Design and synthesis of hollow nanostructures as highly efficient hosts for advanced lithium-sulfur/selenium sulfide batteries

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**NANYANG
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SINGAPORE

**DESIGN AND SYNTHESIS OF HOLLOW
NANOSTRUCTURES AS HIGHLY EFFICIENT HOSTS
FOR ADVANCED LITHIUM-SULFUR/SELENIUM SULFIDE
BATTERIES**

ZHANG JINTAO

**SCHOOL OF CHEMICAL AND BIOMEDICAL ENGINEERING
2019**

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BATTERIES**

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School of Chemical and Biomedical Engineering

A thesis submitted to the
Nanyang Technological University
in partial fulfilment of the requirement for the degree of
Doctor of Philosophy

2019

Statement of Originality

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

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Supervisor Declaration Statement

I have reviewed the content and presentation style of this thesis and declare it is free of plagiarism and of sufficient grammatical clarity to be examined. To the best of my knowledge, the research and writing are those of the candidate except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

Feb 20, 2019

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Date

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Prof. David Lou Xiong Wen

Authorship Attribution Statement

This thesis contains material from 3 papers published in the following peer-reviewed journals where I was the first author.

Chapter 4 is published as Zhang, J. T.; Hu, H.; Li, Z.; Lou, X. W. Double-shelled nanocages with cobalt hydroxide inner shell and layered double hydroxides outer shell as high-efficiency polysulfide mediator for lithium-sulfur batteries. *Angewandte Chemie-International Edition* 55, 3982-3986 (2016). DOI: 10.1002/anie.201511632

The contributions of the co-authors are as follows:

- Prof David Lou provided the initial project direction and edited the manuscript drafts.
- I prepared the manuscript drafts. The manuscript was revised by Dr Li Zhen.
- I co-designed the study with Prof. Lou and performed all the laboratory work at the School of Chemical and Biomedical. I also analyzed the data.
- All microscopy, including sample preparation, was conducted by me in the Facility for Analysis, Characterization, Testing and Simulation.
- Dr Hu assisted in the synthesis of the materials.

Chapter 5 is published as Zhang, J. T.; Li, Z.; Chen, Y.; Gao, S. Y.; Lou, X. W. Nickel-iron layered double hydroxide hollow polyhedrons as a superior sulfur host for lithium-sulfur batteries. Published online, *Angewandte Chemie-International Edition* 57, 10944-10948 (2018), DOI: 10.1002/anie.201805972.

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- Prof David Lou provided the initial project direction and edited the manuscript drafts.
- I prepared the manuscript drafts. The manuscript was revised by Dr Li Zhen Dr Gao and Chen Ye.
- I co-designed the study with Prof. Lou and performed all the laboratory work at the School of Chemical and Biomedical. I also analyzed the data.
- All microscopy, including sample preparation, was conducted by me in the Facility for Analysis, Characterization, Testing and Simulation.

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Abstract

Due to the overwhelming superiorities in energy density and material cost, lithium-sulfur (Li-S) batteries have been recognized as a potential candidate for next-generation electrochemical energy-storage (EES) technology. The main challenges for Li-S batteries lay in the enhancement of reaction kinetics and the suppression of the polysulfide dissolution at high S loading electrodes. In the first two projects, we have focused on the host materials. Two types of novel hollow nanostructures have been successfully designed and synthesized as efficient hosts for S to improve the electrochemical performance of Li-S batteries. After that, we have used SeS_2 instead of S as the active material to further enhance the performance of Li storage. It is proved that the introduction of a certain proportion of Se into S-based cathodes could obviously improve the integrated battery performance. The main results and new findings in this work are summarized as follows.

1. Double-shelled nanocages with inner $\text{Co}(\text{OH})_2$ shell and outer LDH shell (CH@LDH) have been designed and synthesized as a conceptually new sulfur host for Li-S batteries. Specifically, the hollow CH@LDH polyhedra with complex shell structures not only maximize the advantages of hollow nanostructures for encapsulating a high content of sulfur (75wt%) but also provide sufficient self-functionalized surfaces for chemically bonding with LiPSs to suppress their outward dissolution. When evaluated as cathode material for Li-S batteries, the CH@LDH/S composite shows a significantly improved electrochemical performance.

2. Hollow Ni/Fe LDH polyhedrons have been designed and fabricated as an advanced sulfur host for enhancing the performance of Li-S batteries. The Ni/Fe LDH host shows multiple advantages. First, the Ni/Fe LDH shells can provide sufficient

sulfiphilic sites for chemically bonding with LiPSs. Second, the hollow architecture can provide sufficient inner space for both loading a large amount of sulfur and accommodating its large volumetric expansion. Moreover, once the active material is confined within the host, the shells could easily restrict the outward diffusion of LiPSs, guaranteeing prolonged cycle life even with high sulfur loading. As a result, the S@Ni/Fe LDH cathode has successfully solved the main issues related to sulfur electrodes, and it exhibits significantly improved electrochemical performances with prolonged life over 1000 cycles and excellent rate properties.

3. A freestanding lotus root-like carbon fiber network decorated with CoS₂ nanoparticles (denoted as CoS₂@LRC) has been designed and prepared as the SeS₂ host for enhancing the lithium storage performance. The integrated electrode is constructed by 3D interconnected multichannel carbon fibers, which can not only accommodate high content of SeS₂ (70 wt %), but also promise excellent electron and ion transport for achieving high capacity utilization of 1015 mAh g⁻¹ at 0.2 A g⁻¹. What is more, there are numerous CoS₂ nanoparticles decorated all over the inner walls and surfaces of the carbon fibers, providing efficient sulfiphilic sites for restricting the dissolution of LiPSs and LiPSes during the electrochemical processes, thus successfully suppressing the shuttle effect and maintaining excellent cycling stability over 400 cycles at 0.5 A g⁻¹.

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List of abbreviations

Li-S: lithium-sulfur batteries

LiPSs: lithium polysulfides

LiPSes: lithium polyselenides

Li₂S: lithium sulfide

SeS₂: selenium sulfide

Se_xS_y: selenium-sulfur solid solutions

S: sulfur

Se: selenium

LIBs: lithium-ion batteries

SIBs: sodium-ion batteries

EES: electrochemical energy storage

1D: one-dimensional

2D: two-dimensional

3D: three-dimensional

DSNCs: double-shelled nanocages

TiO₂: titanium dioxide

MnO₂: manganese oxide

CoO/Co₃O₄: cobalt oxide

CoS₂: cobalt sulfide

MoS₂: molybdenum sulfide

NiS: nickel sulfide

VN: vanadium nitride

TiN: titanium nitride

WN: tungsten nitride

C_3N_4 : carbon nitride

$Co(OH)_2$: cobalt hydroxide

$Ni(OH)_2$: nickel hydroxide

LDH: layered double hydroxides

ZIF-67: zeolitic imidazolate framework-67

MIL-88A: matériaux institut lavoisier-88A

$FeCl_3$: iron chloride hexahydrate

$Co(Ac)_2$: cobalt acetate tetrahydrate

$Ni(NO_3)_2$: nickel nitrate hexahydrate

$Co(NO_3)_2$: cobalt nitrate hexahydrate

Na_2MoO_4 : sodium molybdate dihydrate

Li^+ : lithium cation

OH^- : hydroxide

Fe^{3+} : ferric cation

Ni^{2+} : nickel cation

Co^{2+} : cobaltous cation

MoO_4^{2-} : molybdate ion

PAN: polyacrylonitrile

PS: polystyrene

DMF: N,N-dimethylformamide

DI: deionized

NMP: N-methyl pyrrolidone

super-P-Li/Ketjen black: carbon black

PVP: polyvinylpyrrolidone

PVDF: polyvinylidene fluoride

CNTs: carbon nanotubes

CNFs: carbon nanofibers

GO: graphene oxide

rGO: reduced graphene oxide

LRC: lotus root-like carbon fibers

PC: propylene carbonate

EC: ethylene carbonate

DEC: diethyl carbonate

LiPF₆: lithium hexafluorophosphate

DME: 1,2-dimethoxyethane

DOL: 1,3-dioxolane

LiTFSI: bis(trifluoromethane)sulfonimide lithium salt

LiNO₃: lithium nitrate

Ar: argon

N₂: nitrogen

H₂: hydrogen

XRD: X-ray diffraction

FESEM: field-emission scanning electron microscope

EDX: energy-dispersive X-ray spectroscopy

TEM: transmission electron microscope

SAED: selected-area electron diffraction

HRTEM: high-resolution transmission electron microscope

TGA: thermogravimetric analysis

BET: Brunauer-Emmett-Teller

DFT: density functional theory

XPS: X-ray photoelectron spectroscopy

UV-Vis: ultraviolet-visible

CV: cyclic voltammetry

EIS: electrochemical impedance spectroscopy

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Chapter 1. Introduction

1.1. Background

The continuous increase of energy consumption all over the world has generated a clear environmental fingerprint of humanity on the climate of earth.^[1] As a result of fossil combustion, the world confronts with the energy crisis and environmental pollution.^[2] In the past decades, great efforts have been devoted to investigating various electrochemical energy storage (EES) systems to utilize sustainable but intermittent renewable sources such as solar, wind and tide.^[2] Among different electrochemical energy storage and conversion systems, the rechargeable batteries are generally considered as one of the most important technologies for powering consumer electronics, portable devices, electric vehicles, et al.^[2] In the field of rechargeable batteries, high energy density electrochemical systems have been a research focus over the past decades. After two decades of development, lithium-ion batteries (LIBs) based on intercalation compounds are approaching their energy density limit,^[3] and hence are unable to further satisfy the ever-growing demands of mobile electronic devices with increased power consumption, or electric vehicles with an extended driving range.^[4] New systems with higher energy densities are urgently required for the rapidly evolving markets. As one of the most promising next-generation EES technologies, Li-S batteries has been studied all around the world and the numbers of publications/patents have increased exponentially.^[1] It is generally accepted that S exhibit the highest theoretical gravimetric energy density among all solid-state cathode materials, which is theoretically double that of the state-of-art cathode materials of LIBs (**Figure 1.1**).^[5] Moreover, the material cost of S could be greatly reduced compared with that of conventional LIBs, due to the

abundance of S in the earth's crust, making it suitable for both transportation and large-scale (grid-level) energy storage applications.^[6]

Figure 1.1. Energy density of various electrochemical storage systems. Reproduced with permission.^[7] Copyright 2015, John Wiley and Sons.

Li-S batteries demonstrate remarkable superiorities compared with traditional LIBs.^[1] First of all, S atoms could accept two electrons resulting in the conversion of elemental S to lithium sulfide (Li_2S) in an ideal cell.^[6] Therefore, the theoretical specific capacity of S cathode (1672 mAh g^{-1}) is a magnitude higher than that of the cathode materials (such as lithiated transition-metal oxide and phosphate cathode materials) in LIBs.^[8] Moreover, S is abundant in nature, and its production cost is much cheaper compared with the common cathode materials composing of Co, Ni in LIBs, which makes it rather favorable for EES applications.

However, the commercialization of the rechargeable Li-S battery is still hindered by three main issues of: (a) the inherent poor electronic conductivity of S and its end products of discharge ($\text{Li}_2\text{S}/\text{Li}_2\text{S}_2$), (b) the dissolution of intermediate lithium polysulfides (LiPSs), and (c) large volumetric expansion of $\sim 80\%$ upon full lithiation. These issues bring about serious self-discharge, low Coulombic efficiency and rapid

decline of capacity upon cycling.^[9] Thus, there is a great challenge to enhancing the performance of Li-S batteries, especially in the high loading and high S content electrodes.

As a congener of S, Se is also considered as a potential alternative in reactions with Li ions with promising electrochemical performance.^[10] Se shows higher conductivity with better reaction kinetics than S, but its lower gravimetric capacity and higher cost limit the application of Li-Se batteries.^[11] The introduction of a certain proportion of Se into S-based cathodes is an effective strategy for enhancing the integrated battery performance.^[12] However, the study of Se_xS_y -based materials is still in a very early stage, and the ideas of recent studies are usually limited to the formation of composites of pristine carbonaceous materials with Se_xS_y , so the application potential of the Se_xS_y cathode has not yet been fully demonstrated.^[12-13] It has been found that, as for S cathodes with an ether-based electrolyte, Se_xS_y cathodes also suffer serious dissolution of the reaction intermediate products during charging/discharging processes, which could not be readily controlled simply by using ordinary pure carbonaceous hosts.^[14] As inspired by the idea of chemically binding soluble LiPSs to polar substrates in Li@S batteries, it is believed that some rationally selected polar materials might also be effective for Se_xS_y cathodes.

1.2. Motivation

The popular strategy to offset the shortcomings of Li-S and Li- SeS_2 batteries is loading S or SeS_2 on other auxiliaries with high conductivity and LiPSs absorbability for achieving high utilization of S or SeS_2 and enhanced cycling stability. In the early years, plenty of carbon materials such as porous carbon,^[15-16] graphene,^[17] carbon nanotubes,^[18] hollow carbon nanofibers/nanospheres^[19-20] have been employed as

support materials for Li-S and Li-SeS₂ batteries due to their superior electrical conductivity and physical absorbability. Although the specific capacity of these S@C and SeS₂@C nanohybrids is much superior over that of pure S and SeS₂ cathodes in initial cycles, rapid capacity decay occurs in the following discharge/charge process because of the weak interaction between nonpolar carbonaceous supports and polar LiPSs.^[21] More recently, transitional metal compounds (oxides,^[22] sulfides,^[23] carbides,^[24] nitrides,^[25] and hydroxides^[26]) have been introduced to S cathode to provide much stronger chemical immobilization toward LiPSs. However, most transition metal compounds could not provide sufficient active sulfiphilic sites to immobilize the LiPS, especially at a high S loading, because of their limited surface areas.^[27] Hollow structures have the structural advantages that once the LiPSs near the shell are immobilized, the shell and the LiPSs near the shell would act as dams and then the inner LiPSs will be controlled naturally.^[27] Therefore, it is desirable to fabricate effective transitional compounds with hollow structures to achieve high-performance Li-S and Li-SeS₂ batteries without sacrificing active mass loading.

1.3. Overall objective

The main objective of this research is to find suitable transitional metal materials with unique structures as host materials for high-performance Li-S or Li-SeS₂ batteries. This Ph.D. project focuses on developing different LDH with controlled shell numbers and compositions as S host materials to improve the electrochemical performance of Li-S batteries. Moreover, in order to further improve the electrochemical performance of Li-S batteries, the host materials are optimized by using conductive CoS₂ decorated carbon fibers, and the active materials are also optimized via introducing conductive Se

in S. Specifically, the objective of this project can be categorized into the following three aspects.

1.3.1. Synthesis of $\text{Co}(\text{OH})_2@ \text{Ni/Co LDH}$ (noted as CH@LDH) with double shells as S host materials for high-performance Li-S batteries

The employment of transition-metal hydroxides as potential S hosts is a satisfying direction to improve the electrochemical performance of Li-S batteries due to the abundant hydrophilic and hydroxy groups with strong chemical interactions to LiPSs. Moreover, the layered double hydroxide (LDH) with high anion exchange capability may be superior to normal transition-metal hydroxide due to the possibility of entrapment of LiPSs within the interlayers. Motivated by the structural features of hollow structures for encapsulation of a large amount of S, double-shelled nanocages with an internal layer of $\text{Co}(\text{OH})_2$ and an outermost layer of Ni/Co LDH are designed and fabricated as LiPSs mediator for Li-S batteries.

1.3.2. Exploring Ni/Fe LDH with a single-shell structure as S host materials for long cycle life Li-S batteries.

The LiPSs in the single shell might possess shorter electron and ion transfer path compared to double shells. Moreover, Ni/Fe LDH shows superior electrocatalytic activity in OER. Considering these factors, novel hollow Ni/Fe LDH polyhedrons are designed as an S host to restrict the dissolution of LiPSs. The enhanced electrochemical data indicate the Ni/Fe LDH shell could offer plenty of sulfiphilic sites to link with LiPSs through chemical bonds and effectively accelerate the redox reactions of LiPSs. Moreover, the hollow configuration could offer sufficient internal cavity to load a large amount of S and address the pronounced volume changes. More importantly, the LiPSs are confined within the shell to form a barrier for the inner active materials. Therefore,

the inner active LiPSs will be controlled naturally. When evaluated as cathodes for Li-S batteries, the S@Ni/Fe LDH hybrid structure can achieve remarkably enhanced lithium storage properties in terms of cycling life over 1000 times and remarkable capacity retention at high current density.

1.3.3. Construction of a freestanding CoS₂@LRC/SeS₂ electrode for high-performance Li-SeS₂ batteries

CoS₂ has proven as excellent S host for inhibiting the dissolution of LiPSs dissolution in Li-S batteries due to its inherent metallic conductivity and catalytic activity. During the discharge/charge cycles, CoS₂ can not only link strongly with LiPSs through chemical bond, but also effectively expedite the redox reactions of LiPSs. Inspired by these results, CoS₂ might be useful for Se_xS_y cathodes. Therefore, we report the synthesis of a 3D carbonaceous network constructed from CoS₂ decorated lotus root-like nanofibers (denoted as CoS₂@LRC) as binder-free host material for SeS₂ cathode in Li-SeS₂ batteries. The as-prepared 3D conductive network exhibits obvious structural advantages. On the one hand, the interwoven LRC fibers within the network could ensure fast electron and ion transport for high rate capabilities. On the other hand, the parallel channels within the carbon nanofiber could offer enough void space to well address the volumetric changes of active materials during lithiation reaction. Moreover, the decorating CoS₂ nanoparticles in the LRC can provide plenty of sulfiphilic sites to confine LiPSs and LiPSes during the discharge/charge processes, leading to good conservation of Se_xS_y and remarkable cycling stability.

1.4. Organization

The layout of this thesis is shown below:

In Chapter 1, a brief introduction of the study is provided including the background, motivation, and objectives of the research project. After that, some recent advances in the strategies used to improve the electrochemical performance of Li-S batteries are reviewed in Chapter 2. The general synthetic methodology, materials characterization techniques, and electrochemical measurement procedures applied in this project are summarized in Chapter 3. For Chapter 4 and 5, two novel LDH host materials are presented as high-efficiency polysulfide mediators for Li-S batteries, including double-shelled nanocages with Co(OH)_2 inner shell and Ni/Co LDH out shell, and single-shelled polyhedrons with Ni/Fe LDH. Chapter 4 firstly demonstrate the effectiveness of LDH towards LiPSs. To further improve the electrochemical performance of Li-S batteries, the compositions of LDH are optimized in Chapter 5. In Chapter 6, to further improve the electrochemical performance, the cathode materials are optimized from both the host and active materials. We use integrated CoS_2 decorated multichannel carbon fibers as host materials to improve the conductivity of the host, and introduce Se in active S to improve the conductivity of active materials. The electrochemical performance of all the three electrodes are investigated systematically. Finally, the overall conclusion of the three works is drawn in Chapter 7, together with some prospects for future studies in this research area.

Chapter 2. Literature Review

2.1. Mechanisms of Li-S batteries

Li-S batteries consist of three parts, which are an S cathode, a Li anode, and electrolyte.^[28] **Figure 2.1** describes the components and the operating principles. The electrical energy can be stored in the S electrode through a reversible electrochemical reaction between Li^+ and S.

Figure 2.1. Schematic diagram of a Li-S cell showing its components and the chemical reaction.

After assembly, the Li-S cell is in a charged state. When connected with an extra load, the Li-S system will discharge to initiate the oxidation reaction at the anode surface by losing one electron to generate Li^+ . This derived electron will transfer through the load and arrive in the cathode to reduce S into Li_2S with the assistance of Li^+ in the electrolyte. As for the charging process, the opposite phenomena will occur.^[9]

On the surface, the overall discharge/charge process seems a single-step reaction, but in reality, the process contains multiple steps. For example, the reduction of S includes 4 steps, which can be divided into two classes: single-phase reaction and two-phase reaction.^[8] The information about the reduction steps, the related products, and the mechanism is shown in **Figure 2.2** and illustrated below.

Step I: A two-phase reaction where solid S_8 is reduced to liquid Li_2S_8 . Because of the high polarity, the resultant Li_2S_8 is highly soluble in the liquid organic electrolyte. This Li_2S_8 solution will act as catholyte for the sequential reduction.

Step II: A single-phase reaction where the liquid Li_2S_8 is reduced to liquid Li_2S_6 and Li_2S_4 .

Step III: A two-phase reaction where the liquid Li_2S_6 and Li_2S_4 are further reduced to solid Li_2S_2 .

Step IV: A single-phase reaction where solid Li_2S_2 is finally reduced to solid Li_2S .

Generally speaking, the lower plateau reaction for step III is sluggish compared to the upper plateau reaction for step I and step II because extra energy is required for nucleation of the solid phase and solid-state diffusion is rather slow during the conversion from solid Li_2S_2 to solid Li_2S .^[8] Based on the total mass of S and 2Li, the theoretical specific capacity for the integral Li-S full cell is about 1166 mAh g^{-1} .^[29] As the average discharge voltage plateau of the multiple plateaus is $2.2 \text{ V vs Li}^+/\text{Li}$, the

gravimetric energy density of a Li-S full cell is about 2600 Wh kg⁻¹. Accordingly, the average volumetric energy density of a Li-S full cell is about 2200 Wh L⁻¹.^[6]

Figure 2.2. Voltage of a Li-S cell during discharge at 0.05 C and the formation of various intermediates. Reproduced with permission.^[30] Copyright 2015, The Electrochemical Society.

It should be mentioned that there is a huge controversy among the scientific community about the reaction mechanism and detailed steps of the Li-S batteries. Some research groups believe the existence of Li₂S₆ along with Li₂S₈ in the first discharge plateau.^[6] Others think the individual steps will generate multiple reduction products instead of any one specific product.^[31] In general, the charge/discharge process is not a simple single reaction but combine multiple steps with many soluble intermediates.

2.2. Challenges of Li-S batteries

Although Li-S batteries have attracted plenty of research interests all over the world since the early 2000s, many critical challenges still exist to impede commercialization of Li-S batteries. Generally, researchers need to solve the following three main obstacles for practical application of Li-S batteries.

a. Insulating nature of S and Li₂S

The first challenge is the poor electron/ion conductivity of elemental S and solid reduced product (Li_2S_2 and Li_2S). The non-conducting S shows an electrical conductivity of $5 \times 10^{-30} \text{ S cm}^{-1}$, leading to the huge internal resistance of the Li-S battery. Due to their insulating nature, Li-S batteries confront with two serious problems.

(i) Low utilization

The real utilization of active material is hampered by the essential insulating nature of S and Li_2S . The generation of insoluble and insulating Li_2S during discharge will cover the cathode surface, forming a passivation layer. Due to this passivation layer, the full utilization of S in the electrode is impeded, resulting in low capacity and low rate capacity.

(ii) Sluggish kinetics

Usually, in common Li-S voltage profiles, there is a higher polarization at the lower discharge plateau because of the limited kinetics for both electrons and lithium ions, which will lead to inferior rate capabilities.

b. Diffusion of the soluble intermediates

As mentioned before, the intermediate long-chain LiPSs species (Li_2S_4 - Li_2S_8) could become soluble in ether-based electrolytes during the cycling process. However, some of them will diffuse to the anode side, resulting in some undesirable side reactions. After reacting at anode side, the solid products (Li_2S or Li_2S_2) will deposit on the anode surface, leading to the loss of active materials and the passivation of Li metal anode. Moreover, some high-order LiPSs get electrons and Li^+ at anode side and be reduced to low-order LiPSs during charging process. The reduced soluble LiPSs will diffuse back to the cathode, which is called “shuttle effect”, this process will lead to low Coulombic efficiency.^[5] In general, the diffusion of the soluble LiPSs is the main challenge of the Li-S batteries, which will cause the rapid capacity decay during cycling.

c. Large volumetric expansion of S upon lithiation

Due to the discrepancy in density between S (2.03 g cm^{-3}) and Li_2S (1.66 g cm^{-3}), elemental S will experience a high volumetric expansion of about 80% upon full lithiation to Li_2S . The huge volume change will cause pulverization, exfoliation and lose the contact of the electrode materials with the current collector. As a result, a significant capacity fade will be observed.

2.3. Cathodes fabrication for Li-S batteries

The S cathode is the key component of Li-S batteries to ensure the whole device with high energy density. However, as we mentioned above, three critical issues needed to be overcome. First, the low electrical conductivities of S and Li_2S cause low utilization of S, larger polarization and inferior rate capabilities, making S unsuitable for direct use as a conductive cathode. Second, dissolution of LiPSs leads to the loss of active materials, shuttle effect, and the passivation of Li metal anode. Third, the repeated volume expansion of S leads to the pulverization of cathode. To cope with these shortcomings, S is usually combined with host materials, which can improve the conductivity, effectively trap LiPSs, and accommodate the volume change. According to the confining mechanisms, the functions of developed S hosts could be generally classified into two categories: the physical confinements and chemical immobilization.

2.3.1. Physical Confinements

Physical confinement of S in pores of the conductive material (usually a carbonaceous material or conductive polymer) has been considered as one of the most effective approaches to overcome the problems from an early stage. Commonly, these host materials can not only ameliorate electron/ion transport in the discharge/charge processes but also trap LiPSs with the help of their physical adsorption capability. The

porous carbonaceous materials, considering their pore size, can be divided into three categories: microporous carbons (< 2 nm), mesoporous carbons (2-50 nm), macroporous carbons (> 50 nm).^[5] Since S cathode within various pore sized hosts shows different electrochemical behaviors, in this section, cathode structures with various pore sizes are introduced.

2.3.1.1. Microporous carbon

For the microporous carbon hosts, the electrochemical behavior of S/carbon composite is very different from that of the normal S electrodes, especially when the pore size decreases to around 0.5 nm. A lower voltage plateau could be observed on this type of cathode system, and the S content should be kept below a certain level for good lithium storage properties. Due to their smaller size than S₈ crown rings, the S₂₋₄ molecules are preferentially confined in the ultrafine micropores of carbon matrixes instead of cyclo-S₈ molecules (**Figure 2.3a**).^[32] Zhang et al. reported a primitive study about the infusion of S₂₋₄ into microporous carbon matrix.^[33] In their study, carbon spheres with narrow micropores are selected as the conductive matrix. After thermal treatment of a mixture of S and microporous carbon at 149 °C for 6h and at 300 °C for 2h, the S with a highly dispersed state is successfully loaded within the micropores of carbon spheres (**Figure 2.3b**). When tested as cathode materials, the S₂₋₄/microporous carbon spheres demonstrate a sole discharge plateau at 1.8 V, which is quite different from the conventional S cathodes with two discharge plateaus at 2.3 and 2.1 V. This result indicates S₂₋₄ is directly changed into Li₂S without the formation of soluble LiPSs. Accordingly, only one plateau at about 2 V can be found in the charging branch, which refers to the oxidation reaction from Li₂S to S₂₋₄ without the formation of S₈ molecules (**Figure 2.3c**).^[34]

Figure 2.3. (a) A scheme of small S molecules and their redox reaction process confined inside the micropores. (b) Discharge-charge voltage profiles of S/microporous carbon in glyme-based electrolyte. (c) Only small LiPSs species can enter the confined space of ultramicropores. (d) Schematics of the lithiation process in an S microporous carbon cathode in carbonate-based electrolyte. (a) Reproduced with permission.^[32] Copyright 2012, American Chemical Society. (b) Reproduced with permission.^[33] Copyright 2010, Royal Society of Chemistry. (c) Reproduced with permission.^[34] Copyright 2013, John Wiley and Sons. (d) Reproduced with permission.^[35] Copyright 2014, John Wiley and Sons.

The process without the formation liquid LiPSs is designed as ‘solid-solid reaction’. As a result, the dissolution of LiPSs in the liquid electrolyte could be totally avoided, resulting in an impressive cyclic capacity for the microporous carbon/S₂₋₄ electrodes. It should be noted that S₂₋₄ based cathode displays similar cycling stability in both ether and carbonate-based electrolytes because the micropores can prevent the access between S₂₋₄ molecules within the solvents in the electrolyte (Figure 2.3 d, e).^[34-35] By contrast, the S₈ based electrode could only work well in ether-based electrolyte because the nucleophilic LiPSs could react with carbonate-electrolyte irreversibly.

2.3.1.2. Mesoporous carbon

The cathode made of S on the microporous carbons demonstrates excellent cyclability, however, its rate capability is largely compromised.^[36] Earlier reports suggest that the S cathode loading on mesoporous carbon host could exhibit an excellent rate performance with good cyclability.^[37] Mesoporous carbon with interconnected porous structures possesses high pore volumes, high surface areas, and high electrical conductivity, which has been issued as host materials for Li-S batteries.^[38] Wang et al. used active carbon with a high surface area of 1080 m² g⁻¹ to load elemental S by a melt-diffusion method. The mixture is firstly annealed to 200 °C for 6 h to melt S and maximize its diffusion into the mesopores of carbonaceous host. After that, the temperature is increased to 300 °C for 3 h to consume the redundant S remaining on the outside surface of host materials. The coin cell is assembled by using liquid electrolyte of PC-ED-DEC (1:4:5, v/v) containing 1 M LiPF₆. As the carbonate-based solvents can chemically react with the reduced S species (LiPSs), the cathodic peak near 2.3 V appears only in the 1st cycle. After that, the specific capacity can be stabilized at 400 mAh g⁻¹ for the following 25 cycles. In 2009, Nazar et al. used mesoporous carbon with highly ordered channels (CMK-3) as S host materials (**Figure 2.4a**).^[16] They reported

that the melted S is encapsulated within the mesopores of CMK-3 by capillary effect, and the dissolved LiPSs are largely confined in the mesoporous carbon host during cycling. The CMK-3 framework can not only act as an electronic conduit to the active S, but also serve as a mini-electrochemical reaction chamber. Benefitting from these advantages, the Coulombic efficiency for CMK-3/S in the first discharge-charge cycle is 99.94% without any overcharge, and the specific capacity can be stabilized at 800 mAh g⁻¹ for 20 cycles.

Figure 2.4. (a) A schematic diagram of S confined within the interconnected pore structure of CMK-3. (b) Illustration of the S/C composite by using a bimodal porous carbon as the support. (c) S mesoporous carbon cathode in the carbonate-based electrolyte. (a) Reproduced with permission.^[16] Copyright 2009, Nature Publishing Group. (b) Reproduced with permission.^[39] Copyright 2009, American Chemical Society. (c) Reproduced with permission.^[35] Copyright 2014, John Wiley and Sons.

Liang et al. used bimodal porous carbon materials as suitable substrates for the S/C composite cathode, which shows high energy and high-power density (Figure 2.4b).^[39] Moreover, the bimodal mesoporous carbon/S composites proposed by Nazar's group

also exhibit high rate properties without compromising the capacity and cycle stability.^[40-41] Notably, the pore size of mesoporous carbon is higher than EC or DMC (Figure 2.4c), which can chemically react with LiPSs. Moreover, the electrolytes used in these works are no longer carbonates but ethers, which show superior stability than carbonates toward LiPSs.^[42]

2.3.1.3. Hybrid structures

Although mesoporous carbons are widely explored as S host with high S loading, the cycle stabilities are not always good compared with microporous carbon. One important reason is that the S species in mesopores can still be contacted by organic liquid electrolyte solvents, leading to inevitable dissolution of polysulfide into the electrolyte. Whereas, S hosts based on microporous carbons are capable to prevent the dissolution of LiPSs for enhanced cycling stability. Nevertheless, their S loading content is usually low (~ 40 wt%), and the reaction kinetics is quite sluggish due to the “solid-solid” process. As a result, the energy density in these systems is always quite low. To better balance the advantages and disadvantages of mesoporous and microporous carbons, hybrid nanoarchitectures based on these two nanostructures are designed to not only prolong the cycle life but also improve the rate performances at a relatively high S loading.

For example, Li et al. reported highly ordered meso-microporous core-shell carbon as S host (**Figure 2.5 a,b**).^[15] Such a hierarchical carbon container combines the advantages of both mesoporous carbon and microporous carbon. Specifically, the mesoporous core ensures sufficient space for high S loading and realize a high utilization of S. On the other hand, the external microporous layer serves as a physical barrier to enable long lifespan. Moreover, the hybrid core-shelled meso-microporous structure can ensure the high specific capacity of the whole cathode at high rates. As a

result, the S/meso-microporous hybrid delivers a high capacity of 837 mAh g⁻¹ at 0.5 C over 200 cycles with a minor capacity fading of 20%, demonstrating that the success of the proposed structural design. There are also some other micro-mesoporous carbon nanostructures reported as S hosts in Li-S systems, such as carbon spheres with dual-pore size features,^[43-44] graphene,^[45] CNFs,^[46-47] and CNTs.^[48]

Figure 2.5. (a,b) Schematic illustration for the highly ordered meso-microporous core-shell carbon and S@carbon composite. (c) TEM image of single-shelled S@ carbon spheres. (d,e) TEM image of double-shelled S@carbon spheres. (a,b) Reproduced with permission.^[15] Copyright 2014, American Chemical Society. (c) Reproduced with permission.^[19] Copyright 2011, John Wiley and Sons. (d,e) Reproduced with permission.^[20] Copyright 2012, John Wiley and Sons.

It should be mentioned that macroporous carbons with large open pores cannot stabilize LiPSs efficiently, which lead to fast capacity fade in the continuous discharge/charge processes. Despite these disadvantages, it has been reported that

microporous hollow nanostructures composed of micro or mesoporous shells show great potential as S hosts. On the one hand, the inside hollow cavity with a large space could enable the high loading of S. On the other hand, the micro or mesoporous shells have two important roles: physical barrier for restricting the outward diffusion of LiPSs and channels for carrying the electron and Li ions into the internal space. As a result, the hollow nanostructures with micro or mesoporous features could exhibit the superiorities from both macropores and micro/mesopores to realize high S loading and good cycling stability.

Archer et al. reported using single-shelled mesoporous hollow carbon spheres as S host materials for Li-S battery.^[19] The mesoporous hollow carbon spheres can encapsulate and sequester active S in their interior and porous shell (Figure 2.5 c), thereby minimizing LiPSs dissolution and shuttling in the electrolyte. When evaluated at the cathode materials in Li-S batteries, the as-prepared S@single-shelled mesoporous hollow carbon spheres display outstanding electrochemical performance at both low and high current densities. In another case, Lou and co-workers prepared double-shelled hollow carbon spheres using SnO₂ hollow spheres as the hard templates (Figure 2.5 d).^[20] When evaluated as S host materials for Li-S batteries, the double shells could effectively encapsulate a relatively high amount of active S, suppress the outward diffusion of LiPSs, and withstand volume variation upon prolonged cycling. As a result, the S@double-shelled hollow spheres exhibit significantly improved electrochemical performance.

2.3.2. Chemical Immobilization

Physical prevention of the dissolution of LiPSs in porous carbonaceous host has been verified as effective strategies to improve the lithium storage performance of Li-S

batteries. Nevertheless, the physical confinement could not completely inhibit the dissolution of LiPSs because of the poor interactions between polar LiPSs and nonpolar carbonaceous matrix. Therefore, strategies using carbon hosts via physical confinement are only appropriate for short-term cycling.

In recent studies, approaches for confining LiPSs based on strong chemical interactions between host materials and LiPSs have been reported to prolong the cycling life of Li-S batteries. Different from the previously mentioned physical strategies in limited spaces, the chemical anchoring approaches rely to strong interactions between polar host materials and LiPSs on the interface. During battery operation, two vital parameters including surface functionality, intrinsic polarity, and nucleophilicity could largely influence the bond strength between the polar host materials and LiPSs. In this section, we focus on various types of chemical strategies for anchoring LiPSs on different polar hosts. One is the chemical affinity by polar interaction; another is the catalytic effect on enhancing the conversion of LiPSs.

2.3.2.1 Chemical Affinity by polar interaction

This section covers researches on various strategies using polar-polar interactions between host and LiPSs, including modified carbonaceous materials, oxides, sulfides, carbides, nitrides and hydroxides. Benefiting from the strong chemical interaction between S and polar support materials by forming functional group-S or metal-S bonds, Li-S batteries with improved cycling durability can be realized.

Modified carbonaceous materials

At an initial stage of developing S cathodes, some researchers introduced graphene oxide as the host materials. Zhang and co-workers demonstrated that the soluble LiPSs

Figure 2.6. (a) The calculated interaction between Li_2S cluster and different host materials based on DFT calculations. (i) single-layer graphene, (ii, iii) EFG, and (iv) stability test of EFG-S nanocomposites with different S loading and rGO-S composite. (b) (i) Scheme of the synthetic procedures of the LRC/S@EFG electrode; electrochemical performance of: (ii) cycling comparison between of LRC/S and LRC/S@EFG, (iii, iv) rate performance of LRC/S@EFG, (v) areal capacity of LRC/S@EFG electrodes with different S loading. (a) Reproduced with permission.^[49] Copyright 2014, Nature Publishing Group. (b) Reproduced with permission.^[50] Copyright 2015, Nature Publishing Group.

could be bonded with the GO through a polar-polar interaction since the epoxy and hydroxyl groups functionalized on the GO could strengthen the binding of S with the C-C bond.^[17] In 2014, Wang et al. fabricated an S-C cathode by covalently binding the LiPSs on amino-functionalized reduced GO (denoted as rGO).^[49] As shown in **Figure 2.6a** (i-iii), the density-functional theory (DFT) calculations demonstrate the enhanced affinity of LiPSs to ethylenediamine (denoted as EDA)-functionalized rGO. These highly active molecules enable it as a perfect crosslinker to covalently bridge polar LiPSs and nonpolar carbonaceous matrix. As a result, the dissolution of active materials could be effectively prevented. As expected, the S@EDA-functionalized rGO composites exhibit exceptionally stable cycling performance over 350 cycles with high capacity retention of 80% and good rate capability (Figure 2.6a (iv)).

Lou and co-workers reported the design and synthesis of a free-standing pie-like electrode constructed from lotus root-like carbon (LRC) nanofibers with S as ‘fillings’, and amino-functionalized rGO as the ‘crust’ (Figure 2.6b).^[50] The active materials are confined in channels within the interconnected LRC nanofibers. The unique design exhibits many superiorities. Firstly, the multichannel LRC could offer sufficient space to achieve a high mass loading of S. Secondly, the 1D channel-like carbon nanofibers with close contact of internal S species and external conductive frameworks of rGO could ensure excellent electron and ion transport for fast electrochemical redox reactions. Also, the crust with functional amino groups can effectively suppress the loss of soluble LiPSs from the cathode, leading to enhanced cycling stability. Benefiting from these advantages, the as-prepared freestanding pie-like electrode exhibits a high specific capacity of 1215 mAh g⁻¹ in the first cycle at 0.2 C with good capacity retention of 78.2% over 200 cycles. It should be mentioned that the capacity decay rate is as low as 0.1% per cycle.

Metal Oxides

Different from carbon materials, many metal oxides are inherently polar materials with strong interaction force with LiPSs species. Nevertheless, most of the metal oxides possess a much lower conductivity, which largely compromises the lithium storage properties of Li-S batteries, especially at high current density. A potential solution to bring the superiority of metal oxides into full play is fabricating hybrid structures of metal oxides and highly conductive materials. Inspired by these, Lou's group designed and fabricated a 1D composite within hollow carbon nanofibers filled with MnO₂ nanosheets (denoted as MnO₂@HCF) to load S (**Figure 2.7a**).^[51] The MnO₂@HCF composites have various advantages. To be specific, the 3D interconnected conductive network composed of 1D carbon nanofibers could largely improve the electron and ion transport, leading to high capacity at high current density. Besides, the MnO₂ nanosheets in the hollow carbon nanofibers can provide efficient surface bonding towards LiPSs, thereby keeping the LiPSs inside the hollow carbon nanofibers. Remarkably, the MnO₂@HCF/S cathode with a very high areal S density of 3.5 mg cm⁻² delivers high capacity retention at a high rate and excellent cycling stability for 300 cycles.

Wang et al. reported a ternary hybrid material (NiFe₂O₄/CNTs) as S host for Li-S batteries (**Figure 2.7b**).^[52] Specifically, the NiFe₂O₄ nanosheets can offer sufficient and strong binding sites to anchor LiPSs species. Moreover, the CNTs can enhance the ionic/electronic conductivity for the whole electrode, thereby ensuring the high specific capacity. Benefiting from these advantages, the S/NiFe₂O₄/CNTs cathode exhibits high reversible specific capacity, good rate capability, and excellent cycling life. Moreover, the battery delivers a minor capacity loss of about 4.5% over 500 cycles at 1 C.

Usually, most metal oxides are semiconductors. Cui et al. introduce oxygen defects to improve the conductivity of TiO₂ (**Figure 2.7c**).^[53] After being treated in reductive

conditions, TiO_2 with oxygen defect reveals a remarkable rise in electrical conductivity, which becomes a potential current collector for S cathode. Moreover, the generated oxygen vacancies could facilitate the interaction between TiO_2 and S, resulting in the improved chemical adsorption of LiPSs at the interface. Also, the hollow structure offers enough space to load a large amount of active material and mediate the volume expansion of S during cycling. Benefiting from these advantages, the S/reduced TiO_2 inverse opal cathode delivers excellent electrochemical performances with remarkable cycling stability and high capacity.

Figure 2.7. (a) Advantages of the $\text{MnO}_2@\text{HCS}/\text{S}$ composite over HCF/S . (b) Schematic illustration of the formation process of the $\text{CNT}/\text{NiFe}_2\text{O}_4/\text{S}$ ternary materials structure. (c) Scheme of the encapsulation of S into the reduced TiO_2 inverse opal arrays. (a) Reproduced with permission.^[51] Copyright 2015, John Wiley and Sons. (b) Reproduced with permission.^[52] Copyright 2015, American Chemical Society. (c) Reproduced with permission.^[53] Copyright 2014, American Chemical Society.

Metal Sulfides

Transition metal sulfides have also drawn huge research interests as potential S hosts to adsorb LiPSs effectively. As revealed by computational calculations, the LiPSs could be anchored on metal sulfides through polar-polar interaction between the transition metal and the LiPSs.^[54] Although the 2D metal sulfides exhibit improved

adsorption of LiPSs and fast charge transfer within the layers, the charge transfer through different layers is still lagging. Besides, the 2D nanostructures tend to form aggregation during the electrode preparation. Thus, fabricating the metal sulfides-based hosts with a conductive additive and favorable nanostructures might be helpful to improve the charge transfer and be robust. Qiao and co-workers designed a composite structure composed of 3D carbon hollow spheres decorated with nanosized nickel sulfide (NiS@C-HS) as host materials for Li-S batteries (**Figure 2.8a**).^[55] The hollow carbon spheres with enough internal space are utilized to enable a high loading amount of S and high the electrical conductivity for the whole cathode. The nanosized NiS can optimize the chemical adsorption of LiPSs. Benefiting from these unique designs, the S@NiS@C-HS electrode realizes good cycling performance with a high capacity of 695 mAh g⁻¹ over 300 cycles and a low capacity decay of 0.013% per cycle.

Figure 2.8. (a) Schematic illustration of the fabrication process of NiS@C-HS. (b) Schematic of i) the synthesis process of MoS₂-encapsulated hollow S sphere, ii) effective soluble LiPSs entrapment and structural integrity of MoS₂-entrapsulated hollow S sphere upon lithiation/de-lithiation. (a) Reproduced with permission.^[55] Copyright 2017, John Wiley and Sons. (b) Reproduced with permission.^[56] Copyright 2017, American Chemical Society.

Zheng et al. demonstrated the strong interactions of MoS₂ layers on LiPSs during lithiation/de-lithiation processes via *in situ* TEM (Figure 2.8 b).^[56] The results provide

visual evidence that the participation of MoS₂ within the host could effectively reduce the leakage/sublimation of S under high-vacuum conditions, which indirectly demonstrates the favorable chemical interaction between MoS₂ and LiPSs.

Carbide

As a new class of 2D materials, MXenes have attracted growing research interest in various electrochemical energy storage systems such as supercapacitors, LIBs, and SIBs due to their high conductivity, good flexibility, and easy processing. In 2015, Nazar group reported a pioneering work of 2D early-transition-metal carbide conductive MXene phases with a hydrophilic surface as excellent S host materials (**Figure 2.9a**).^[24, 57] As confirmed by XPS investigations, there are strong interactions between LiPSs species and “acid” Ti atoms on the surface of the MXene. Moreover, the hydroxy groups are replaced by S/sulfide species to form a strong Ti-S bond with the core. Benefiting from the powerful chemisorption capability toward LiPSs onto the Ti sites and hydroxy surface groups, the dissolution of LiPSs is effectively mitigated and the obtained S/d-Ti₂C cathode demonstrates high cycling stability with a fine capacity decay rate of 0.05% per cycle.

Recently, Wang et al. reported the design and synthesis of highly crumpled nitrogen-doped MXene (denoted as N-Ti₃C₂T_x) nanosheets as a host material for S cathode (**Figure 2.9b**).^[58] The as-prepared N-Ti₃C₂T_x nanosheet has a large surface area of 385 m² g⁻¹ with a pore volume of 0.342 cm³ g⁻¹. Also, XPS analysis demonstrates that heteroatom nitrogen is successfully loaded into the lattice of Ti₃C₂T_x nanosheets. Besides, the doping could effectively ameliorate the adsorption capability of MXene nanosheets toward Lewis acid. Therefore, the doped MXene sample demonstrates the strong adsorption of N-Ti₃C₂T_x toward LiPSs, which is verified by visible adsorption test and UV spectra. When tested as a potential host material for S cathode, the sheet-

like crumpled N-Ti₃C₂T_x sample could realize a high S loading of 5.1 mg cm⁻², a high specific capacity of 1144 mAh g⁻¹ at 0.2 C, good rate performance, and excellent cycling stability over 1000 cycles.

Figure 2.9. (a) Schematic illustration of the binding with S on the MXene surface and the change of S species during the discharge process. (b) Illustration of synthesis of the crumpled N-Ti₃C₂T_x/S composites. (a) Reproduced permission.^[24] Copyright 2015, John Wiley and Sons. (b) Reproduced permission.^[58] Copyright 2018, John Wiley and Sons.

Nitrides

Transition metal nitrides own better electrical conductivity than metal oxides and metal sulfides, which enables them as good electrode materials in supercapacitors and

LIBs.^[59-61] The recent investigations have demonstrated that the highly conductive transition metal nitrides could be good S host materials for Li-S batteries due to their good structural stability and strong chemisorption capability toward LiPSs. Huo and co-workers have coated mesoporous VN nanowires with a carbonaceous layer into a hybrid host material (MVN@C NWs) for Li-S batteries (**Figure 2.10a**).^[59] The inner mesopores of the core can not only load a large amount of active S but also buffer the volume change of S during charging/discharging processes. Also, the MVN core also possesses strong physical and chemical adsorption toward LiPSs, which could effectively prevent the loss of LiPSs. Furthermore, the intertwined conductive and long S/MVN@C NWs form a 3D conductive network, thereby enhancing electron/ion transfer for the whole freestanding electrode. Benefiting from these advantages, the freestanding S/MVN@C NWs electrode with a high S loading of 2.8 mg cm⁻² delivers a specific capacity of 1305 mAh g⁻¹ at 0.2 C, and a long cycling life over 200 repeated cycles.

TiN exhibits many desirable features as a promising S host. Firstly, TiN possesses superior electrical conductivity over titanium oxide and carbon. Moreover, TiN could generate an oxide passivation layer during cycling to increase the chemical stability. For example, Goodenough et al. synthesized mesoporous TiN through a solid-solid phase separation method with zinc titanate as a precursor (**Figure 2.10b**).^[60] Owing to the enhanced conductivity, robust structural stability and improved adsorption properties of the TiN host, the derived TiN-S hybrid cathode shows largely enhanced specific capacity even at high current densities. As shown by EIS spectra, TiN-S electrode shows smaller resistance than that of mesoporous TiO₂-S and Vulcan C-S electrodes, leading to the smallest electrochemical polarization and fastest lithium storage kinetics.

Figure 2.10. (a) i) Schematic illustration of the preparation of S/MVN@C NWs. ii) The comparison of discharge/charge process within S/MVN@C NWs and S/MVN NWs cathodes. (b) i) Schematic diagram illustrating the discharge/charge process for TiN-S. ii) Charge/discharge profiles of TiN-S and control samples at 0.2 C, iii) Nyquist plot of TiN-S and control samples, iv) rate performance of TiN-S, and control samples. (a) Reproduced with permission.^[59] Copyright 2017, American Chemical Society. (b) Reproduced with permission.^[60] Copyright 2016, John Wiley and Sons.

As it is still a challenge to get a high specific surface area for the heavy metal nitrides to maximize their chemical adsorption for LiPSs, the design, and synthesis of a

Figure 2.11. (a) First-principles calculations i) pristine carbon, ii) N-doped carbon, iii) g-C₃N₄ substrates; iv) The binding energies between Li₂S₂ molecules and different host substrates. (b) The calculated band structures of i) g-C₃N₄ and ii) graphene-C₃N₄ hybrid with relaxed configurations. iii) The comparison of Li₂S₄ adsorptivity between of the NG-CN, g-C₃N₄, porous N-doped carbon, Vulcan carbon, and Super P carbon. iv) The comparison of the binding energy of Li₂S, Li₂S₂, and Li₂S₄ on NG-CN hybrid structures and pristine graphite. v-viii) The fully relaxed structures of Li₂S₂ binding on v) graphite, vi) NG-CN, vii) Li₂S, viii) Li₂S₄ binding on NG-CN. (a) Reproduced with permission.^[25] Copyright 2016, American Chemical Society. (b) Reproduced with permission.^[62] Copyright 2017, John Wiley and Sons.

light-weight S host material with numerous chemisorption sites is highly needed to realize an enhanced Li-S battery. Amongst available candidates, the low-mass polar graphitic carbon nitride ($\text{g-C}_3\text{N}_4$) with a similar structure to layered graphite could be a good choice. Nazar and co-workers reported $\text{g-C}_3\text{N}_4$ as host materials for S cathodes.^[25] Both the spectroscopic experimental and DFT studies reveal the strong chemical interaction between $\text{g-C}_3\text{N}_4$ with LiPSs (**Figure 2.11a**). Compared to pristine carbon and N-doped carbon, $\text{g-C}_3\text{N}_4$ with more pyridinic N active sites for chemical adsorption towards LiPSs possess higher binding energy toward Li_2S_2 molecules. Benefiting from the nature interaction between $\text{g-C}_3\text{N}_4$ and LiPSs, the thick electrode with a high S loading ($3\text{-}5\text{ mg cm}^{-2}$) is fabricated and shows high areal capacity and excellent cycling stability at 0.5 C with a minor capacity fade rate of 0.04% per cycle over 1500 cycles. Considering the low conductivity of both $\text{g-C}_3\text{N}_4$ and S, highly conductive graphene is used as an additive to create a direct pathway for electron transfer. Besides, the 3D graphene network could effectively facilitate the penetration of electrolyte through the thick cathode.

In order to improve the conductivity of C_3N_4 -based host, a highly conductive network could be incorporated as integrated support for S cathodes. For example, Nazar et al. further developed an N-doped graphene/graphitic C_3N_4 (denoted as NG/CN) hybrid as support to load S (Figure 2.11b).^[62] The NG/CN composite is fabricated through thermal pyrolysis from the mixture of cyanamide and GO. XPS results confirm the simultaneous formation of $\text{g-C}_3\text{N}_4$ and N-doped graphene. To demonstrate the high electrical conductivity, the band structures of NG/CN composite and sole $\text{g-C}_3\text{N}_4$ are further examined by first-principles calculations based on DFT. Notably, the NG/CN composite shows a metallic feature with zero band gap. Whereas, pure $\text{g-C}_3\text{N}_4$ shows semiconducting behavior with a band gap of 2.1 eV . Benefiting from the advantages of

the improved conductivity and strong chemical LiPSs adsorption of the NG/CN composite, the NG/CN-S electrode with a high S loading of 5.2 mg cm^{-2} demonstrates high capacity retention over 80 cycles.

Metal Hydroxides

The hydroxides possess abundant functional hydrophilic and polar groups, which make them be effective immobilizers for LiPSs. In 2015, Wang et al. reported $\text{Co}(\text{OH})_2$ as a new host for constructing Li-S batteries with enhanced performances (**Figure 2.12a**).^[63] In this work, the S is firstly diffused into conductive carbon black (CCB) as the conductive support of the composite. Furthermore, the $\text{Co}(\text{OH})_2$ nanosheets are grown between the S/CCB small nanoparticles forming a 3D connected network via a hydrothermal method. As a result, the S/CCB small nanoparticles are decorated in the 3D $\text{Co}(\text{OH})_2$ network. The 3D network in the $\text{Co}(\text{OH})_2$ @S/CCB hybrid can not only provide intersected blocks for LiPSs, but also adjust the diffusion of LiPSs. Benefiting from the above advantages of both CCB and $\text{Co}(\text{OH})_2$ nanosheets, the $\text{Co}(\text{OH})_2$ @S/CCB cathodes reveal lithium storage properties with high specific capacity, and enhanced cycling stability over 200 cycles.

After that, Yu group designed a feasible and effective host matrix using thin-layered nickel-based hydroxide for Li-S batteries (Figure 2.12b).^[26] Firstly, the S_8 @CB particles are fabricated through an impregnation method to load S_8 molecules into conductive and high porous CB matrices. The CB can not only provide abundant meso- or macro-porous places to accommodate S, thereby restraining their aggregation, but also improve the electron transfer of S. Next, thin-layered nickel nitrate hydroxide (NNH) nanosheets were packed on the S_8 @CB particles. The NNH has several advantages for restricting the dissolution of LiPSs. Firstly, the NNH can electrochemically react with Li^+ irreversibly, thereby generating a more stable shelly structure on the S_8 @CB. The shelly

structure can serve as a robust protective layer with abundant functional polar/hydrophilic groups to restrict the LiPSs, hence achieving drastic improvements in cell behaviors.

Figure 2.12. (a) Schematic illustration of the formation of $\text{Co}(\text{OH})_2@\text{S}/\text{CCB}$ composite. (b) Schematic illustration of i) the entire fabrication procedures, and ii) the working mechanisms of NNH in Li-S cathodes. (c) Schematic illustration of i) the fabrication of $\text{S}@\text{Ni}(\text{OH})_2$ double-shell hollow composite spheres, and ii, iii) the structural and chemical advantages of ultrathin $\alpha\text{-Ni}(\text{OH})_2$ nanosheets. (a) Reproduced with permission.^[63] Copyright 2015, Royal Society of Chemistry. (b) Reproduced with permission.^[26] Copyright 2015, Nature Publishing Group. (c) Reproduced with permission.^[64] Copyright 2017, Elsevier.

Xu and co-workers reported hierarchical hollow spheres constructed with ultrathin α -Ni(OH)₂ nanosheets as encapsulation matrix for S cathode.^[64] As shown in Figure 2.12c, S nanospheres coated by PVP (S@PVP) are firstly obtained through a facile chemical strategy. Then, the obtained S@PVP sample is further covered by a layer of ultrathin α -Ni(OH)₂ nanosheets through a solution-based method. The hierarchical shell could not only provide sufficient void space to mediate the volume change during the discharge/charge cycles, but also anchor the movable LiPSs via strong chemical interactions, thereby efficiently reduce the loss of active S. Thus, the as-prepared S@ α -Ni(OH)₂ electrode demonstrates a high reversible discharge capacity of 1020 mAh g⁻¹ at 0.2 C and long cycle life over 1000 times with a capacity of 0.04% per cycle.

2.3.2.2. Catalytic effects on enhancing the kinetics of LiPSs conversion reactions

As both the initial S and final product Li₂S exist in solid states, they are more stable than soluble LiPSs. However, the sluggish reaction kinetics limit the conversion of soluble LiPSs to stable S or Li₂S. As mentioned before, the sluggish reaction kinetics come from the slow electron and Li ions transfer caused by deposition of insulating Li₂S₂ or Li₂S. Using catalytic host materials might help to enhance the rate of LiPSs conversion reactions, thereby shortening the duration of LiPSs and limiting the loss of LiPSs. Based on these considerations, many materials with catalytic properties have been introduced into Li-S systems to improve the conversion rate between S and Li₂S.

In 2014, Nazar group demonstrated Ti₄O₇ was a good host material for S cathode (**Figure 2.13a**).^[65] Ti₄O₇ is a member of Ti_nO_{2n-1} Magnéli phases with metallic properties. Compared with an insulating oxide such as TiO₂, this metallic oxide plays a different role as an S host. The function of insulating metal oxide is just as a LiPSs reservoir to bind LiPSs via chemical interactions between the LiPSs and the metal centers. The metallic Ti₄O₇ can not only provide a polar S for strong LiPSs binding but

also enhance the redox electron transfer, thereby triggering the surface-mediated reduction of LiPSs. This work points out the importance of introducing a LiPSs mediator with both sulfiphilic and metallic properties, which can both provide a strong interaction toward LiPSs but also facilitate the redox reactions of LiPSs.

Figure 2.13. (a) Schematic illustration of surface-mediated reduction of Li_2S from LiPSs on carbon and Ti_4O_7 . (b) Schematic illustration of the synthetic procedure for the hybrid host composed of electrocatalyst and graphene and its working mechanism. (c) Schematic illustration of working mechanism for the CoS_2 -incorporated C/S cathode to promote the polysulfide reduction and prevent polysulfide diffusion. (a) Reproduced with permission.^[65] Copyright 2014, Nature Publishing Group. (b) Reproduced with permission.^[66] Copyright 2015, American Chemical Society. (c) Reproduced with permission.^[67] Copyright 2016, American Chemical Society.

In 2015, Arava et al. used Pt/graphene and Ni/graphene as electrocatalyst in S cathode to hold back the dissolution of the LiPSs and promote the reaction kinetics at a high rate.^[66] Pt/graphene exhibits superior lithium storage properties over pristine graphene electrodes with reduced overpotential and excellent specific capacity. Besides, the enhanced rate of LiPSs conversion reactions is confirmed by the change in the exchange current densities in both lithiation/de-lithiation processes. Furthermore, EIS results also confirm the smaller charge-transfer resistance, revealing the electrocatalyst

influence of Pt/graphene. Compared with pristine graphene/S electrode, the Pt/graphene/S electrode demonstrates higher specific capacity with a Coulombic efficiency above 99.3%. This work opens a new avenue for improving electrochemical performance by incorporating a catalyst in the cathode for Li-S batteries.

Zhang and co-workers also verified that CoS₂ with high electrical conductivity could not only provide strong CoS₂-LiPSs interaction but also dynamically enhance the LiPSs' redox reactions. The strong CoS₂-LiPSs interaction is confirmed by visualized adsorption test and first-principle calculations based on DFT. Notably, the enhanced redox reactions of LiPSs on CoS₂ surface are investigated by CV tests of symmetrical Li₂S₆-Li₂S₆ cells by comparing the onset potential, other than the position of cathodic/anodic peaks. As a result, the enhanced LiPSs redox facilitates the conversion from S to LiPSs and LiPSs to Li₂S, mitigating the electrochemical polarization of Li-S batteries and thereby higher discharge capacity and enhanced cycling stability.

2.3.3. Summary

In summary, the strategies used to restrict the dissolution of LiPSs are mainly divided into two types: physical confinements and chemical immobilization. The advantages and disadvantages of physical confinements and chemical immobilization are listed in **Table 2.1**. Specifically, the physical confinements have acquired great attention since 2009. Most physical confinements refer to carbonaceous materials with porous structures, which can physically absorb LiPSs and meanwhile improve the conductivity of the S. Nevertheless, the capillary action by pores for LiPSs is rather limited due to the weak physical effect. Since 2014, the chemical immobilization on LiPSs has aroused increasing research interest. The chemical immobilization toward LiPSs are further divided into two types: chemical affinity by polar interactions, and

catalyst effect. The chemical affinity refers to the compound with polar chemical bonding, which can provide strong interaction toward LiPSs. The catalyst effect toward LiPSs refers to the host materials can facilitate the redox reaction of LiPSs, thereby help them transfer to a more stable solid phase (S or Li₂S). Normally, the host materials can not only provide strong interaction with LiPSs, but also possess intrinsic metal conductivity or superior catalytic activity.

Table 2.1. The advantages and disadvantages of physical confinements and chemical immobilizations.

Strategies	Advantages	Disadvantages	Classic examples
Physical confinements	Improve the conductivity of the composite Adsorbing LiPSs by adsorption effect of micro or mesoporous	Weak interactions between polar LiPSs and non-polar carbon	CMK-3/S
Chemical immobilization	Strong chemical interactions to LiPSs Enhance the reaction kinetics of LiPSs	Limited sulfiphilic sites Usually weak electron conductivity	MnO ₂ /S

2.4. Li-SeS₂ batteries

2.4.1. Mechanisms and challenges of Li-SeS₂ batteries

As a congener of element S, Se is a prospective cathode material for lithium storage. As shown in **Figure 2.14**, the pioneering work by Amine's group demonstrated that Li-Se batteries using Se as the cathode material have a higher utilization rate, better electrochemical activity, and faster electrochemical reaction.^[12] In principle, Se has

higher electrical conductivity ($1 \times 10^{-3} \text{ S m}^{-1}$), compared with S ($5 \times 10^{-28} \text{ S m}^{-1}$).^[68] It is reported that Li-Se batteries deliver a higher output voltage than that of Li-S batteries (approximately 0.5 V), and thus a higher energy density.^[11] In addition, benefiting from the higher density (2.5 times that of S), Se has a comparable volumetric capacity (3253 Ah L⁻¹) to S (3467 Ah L⁻¹).^[11]

Figure 2.14. Comparison of S, Se, and SeS₂.

Although Li-Se batteries have been widely investigated, they still suffer from relatively lower mass capacity (Se_{theoretical capacity}: 678 mAh g⁻¹), compared with the Li-S batteries (S_{theoretical capacity}: 1672 mAh g⁻¹). Moreover, Se has higher cost than S. Generally, Se promises a higher reaction kinetic but a lower reversible capacity; while S shows a high reversible capacity but a lower reaction kinetic. As a result, the heteroatomization of Se and S, which utilizes the advantages of both Se and S, is a promising strategy to maximize the electrochemical performance of Se and S electrodes for LIBs. However, similar to the S cathode, the Se_xS_y-based cathodes also endure the dissolution of reaction intermediates (LiPSs and LiPSes) into the organic electrolytes with a rapid capacity fading.

2.4.2. Strategies for Li-SeS₂ batteries

Amine group demonstrated that the solid solution of Se_xS_y could be a new class of cathode materials for lithium storage with higher theoretical capacities than pure Se cathode and improved conductivity compared to pure S cathode.^[12] After that, various carbonaceous materials are introduced as Se_xS_y host materials to inhibit the dissolution of LiPSs and LiPSes for better Li-Se_xS_y batteries, such as various mesoporous carbons,^[69-70] micro/mesoporous carbon matrix,^[14] and double-layered hollow carbon spheres.^[71] Wang et al. employed carbonized PAN as the host materials for SeS_x via heating the mixture of SeS_x and PAN at 600 °C under vacuum.^[72] The resultant SeS_x molecules are encapsulated by heterocyclic -CN ring within the PAN-derived carbon materials to slow down the dissolution of LiPSs and LiPSes. In addition, the heterocyclic ring can also accommodate the volume change during lithiation/de-lithiation. As a result, the SeS_{0.7}/CPAN composite delivers a high capacity of 780 mAh g⁻¹ and retains for 1200 cycles in the carbonate-based electrolyte. It should be noted that Se can work well in carbonate-based electrolytes, but S cannot.^[68] Considering both S and Se can operate normally in ether-based electrolytes, it would be better to use ether-based electrolytes if S content comes up to a certain ratio. Shi and co-workers reported N-doped mesoporous carbons (denoted as NMCs) as the encapsulation materials for Se_nS_{8-n} using an ether-based electrolyte for lithium storage.^[73] It has been demonstrated that the Se-S molecules confined in NMCs are able to recover after charge/discharge process in ether-based electrolyte. Moreover, the heteroatomic Se-S molecules with higher polarizability show more electrochemical stability than pure S because of stronger surface interactions with the N-doped carbon host materials. Benefiting from these advantages, the Se₂S₆/NMCs composite delivers a high reversible capacity of 883 mAh g⁻¹ after 100 cycles. Moreover, it still delivers a high specific capacity of 780 mAh g⁻¹ after 200 cycles.

2.4.3. Summary

In summary, the strategies to improve the stability of Se_xS_y are mainly focused on employing various carbonaceous materials as the host materials. That means the study of Se_xS_y -based cathode is still in an infant stage, so the application potential of the Se_xS_y cathode has not yet been fully achieved. Inspired by the idea of introducing polar substrates to bind soluble LiPSs in Li-S batteries chemically, it is believed that some rationally selected polar materials might also be effective for Se_xS_y cathodes.

Chapter 3. Experimental Section

3.1. Synthesis Methodology

The active materials (S or SeS₂) was infused into the host materials by melt-diffusion method. Specifically, after well mixed the S (SeS₂) with the host materials, the mixtures of S (SeS₂) and host were heated to 155 °C and then maintained at this temperature for 5-24 h to infuse the S (SeS₂) into the inner space of the host materials.

3.2. Materials Characterizations

The morphologies and structures were characterized by field-emission scanning electron microscopy (FESEM; JEOL, JEM-6701F, 5 kV) and transmission electron microscopy (TEM; JEOL, JEM-2010, 200 kV). Elemental mapping was collected using EDX spectroscopy attached to TEM (JEOL, JEM-2100F). Powder X-ray diffraction (XRD) patterns were recorded using a Bruker diffractometer with Cu K α radiation (D2 phaser, Cu K α , $\lambda=1.5406$ Å) to study the crystallographic structure. The composition of the samples was analyzed by energy-dispersive X-ray spectroscopy (EDX) attached to the FESEM instrument. Raman spectra of the dried samples were collected using a Renishaw System 1000 micro-Raman spectroscopy. Thermogravimetric analysis (TGA, Perkin Pyris Diamond) was performed under air or N₂ flow (200 ml min⁻¹) with a temperature ramp of 10 °C min⁻¹.

3.3. Electrochemical Measurements

The electrochemical measurements were carried out using 2032-type coin cells with pure lithium metal as the counter and also the reference electrodes at room temperature.

The electrolyte used was 1.0 M LiTFSI in a mixed solution of DOL/DME (1:1 by volume) with 0.2 wt% LiNO₃ additives. Cell assembly was carried out in an Ar-filled glovebox with concentrations of moisture and oxygen below 1.0 ppm. Cyclic voltammetry was performed using an electrochemical workstation (CHI 660C). The charge/discharge tests were performed using a NEWARE battery tester at different current densities with specific voltage windows.

Chapter 4. A double-shelled host with Co(OH)₂ inner shell and Ni/Co LDH outer shell for Li-S batteries[†]

4.1. Introduction

After two decades of optimization, the current LIBs based on intercalation reactions have approached their energy density limit and will be unable to meet the demands of fast-developing electric vehicles, large-scale energy storage devices, and advanced portable electronics.^[1] Due to the overwhelming advantages in energy density, Li-S batteries have been considered as a promising candidate for the next-generation electrochemical energy storage technologies.^[1, 9] In addition, some valuable characteristics of S, such as the high natural abundance, low cost and nontoxicity, make Li-S batteries even more commercially competitive than the current LIBs.^[5] However, practical applications of the rechargeable Li-S battery are still hindered by a multitude of issues, including low utilization of the active material, short cycle life, fast self-discharge, and poor Coulombic efficiency.^[8] The insulating nature of both S and its end products of discharge (Li₂S/Li₂S₂), as well as the dissolution of intermediate LiPSs generated during cycling are the two primary reasons for poor performance of Li-S batteries. To solve these challenges, extensive research efforts have been exerted on cathodes,^[6, 74-75] electrolytes,^[76-78] separators,^[79-81] and lithium metal anodes^[82-83] for preventing the migration of LiPSs and enhancing the utilization ratio of S. Among these approaches, composing S with conductive carbon frameworks has been proven promising.^[84-86] In the pioneering work by Nazar's group, S is confined within highly

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ordered mesoporous carbon (CMK-3), and exhibits a reversible capacity over 1000 mAh g⁻¹ for 20 cycles.^[16] Encouraged by that, various carbon materials have been further investigated thoroughly for improving the performance of Li-S batteries, including porous carbon,^[15, 34-35] carbon nanotubes/fibers,^[50, 87-89] graphene,^[49, 90] hollow carbon structures,^[19-20] and combined carbon structures,^[91-92] and great progress in both electrochemical properties and the reaction mechanisms have been achieved.

Although these carbon/S composite cathodes exhibit high specific capacities during the initial cycles, they usually decay rapidly in the subsequent cycles, and the cycling stability remains a significant challenge for practical applications. This problem is often attributed to the dissolution of the reaction intermediate LiPSs in the organic electrolyte. In fact, the weak physical adsorptions provided by the nonpolar carbon substrates could not efficiently suppress the dissolution of polar natured LiPSs during the whole charge-discharge cycling process.^[65] In contrast, it has been discovered that some metal oxides/sulfides with polar surfaces can form strong chemical bonds with the lithium polysulfide species. Introducing inorganic anchoring materials as S hosts, such as Ti₄O₇,^[65, 93] MnO₂,^[51, 94] and TiS₂,^[95] has been demonstrated as an effective way to slow down LiPSs dissolution and therefore achieve long-term cycling stability. However, considering the high volume ratio of S and the metal oxides/sulfides, it is often concerned that the anchoring powder, even with nanoscale particle sizes, would not be able to provide sufficient interfaces to fix all of polysulfide species in the electrode. A more practical way is to apply the limited anchoring materials as the coating layers. More recently, thin-layered metal hydroxides, including Co(OH)₂^[63] and Ni₃(NO₃)₂(OH)₄,^[26] have been demonstrated as effective encapsulation materials for the S cathodes. In one case, Yu's group demonstrated that Ni₃(NO₃)₂(OH)₄ could turn into layered (Li, Ni)-mixed hydroxide compounds by irreversibly reacting with Li⁺ during

the early cycles.^[26] This result suggests the possibility of using layered transition metal hydroxides as promising encapsulation materials to build better Li-S cells. Unfortunately, restricted by the undesired polarizations of the electrode and the inevitable process of the slow transformation from $\text{Ni}_3(\text{NO}_3)_2(\text{OH})_4$ to layered (Li, Ni)-mixed hydroxides, this hybrid cathode material is still far away from the real world production and application.^[26] Therefore, it is still in urgent need of exploring new materials as S hosts for the practical use of Li-S batteries.

LDH is a class of anionic clays with 2D structures, which have been widely used in the disciplines of catalysis, catalyst precursors, bioactive nanocomposites, electroactive and photoactive materials.^[96] The general formula of LDHs is $[\text{M}^{2+}_{1-x}\text{M}^{3+}_x(\text{OH})_2] [\text{A}^{n-}_{x/n}] \cdot m\text{H}_2\text{O}$, where M^{2+} is a divalent cation and M^{3+} a trivalent cation, while A^{n-} is a charge-balancing interlayer anion.^[96] Benefitting from the abundant hydrophilic groups and hydroxyl groups, LDHs might be an ideal polysulfide mediator based on previous findings.^[26, 63, 97] In addition, the electrocatalysis of LDHs may also enhance the reaction kinetics of LiPSs redox reactions,^[66, 96] and the high anion exchange capability may entrap polysulfide anions within the interlayers,^[86, 98] effectively suppressing the dissolution of LiPSs into the organic electrolyte. To the best of our knowledge, rare investigations have been reported on utilizing LDHs as S hosts for Li-S batteries.

In this chapter, we have designed and synthesized a novel type of double-shelled $\text{Co}(\text{OH})_2/\text{LDH}$ (noted as CH@LDH) nanocages as a new S host for Li-S batteries. The concept of the CH@LDH/S composite cathode has multiple advantages. Specifically, the outer LDH and inner $\text{Co}(\text{OH})_2$ hollow polyhedrons with complex shell structures not only maximize the advantages of hollow nanostructures for encapsulating a large amount of S,^[20] but also provide a relatively larger functional surface for chemically

bonding with LiPSs to suppress their outward dissolution. When evaluated as the cathode material for Li-S batteries, the CH@LDH/S composite shows significantly improved electrochemical performances.

4.2. Experimental Measurements

4.2.1. Materials Synthesis

Synthesis of ZIF-67 nanocrystals. All the chemicals were directly used after purchase without further purification. Typically, 1 mmol of $\text{Co}(\text{NO}_3)_2$ and 4 mmol of 2-methylimidazole were dissolved in 25 mL of methanol, respectively. Then, the solution of 2-methylimidazole was quickly poured into the solution of $\text{Co}(\text{NO}_3)_2$ under vigorous stirring. The well-mixed solution was aged for 24 h at room temperature. Finally, the purple precipitate of ZIF-67 was washed with ethanol for 3 times by centrifugation, and then dried at 70 °C for 6 hours.

Synthesis of yolk-shelled ZIF-67@LDH. 40 mg of ZIF-67 was first dispersed in 20 mL of ethanol, and then 5 mL of ethanol solution containing 90 mg of $\text{Ni}(\text{NO}_3)_2$ was quickly poured into the former purple dispersion. After stirring for 30 min, the product was washed with ethanol for 3 times by centrifugation and dried at 70 °C for 10 hours.

Synthesis of Double-shelled CH@LDH nanocages. 40 mg of the yolk-shelled ZIF-67@LDH was dispersed in 20 mL of ethanol, and then 5 mL of deionized water solution containing 50 mg of Na_2MoO_4 was quickly poured into the former dispersion under stirring. The mixed solution was heated to 85 °C until the purple color disappeared entirely. The products were washed with water 3 times by centrifugation and dried at 70 °C overnight to get double-shelled CH@LDH nanocages. As to remove ZIF-67 cores

for the synthesis of pure hollow LDH, 40 mg of the yolk-shelled ZIF-67@LDH was dispersed in 20 mL of ethanol and 5 mL of deionized water, and then treated by the same method as mentioned above.

Synthesis of CH@LDH/S composites. The CH@LDH/S composites were prepared via a melt-diffusion method. A mixture of S powder and double-shelled CH@LDH with a mass ratio of 3 : 1 was sealed in a glass bottle, and heated at 155 °C for 12 hours in an oven.

4.2.2. Electrode Preparation and Adsorption test

To make the cathode electrode, CH@LDH/S, Super P, carbon nanotubes (CNTs) and PVDF binder were mixed in NMP with a weight ratio of 70 : 10 : 10 : 10. And then the slurry was spread onto an aluminum foil with the areal S loading of 2.8-3.2 mg cm⁻². The electrode film was dried in an oven at 70 °C overnight, and cut into round disks with a diameter of 8 mm. The 2032-type coin cells were assembled using Celgard 2300 membrane as separator and Li metal as the anode. The electrolyte was composed of 1 M LiTFSI in a mixture of DOL and DME (1:1, v/v) with 0.2 M of LiNO₃. The cells were assembled in an Ar-filled glovebox with a concentration of moisture and oxygen below 5 ppm. Galvanostatic discharge-charge tests were performed on a Neware Battery Measurement System (Neware, China) in the voltage range of 2.8-1.7 V. The current density was based on the weight of S (1C = 1675 mA g⁻¹), and the specific capacities were calculated on the mass of S. The electrode and coin cells of pure CH@LDH were prepared by the same method to CH@LDH/S sample.

To carry out the visualized adsorption test, Li₂S₆ solution was prepared by adding Li₂S and S at a molar ratio of 1:5 in DME/DOL (1:1 by volume) followed by vigorous

magnetic stirring at 50 °C. Solutions with Li_2S_6 concentration of 0.1 wt% were used for adsorption test. 10 mg of CH@LDH and conductive carbon were added into two glass vials, respectively, and then 2 mL $\text{Li}_2\text{S}_6/\text{DME}/\text{DOL}$ solution was poured into these glass vials. A blank glass vial was also filled with the same Li_2S_6 solution for reference.

4.3. Results and Discussion

4.3.1. Formation Processes

The synthesis process of double-shelled CH@LDH nanocages and CH@LDH/S is shown in **Figure 4.1**. First, rhombic dodecahedral ZIF-67 particle is fabricated as a sacrificial template. Then, hollow polyhedral LDH shells are formed on ZIF-67 (denoted as ZIF-67@LDH) by reacting with $\text{Ni}(\text{NO}_3)_2$ in ethanol. Following that, double-shelled CH@LDH nanocages are fabricated by reacting the yolk-shelled ZIF-67@LDH with the aqueous solution of Na_2MoO_4 . Finally, S is loaded into double-shelled CH@LDH nanocages by a melting-diffusion method.

Figure 4.1. Schematic illustration of the synthesis of the CH@LDH/S composite.

4.3.2. Materials Characterizations

ZIF-67 particles are fabricated as previously reported.^[99] The morphology of ZIF-67 is shown in **Figure 4.2a, b and c**. The low-magnification FESEM image of the as-prepared ZIF-67 (Figure 4.2a) shows that the sample consists entirely of uniform polyhedron with an average size of about 800 nm. The particle in Figure 4.2b clearly shows that this

polyhedron is rhombic dodecahedron, and the surface is very smooth. The crystallographic structure and phase purity of the ZIF-67 sample are determined by XRD, as shown in Figure 4.2d. All the diffraction peaks can be assigned to the simulated pattern. What's more, the main chemical composition of the crystals can be evidenced by the EDX (Figure 4.2 e), the result demonstrates a high purity of the material phase.

Figure 4.2. (a,b) FESEM images, (c) TEM image, (d) XRD patterns and (e) EDX spectrum of ZIF-67 nanoparticles.

By using ZIF-67 as the sacrificial template and reacting with $\text{Ni}(\text{NO}_3)_2$ in ethanol solution for 30 min, the Ni/Co LDH polyhedral nanoshells are successfully formed. Figure 4.3a, b show the morphology of as-prepared Ni/Co LDH that is in the same morphology and dimension of ZIF-67.^[99] FESEM image shows the rougher surface assembled by small nanosheets indicating the thin layer-shaped LDH morphology (Figure 4.3a). The yolk-shell structure of the sample can be revealed through TEM observation (Figure 4.3b), from which a well-developed inner cavity can be clearly identified. The core with smooth surface has similar polyhedral shape with original ZIF-67, while the shell is composed of interconnected small nanosheets. According to the

XRD pattern (Figure 4.3c), the crystalline phase of the yolk-shelled product is still mainly composed of ZIF-67, which is further supported by the EDX result showing the similar elemental composition with ZIF-67 (Figure 4.3d).

Figure 4.3. (a) FESEM image, (b) TEM image, (c) XRD pattern and (d) EDX spectrum of yolk-shelled ZIF-67@LDH.

Figure 4.4. (a) The TEM image and (b) EDX spectrum of pure out-shelled LDH without a core.

To determine the composition of the outer shell, the ZIF-67 core with poor water stability is removed by refluxing in a mixed solvent of ethanol and water at elevated temperature.^[99] After that, the TEM image shows the fully hollowed LDH shell (**Figure 4.4a**), which indicates the complete removal of the ZIF-67 cores. EDX spectrum of the LDH shell shows a Ni/Co molar ratio of around 1:2 (Figure 4.4b), indicating the chemical formula of the LDH shell might be expressed as $[\text{Ni}^{2+}_{1/3}\text{Co}^{3+}_{2/3}(\text{OH})_2] [\text{NO}_3^{2-}_{1/3}] \cdot \text{mH}_2\text{O}$.

Figure 4.5. (a) FESEM image, (b) TEM image, (c) XRD pattern and (d) EDX spectrum of CH@LDH.

After the reaction with an aqueous solution of Na_2MoO_4 , the product well inherits the morphology and dimensions of the integrated nanosheets-assembled shells (**Figure 4.5a**). The inner ZIF-67 yolk is transformed into hollow structured nanocages, forming novel double-shell structured nanocages (Figure 4.5b). Figure 4.5c shows the XRD result of the as-prepared double-shelled CH@LDH nanocages. After the reaction of

ZIF-67@LDH with a water solution of Na_2MoO_4 , the diffraction peaks of ZIF-67 totally disappear, and the diffraction peak at 18.9° corresponds relatively well to $\text{Co}(\text{OH})_2$.^[63] It is interesting to note that MoO_4^{2-} anions are not directly involved in the chemical reaction with the inner ZIF-67; instead, the OH^- ions generated by hydrolysis of MoO_4^{2-} anions precipitate with Co^{2+} ions released from ZIF-67 to form $\text{Co}(\text{OH})_2$. On the other hand, the distinguishable (003), (006), (009) and (110) peaks of the product can be clearly ascribed to a typical Ni/Co LDH structure.^[99] EDX spectrum of the CH@LDH nanocages indicates that Ni and Co are the two major metal elements in the double-shelled framework with a small amount ($< 5 \text{ wt\%}$) of Mo incorporated (Figure 4.5d). To investigate the surface area of the double-shelled CH@LDH, N_2 physical adsorption tests are carried out. As depicted in **Figure 4.6**, the double-shelled nanocages have a specific surface area of $117 \text{ m}^2 \text{ g}^{-1}$, which could provide sufficient surface for chemically bonding with LiPSs.

Figure 4.6. N_2 adsorption-desorption isotherms of double-shelled CH@LDH nanocages.

After S is loaded into the double-shelled CN@LDH nanocages, the CH@LDH/S composite particles well maintain the polyhedral shape (**Figure 4.7a**). The darker contrast of the inside region of the CH@LDH/S composite indicates the diffusion of S into the inner space (Figure 4.7b), revealing that S has been homogeneously

encapsulated within the LDH shells. XRD is used to investigate the phase of the CH@LDH/S composite, as shown in Figure 4.7c, the diffraction peaks of $\text{Co}(\text{OH})_2$ and LDH become relatively weak, all strong diffraction peaks come from the crystalline S in the CH@LDH/S composite. The mass loading of S in the CH@LDH/S composite is determined by TGA to be as high as 75 wt% (Figure 4.7d), which may promise both high volumetric and gravimetric energy densities of the electrode material for Li-S batteries.^[100]

Figure 4.7. (a) FESEM image, (b) TEM image, (c) XRD pattern and (d) TGA curve of CH@LDH/S composite. The TGA curve was tested in an N_2 atmosphere with a heating rate of $10\text{ }^\circ\text{C min}^{-1}$.

The distribution of different elements in the CH@LDH/S composite is investigated by EDX mapping analysis under FESEM observation (**Figure 4.8a**). The uniform distributions of Co and Ni elements suggest that the double-shelled CH@LDH structures are formed in almost all particles. The signal of S is uniformly matched with the CH@LDH region, indicating the good confinement of S within the CH@LDH

frameworks. The strong EDX signal of S in the CH@LDH/S composite indicates a large amount of S in the final cathode electrode material (Figure 4.8b).

Figure 4.8. (a) FESEM image of CH@LDH/S and corresponding EDX elemental mappings, (b) EDX spectrum of CH@LDH/S composites.

Figure 4.9. Cross-section FESEM image of the CH@LDH/S electrode film.

4.3.3. Electrochemical Measurements

To evaluate the electrochemical cycling performance of the CH@LDH/S composite, 2032-type coin cells are fabricated with thick coated electrode films, in which the areal mass loading of S is controlled to be $\sim 3 \text{ mg cm}^{-2}$. To investigate the thickness of the electrode, FESEM analysis was employed to reveal the cross-sectional view of the electrode, as shown in **Figure 4.9**, the thickness of the electrode is about $45 \text{ }\mu\text{m}$.

Figure 4.10. Cycling performance comparison between CH@LDH/S and C/S.

To show the effects of CH@LDH on retarding polysulfide dissolution, a mesoporous carbon/S composite (denoted as C/S) is also measured by the same conditions for comparison. As shown in **Figure 4.10**, when cycled at 0.1 C, the CH@LDH/S composite delivers an initial discharge capacity of 1014 mAh g^{-1} , which is very close to the initial discharge capacity of 1068 mAh g^{-1} achieved by the C/S composite, revealing that the CH@LDH host would not obviously increase the polarization of the cells in the early stage of cycling. Different from the Ni-based hydroxide ($\text{Ni}_3(\text{NO}_3)_2(\text{OH})_4$), which gradually transformed into (Ni, Li)-mixed hydroxides during dozens of charge-discharge cycles,^[26] the CH@LDH framework exhibits stable electrochemical property at the beginning of the electrochemical tests. In

the following cycles, the C/S composite shows a reversible capacity of 450 mAh g^{-1} after only 60 cycles. In contrast, the CH@LDH/S composite maintains much better capacity retention of 736 mAh g^{-1} after the same number of cycles, and still delivers a reversible capacity of 653 mAh g^{-1} at the 100th cycle, indicating that the CH@LDH host successfully suppresses the outward diffusion of soluble LiPSs. When cycled at 0.5 C (Figure 4.10a), the CH@LDH/S composite also exhibits stable cycle life, over which the discharge capacity slowly decreases from initially 747 mAh g^{-1} to 491 mAh g^{-1} by the 100th cycle. Considering the relatively high areal mass loading of S, the cycling performance is competitive to previously reported works.^[20]

To investigate the stability of the CH@LDH host in the electrolyte of the Li-S batteries, a pure CH@LDC electrode is fabricated using the same electrolyte to CH@LDH/S cells. As shown in **Figure 4.11**, the stable cyclic voltammetry (CV) curves of a pure CH@LDH electrode further confirm its electrochemical stability. Moreover, based on recently reported electrocatalysis principles to the Li-S batteries,^[66] the CH@LDH host may also enhance the reaction kinetics of S cathode due to its inherent catalytic properties.^[96]

Figure 4.11. CV plots of pure CH@LDH in the voltage range of 1.7-2.8 V with a scan rate of 0.2 mV s^{-1} .

Visual observation of solution phase LiPSs adsorption further demonstrates that CH@LDH has a much better capability of adsorbing LiPSs than the carbon material (**Figure 4.12**).

Figure 4.12. Visualized adsorption of Li_2S_6 on CH@LDH and C.

When cycled in the electrolyte without LiNO_3 additive, the C/S composite shows an obvious overcharge (**Figure 4.13b**), indicating significant dissolution of LiPSs; while the CH@LDH/S composite still exhibits a high Coulombic efficiency (**Figure 4.13a**), further revealing that the CH@LDH host can effectively restrict the dissolution of LiPSs. The results show that the CH@LDH/S composite has much weaker “shuttle effect” than the C/S composite, revealing that CH@LDH can effectively restrict the diffusion of LiPSs.

To evaluate the rate capability of CH@LDH/S, cells with S mass loading of 3 mg cm^{-2} are cycled at various current densities for 0.1 to 1 C (**Figure 4.14a**). The discharge capacity of CH@LDH/S is stabilized at $> 900 \text{ mAh g}^{-1}$ at 0.1 C, corresponding to an areal capacity of 2.7 mAh cm^{-2} . Further cycling at 0.2, 0.5 and 1 C shows high reversible

Figure 4.13. Voltage profiles of the second cycle of (a) CH@LDH/S and (b) C/S with the LiNO₃-free electrolyte.

capacities of 800, 650 and 500 mAh g⁻¹, respectively (Figure 4.14a and b), indicating excellent reaction kinetics of the CH@LDH/S electrode. When the current density is reduced back to 0.1 C, a reversible capacity of 904 mAh g⁻¹ is achieved, indicating good stability of the electrode material after high current density tests. The excellent electrochemical performance is attributed to the multiple advantages of this novel cathode structure. First, the hollow structure provides sufficient void space for loading a large amount of active materials. Second, the hydroxyl-functioned polar surfaces have strong binding affinities toward LiPSs, which can efficiently suppress the dissolution of LiPSs and thus keep good cycling stability. Third, the CH@LDH host can enhance the

reaction kinetics of the S electrode, giving rise to high rate properties even with high areal mass loading of S.

Figure 4.14. (a) Discharge capacities and (b) voltage profiles of CH@LDH/S at various current densities from 0.1 to 1 C.

4.4. Summary

In this chapter, we have demonstrated a new concept of using double-shelled CH@LDH nanocages as an S host for Li-S batteries. With this novel design, a high content of S (75 wt%) is loaded within the CH@LDH/S composite, and the Li-S battery with the CH@LDH/S cathode can maintain excellent cycling stability at both 0.1 and 0.5 C over 100 cycles, and deliver high rate capacities with relatively high S loading of $\sim 3 \text{ mg cm}^{-2}$. It is believed that the concept of introducing LDH in the Li-S battery system will inspire a new avenue for future development of high-performance Li-S batteries.

Chapter 5. A single-shelled host based on Ni/Fe LDH for Li-S batteries[†]

5.1. Introduction

Li-S batteries have been regarded as one of the most promising candidates for next-generation electrochemical energy storage systems owing to their high energy density of 2600 Wh kg⁻¹ in theory and the low material cost of S.^[1, 4] However, the practical application of Li-S batteries is still hindered by insufficient S utilization, poor cycling stability, limited high rate property, and low Coulombic efficiency, especially in the electrode films with both high content and high areal mass loading of S.^[101] During the past decades, tremendous attempts have been made to enhance the reactivity of S and mitigate the polysulfide dissolution, including modulating cathode structures,^[16, 19, 33, 102] decorating separators,^[103-105] introducing interlayers,^[106] and developing new electrolyte additives.^[107-108] Employing meso- or micro- porous carbon as the host materials for S is the most common strategy.^[15, 35, 109] The porous carbon hosts can not only improve the conductivity of S cathode, but also provide physical adsorption to LiPSs by retaining them within the porous structures. However, when the S content reaches 70 wt% or above, the carbon/S composite cathodes usually suffered from rapid capacity decay because of the repulsion between the polar LiPSs and the nonpolar carbonaceous substrates. Once LiPSs are solvated, these intermediate reactants will easily detach from the electrode surface and diffuse away, leading to serious capacity loss of cathode and the passivation on anode interfaces. Therefore, rational design of proper S host materials

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which can provide stronger adsorption/binding for LiPSs is required to achieve stable long-term cycling performance for Li-S batteries.

More recently, it has been realized that some polar inorganic materials including transition-metal oxides,^[22, 51, 94, 110] sulfides,^[23, 55, 67] carbides,^[111-112] and hydroxides^[26, 113] can offer abundant adsorption sites to chemically adsorb LiPSs, retaining their capability as effective S hosts. Moreover, it has been demonstrated that the polysulfide dissolution process could be controlled by electrocatalytic effects on the conversion of LiPSs.^[67] LDH represents a promising S host owing to their structural advantages of inorganic cationic sheets.^[113-115] Specifically, the abundant hydrophilic and hydroxyl groups in LDH can chemically bond LiPSs.^[113] The metal sites exposed in LDH can provide sufficient “sulfiphilic” sites to kinetically enhance the redox reactions of LiPSs.^[115] Moreover, the inorganic cationic sheets may entrap polysulfide anions with the interlayers.^[115] Very recently, Ni/Fe LDH coated separators have been proposed to afford superior LiPSs absorptivity for enhanced Li-S batteries.^[116] Unfortunately, considering most S species are in the cathode, only a relatively small part of LiPSs can touch the sulfiphilic materials coated on separators. Therefore, the electrocatalytic effect from the materials coated on separator might be limited.

In this chapter, we have designed and synthesized novel single-shelled Ni/Fe LDH polyhedrons as an S host for enhancing the performance of Li-S batteries. The single-shelled Ni/Fe LDH host can not only inherit the advantages of double-shelled CH@LDH host, but also possess other unique advantages. Firstly, similar to double-shelled nanostructure, the hollow architecture itself is a wonderful physical host, since it can provide enough inner space for both loading large amounts of S and accommodating its large volumetric expansion. Moreover, once the active material is confined within the host, the shells would act as a dam and easily restrict the outward

diffusion of LiPSs. More importantly, better than double-shelled CH@LDH host, the Ni/Fe LDH shells can provide more sufficient sulfiphilic sites for chemically bonding with more LiPSs during the whole reaction processes, and also kinetically accelerating the redox reactions from long-chain LiPSs to $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$, which can effectively minimize the LiPSs loss and achieve homogeneous deposition of solid products. As a result, although within a simple configuration, Ni/Fe LDH host has successfully solved issues mentioned above in high S loading electrodes, and it shows significantly improved electrochemical performance with prolonged life over 1000 cycles and excellent rate properties.

5.2. Experimental Measurements

5.2.1. Materials Synthesis

Synthesis of MIL-88A nanocrystals. All the chemicals were directly used after purchase without further purification. Typically, 116 mg of fumaric acid and 162 mg of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ were dissolved in 10 mL of DMF at room temperature to form a clear yellow solution. Then, the well-mixed solution was heated in an oil bath at 100 °C for 2 h. Finally, the yellow precipitate of MIL-88A was obtained via centrifugation at 4000 rpm for 2 min, washed with DMF 2 times with the same centrifugation conditions.

Synthesis of hollow Ni/Fe LDH polyhedrons. The obtained MIL-88A was dispersed in 4 mL of ethanol (solution A), and 50 mg of urea were dissolved in 6 mL of DI water (solution B). Then, solution A and solution B were mixed via stirring at room temperature (solution C). At last, solution C was heated at 90 °C for 5-6 h without stirring. The product was washed with water and ethanol 3 times by centrifugation and dried at 70 °C for 10 hours.

Synthesis of S@Ni/Fe LDH composites. The S@Ni/Fe LDH composites were prepared *via* a melt-diffusion method. A mixture of S powder and hollow Ni/Fe LDH polyhedrons with a mass ratio of 7 : 3 was sealed in a glass bottle, and heated at 155 °C for 5 hours in an oven.

5.2.2. Electrode Preparation and Adsorption test

To make the cathode electrode, S@Ni/Fe LDH, Ketjen black, and PVDF binder were mixed in NMP with a weight ratio of 70 : 20 : 10. And then the slurry was spread onto a carbon paper with the areal S loading of 2-3 mg cm⁻². The electrode film was dried in an oven at 70 °C overnight. The 2032-type coin cells were assembled using Celgard 3501 membrane as separator and Li metal as anode. The electrolyte was composed of 1 M LiTFSI in a mixture of DOL) and DME (1:1, v/v) with 0.2 M of LiNO₃. The electrolyte/S ratio used in the coin cell is 30:1 (μL:mg). The cells were assembled in an Ar-filled glovebox with concentration of moisture and oxygen below 5 ppm. Galvanostatic discharge-charge tests were performed on a Neware Battery Measurement System (Neware, China) in the voltage range of 2.8-1.8 V (0.1, 0.2, 0.5 C), 2.8-1.7 V (1, 2 C). The cells used for cycling tests (at 0.2 and 1 C) were first activated at 0.1 C for 3 cycles. The current density was based on the weight of S (1C = 1675 mA g⁻¹), and the specific capacities were calculated on the mass of S. The electrode and coin cells of S@Ketjen black were prepared by the same method to S@Ni/Fe LDH sample.

To carry out the visualized adsorption test, Li₂S₆ solution was prepared by adding Li₂S and S at a molar ratio of 1:5 in DME/DOL (1:1 by volume) followed by vigorous magnetic stirring at 50 °C. Solutions with Li₂S₆ concentration of 0.2 wt% were used for adsorption test. 30 mg of Ni/Fe LDH and Ketjen black were added into two glass vials,

respectively, and then 3 mL $\text{Li}_2\text{S}_6/\text{DME}/\text{DOL}$ solution was poured into these glass vials. A blank glass vial was also filled with the same Li_2S_6 solution for reference. The strong capability of Ni/Fe LDH to adsorb Li_2S_6 is characterized by ex situ UV-Vis spectroscopy (Shimadzu, UV-2450).

5.3. Results and Discussion

5.3.1. Formation Processes

Figure 5.1. Schematic illustration of the synthesis of S@Ni/Fe LDH and proposed advantages of Ni/Fe LDH.

The synthesis process of hollow Ni/Fe LDH polyhedrons and S@Ni/Fe LDH is shown in **Figure 5.1**. First, a MIL-88A particle is fabricated as a sacrificial template. Then, polyhedral Ni/Fe LDH shells are formed on MIL-88A by reacting with $\text{Ni}(\text{NO}_3)_2$ and urea in a mixed solution of ethanol and DI water. Finally, S is loaded into the Ni/Fe LDH polyhedrons by a melting-diffusion method. The design of the S@Ni/Fe LDH composites has multiple advantages. First, the hollow polyhedrons can provide sufficient void space to not only encapsulate a large number of S, but also accommodate the volume expansion of S during lithiation. Second, the thin Ni/Fe LDH shells can provide a relatively large amount of functional surface and abundant sulfiphilic sites for

chemically bonding with LiPSs and kinetically enhancing the redox reactions of LiPSs, thereby suppressing their outward diffusion and maintaining enhanced cycling stability.

5.3.2. Materials Characterizations

MIL-88A templates are fabricated by mixing FeCl_3 and fumaric acid in DMF solution in an oil bath and stirred for 2 h at 100 °C. XRD measurement is performed to examine the crystalline structure of the resulted MIL-88A samples. The XRD pattern matches well with the published pattern (**Figure 5.2a**),^[117] demonstrating that the as-synthesized templates are phase-pure. Figure 5.2b shows the FESEM image of MIL-88A crystals. The as-prepared MIL-88A particles have the uniform shape of spindle-like polyhedrons with a smooth surface and an average diameter of 750 nm. The products exhibit a remarkably narrow size distribution with an average particle length of 1.5 μm . Besides, a uniform-contrast TEM image of the MIL-88A demonstrates their solid and dense nature (Figure 5.2c).

Figure 5.2. (a) XRD pattern, (b) FESEM image and (c) TEM image of MIL-88A crystals.

The hollow Ni/Fe LDH polyhedrons are fabricated by using the spindle-like MIL-88A as both sacrificial templates and iron precursor. In this step, MIL-88A particles are dispersed in ethanol/DI water solution of nickel nitrate and urea and heated at 90 °C for 5h to produce Ni/Fe LDH polyhedrons. During the process, OH^- ions generated from

the hydrolysis of urea can gradually etch MIL-88A templates, then the released Fe^{3+} ions will coprecipitate with Ni^{2+} and OH^- ions to form thin layered Ni/Fe LDH shells.

Figure 5.3. (a) XRD pattern and (b) EDX spectrum of as-prepared Ni/Fe LDH.

Figure 5.4. (a,b) FESEM images and (c,d) TEM images of the as-prepared Ni/Fe LDH.

The structure of Ni/Fe LDH polyhedrons is characterized by XRD, as shown in **Figure 5.3a**, the XRD pattern of Ni/Fe LDH polyhedrons matches well with the Ni/Fe LDH phase, indicating the complete consumption of the Ni precursor template during the reaction. In addition, all of the diffraction peaks are significantly broadened, which

might be due to small crystallite sizes and stacking faults. EDX analysis (Figure 5.3b) validate the presence of Ni, Fe, C and O in these hollow Ni/Fe LDH polyhedrons, and the molar ratio of Ni/Fe is about 3:1, which indicates the possible chemical formula of the hollow Ni/Fe LDH polyhedrons might be expressed as $\text{Ni}^{2+}_3\text{Fe}^{3+}_1(\text{CO}_3^{2-})_{1/2}(\text{OH})_8 \cdot x\text{H}_2\text{O}$.

FESEM image shows that the Ni/Fe LDH polyhedral shells are successfully formed in the same spindle-like morphology of MIL-88a (**Figure 5.4a**). A magnified FESEM image (Figure 5.4b) clearly shows that the smooth surface of the spindle-like precursor is finally turned into a hierarchical shell with a rougher surface assembled by small nanosheets. The hollow interior of these spindle-like Ni/Fe LDH polyhedrons is unambiguously elucidated by the sharp contrast between the shell and the inner cavity under TEM observations (Figure 5.4c). An enlarged TEM image confirms that the thickness of the shell is around 4 nm (Figure 5.4d).

Figure 5.5. (a, b) FESEM images and (c) TEM image of S@Ni/Fe LDH nanoparticles.

S is loaded within the Ni/Fe LDH host by a melt diffusion method. The morphology of the S@Ni/Fe LDH composites is determined by FESEM and TEM images. As depicted in **Figure 5.5a**, low-magnification FESEM image reveals that no obvious S particles are found in the S@Ni/Fe LDH composite. A close-up FESEM image reveals S@Ni/Fe LDH composite well maintains the spindle shape (Figure 5.5b). The darker contrast of the inside region of the S@Ni/Fe LDH composite indicates the diffusion of

S into the inner space (Figure 5.5c), revealing that S has been homogeneously encapsulated within the Ni/Fe LDH shells.

Figure 5.6. (a) TGA curve and (b) XRD pattern of as-prepared S@Ni/Fe LDH nanoparticles.

Figure 5.7. (a) EDX spectrum, (b) STEM image, and (c) the corresponding elemental mappings of S@Ni/Fe LDH.

TGA is used to determine the percentage of S in the S@Ni/Fe LDH composites (**Figure 5.6a**). The weight loss for S@Ni/Fe LDH is due to the evaporation of S occurs in a wide temperature range mainly between 180 and 300 °C with a total S content of about 70 wt%, which may promise both high volumetric and gravimetric energy densities of the electrode material for Li-S batteries. The structure phase of S@Ni/Fe LDH composite is determined by XRD, as shown in Figure 5.6b, the diffraction peaks of Ni/Fe LDH become relatively weak, all strong diffraction peaks come from the

crystalline S in the S@Ni/Fe LDH composite, which further confirms the high S content of S@Ni/Fe LDH composite.

The EDX spectrum of the S@Ni/Fe LDH composites (**Figure 5.7a**) indicates the strong signal of S, which also confirms the large amount of S in the final cathode electrode material. The STEM (Figure 5.7b) and the corresponding elemental mapping images (Figure 5.7c) further show the well-matched spatial distributions of Ni, Fe, O and S in the S@Ni/Fe LDH sample. These observations verify that the S has been homogeneously trapped inside the void space of the Ni/Fe LDH hollow polyhedrons.

5.3.3. *Electrochemical Measurements*

To evaluate the electrochemical performance of the S@Ni/Fe LDH electrode, 2032-type coin cells are fabricated with S@Ni/Fe LDH as the cathode and lithium as the anode. The areal mass loading of S is kept at 2-3 mg cm⁻². To show the effect of Ni/Fe LDH on retarding polysulfide dissolution, a S@Ketjen black composite is also measured by the same conditions for comparison. When cycled at a current density of 0.2 C, as shown in **Figure 5.8 a,b**, the S@Ni/Fe LDH electrode delivers an initial capacity of 1091 mAh g⁻¹, corresponding to a desirable areal capacity of 2.47 mAh cm⁻². After 200 cycles, a capacity of 724.5mAh g⁻¹ (1.64 mAh cm⁻²) is maintained with Coulombic efficiency of more than 99%. In contrast, although the S@Ketjen black electrode has a comparable initial capacity (Figure 5.8 a,c), it suffers a rapid capacity decay after 50 cycles, and only maintains a discharge capacity of 616 mAh g⁻¹ after 115 cycles. To investigate the redox kinetics of LiPSs in the S@Ni/Fe LDH cells. The 2nd cycle discharge-charge voltage profiles are compared as shown in **Figure 5.9**. S@Ni/Fe LDH shows a smaller polarization of 182 mV compared to S@Ketjen black cell (221 mV), suggesting the enhanced redox kinetics of LiPSs. The superior cycling stability of the S@Ni/Fe LDH

electrode is attributed to the unique Ni/Fe LDH polyhedrons, which can provide strong interaction with LiPSs and propel the redox reactions of LiPSs, thereby effectively suppressing the outward diffusion of the soluble LiPSs.

Figure 5.8. (a) Cycle performance of S@Ni/Fe LDH and S@Ketjen black at 0.2 C. Discharge-charge voltage profiles of (b) S@Ni/Fe LDH and (c) S@Ketjen black at 0.2 C.

To confirm the strong Ni/Fe LDH-LiPSs interaction, the same amount of Ni/Fe LDH polyhedrons and ketjen black (30 mg) was added to the Li₂S₆/DOL/DME solution.

Figure 5.9. The 2nd cycle charge-discharge voltage profiles comparison of S@Ni/Fe LDH and S@Ketjen black at 0.2 C. ΔE indicates the difference between the mid-point voltage of charge profile and discharge profile.

Figure 5.10. Visualized adsorption of Li_2S_6 solution with Ni/Fe LDH and ketjen black.

Figure 5.11. UV-vis spectra of blank Li_2S_6 solution and Li_2S_6 solution with Ni/Fe LDH and ketjen black.

The color changes of Li_2S_6 solution are shown in **Figure 5.10**, Ni/Fe LDH thoroughly decolors dissolved LiPSs, while ketjen black has no observable effect on the Li_2S_6 solution since the tawny color still remains. The strong capability of Ni/Fe LDH to adsorb Li_2S_6 is further demonstrated by ex-situ UV-vis spectroscopy investigation (**Figure 5.11**), where strong absorbance peaks of Li_2S_6 solution in 400-500 nm region disappear,^[118] indicating strong adsorption ability of LiPSs in the S@Ni/Fe LDH cathode.

Figure 5.12. (a) C-rate properties and (b) voltage profiles of S@Ni/Fe LDH at various current densities from 0.1 to 2 C.

The rate capability of the S@Ni/Fe LDH electrode is evaluated by cycling the cells at various rates from 0.1 to 2 C (**Figure 5.12a, b**). At 0.1 C, the discharge capacity stabilizes quickly at 1050 mAh g⁻¹, (corresponding to a high areal capacity of 3.19 mAh cm⁻²). Then, the S@Ni/Fe LDH electrode delivers the discharge capacities of 931 (2.83), 853 (2.59), 801 (2.43), and 633 mAh g⁻¹ (1.92 mAh cm⁻²) at 0.2, 0.5, 1, and 2 C,

respectively. This excellent rate performance confirms the enhanced electrochemical reaction kinetics and excellent electronic/ionic transport properties of the electrode. When the current density is abruptly switched back to 0.1 C, most of the original capacity can be recovered, indicating the excellent stability and reliability of the S@Ni/Fe LDH electrode.

Figure 5.13. Prolonged cycling performance of S@Ni/Fe LDH at 1 C.

Figure 5.14. A TEM image of S@Ni/Fe LDH particles after the long-term cycling test.

The prolonged cycling life of the S@Ni/Fe LDH electrode is measured at 1 C (Figure 5.13). The S@Ni/Fe LDH electrode delivers an initial discharge capacity of 844

mAh g^{-1} . Then, the cell maintains a very stable cycle life, and achieves a capacity of 501 mAh g^{-1} after 1000 cycles, corresponding to a small capacity decay rate of only 0.04% per cycle. In addition, the Coulombic efficiency of the S@Ni/Fe LDH cell is higher than 99% during the whole cycle life, revealing good suppression of the outward diffusion of LiPSs. To demonstrate the structural stability of the electrode, TEM image of S@Ni/Fe LDH after cycling test is performed. As shown in **Figure 5.14**, the spindle-like S@Ni/Fe LDH morphology is well maintained, revealing the robust and reliable feature of the composite cathode.

5.4. Summary

In this chapter, we have designed and synthesized a high-performance composite cathode based on hollow Ni/Fe LDH polyhedrons for Li-S batteries. This rationally designed host can maximize the effectiveness of restricting diffusion of LiPSs and enhancing the redox reaction kinetics of S species at the same time. As a result, the S@Ni/Fe LDH cathode delivers a high discharge capacity of 1091 mAh g^{-1} at 0.2 C, and exhibits stable cycle life over 1000 cycles at 1.0 C with a small capacity decay rate of 0.04% per cycle. The new concept of applying hollow LDH-based hosts may further inspire researchers for developing more efficient and cost-effective materials for Li-S batteries and other S-based high energy density electrochemical systems.

Chapter 6. A freestanding host based on CoS₂-decorated multichannel carbon fibers for Li-SeS₂ batteries[†]

6.1. Introduction

Due to the ever-growing demand for higher energy densities to power the emerging electric vehicles and mobile electronics, high-performance rechargeable batteries have attracted remarkable attention in the last ten years.^[1-3, 5] Li-S batteries, with high theoretical energy density and cost-effective materials, are considered to be one of the most promising candidates for next-generation energy storage systems.^[9, 119] To promote the commercialization of Li-S batteries, various strategies have been tried to enhance the capacity utilization rate of S and restrict the dissolution of LiPSs.^[27, 76-77, 120-121] Benefiting from the developments on electrolytes, separators, and host materials, the problems of LiPSs dissolution and shuttle effect have been largely addressed.^[21, 79, 84, 106, 122] However, it is still a great challenge to enhance the energy density of Li-S batteries to a practical level, because, in commercial high loading electrodes, the intrinsic low electrical and ionic conductivity of S and Li₂S usually lead to an insufficient capacity releasing.^[7, 123-124] Based on the thought of introducing high conductive active material instead of S, Se has been chosen as an alternative cathode for lithium storage, and, as expected, the Li-Se batteries promise much better reaction kinetics.^[125-126] However, the relatively lower gravimetric capacity and higher cost of Se limit the application scope of Li-Se batteries.^[127-128]

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To rationally balance the opposite but complementary features of Se and S, a class of Se-S solid solutions (noted as Se_xS_y) has been proposed as the cathode candidate for lithium storage.^[12] Some pioneering works on Se_xS_y -based cathodes have shown the attractive advantages of Se_xS_y for both Li and Na storage.^[12, 68-69, 73, 129] However, similar to the S cathode, the Se_xS_y -based cathodes also suffer from the rapid capacity fading due to the dissolution of reaction intermediates into the organic electrolyte.^[14, 68-69] Since Se_xS_y has similar chemical properties to S, it is expected that the strategies used for stabilizing the S cathode might also be effective for suppressing the dissolution of LiPSs/LiPSes in the Se_xS_y -based cathodes. Recently, some metal oxides/nitrides/sulfides have been demonstrated as good host materials for addressing the LiPSs dissolution issue of Li-S batteries.^[22, 65, 67, 94, 130-132] Among them, cobalt disulfide (CoS_2) is thought as a very efficient host choice for Li-S batteries due to its unique physical and chemical properties.^[67, 133] With the inherent metallic conductivity ($6.7 \times 10^3 \text{ S cm}^{-1}$, 300 K) and catalytic property, CoS_2 can not only provide strong chemical adsorption to LiPSs, but also kinetically enhance the LiPSs redox reactions, thereby significantly improving the cycle stability and high rate property of Li-S batteries. These results suggest the possibility of using CoS_2 as a host material to build better Li- Se_xS_y batteries.

In this chapter, we design and synthesize a freestanding lotus root-like carbon fiber network decorated with CoS_2 nanoparticles (noted as $\text{CoS}_2\text{@LRC}$) as SeS_2 host for enhancing the performance of Li- SeS_2 batteries. The integrated electrode is constructed by 3D interconnected multichannel carbon fibers, which could not only accommodate high content of SeS_2 , but also promise excellent electron and ion transport for achieving high capacity utilization. What is more, there are numerous CoS_2 nanoparticles decorated all over the inner walls and surfaces of the carbon fibers, providing efficient

sulphilic sites for restricting the dissolution of LiPSs and LiPSes during the electrochemical processes, thus successfully suppressing the shuttle effect and maintaining excellent cycling stability.

6.2. Experimental Measurements

6.2.1. Materials Synthesis

Synthesis of Co(Ac)₂/PAN/PS. All the chemicals were directly used after purchase without further purification. The Co(Ac)₂/PAN/PS fibers were synthesized according to a previously reported method.^[50] Typically, 340 mg of Co(Ac)₂, 400 mg of PS, and 500 mg of PAN were dissolved in 5 mL of DMF with vigorous stirring at 65 °C overnight to form the precursor solution. Then the precursor solution was electrospun on aluminum foil collector. The distance between the syringe and the collector was fixed at 15 cm, and the voltage of 17 kV was applied with a flow rate of 1 mL h⁻¹. Finally, the Co(Ac)₂/PAN/PS fibers paper was stabilized at 200 °C for 2 h in air.

Synthesis of Co@LRC. The stabilized Co(Ac)₂/PAN/PS paper was annealed at 800 °C for 4 h in a tube furnace with a heating rate of 5 °C min⁻¹ under Ar/H₂ flow (95%/5% in volume ratio). Afterwards, the furnace was cooled down to room temperature naturally.

Synthesis of CoS₂@LRC. The Co@LRC paper was mixed with S powder with a mass ratio of 1:2. Then, the mixture was transferred into a sealed glass vial and heated at 400 °C and maintained for 6 h in a tube furnace under a N₂ flow.

Synthesis of the CoS₂@LRC/SeS₂ electrode. Firstly, the CoS₂@LRC paper was cut into small pieces. Then, 25 mg of SeS₂ powder was dissolved into 5 mL of toluene with stirring at 110 °C. An appropriate amount of the SeS₂ solution was dripped to the pre-cut CoS₂@LRC piece. After evaporation of toluene, the CoS₂@LRC/SeS₂ was heated at 155 °C for 12 h in a sealed glass vial. The volume of the SeS₂ solution dripped was determined by the mass of the pre-cut CoS₂@LRC. For instance, when the mass of the pre-cut CoS₂@LRC was 1.2 mg, 2.8 mg of SeS₂ was needed to obtain an electrode containing 70% SeS₂. Therefore, 560 μL of SeS₂ solution (5 mg mL⁻¹) was dripped to the CoS₂@LRC fiber piece.

6.2.2. Electrode Preparation and Adsorption test

The CoS₂@LRC/SeS₂ papers were directly used as working electrodes after drying at 70 °C overnight. The areal mass loading of SeS₂ was controlled to be 2.3-2.5 mg cm⁻². CR2032 coin cells were assembled in an Ar-filled glovebox with lithium metal as an anode and Celgard 2400 membrane as a separator. The electrolyte was 1 mol L⁻¹ LiTFSI in DOL and DME (v/v=1:1) with 0.2 mol L⁻¹ LiNO₃. The electrolyte volume was controlled to be 30 μL per 1 mg of SeS₂. Cells were operated in a voltage window of 1.8-2.8 V vs. Li/Li⁺ using a NEWARE battery tester, except for low-rate (0.1 A g⁻¹) study that was conducted between 1.9 and 2.8 V vs. Li/Li⁺. The cells used for cycling tests (at 0.2 and 0.5 A g⁻¹) were activated at 0.1 A g⁻¹ for 3 cycles firstly. All the capacity values were based on the mass of SeS₂.

To carry out the visualized adsorption test, Li₂S₆ solution was prepared by adding Li₂S and S at a molar ratio of 1:5 in DME/DOL (1:1 by volume) followed by vigorous magnetic stirring at 50 °C. Solutions with Li₂S₆ concentration of 0.1 wt% were used for

adsorption test. 15 mg of $\text{CoS}_2\text{@LRC}$ and LRC were added into two glass vials, respectively, and then 3 mL $\text{Li}_2\text{S}_6/\text{DME}/\text{DOL}$ solution was poured into these glass vials. A blank glass vial was also filled with the same Li_2S_6 solution for reference.

6.3. Results and Discussion

6.3.1. Formation Processes

Figure 6.1. (a) Schematic illustrates of the synthesis process of $\text{CoS}_2\text{@LRC}/\text{SeS}_2$. (b) Digital photos of (1) toluene, (2) the mixture of SeS_2 and toluene before heat treatment, and (3) the as-prepared $\text{SeS}_2/\text{toluene}$ solution.

The synthesis procedure of $\text{CoS}_2\text{@LRC}$ is schematically illustrated in **Figure 6.1a**. First, an interwoven fiber paper of $\text{Co}(\text{Ac})_2$, PAN and PS are fabricated by electrospinning. After annealed at $800\text{ }^\circ\text{C}$ in a reductive atmosphere, $\text{Co}(\text{Ac})_2$ is reduced to metallic Co, and LRC fibers are formed.^[50] Then, $\text{CoS}_2\text{@LRC}$ is gained by annealing

Co@LRC with S power at 400 °C in a nitrogen atmosphere. Finally, SeS₂ is loaded within CoS₂@LRC through a modified melt-diffusion method.

Figure 6.2. Proposed advantages of CoS₂@LRC/SeS₂ over LRC/SeS₂.

The design of the CoS₂@LRC/SeS₂ cathode has multiple advantages (**Figure 6.2**). First, the interwoven LRC fibers construct an excellent 3D conductive network, ensuring excellent electron and ion transport for high capacities. Moreover, since there is no binder or conductive additives needed, the overall mass ratio of SeS₂ in the free-standing electrode can reach as high as 70 wt%. Second, there are numerous CoS₂ nanoparticles uniformly decorated all over the inner walls and outer surfaces of the carbon fibers, providing efficient sulfiphilic sites for restricting the dissolution of LiPSs and LiPSes during the electrochemical processes, which can effectively suppress the loss of active materials, leading to excellent cycling stability. In addition, the parallel channels inside the CoS₂@LRC fiber can provide enough void spaces to accommodate the volume expansion of SeS₂ during lithiation.

6.3.2. Materials Characterizations

The phase purity of the as-prepared $\text{Co}(\text{Ac})_2/\text{PAN}/\text{PS}$ fibers is confirmed by XRD (**Figure 6.3a**), where only a broaden peak of PAN appears,^[134] while no signals from $\text{Co}(\text{Ac})_2$ and PS are detected, noting the uniform distribution of amorphous $\text{Co}(\text{Ac})_2$ in the fibers. Figure 6.3b,c depict the morphology of $\text{Co}(\text{Ac})_2/\text{PAN}/\text{PS}$ fibers through FESEM images. As can be seen, the electrospun $\text{Co}(\text{Ac})_2/\text{PAN}/\text{PS}$ fibers have a smooth surface with an average diameter of 1.5 μm , and the fibers are interweaved with each other. The uniformity of $\text{Co}(\text{Ac})_2/\text{PAN}/\text{PS}$ fibers is confirmed by TEM observation, as shown in Figure 6.3d, it is verified that amorphous $\text{Co}(\text{Ac})_2$ is uniformly distributed in the fibers.

Figure 6.3. (a) XRD pattern, (b,c) FESEM images, and (d) TEM image of $\text{Co}(\text{Ac})_2/\text{PAN}/\text{PS}$ fibers.

The phase purity of the as-prepared Co@LRC fibers is confirmed by X-ray diffraction (XRD; **Figure 6.4a**). Apparently, after annealed at 800 $^\circ\text{C}$ in Ar/H_2

atmosphere, the identified peaks can be perfectly assigned to Co (JCPDS card no. 01-1255), noting $\text{Co}(\text{Ac})_2$ is reduced to Co. Moreover, the wide broaden peak at 26° comes from amorphous carbon, indicating the PAN has been successfully carbonized to amorphous carbon. The morphology of Co@LRC fibers is displayed in Figure 6.4b. As can be seen, the interwoven network of Co@LRC fibers is well preserved, and a higher magnification FESEM image shows that the surface of the Co@LRC fiber becomes rough (Figure 6.4c). The lotus root-like interior of Co@LRC fibers is revealed by TEM. As shown in Figure 6.4d, multichannel structures can be clearly observed in the fiber, suggesting the complete removal of the PS. Moreover, TEM observation also indicates that numerous Co nanoparticles with a size of < 20 nm are uniformly distributed all over the surface and inner walls of LRC fibers.

Figure 6.4. (a) XRD pattern, (b,c) FESEM images and (d) TEM image of Co@LRC fibers.

The phase purity of the CoS_2 @LRC sample is identified by XRD analysis, as shown in **Figure 6.5a**, apparently, the identified peaks can be perfectly assigned to CoS_2

(JCPDS card no. 89-3056), confirming the Co phase is completely converted into CoS_2 as designed after annealed at 400 °C with S powder in N_2 atmosphere. The CoS_2 weight percent in the $\text{CoS}_2\text{@LRC}$ was determined by TGA analysis at 800 °C, as displayed in Figure 6.5b. The final solid product after TGA test corresponds to Co_3O_4 , thus the weight percent of CoS_2 is about 38 wt%, and the carbon content is about 62 wt%.^[135-136] Nitrogen adsorption-desorption tests were used to further examine the surface of the $\text{CoS}_2\text{@LRC}$ samples. Figure 6.5c shows the BET adsorption/desorption curves of the $\text{CoS}_2\text{@LRC}$, the specific surface area of $\text{CoS}_2\text{@LRC}$ is 77.6 $\text{m}^2 \text{g}^{-1}$. The Raman spectrum of $\text{CoS}_2\text{@LRC}$ was collected to illustrate the structure of the $\text{CoS}_2\text{@LRC}$, as shown in Figure 6.5d, the similar intensity of D and G bands reveals the amorphous feature of the LRC carbon substrate.

Figure 6.5. (a) XRD pattern, (b) TGA curve, (c) BET curves and (d) Raman spectrum of $\text{CoS}_2\text{@LRC}$.

Figure 6.6. (a-d) FESEM images, (d-g) TEM images and (h) HRTEM image of CoS₂@LRC. (i) EDX spectra comparison between CoS₂@LRC and Co@LRC.

The morphology of CoS₂@LRC fibers is characterized by FESEM and TEM. As shown in **Figure 6.6a**, a panoramic FESEM image demonstrates that the CoS₂@LRC fibers well inherit the morphology and dimensions of Co@LRC. A closer FESEM image indicates the particle size of CoS₂ on the surface becomes larger (Figure 6.6b). To investigate the lotus root-like structures visually, a cross-sectional view of CoS₂@LRC fiber is characterized by FESEM, as shown in Figure 6.56, the lotus root-like structure can be directly observed. To study the distribution of CoS₂ particles in the multichannel fibers, the CoS₂@LRC fibers were ground in a mortar, and the broken fibers were

characterized by FESEM. As shown in Figure 6.6d, the longitudinal-section observation clearly reveals that the CoS₂ nanoparticles are not only distributed on the surface of the fiber but also uniformly located in the inner walls of the LRC fiber.

The multichannel structures of CoS₂@LRC fibers are determined by TEM characterization directly, as shown in Figure 6.6e, a low magnification TEM image indicates that there are many highly parallel channels in each CoS₂@LRC fiber with no breaks. A closer TEM image further reveals the CoS₂ particles are distributed all over the multichannel fibers (Figure 6.6f). A high magnification TEM image of CoS₂@LRC fiber further indicates the size changing of the CoS₂ nanoparticles, as shown in Figure 6.6g, the average size of CoS₂ nanoparticles increases to around 40 nm, which might be caused by the crystalline phase transformation and reforming from Co to CoS₂. A representative HRTEM image clearly shows lattice fringes with an interplanar distance of 0.195 nm, corresponding to the (220) planes of CoS₂ (Figure 6.6h). The phase purity and chemical composition of the CoS₂@LRC fibers are confirmed by EDX analysis, as shown in Figure 6.6i, the EDX spectrum of CoS₂@LRC evidently shows strong Co and S signals, while there is no S signal from the EDX spectrum of Co@LRC, indicating the successful sulfidation process.

SeS₂ is infused into the CoS₂@LRC fibers via a modified melt diffusion method. Firstly, the SeS₂ is dissolved in toluene solution with ultrasound, followed by stirring at 110 °C in a sealed vial. After that, an appropriate amount of SeS₂/toluene solution is dripped into the pre-cut CoS₂@LRC paper. After evaporation of toluene, the CoS₂@LRC/SeS₂ composite is made through a melt diffusion method at 155°C.

After loaded with SeS₂, the CoS₂@LRC/SeS₂ paper is directly used as a binder-free electrode, as shown in the inset of **Figure 6.7a**. FESEM analysis is employed to investigate the morphology of the CoS₂@LRC/SeS₂ electrode. Figure 6.7a displays the

Figure 6.7. (a) Cross-section FESEM image of the $\text{CoS}_2\text{@LRC/SeS}_2$ electrode. (b-d) FESEM images of $\text{CoS}_2\text{@LRC/SeS}_2$ fibers. Inset of (a): a photograph of the freestanding $\text{CoS}_2\text{@LRC/SeS}_2$ electrode. Inset of (c): a cross-section FESEM image of $\text{CoS}_2\text{@LRC/SeS}_2$ fibers.

cross-sectional view of the electrode. Apparently, the thickness of the electrode is about 300 μm . A low-magnification FESEM observation (Figure 6.7b) reveals the freestanding electrode is composed of randomly oriented and interwoven $\text{CoS}_2\text{@LRC/SeS}_2$ fibers, forming a 3D interconnected network with abundant void spaces, which allows for the penetration of the electrolyte into the inner structure. Moreover, no large SeS_2 particles could be found on the surface of the $\text{CoS}_2\text{@LRC/SeS}_2$ fibers. A closer FSEM examination indicates that only a small amount of agglomerated SeS_2 can be observed on the surface of $\text{CoS}_2\text{@LRC/SeS}_2$ (Figure 6.7c), which demonstrates that most of SeS_2 have been successfully diffused into the inner space of the $\text{CoS}_2\text{@LRC}$ host. The cross-section image of the $\text{CoS}_2\text{@LRC/SeS}_2$ fiber indicates that SeS_2 adheres to the inside of the carbon channels (Inset of Figure 6.7c). Better revealed by a high-magnification FESEM image (Figure 6.7d), CoS_2 particles still

expose on the surface of $\text{CoS}_2\text{@LRC/SeS}_2$ fiber, which also confirms that most SeS_2 are infused into the inner channels of the $\text{CoS}_2\text{@LRC}$ fiber.

TGA analysis is employed to investigate the content of SeS_2 in the $\text{CoS}_2\text{@LRC/SeS}_2$ electrode, as shown in **Figure 6.8a**, the content of SeS_2 in the electrode is around 70 wt%, which is higher than many previously reported works.^[69-70, 73, 129] The phase purity of the $\text{CoS}_2\text{@LRC/SeS}_2$ electrode was investigated by XRD, as shown in Figure 6.8b, where all the identified peaks can be perfectly assigned to pristine SeS_2 , confirming the high amount of SeS_2 in the $\text{CoS}_2\text{@LRC/SeS}_2$ electrode.

Figure 6.8. (a) TGA curve, (b) XRD pattern, (c) TEM image and (d) elemental mappings of $\text{CoS}_2\text{@LRC/SeS}_2$ fibers.

TEM observation of the $\text{CoS}_2\text{@LRC/SeS}_2$ fiber shows an darker contrast of the inner space compared to $\text{CoS}_2\text{@LRC}$ (Figure 6.8c), further revealing the diffusion of SeS_2 into the channels. Moreover, some void spaces remain in the inner channels of the $\text{CoS}_2\text{@LRC/SeS}_2$ fiber, which might be beneficial for accommodating the volume variation during the charge/discharge processes. The TEM elemental mapping images

in Figure 6.8d reveals the homogeneous distribution of SeS_2 in the $\text{CoS}_2@\text{LRC}$ host. In one word, the above finding indicates that SeS_2 is well embedded into the inner channels of the $\text{CoS}_2@\text{LRC}$ host materials, which presents similar structures to the previous reported $\text{S}@\text{LRC}$ nanocomposites.^[50]

To show the significant function of the CoS_2 nanoparticles, a control group of pure LRC fibers with similar multichannel structure is prepared. **Figure 6.9a** shows the FESEM image of LRC fibers, demonstrating the LRC fibers are interweaved with each other similar to the $\text{CoS}_2@\text{LRC}$. A closer FESEM image reveals the smooth surface of the fiber as same as the reported work.^[50] Moreover, the lotus root-like multichannel structures of the LRC fibers could be demonstrated by the cross-sectional view of the FESEM image (Figure 6.9c) and TEM images (Figure 6.9 d-e).

Figure 6.9. (a,b) FESEM images, (c) a cross-sectional FESEM image, (d-f) TEM images of LRC.

The phase purity of the LRC is determined by XRD analysis, as shown in **Figure 6.10a**. The broad peak at 26° demonstrates the amorphous phase of the as-prepared carbon. The structure of the LRC fiber is further investigated by the Raman spectroscopy (Figure 6.10b). The disordered D band and G band are the intrinsic

characteristic peaks for carbonized PAN, which can enhance the electron transportation to the electrode.

Figure 6.10. (a) XRD pattern and (b) Raman spectrum of LRC.

Figure 6.11. (a) XRD pattern, (b,c) FESEM images, (d) TGA curve, (e) a cross-sectional FESEM image, and (f) TEM image of LRC/SeS₂ fibers.

SeS₂ is impregnated into the LRC fibers via the same method to CoS₂@LRC/SeS₂ electrode. **Figure 6.11** shows the characteristic features of the LRC/SeS₂ electrode. The XRD patterns, shown in Figure 6.11a, reveal the successful infusion of SeS₂ in the LRC/SeS₂ electrode. TGA curve demonstrates the SeS₂ content in the LRC/SeS₂ electrode is about 70 wt% (Figure 6.11d). FESEM images exhibit that there is no extra

SeS₂ on the smooth surface of the LRC fibers (Figure 6.11b,c). The blocked channels in the fiber (Figure 6.11e) demonstrate the successful infusion of active SeS₂ into the inner space of the LRC fibers, which is also confirmed by the dark contrast of the TEM image of LRC/SeS₂ (Figure 6.11f).

6.3.3. Electrochemical Measurements

Figure 6.12. (a) Voltage profiles of CoS₂@LRC/SeS₂ electrode at 0.1 A g⁻¹. (b) Cycle performance comparison between CoS₂@LRC/SeS₂ and LRC/SeS₂.

To evaluate the electrochemical performance of the CoS₂@LRC/SeS₂ electrode, 2032-type coin cells are fabricated. The areal mass loading of SeS₂ is kept at 2.3-2.5 mg cm⁻². The representative discharge-charge voltage profiles of the CoS₂@LRC/SeS₂ electrode are shown in **Figure 6.12a**. The discharge curves show four plateaus at around 2.30, 2.14, 2.12 and 2.05 V, respectively. The first two plateaus at around 2.30 V and

2.14 V are assigned to the conversion of SeS₂ solid solution to soluble long-chain LiPSs and LiPSes, respectively. The following two plateaus at 2.12 V and 2.05 V are attributed to dissociation of the long-chain LiPSs and LiPSes into short-chain LiPSs and LiPSes.^[68, 70, 72] Figure 6.12b shows the cycling performance of CoS₂@LRC/SeS₂ electrode. When cycled at 0.2 A g⁻¹, the CoS₂@LRC/SeS₂ electrode delivers an initial capacity of 1015 mAh g⁻¹, which is very close to the theoretical value (1123 mAh g⁻¹), corresponding to a desirable areal capacity of 2.33 mAh cm⁻². Importantly, the overall content of SeS₂ and the capacity of the CoS₂@LRC electrode are both higher than that of previously reported Se_xS_y-based cathodes (**Table 6.1**). After 100 cycles, a capacity of 745 mAh g⁻¹ (1.73 mAh cm⁻²) is maintained with Coulombic efficiency of > 98%. In contrast, although the LRC/SeS₂ electrode has a comparable initial capacity, it suffers a rapid capacity decay after only 20 cycles, and only maintains a discharge capacity of 494 mAh g⁻¹ after 76 cycles. The superior cycling stability of CoS₂@LRC/SeS₂ electrode is profited from introducing the CoS₂ nanoparticles, which can effectively suppress the outward diffusion of the soluble LiPSs/LiPSes.

To obtain additional evidence of the capture ability of CoS₂@LRC to bind LiPSs, visual discrimination is employed to investigate the interaction of different S host materials (LRC, CoS₂@LRC) with LiPSs (taking Li₂S₆ as the representative polysulfide). Considering that DME and DOL are generally used electrolyte solvent in the Li-S battery, the Li₂S₆ is prepared in DME/DOL solution using the previously reported method (seen in Experimental section). An equivalent amount of each material is added to a fixed volume of solution containing a fixed amount of Li₂S₆. As shown in **Figure 6.13**, the addition of CoS₂@LRC renders the Li₂S₆ solution almost completely colorless indicating strong adsorption of Li₂S₆ by the solid, whereas the LRC solution remains slightly colored, indicating lower adsorption capacity for Li₂S₆ than the

CoS₂@LRC composite. The better adsorption capability of CoS₂@LRC composite further explains well the observed better cycling performance than LRC cathodes in batteries.

Table 6.1. Performance comparison between CoS₂@LRC/SeS₂ and representative Li-SeS₂ cathodes employing various carbon-based hosts.

Sample	SeS ₂ ratio in electrode (wt%)	Areal mass loading of SeS ₂ (mg cm ⁻²)	Capacity based on SeS ₂ (mAh g ⁻¹)	Capacity based on electrode materials (mAh g ⁻¹)	Ref.
SeS ₂ /MCA	40%	1.5-2	816 (0.5 A g ⁻¹)	326.4 (0.5 A g ⁻¹)	[70]
SeS ₂ /MWCNTs	49%	NA	>1200 (0.05 A g ⁻¹)	588 (0.05 A g ⁻¹)	[68]
SeS ₂ /DLHC	60%	0.8-1	1100 (0.2 A g ⁻¹)	660 (0.2 A g ⁻¹)	[71]
SeS ₂ /CMK-3@PDA	56%	2.6-3	1234 (0.2 A g ⁻¹)	691 (0.2 A g ⁻¹)	[69]
CoS ₂ @LRC/SeS ₂	70%	2.3-3	1015 (0.1 A g ⁻¹)	711 (0.1 A g ⁻¹)	This work

Figure 6.13. Visualized adsorption of Li₂S₆ solution with CoS₂@LRC and LRC.

The rate capability of CoS₂@LRC/SeS₂ electrode is evaluated by cycling the cells at various current densities from 0.1 A g⁻¹ to 2 A g⁻¹ (**Figure 6.14** a,b). It is pronounced that the sample shows magnificent cyclic capacity retention at each rate. Remarkably, at 0.1 A g⁻¹, the discharging capacity stabilizes quickly at 1096 mAh g⁻¹ (corresponding

to a high areal capacity of 2.63 mAh cm^{-2}). Then, $\text{CoS}_2\text{@LRC/SeS}_2$ delivers the discharging capacities of 1038 (2.49), 846 (2.03), 686 (1.64), and 526 mAh g^{-1} (1.26 mAh cm^{-2}) at 0.2, 0.5, 1, and 2 A g^{-1} , respectively, confirming the enhanced electrochemical reaction kinetics and excellent electronic/ionic transport properties of the integral electrode.

Figure 6.14. (a) Voltage profiles and (b) rate capabilities of $\text{CoS}_2\text{@LRC/SeS}_2$ at various current densities from 0.1 to 2 A g^{-1} .

The prolonged cycle life of the $\text{CoS}_2\text{@LRC/SeS}_2$ electrode is measured at 0.5 A g^{-1} (**Figure 6.15**). The $\text{CoS}_2\text{@LRC/SeS}_2$ electrode delivers an initial discharge capacity of 868 mAh g^{-1} , and slightly decreases to 787 mAh g^{-1} after 10 cycles. Then, the cell maintains a very stable cycle life, and achieves a capacity of 470 mAh g^{-1} after 400 cycles, corresponding to a small capacity decay of only 0.10% per cycle. In addition, the Coulombic efficiency of the $\text{CoS}_2\text{@LRC/SeS}_2$ cell is larger than 97% during the cycling process, revealing a good control of the shuttle effect.

Figure 6.15. Prolonged cycle life of $\text{CoS}_2@\text{LRC}/\text{SeS}_2$ at 0.5 A g^{-1} .

Figure 6.16. FESEM images of $\text{CoS}_2@\text{LRC}/\text{SeS}_2$ electrode after cycling test.

In order to further understand the enhanced cycling stability of the $\text{CoS}_2@\text{LRC}/\text{SeS}_2$ electrode, we have carried out post-mortem studies after 100 charge-discharge cycles at 0.2 A g^{-1} . As shown in **Figure 6.16**, the $\text{CoS}_2@\text{LRC}/\text{SeS}_2$ electrode well maintains its original morphology after the cycling test, indicating the excellent structural stability of the electrode, which also ensures the enhanced cycling stability of the $\text{CoS}_2@\text{LRC}/\text{SeS}_2$ electrode.

6.4. Summary

In this chapter, we have developed a freestanding $\text{CoS}_2@\text{LRC}/\text{SeS}_2$ electrode with well-integrated features of the high content of electroactive SeS_2 , numerous functional CoS_2 nanoparticles and conductive LRC network. Specially, SeS_2 is essentially more reactive than S; the conductive LRC network further ensures the capability utilization,

and the CoS₂ nanoparticles promise excellent cycling stability. Benefiting from the above-mentioned advantages, the CoS₂@LRC/SeS₂ cathode delivers a high discharge capacity of 1015 mAh g⁻¹ (2.3 mg cm⁻²) at 0.2 A g⁻¹, accompanied by excellent high rate performance and prolonged cycle life over 400 cycles. We hope that this work will provide some meaningful inspiration for the rational design of SeS₂-based batteries with high energy density and enhanced lithium storage performance.

Chapter 7. Concluding Remarks and Outlook

7.1. Concluding Remarks

This research work focuses on the development of hollow polar host materials for high-performance Li-S and Li-SeS₂ batteries via suppressing the dissolution of soluble active intermediates (LiPSs/LiPSes). Many polar transition metal compounds show strong chemical affinity to LiPSs, but their limited surface area restricts their interaction with these active materials. Hollow nanostructures have been demonstrated their unique structural advantages to controlling the loss of the active materials. They just need to anchor a small number of LiPSs/LiPSes near the shell, and then the inner active species will be protected by the dams of the shell and the outer anchored LiPSs. In my thesis, a series of polar hosts with unique hollow structures have been designed and employed as LiPSs/LiPSes mediators for Li-S and Li-SeS₂ batteries.

Firstly, we have demonstrated a new concept of using double-shelled CH@LDH nanocages as an S host for Li-S batteries. With this novel design, a high content of S (75 wt%) is loaded within the CH@LDH/S composite, and the Li-S battery with the CH@LDH/S cathode can maintain excellent cycling stability at both 0.1 and 0.5 C over 100 cycles and delivers high rate capacities with relatively high S loading of ~ 3 mg cm⁻². The concept of introducing LDH in the Li-S battery system might represent a new avenue for future Li-S batteries with high performances.

Moreover, we have designed an S host based on hollow Ni/Fe LDH polyhedrons for Li-S batteries. Better than Ni/Co LDH, Ni/Fe LDH can maximize the effectiveness of moderating LiPSs diffusions and enhance the redox reaction kinetics of S species at the same time. Therefore, although within a simple configuration, the S@Ni/Fe LDH composite cathode delivers high discharge capacities of 1091 mAh g⁻¹ at 0.2 C, and

exhibits stable cycle life up to 1000 cycles at 1 C with a small capacity decay rate of 0.04% per cycle.

To further enhance the electrochemical performance, we optimized the cathode from both the active materials and host materials. We introduce conductive Se in the active S, and use CoS₂ decorated LRC fibers as host materials. The obtained CoS₂@LRC/SeS₂ electrode combines unique structural advantages from the high content of electroactive SeS₂, numerous functional CoS₂ species, and conductive LRC network. Especially, SeS₂ is essentially more reactive than S; the conductive LRC network further ensures the capability utilization, and the CoS₂ nanoparticles promise excellent cycling stability. Benefiting from the above-mentioned advantages, the CoS₂@LRC/SeS₂ cathode delivers a high discharge capacity of 1015 mAh g⁻¹ (2.3 mg cm⁻²) at 0.2 A g⁻¹, accompanied by excellent high rate performance and prolonged cycle life over 400 cycles. We hope that this work will provide some meaningful inspiration for the rational design of SeS₂-based batteries with high energy density and enhanced lithium storage performance.

In summary, this research project has systematically investigated the Li-S and Li-SeS₂ batteries employing hollow LDH or CoS₂/LRC fibers as host materials to inhibit the dissolution of active intermediates. We compare our three works and the state-of-the-art Li-S works from the capacity based on the mass of cathode and the S content in the cathode (**Table 7.1**). Firstly, double-shelled CH@LDH host can load a high content of S than the single-shelled structure. But the S@Ni/Fe LDH composite shows higher capacity than CH@LDH/S demonstrate that the capacity can be improved by optimization of the compositions of LDH although within a simple configuration. Generally, the two Li-S works show comparable performance to the state-of-the-art Li-S batteries. More importantly, the freestanding CoS₂@LRC/SeS₂ electrode exhibits very

excellent specific capacity and S content, which is superior than the state-of-the-art Li-S batteries. It is demonstrated that remarkable lithium storage properties can be achieved by properly designing and synthesizing the polar nanostructures of LDH or CoS₂/LRC host materials. These findings in this project will greatly expand our knowledge in the synthesis of polar host materials with hollow structures, and also serve as evidence confirming the advantages of polar hollow host for effectively inhibiting the dissolution of LiPSs or LiPSeS to generate high-performance Li-S and Li-SeS₂ batteries.

Table 7.1. Comparison of the capacity and cycling stability of our works with others.

	Sample	Capacity (mAh g ⁻¹), 0.2 C		S content in cathode
		Sulfur	Cathode	
Chapter 4	Li-CH@LDH/S	800	420	0.53
Chapter 5	Li-Ni/Fe LDH/S	939	460	0.49
Chapter 6	Li-CoS ₂ @LRC/SeS ₂	1015	711	0.70
[111]	Li-TiC@G/S	1032	619	0.60
[137]	Li-CG/S	1024	451	0.44
[80]	Li-TiO ₂ /NPs-S	700	336	0.48
[138]	Li-Li ₂ S/PPy	695	348	0.50
[139]	Li-HMT@CNT/S	1100	495	0.45

7.2. Outlook

A variety of hollow inorganic structures have been approved as effective host materials for building high-performance Li-S and Li-SeS₂ batteries via successfully preventing the outward diffusion of dissolved active materials. Nevertheless, there are

still some problems that need to be tackled regarding the commercial application of Li-S and Li-SeS₂ batteries. The future researches are proposed in the following aspects:

1) Considering the practical application, high gravimetric and volumetric capacity is required to realize high energy/power density for real Li-S batteries. To improve the gravimetric capacity of Li-S batteries, the S fraction in the electrode and S utilization should be further enhanced without degrading the capacity. To realize high energy density of Li-S batteries, the S load and S/electrolyte ratio are the most important parameters. Of note, the utilization of S is typically directly linked to the S fraction and S load, and the ratio of S/electrolyte. For the requirement of high volumetric capacity, the thickness of S cathode is a crucial parameter. If looked at from the hollow host based S cathode, the loading content of S within the hollow host materials should be optimized to reserve proper space for the volumetric expansion. Besides, the morphologies of the S-based composite materials should be rationally designed to achieve high tap/press density for the electrode films. Furthermore, enhancing the robustness of hollow hosts is another aspect need to note to maintain the integrity and functionality after rolling press during the conventional electrode fabrication process. Last but not least, cost-effective and scalable fabrication techniques are yet to be developed for practical applications of these hollow micro/nanostructures for use in Li-S batteries.

2) Recent years, most works are focused on the design of novel S-based cathodes via employing a variety of host materials. However, the complicated conversion mechanisms of the active materials and the changes of the electrode/electrolyte interfaces are still not very clear. Therefore, advanced characterizations should be developed and introduced to investigate the detailed reaction processes, such as: (a) whether S₈ is re-formed at the end of the charging process, and its crystalline form; (b) how to demonstrate the enhanced conversion rate come from the catalyst effect, rather

than the enhanced electrical conductivity; (c) how could the inorganic materials affect the deposition of active materials. More advanced characterization techniques, such as in-situ and operando ones, are needed to allow in-depth mechanistic understanding of the electrochemistry involved, which can then be used as guidelines to design better Li-S batteries.

3) Further optimization of the ratio of Se and S. The solid solution Se_xS_y shows so many advantages in improving the conductivity of active materials and keeping high capacity. The ratio of x/y should be further investigated for higher conductivity and higher capacity.

4) Electrolyte development. The addition of LiNO_3 in the electrolyte effectively suppress the electrochemical reaction between LiPSs with Li anode via the formation of SEI film on the surface of Li anode. However, as the huge volume change of Li anode during charge/discharge process, the SEI film is usually not stable for long-term cycling. Therefore, there are still some LiPSs can touch Li anode when the cycling number is long enough. Besides that, the traditional liquid electrolyte is usually composed of organic solvents, which are highly flammable and may lead to serious safety issues. As such, there is an urgent need to develop some solid electrolyte for guaranteeing the reliability and safety of high energy density Li-S batteries. Considering the low ionic conductivity of the solid electrolyte, the integration of solid electrolyte and liquid organic electrolyte might be an attractive research direction.

5) Separator/interlayer development. The separator is placed between anode and cathode, which plays a great role in inhibiting the diffusion of active materials. Therefore, the development of separator or the introduction of interlayer is also an interesting direction. In the early years, various microporous carbon materials have been coated on separators to suppress the diffusion of LiPSs from cathode to anode, because

their small pores do not permit the pass of LiPSs. More recently, with the development of polar materials, various polar materials have also been introduced in modifying separator or serving as interlayer. It should be noted, the polar materials on separator/interlayer can only provide strong chemical affinity to LiPSs, but could not promote the reaction kinetics of active materials, because they are far from cathode, thereby could not get or lose electrons from the external circuit.

6) The development of Li metal anode. For the full Li-S batteries, the issue of Li metal anode is also a very significant problem. Different from LIBs, Li metal in Li-S batteries firstly suffers from stripping process without the formation of protective SEI film, after that it begins to plate with the formation of SEI film. During the repeated stripping and plating processes, Li metal anode encounters several challenges, such as the safety issues coming from the dendrite growth and the volume changes, together with the corrosion of Li due to the continuous formation of dead Li and SEI. To solve these problems, one possible direction is developing advanced electrolyte to stabilize the surface of Li anode, for example employing solid-state electrolyte, which can block the growth of Li dendrite. Another method is introducing stable host materials in Li metal anode to minimize its volume change, such as using 3D scaffold of other metals or carbon materials to control Li stripping and plating.

Complete List of Publications

- [1] **Zhang, J. T.**; Hu, H.; Li, Z.; Lou, X. W. Double-shelled nanocages with cobalt hydroxide inner shell and layered double hydroxides outer shell as high-efficiency polysulfide mediator for lithium-sulfur batteries. *Angew. Chem., Int. Ed.* **2016**, *55*, 3982-3986.
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