decrease the contact resistance. Therefore, this uniquely designed electrode allows us to push the rate tolerance capability and cyclability in sodium storage.

Figure 7.11 Schematic illustration of the additional active sites of MoS₂-nanosheet-decorated MoS₂ nanobelts wrapped Ni₃S₂ nanofibers, the electron transfer and sodium ion transportation in the hybridized electrodes, as well as the derived active materials of metallic Mo and sulfur on Ni₃S₂ nanofibers after cycling.

7.3 Conclusion

We have successfully fabricated a novel nanofiber superstructure composed of few-layer MoS₂ nanosheets decorated elongated Ni₃S₂@MoS₂ coaxial nanofibers by a one-step PVP-assisted hydrothermal reaction. Such hierarchical nanofibers possess the homogeneous heterointerface with a porous structure, leading to the maximization of synergistic interaction. Such unique architecture with maximized synergistic effect as the anode of SIBs manifests remarkable performance with high specific capacity, superior cycling stability, and excellent rate capability. Compared to the Ni₃S₂/MoS₂ (430 mAh g⁻¹) and the Ni₃S₂@MoS₂ (342 mAh g⁻¹) electrodes, it exhibits high specific capacities of 568 and 283mAh g⁻¹ at 200 mA g⁻¹ and 5 A g⁻¹, respectively. More interestingly, strong heterointerface synergistic effect of our MoS₂/Ni₃S₂@MoS₂

heterostructure can perform stable performance for SIBs. Even after 400 cycles, a specific capacity of 207 mAh g⁻¹ can be maintained at 5 A g⁻¹. The improved performance is probably due to the maximized synergetic effect from the porous hierarchical structure and homogeneous atomic heterointerface. Our detailed study fundamentally establishes a relationship between the heterointerface/chemistry of heterostructures and their properties. It is anticipated that our strategy can provide a new idea to prepare other heterostructures for energy storage devices.

Chapter 8

Active Sites–Enriched Hierarchical MoS₂ Nanotubes: Highly Active and Stable Architecture for Boosting Hydrogen Evolution and Lithium Storage

The design of nanostructures with sufficient active sites is considerably challenging but highly desirable for energy applications. Herein, highly active tubular MoS₂ structures on flexible 3DGF are firstly produced by a bottom–up approach using Ni₃S₂ nanowires as precursor and self–sacrificial template. The hierarchical tubular structures with high surface curvature expose a large fraction of edge sites and defects, which, along with high surface area, lead to excellent activity for electrocatalytic hydrogen evolution. When evaluated as anode materials for LIBs, these hierarchical MoS₂ nanotubes manifest high specific capacity and excellent rate capability as well as extremely long–term cycle stability. This work elucidates how structure design of nanomaterials can significantly impact the surface structure at the atomic scale, enabling new opportunities for other tubular structures.

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8.1 Introduction

Since the discovery of CNTs in 1991, intensive efforts have been motivated to fabricate various types of nanotubes due to their unique physical/chemical properties and expansive applications in a variety of fields.²⁶⁶⁻²⁶⁷ Similar to carbon, fullerene-like and tubular TMDs have been increasingly investigated both theoretically and experimentally.²⁶⁸⁻²⁷³ MoS₂ as a typical layered metal dichalcogenide has been widely recognized as a universal material for energy applications. Novel applications of tubular MoS₂ structure in catalysis, energy storage, lubricants, electronics, and optoelectronics have driven the development of synthetic strategies that enable control of its structure and morphology.²⁷⁴⁻²⁷⁶ MoS₂ nanotubes were firstly synthesized by Tenne *et al.* by a gas reaction of MoO_{3x} and H₂S under a reducing atmosphere at elevated temperatures (800–950 °C).^{271, 277} Chen and co-workers also reported the synthesis of open-ended MoS₂ nanotubes by a gas-solid reaction.²⁷⁴ However, these approaches for the fabrication of MoS₂ nanotubes always require complicated procedures with high temperatures or dangerous gases (H₂ and H₂S). Besides, extensive research has proved that hollow nanotubes with abundant active edge sites and high SSA can achieve excellent performance in many applications. Recently, a variety of solution-phase strategies have also been adopted to synthesize tubular MoS₂ structures with high surface area. For example, Zhang *et al.* reported an anion-exchange method for the synthesis of hierarchical tubular MoS₂ structures, which exhibit high activity and stability for photoelectrocatalytic and electrocatalytic HER.²⁷⁶ Wang *et al.* synthesized 3D assembled tubes constructed by single-layered MoS₂ nanosheets through a solvothermal method.¹⁰⁰ The assembled tubular architecture exhibits excellent electrochemical performance as anode materials of LIBs and high activity in hydrodesulfurization (HDS) catalysis. The excellent properties are probably attributed to the porous tubular architecture, which can shorten the transport path of lithium ions, and provide sufficient exposed active sites for reactions. These important results represent that it is a

significant topic to tune the properties of MoS₂ nanotubes by controlling their microstructures. Despite these advances in the fabrication of tubular nanostructures, it is still a considerable challenge to obtain MoS₂ nanotubes with sufficient exposed active sites, high SSA and robust stability by a facile method. Herein, we develop a facile template-assisted approach for the construction of hierarchical MoS₂ hollow nanotubes implanted with exceptional active sites. The synthesized hierarchical nanotubes are constructed by MoS₂ hollow nanotubes decorated with MoS₂ nanosheets, which are self-supported on flexible 3DGF. We denote it as MT@MS/GF. The obtained hierarchical MT@MS/GF exhibits excellent electrocatalytic activity and high stability with low overpotential in the acidic electrolyte for the electrochemical HER. In addition, when evaluated as anode materials for LIBs, the binder-free hierarchical MoS₂ electrode manifests high specific capacity and excellent rate capability as well as extremely long-term cycle stability.

8.2 Results and Discussions

The synthesis strategy of hierarchical MT@MS/GF is schematically depicted in **Section 3.1.5**. First, few-layer MoS₂ nanosheets decorated Ni₃S₂@MoS₂ coaxial nanofibers on 3DGF/Ni are employed as the template, which is synthesized by a facile hydrothermal method. SEM and TEM images show the as-synthesized sample with an obvious core-shell structure, in which a large amount of ultra-small few-layer MoS₂ nanosheets decorate elongated Ni₃S₂@MoS₂ coaxial nanofibers (denoted as MoS₂/Ni₃S₂@MoS₂) (**Figure 8.1a–d**). It should be notified that MoS₂/Ni₃S₂@MoS₂ nanofibers are self-supported on 3DGF/Ni. The as-prepared hierarchical MoS₂/Ni₃S₂@MoS₂ nanofibers are transformed into hierarchical MoS₂ tubular architectures by selectively removing the Ni₃S₂ sacrificial template after a FeCl₃-assisted etching process, while MoS₂ is chemically stable during the etching process. In the meanwhile, nickel substrate from 3DGF/Ni can be effectively etched. Then, we can obtain hierarchical MoS₂ tubular architectures directly supported on 3DGF. The detailed reaction

equations are described as follows.²⁷⁸

Figure 8.1 SEM and TEM images of (a-d) MoS₂/Ni₃S₂@MoS₂ and (e-i) Ni₃S₂@MoS₂.

Detailed procedures are given in the **Section 3.2.5**. The phase and morphology of the as-prepared sample were systematically investigated by XRD and SEM. XRD pattern of the obtained sample can be assigned to the hexagonal phase MoS₂ ($a=b=0.316$ nm, $c=1.230$ nm, JCPDS card no. 37-1492) and GF (**Figure 8.2a**). SEM image reveals its tubular morphology with uniform diameters of 50–100 nm and lengths of above 2 μm (**Figure 8.2b**). The MT@MS/GF composites were sonicated in ethanol for 10 min. The hierarchical tubular structures were collapsed due to the ultrasonication effect, which was then dropped onto a TEM grid and dried at ambient conditions. TEM image shows uniform nanotubes with inner and outer diameters of 30 and 50 nm (**Figure 8.2c**). Close examination clearly indicates a typical nanotube is composed of MoS₂ layers (5~8 layers) with an interlayer spacing of 0.68 nm, which are further decorated with a large amount of ultra-small MoS₂ nanosheets (**Figure 8.2d** and **e**). Partial nanotube walls show obviously broken layers with rich defects, highlighted by the dashed lines in **Figure 8.2d**, which are probably caused by the detachment of Ni₃S₂ nanofibers during the etching treatment. Further HRTEM image shows the atomic structures of the nanotube (**Figure 8.2e**). The (001) planes are parallel to each other and

together constitute the tubular structure with an interlayer distance of 0.68 nm. Enlarged HRTEM image shows the regular hexagonal lattice orientation of 2H-MoS₂ (**Figure 8.2f**). The inserted FFT pattern reveals the orientation along [001] zone axis. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images can clearly confirm the hollow tube-like morphologies and uniform composition distribution of the obtained nanotubes (**Figure 8.2g–i**). The EDX results also confirm the composition of MoS₂ (**Figure 8.2j**).

Figure 8.2 a) XRD pattern and b) SEM image of MT@MS/GF. c) TEM image of MT@MS showing a similar structure as (a). d) HRTEM images of MT@MS, showing broken surface layers and crystal planes of MT@MS. e) HRTEM images of MoS₂ walls in MT@MS. The image plane is the (010) plane stacking with the interlayer distance of 0.68 nm. f) HRTEM images of a MoS₂ sheet in MT@MS showing the viewed parallel to the c axis of MoS₂ nanocrystals. Inset (f): the corresponding SAED image. g)

HAADF-STEM image, corresponding EDX maps of MT@MS for S (h), Mo (i), and the EDX spectrum (j).

Figure 8.3 Detailed microstructure characterization. (a) Raman spectra of MT@MS /GF. XPS spectra of (b) S 2p peaks and (c) Mo 3d peaks of MT@MS/GF. (d) N₂ adsorption/desorption isotherms, and the insert corresponding pore size distribution of MT@MS/GF.

Raman spectroscopy was used to further investigate the structures of the MT@MS/GF and bare GF. Two obvious peaks at 1580 and 2720 cm⁻¹ are attributed to the G and 2D bands of GF, respectively (**Figure 8.3a**). The high 2D/G intensity ratio as well as the absence of the D band at 1350 cm⁻¹ in the GF spectrum demonstrates the high quality of GF before MoS₂ growth. By contrast, the appearance of D band at 1350 cm⁻¹ after MoS₂ growth indicates the presence of sp³ bonding which successively corroborates a strong coupling between MoS₂ and GF. Two characteristic peaks at 380 and 405 cm⁻¹ in the MT@MS/GF sample are attributed to E₁2g and A₁g modes of MoS₂, respectively. X-ray

photoelectron spectroscopy (XPS) was employed to further probe the chemical states of S and Mo in MT@MS/GF (**Figures 8.3b** and **c**). Two peaks of Mo 3d_{3/2} and Mo 3d_{5/2} at binding energies of 232.5 and 229.3 eV correspond to the characteristic peaks of Mo⁴⁺ in MoS₂. The S 2p peaks at 162 and 163.2 eV are ascribed to the characteristic peaks of S²⁻ in MoS₂.^{36, 37} In virtue of the hollow tubular structure and ultrathin nanosheets, the MT@MS/GF sample with hierarchical hollow structure exhibits a high BET surface area of 89.6 m² g⁻¹ with abundant mesoporous channels (**Figure 8.3d**).

Figure 8.4 a) and b) TEM images of MT/GF. c) HRTEM images of tubular MoS₂, showing regular crystal planes of MoS₂. d) HRTEM images of tubular MoS₂, showing the viewed parallel to the c axis of MoS₂ nanocrystals. Inset (d): the corresponding SAED image.

The morphology of hierarchical MoS₂ hollow nanotubes on 3DGF can be optimized by the template precursor. This enables us to study the correlation between the microstructure and electrochemical performance. Herein, for comparison, we also fabricate even MoS₂ hollow nanotubes on 3DGF, but without the decorating MoS₂ nanosheets (donated as MT/GF), which are derived from core-shell Ni₃S₂-MoS₂ nanofibers with a homogenous heterointerface on 3DGF/Ni (donated as Ni₃S₂@MoS₂) (**Figure 8.1d-f**). The TEM image of MT/GF shows the typical nanotubes are composed of MoS₂ layers with a wall thickness of 5~10 nm (**Figure 8.4a and b**). Enlarged HRTEM image clearly indicates a typical hollow nanotube is indeed composed of MoS₂ layers (~10 layers) with an interlayer spacing of 0.68 nm (**Figure 8.4c**). Further examination shows the regular hexagonal lattice orientation of 2H-MoS₂ (**Figure 8.4d**). The inserted FFT pattern reveals the orientation along [001] zone axis. XRD pattern can also confirm the pure phase of MT/GF (**Figure 8.5**).

Figure 8.5 XRD pattern of MT/GF.

Recently, MoS₂ and its composites demonstrated their intriguing performance for lithium storage and remarkable efficiency as catalysts of HER.^{160, 165, 183, 279-294} The decent lithium storage and HER properties have been demonstrated. In this study, we investigate the electrocatalytic HER activities of MT@MS/GF in

comparison with MT/GF. A three-electrode setup is employed to evaluate the electrocatalytic HER activities in 0.5M H₂SO₄ electrolyte. Noted that the test is operated in a static state (without rotation) to simulate the real industrial operation. The bare GF shows a negligible background activity for H₂ evolution (**Figure 8.6a**), which is similar to other report.^{280, 295, 296} A reductive scan of the MT@MS/GF sample shows a low overpotential (η) of 77 mV for HER, beyond which a sharp increase in the cathodic current starts to appear, attributing to electrocatalytic H₂ evolution (**Figure 8.6a**). By contrast, the MT/GF catalyst exhibits inferior HER activity with lower catalytic current and larger onset overpotential of 161 mV.

Figure 8.6 Electrocatalytic hydrogen evolution performance of various catalysts. (a) Polarization curves of MT@MS/GF, MT/GF, and GF at a scan rate of 5 mV s⁻¹. (b) Tafel plots of the various catalysts derived from a. (c) Durability test indicating negligible current loss even after 3000 CV cycles. (d) Time dependence of current density under a constant potential of -0.17 V vs RHE.

Table 8.1 Comparison of catalytic parameters of different HER catalysts.

Catalyst	Number of active sites [10 ⁻³ mol g ⁻¹]	TOF [s ⁻¹]	Tafle Slope [mV decade ⁻¹]	Onset overpotential [mV vs RHE]
MT@MS/GF	1.878	0.957	52	77
MT/GF	0.965	0.496	94	161

Figure 8.7 Time dependence of current density for the MT/GF catalyst under a constant potential of -0.17 V vs RHE.

In order to prove the increased active sites provided by the hierarchical MT@MS/GF, the number of active sites for MT@MS/GF and MT@GF was estimated based on voltammetry method (**Figure 8.6**).^{284, 297} The related calculation method is presented in the **Section 3.4.9**. As shown in **Table 8.1**, the MT@MS/GF catalyst exhibits a density of active sites of 1.878×10^{-3} mol g⁻¹, which is obviously higher than that of the MT@GF catalyst (0.965×10^{-3} mol g⁻¹). More active sites implanted in MT@MS/GF can be attributed to its hierarchical nanotubes with massive defects and the inherent reactive surfaces of nanotubes due to their curvature. It has been proved that MoS₂ morphology with a radius of curvature of nanoscale dimensions is expected to engender more exposed edge sites by imposing geometric constraints that can markedly change

the thermodynamic stabilities of different surface features.²⁹⁸ Another possible cause is the hierarchical tubular structure possesses high surface area and diverse mesoporous channels, which are favorable for the fast ion diffusion and close electrode–electrolyte contact, leading to the enhanced electrocatalytic activity. The turnover frequency (TOF) for each active site of the MT@MS/GF catalyst was calculated to be 0.957 s⁻¹ at $\eta = 300$ mV, which is much higher than the TOF value of MT/GF catalyst, indicating its better intrinsic catalytic activity. The HER kinetics of the above various catalysts was investigated by the corresponding Tafel plots ($\log j \sim \eta$) (**Figure 8.6b**). The linear portions in the Tafel plots were fitted according to the Tafel equation ($\eta = b \log |j| + a$) and obtained the Tafel slope (b). Tafel slope of 52 mV per decade was obtained for the MT@MS/GF sample (**Figure 8.6b**), which is far lower than that of 94 mV per decade for the MT/GF sample (**Table 8.1**), testifying the superior HER kinetics of the MT@MS/GF sample. At high current densities, the MT@MS/GF sample also exhibits a more efficient catalyst compared to that of MT/GF. The inherent HER activities of these catalysts were estimated by the exchange current density (j_0). The MT@MS/GF sample exhibits the j_0 of 6.4×10^{-2} mA cm⁻², outperforming the value of 2.5×10^{-2} mA cm⁻² for the MT/GF sample. The outstanding kinetic metrics (low onset overpotential of 77 mV, and Tafel slope of 52 mV per decade) and large j_0 (6.4×10^{-2} mA cm⁻²) highlight the extraordinary hydrogen evolution efficiency of this novel structured MT@MS/GF catalyst. Stability is another significant criterion to evaluate the catalysts. The negligible difference in the J – V curves before and after 3000 CV cycles demonstrates the superior stability of the MT@MS/GF sample in a long-term electrochemical reaction (**Figure 8.6c**). To probe the durability of the MT@MS/GF sample in an acidic environment, the continuous HER measurement at a static overpotential and long-term cycling test were conducted. The curve of the time dependence of current density behaves a typical serrate shape under a constant potential of -0.17 V vs. RHE (**Figure 8.6d**), which is probably related to the alternative processes of bubble accumulation and release. For the hierarchical MT@MS/GF sample, the current density decreases

gradually in the initial 0.5 h, and then increases slightly over 4 h of continuous operation. It is hypothesized that the activation process during the initial 0.5 h can allow more electrolyte to access the MT@MS/GF interfaces by the capillary penetration due to the hierarchical structure, leading to the increased HER current density. In comparison, in the same measured condition, the MT/GF catalyst exhibited a slow but progressive decrease in HER activity (**Figure 8.7**). Besides, XPS and Raman studies of the sample after 4 h of operation revealed no obvious chemical state change of HER-active Mo (**Figure 8.8**). The extraordinary long-term durability of the tubular MT@MS/GF catalyst suggests its promise for realistic hydrogen evolution electrode. Meanwhile, the hierarchical tubular structures of the MT@MS/GF electrode are still detectable even after long-term HER cycling, indicating the good stability of its hierarchical tubular structure (**Figure 8.9**).

Figure 8.8 Detailed microstructure characterization after long-term HER cycling test. XPS spectra of (a) Mo 3d peaks and (b) S 2p peaks of the MT@MS/GF. (c) Raman spectra of the MT@MS/GF. (d) Raman spectra of MoS₂ in the MT@MS/GF.

The experimentally measured high catalytic HER activities ($j_0=6.4 \times 10^{-2} \text{ mA cm}^{-2}$

²⁾ of the MT@MS/GF catalyst prompted us to investigate the enhanced mechanism. Previous DFT calculations indicated that the MoS₂ basal plane was inactive while only edge sites of nanoscale particles with coordinate unsaturated Mo atoms were active for HER, which was later proved by Jaramillo *et al.* experimentally.^{138, 299} Xie *et al.* found that rich defects resulted in partial cracking of the catalytically inert basal planes, leading to the exposure of additional active edge sites.²⁸¹ Herein, our MT@MS/GF sample with high SSA and diverse mesopores possesses cracked MoS₂ nanotube with broken layers and massive defects can extend massive exposed active edge sites, leading to the enhancement of the HER activity. Also, a mass of ultra-small few-layered MoS₂ sheets cover the entire surfaces of nanotubes, which provide accessional catalytic centers for HER. Furthermore, the entire surfaces of nanotubes are regarded to be reactive due to its curvature and a distortion of the bond angles, leading to a preferentially maximum exposure of the catalytically active sites. Meanwhile, the graphene scaffolds may also boost the HER-activity of MT@MS due to the increased electrical conductivity, leading to the fast electron transfer and high electrocatalytic efficiency to HER.

For HER in acidic media, two separate pathways (the Volmer–Tafel or the Volmer–Heyrovsky mechanism) have been proposed for reducing H⁺ to H₂. The Volmer–Heyrovsky mechanism involves two principal steps, referring to the Volmer [Equation (8.3)] and Heyrovsky [Equation (8.4)] while Volmer–Tafel proceeds via the combination of Volmer [Equation (8.3)] and Tafel [Equation (8.5)] reactions.^{59, 60}

Tafel slope, an intrinsic property of electrocatalysts, could be used to probe the rate-determining step and elementary steps involved in the H₂ evolution. In a recent study, under a specific set of conditions, it is reported that Tafel slope of

about 120, 40 or 30 mV per decade will be obtained if the Volmer, Heyrovsky or Tafel reaction is the rate-determining step, respectively.³⁰⁰ Ideally, the Tafel slope is an inherent property of electrocatalytic materials, which is a useful indicator of the rate-limiting step for reactions involving electron transfer. In reality, however, the Tafel slope can be dependent on many factors other than the kinetic exponent of the electrons, such as the coverage of adsorbates and the mass transport effect in the porous structure.³⁰¹ Since, our Tafel slope was determined in the high coverage region, the value of 52 mV may imply Heyrovsky rate-determining step. Due to the complexity of the reaction mechanism, analyzing the Tafel slope is still inconclusive for identifying the HER of MoS₂. However, the Tafel slope of 52 mV per decade obtained in this work is compatible to 36–68 mV per decade of bulk Pt (shape-dependent) in 0.5M H₂SO₄ and close to that of defect-rich MoS₂ ultrathin nanosheets reported previously, which suggests a similar surface chemistry of our hierarchical MT@MS/GF.²⁸¹

Figure 8.9 Detailed morphology characterization after long-term HER cycling test. a) SEM images of MT@MS. b) TEM image of MT@MS. c, d) HRTEM images of MT@MS, showing MoS₂ nanosheets decorating MoS₂ nanotubes and crystal planes of MT@MS.

Figure 8.10 a) The first 4 cycles CV curves of MT@MS/GF at a scan rate of 0.2 mV s⁻¹, b) the first three charge and discharge curves of MT@MS/GF at a current density of 100 mA g⁻¹, c) cycling behavior of the MT@MS/GF and MT/GF electrodes at various current densities, d) cycling behaviors of the MT@MS/GF electrode at a current density of 500 mA g⁻¹.

Figure 8.11 Cycling behaviors of the MT /GF electrode at a current density of 500 mA g⁻¹.

In this study, we also investigate the electrochemical properties of the MT@MS/GF as anode materials for LIBs. The CV curves of MS@MT/GF in the first four cycles are presented in **Figure 8.10a**, which is similar to the reported.^{15, 94} The shape of CV curve and the oxidation/reduction peaks can still retain in the cycles, indicating its good stability. The hierarchical MS@MT/GF delivers initial discharge and charge capacities of 1487 and 1215 mAh g⁻¹, respectively, giving a Coulombic efficiency of 81.7% (**Figure 8.10b**). The Coulombic efficiency rapidly reaches more than 99% after the second cycle. The second and third discharge profiles are almost coinciding with each other, proving excellent cycling performance. The hierarchical MS@MT/GF exhibits excellent rate performance. At high current densities of 1 and 2 A g⁻¹, the specific capacities of 1025 and 916 mAh g⁻¹ can remain, respectively (**Figure 8.10c**). Even cycled at a high current density of 5 A g⁻¹, the specific capacity of 878 mAh g⁻¹ can be maintained. Remarkably, these values are much higher than that of MT/GF (731 mAh g⁻¹). The cycling performance is also outstanding: even after 200 cycles, both discharge and charge capacities of the hierarchical MS@MT/GF can remain at 892 mAh g⁻¹ at a current density of 500 mA g⁻¹, delivering nearly 76.5% of capacity retention (**Figure 8.10d**). In contrast, the MT/GF electrode shows lower capacities and much faster capacity fading under the same testing conditions, and a capacity of only ~727.4 mAh g⁻¹ is retained after 100 cycles (**Figure 8.11**). A complete comparison of electrochemical properties of these two samples, summarized in **Table 8.2**, shows that MS@MT/GF possesses excellent electrochemical properties, including high initial Coulombic efficiency, high specific capacity, excellent rate performance and stable cyclability. The remarkable lithium storage properties of the hierarchical MT@MS/GF catalyst are probably related to its unique tubular architecture constructed by MoS₂ nanosheets-decorated nanotubes. Especially, the hierarchical tubular structure possesses high surface area and massive mesopores, which are favorable for a short diffusion distance of lithium ions and a large electrode-electrolyte contact area, leading to the enhanced rate capability. Meanwhile, the decorating ultrathin

2D nanosheets and the inner void space in the hollow tubular structure not only allow the fast lithium ion diffusion, but also effectively buffer the mechanical stress caused by volume variation during the lithium intercalation/exfoliation, thus leading to the enhanced cycling stability.

Table 8.2 The comparison of electrochemical performances for two electrodes, MT@MS/GF and MT/GF.

Electrode description	1st capacity (mAh g ⁻¹)	Specific Coulombic efficiency	Cycling stability (%)	Rate performance
MT@MS/GF	1487 mAh g ⁻¹ at 100 mA g ⁻¹	81.7%	892 mAh g ⁻¹ after 200 cycles at 500 mA g ⁻¹	1025, 916 and 775 mAh g ⁻¹ at 1000, 2000 and 5000 mA g ⁻¹
MT/GF	1382 mAh g ⁻¹ at 100 mA g ⁻¹	75.2%	727 mAh g ⁻¹ after 100 cycles at 500 mA g ⁻¹	894, 765 and 648 mAh g ⁻¹ at 1000, 2000 and 5000 mA g ⁻¹

8.3 Conclusion

In summary, we have developed a facile method to prepare robust MoS₂ hollow nanotubes implanted with a high density of active sites that exhibit excellent catalytic activity for the HER. The obtained hierarchical nanotubes are constructed by MoS₂ hollow nanotubes decorated with MoS₂ nanosheets, which are self-supported on flexible 3DGF. The hierarchical hollow nanotubes show enhanced lithium storage and excellent electrocatalytic activity towards the HER with quite good stability, arising from preferentially exposed more catalytically active edge sites. Especially, the hierarchical tubular structure possesses high surface area and diverse mesoporous channels, which are favorable for fast ion diffusion and close electrode-electrolyte contact, leading to the enhanced electrocatalytic activity and lithium storage. All these merits undoubtedly contribute to the enhancement of electrochemical properties, including a low

onset overpotential of 77 mV, Tafel slope of 52 mV per decade and large exchange current density of $6.4 \times 10^{-2} \text{ mA cm}^{-2}$. In addition, when evaluated as an anode material for LIBs, these hierarchical MoS₂ nanotubes manifest high specific capacity and excellent rate capability as well as extremely long-term cycle stability. This method can be used for the preparation of other tubular structure for future clean energy applications.

Chapter 9

Conclusions and Future Work

This chapter summarizes the conclusion of the whole research project, together with the proposed future studies. Comprehensive investigations of MoS₂-based composites in different systems demonstrate that the precisely designed structures can rationally tune the electrochemical performance. Meanwhile, the corresponding fundamental studies on the electrochemical mechanisms are proposed in different systems. Based on the scientific results obtained in this thesis, several scientific and technological contributions have been summarized. Moreover, the future work is proposed to investigate the capacity and cycle fade mechanisms of MoS₂-based composites for LIBs and SIBs, and advance the full SIBs with unique electrodes.

9.1 Conclusions

This thesis has aimed to investigate the potential of MoS₂ and its composites as prospective electrode materials and push forward their large-scale application for energy storage and conversion devices. Comprehensive investigations of MoS₂-based composites in different systems exhibit that the precisely designed structures can rationally tune the electrochemical properties. Meanwhile, the corresponding fundamental studies on the electrochemical mechanisms are proposed in different systems.

(1) Ni₃S₂@MoS₂ core/shell nanorod arrays on Ni foam for high-performance electrochemical supercapacitor

A one-step hydrothermal reaction method has been proposed to grow core/shell Ni₃S₂@MoS₂ nanoarrays directly on Ni foam. On the basis of control experiments for Ni₃S₂@MoS₂ arrays with various morphologies, a plausible growth mechanism is proposed which involves self-assembly and oriented attachment of nanocrystalline. The hierarchical Ni₃S₂@MoS₂ core/shell nanorods evidently exhibit higher specific capacitance than the bare Ni₃S₂ sample, as well as more superior cycling stability and more excellent rate capability, which can be ascribed to the porous structure, providing an increased reaction area for enhancing the intimate contact of electrolyte and active materials. Moreover, a novel design with a conductive 1D core material endows the quick electron transportation between Ni₃S₂ nanorods and Ni foam. The present study can be applied to the synthesis of other Ni₃S₂ based hybrid metal sulfides. The obtained hybrids exhibit their prospective potential in the applications of energy storage devices.

(2) High-Performance MoS₂ nanoarchitectures anchored into GF for LIBs

Light-weight, free-standing MoS₂ architectures based anodes for LIBs are developed by growing 3D honeycomb-like MoS₂ structure directly on 3DGF. This is an “all-in-one” highly integrated electrode. All the features are highlighted

as follows: (i) The 3DGF plays dual roles as both the light-weight scaffold for the growth of honeycomb-like MoS₂ structure, and an efficient current collector; (ii) To our best knowledge, it is the first time to report such a new type of MoS₂ nanosheets with a novel 3D honeycomb-like structure, especially obtained directly on 3DGF; (iii) One key point is MoS₂ nanosheets self-assembly into honeycomb-like nanoarchitectures, which can effectively inhibit the aggregation of exfoliated MoS₂ nanosheets and mechanical failure of the active materials. More importantly, the obtained honeycomb-like MoS₂ nanoarchitectures possess a high surface area usable for electrolyte/electrode interfaces, and the ultrathin nature of adjacent MoS₂ walls can effectively reduce the diffusion length of both electrons and ions. With these merits, our 3D honeycomb-like MoS₂ architectures@GF exhibits the high specific capacities, excellent rate capability, and superior cycling stability. Our honeycomb-structured MoS₂ architectures@GF can be extended to further broad applications in electronics, sensors, catalysis, transistors, and supercapacitors

(3) MoS₂ architectures supported on hybrid GF/CNT films for LIBs

We developed light-weight, free-standing MoS₂ nanoarchitecture-based anodes of LIBs by growing 3D worm-like MoS₂ structures directly on 3D GF/CNT hybrid films. The main features are summarized as follows: (i) The 3D porous GF/CNT films act as both the light-weight scaffold for the growth of worm-like MoS₂ nanoarchitectures, and an efficient current collector; (ii) Importantly, this work is the unique worm-like MoS₂ nanoarchitectures anchored onto the skeleton of GF/CNT with a close and robust physical contact, which can effectively inhibit the aggregation of MoS₂ nanosheets and mechanical failure of the active materials, and hence enhance the stability of active materials. Moreover, the obtained worm-like MoS₂ nanoarchitectures possess high surface area and massive pores, which can efficiently facilitate the transportation of electrolyte ions and alleviate the volume change during charge/discharge process; (iii) Another important highlight of this work is the high surface area and strong

bonding energy of GF/CNT films promote high areal loading of active materials but without aggregation, which is verified by first-principle ab initio calculations; (iv) To our best knowledge, it is the first time to report such a novel 3D worm-structured MoS₂ architectures with high areal loading, especially supported directly on 3DGF/CNT.

(4) MoS₂ Nanosheets Decorated Ni₃S₂@MoS₂ Coaxial Nanofibers for Enhanced Na-Ion Storage

A novel synergistic Ni₃S₂-MoS₂ core-shell nanofiber superstructure on 3D Ni/GF has been developed by a one-step PVP-assisted hydrothermal reaction. We summarize the highlight as follows: (i) The nanofibers anchored into Ni/GF substrate can ensure robust mechanical adhesion and provide conductive electrical connection with the current collector, avoiding the use of binders and conducting additives; (ii) Importantly, it is the first time to investigate the correlation between the heterointerface structure and electrochemical performance; (iii) The novel Ni₃S₂-MoS₂ nanofiber architectures possess a homogeneous heterointerface with a porous structure for fast ion/electron transportation, well addressing the key challenging issues on heterostructures for SIBs. More importantly, the unique MoS₂ shell (few-layer MoS₂ nanosheets self-decorating MoS₂ nanobelts) serve as a protecting layer to remedy the cycling instability of Ni₃S₂ nanofiber, while its derived metallic Mo and sulfur can greatly enhance the electrical conductivity for fast charge transfer, and effectively boost the sodium-ion capture/storage, hence improving the electrochemical activity. With these merits, our Ni₃S₂-MoS₂ core-shell nanofiber architectures as novel anodes for SIBs exhibit high capacity, superior rate capability, and stable cycling ability. In addition, the strategy proposed in our study can be extended to prepare other hybrid superstructure for prospective energy storage devices.

(5) Highly Active and Stable Architecture for Boosting Hydrogen Evolution and Lithium Storage:

Controlling nanostructures with sufficiently exposed active sites is paramount for developing effective electrode materials for energy application. For MoS₂, catalytically active sites are limited at the edge sites and thus mainly lies in the surface over the inert basal planes. Nevertheless, the presence of the basal plane is the favorable thermodynamics, which heavily reduces the number of active sites on the surface. Herein, we designed and fabricated a novel hollow tubular structure constructed by MoS₂ nanosheets-decorated nanotubes, which are directly self-supported on flexible 3DGF. The features are highlighted as follows: (i) The 3DGF plays dual roles as both the light-weight scaffold for the support of hierarchal tubular MoS₂ structures, and a current collector; (ii) It is the first report that such a simple sacrificial template method is developed to fabricate tubular MoS₂ structures, especially directly on 3DGF; (iii) Moreover, abundant broken layers and defects in hierarchal MoS₂ nanotubes brings out large surface area and diverse mesopores, which are favorable for fast ion diffusion and close electrode–electrolyte contact, leading to the enhanced number of exposed active edge sites. More importantly, the inherent reactive surfaces of nanotubes derived from their curvature and distortion of the bond angle greatly promote to the exceptionally high density of active sites. All these merits would undoubtedly contribute to the excellent electrocatalytic activity and high stability with low overpotential in the acidic electrolyte for the electrochemical HER. In addition, when evaluated as anode materials for LIBs, these hierarchical MoS₂ nanotubes manifest high specific capacity and excellent rate capability as well as extremely long-term cycle stability. This work unravels the high impact of structure design on the surface structure of nanomaterials, providing guidance for other important technological applications.

9.2 Novel Contributions

Based on the scientific results obtained in this thesis, several scientific and technological contributions have been made and are summarized as below.

9.2.1 Scientific contributions

(1) A novel $\text{Ni}_3\text{S}_2@\text{MoS}_2$ heterostructure was developed by a facile but powerful one-step solution method. By rationally adjusting the thermal treatment conditions or precursor concentration, the morphology of final products can be easily tuned. Hierarchical heterostructures demonstrate enhanced electrochemical performance compared to their counterparts, mainly due to large interfacial areas, rapid ion/ electron transport pathways, and the maximized synergetic effect. The correlation between the heterostructure and electrochemical performance provides fundamental understanding for the rational design of heterostructures.

(2) Due to the light weight, high flexibility and conductivity, 3DGF and GF/CNT films have been chosen as the growth substrates for MoS_2 nanostructures, respectively. By comparing the lithium storage capability of different flexible MoS_2 electrodes based on different substrates, the suitable products can be easily controlled. The corresponding theoretical calculations were providing to analyze the chemical interaction between MoS_2 and different carbon matrixes.

(3) A novel strategy was proposed to obtain hollow nanotubes with abundant active edge sites and high SSA. Compared to bare hollow nanotubes, hierarchical MoS_2 nanotubes with high specific surface and active sites demonstrate enhanced electrochemical performance, due to a short diffusion distance of lithium ions and sufficient electrode–electrolyte contact area, leading to the enhanced rate capability for lithium storage. Besides, they are very beneficial to HER due to the enhanced reactant diffusion, increased active site number, and the significantly lower activation energy barrier for the catalytic rate-determining step. The important results elucidate how structure design of nanomaterials can significantly impact the surface structure at the atomic scale, enabling new opportunities for enhancing structure properties and other important technological applications.

9.2.2 Technological contributions

(1) Hydrothermal reaction method was systematically explored to produce a variety of various MoS₂-based nanostructures with desirable morphologies. Especially, the growth of unique honeycomb-like MoS₂ nanoarchitectures directly on 3DGF was firstly reported by a facile hydrothermal method.

(2) A self-sacrificial template method using Ni₃S₂ nanowires as precursors has been firstly proposed to fabricate tubular MoS₂ structures on flexible 3DGF directly on flexible 3DGF. This method can be extended to prepare other tubular structured materials.

9.3 Future Work

9.3.1 Investigation of capacity and cycling decay mechanism by *n-situ* techniques

MoS₂ has shown vast potential for renewable energy storage and conversion applications, due to its intriguing physicochemical properties. Nevertheless, several issues handicap the commercial application of MoS₂ for LIBs and SIBs, including rapid structure degradation, low electrical conductivity, and sluggish charge transfer kinetics. These strategies are efficient and the decent performance can be achieved in different systems. Nevertheless, the capacity and cycling decay of MoS₂-based composites for LIBs and SIBs are still observed in all systems. Therefore, the more thorough fundamental investigation should be provided and would be significant to figure out the authentic mechanism. In the future, some *in-situ* technologies will be adopted to deeply comprehend the capacity and cycling decay mechanism, including *in-situ* XRD, XPS, Raman and TEM. Specifically, *in-situ* TEM could capture the operando state at a resolution of several nanometers, revealing the structural and the morphologies change involved in LIBs and SIBs. Besides, *In-situ* XRD and XPS can accurately investigate the crystalline structure and valence state of active materials during

lithiation/dethiation or sodiation/desodiation. These technologies can analyze the intermediate phase during cycling, which can help in-depth understanding the electrochemical mechanism, as well as the capacity and cycling decay mechanism. *In-situ* Raman spectroscopy is also a convenient and non-destructive technology for the investigation of electrochemical reaction processes in various energy storage devices. Especially, our group has strong research background of Raman spectroscopy, which can provide convenient facility for further work in this area.

9.3.2 Full sodium cell investigation on $\text{Ni}_3\text{S}_2@\text{MoS}_2$ heterostructures

Since $\text{Ni}_3\text{S}_2@\text{MoS}_2$ heterostructure presents excellent electrochemical performance in half sodium cells, with Na as both reference and counter electrode. To validate the practical applicability of this novel anode material, it would be necessary to further investigate the full sodium cells using $\text{Ni}_3\text{S}_2@\text{MoS}_2$ heterostructure as an anode. Moreover, to obtain an optimized electrochemical performance with a long lifetime, many scientific and technical issues should be firstly addressed, including searching suitable cathodes materials for matching with the $\text{Ni}_3\text{S}_2@\text{MoS}_2$ heterostructure anode. Furthermore, the thermal stability of SIBs is also vital for the commercial application in large scale. Thus, the investigation of the thermal stability of the full cell should be carried out. The electrochemical thermodynamic measurement studies and other thermodynamics studies are employed to characterize the thermal safety of the as-assembled full Na cell.

List of Publications:

- [1] **Wang Jin**, Liu Jilei, Yang Hao*, Chao Dongliang, Yan Jiaxu, Savilov Serguei V., Lin Jianyi, Shen Zexiang*. MoS₂ nanosheets decorated Ni₃S₂@MoS₂ coaxial nanofibers: Constructing an ideal heterostructure for enhanced Na-ion storage. *Nano Energy*, 2016, 20, 1.
- [2] **Wang Jin**, Liu Jilei, Yang Hao*, Chen Zhen, Lin Jianyi, Shen Zexiang*. Active sites-enriched hierarchical MoS₂ nanotubes: highly active and stable architecture for boosting hydrogen evolution and lithium storage. *Journal of Materials Chemistry A*, 2016, 4, 7565.
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Oral Presentations:

- [1] **Wang. J.**; Lin, J.; Shen, Z.; Controlled Synthesis of FeOOH Nanorods and Their Transformation to Mesoporous Fe₂O₃, Fe₃O₄ @ Carbon Nanorods as Anode Materials for Lithium Ion Batteries. *International Conference on Materials for Advanced Technologies (ICMAT 2013)*, 2013, Singapore.
- [2] **Wang. J.**; Lin, J.; Shen, Z.; Ni₃S₂@MoS₂ Nanowire Arrays for High-performance Electrochemical Energy Storage. *Asian Spectroscopy Conference (ASC 2013)*, Dec 17-19, 2013, Singapore
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- [5] **Wang. J.**; Lin, J.; Shen, Z.; Binder-free Nanoarchitected MoS₂ and Composites Supported on various Substrates for High-performance Energy Storage. *International Conference on Materials for Advanced Technologies (ICMAT 2015)*, 2015, Singapore.
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