Defect, interface and stack engineering of two dimensional materials for energy applications

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**NANYANG
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UNIVERSITY**

SINGAPORE

**DEFECT, INTERFACE AND STACK ENGINEERING OF TWO
DIMENSIONAL MATERIALS FOR ENERGY APPLICATIONS**

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2018

DEFECT, INTERFACE AND STACK ENGINEERING OF TWO DIMENSIONAL MATERIALS FOR ENERGY APPLICATIONS

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

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

2018

Statement of Originality

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

...26/01/ 2018.....

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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.

...26/01/ 2018.....

... LIU ZHENG.....

Authorship Attribution Statement

This thesis contains material from papers published/submitted/in preparation in the following peer-reviewed journals where I was/will be the first/co-first and/or contributed co-authors.

Chapter 4 has been submitted as **Cheng Yan**, Jenndy Lim, Chaoliang Tan, Zhi Wei Seh, Hua Zhang, and Zheng Liu. Engineering Ultrathin Two-Dimensional Materials for Energy Storage and Electrocatalysis: From Reaction Mechanisms to Rational Material Design. *Advanced Energy Materials* (2018) submitted. Chapter 4 is also published as Z.Q. Xie, Z.Y. He, X.H. Feng, W.W. Xu, X.D. Cui, J.H. Zhang, **C. Yan**, M.A. Carreon, Z. Liu, and Y. Wang. Hierarchical Sandwich-Like Structure of Ultrafine N-Rich Porous Carbon Nanospheres Grown on Graphene Sheets as Superior Lithium-Ion Battery Anodes. *ACS Appl. Mater. Interfaces* 8, 10324–10333 (2015)

The contributions of the co-authors are as follows:

- Asst/Prof Zheng Liu, Prof Hua Zhang and Asst/Prof Zhi Wei Seh supervised the project and provided the initial project direction and revised the manuscript drafts.
- I prepared the manuscript drafts. The manuscript was revised by Jenndy Lim with some input and Dr. Chaoliang Tan.
- I co-designed the synthesis of the N-rich porous carbon materials with Zhiqiang Xie and Ziyang He and performed Raman and BET measurements at the School of Electrical Electronic and Engineering and at the School of Physical Mathematics Science. I also analyzed the data.
- All microscopy, including sample preparation, was conducted by Zhiqiang Xie and Ziyang He at Louisiana State University, USA.
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- Dr. Haiyong He did SEM characterization and TEM characterization and conducted analysis.
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- Dr Quan Gu and A/Prof Can Xue helped carried out the photocatalytic HER test and analyzed the data.

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The contributions of the co-authors are as follows:

- Asst/Prof Zheng Liu and Prof Shaojun Guo provided the initial project direction and edited the manuscript drafts.
- I prepared the manuscript drafts. The manuscript was revised by Prof Hailiang Yu.

- I designed the study with Asst/Prof Zheng Liu and Prof Shaojun Guo and performed all the laboratory work at the School of Materials Science and Engineering including XRD, SEM and AFM and TEM. I also analyzed the data.
- Prof Hailiang Yu helped prepared the stacking layers by mechanical rolling in Australia and China.
- Mr Yushuai Yu and A/Prof Hui Wu from Tsinghua University assisted in the fruitful discussion during the project and carried out some interpretation.

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Abstract

The emergence of novel two-dimensional (2D) materials triggered by graphene opens a new window and provides an exceptional platform in a large variety of potential applications such as flexible electronics, photodetector and clean energy due to their intrinsic novel and fascinating physicochemical properties compared with their bulk counterparts. So far, various 2D materials with versatile functions have been reported and synthesized with varied success. For example, insulating hexagonal boron nitride (h-BN), semiconducting and metallic transition metal dichalcogenides (TMDCs), black phosphorus (BP) and even non-layered structure 2D materials pure metal nanosheets have aroused tremendous research interests in recent years, further expanding the 2D family.

More importantly, the unique 2D crystal structure and high anisotropy hold great promise for endowing them with tunable electronic and catalytic properties. In this regard, the aim of this PhD thesis is to tune novel 2D materials in a broad regime including defect engineering, interface engineering and stacking engineering and then investigate their possibilities and potential applications for high-performance lithium-ion batteries (LIBs), photocatalytic hydrogen evolution reactions (HER) and electrocatalytic oxygen reduction reactions (ORR).

Firstly, highly nitrogen-doped and defect-rich porous nanocarbon has been synthesized by in-situ simple pyrolysis of zeolitic imidazolate framework nanoparticles grown on graphene oxide as negative electrode in lithium ion batteries (LIBs), which demonstrates extraordinary capacities, remarkable cycling performances and rate capability and surpasses carbon-based electrodes in literature and most of metal oxide-based anodes from metal organic frameworks (MOFs). With an impressive initial capacity of 1378 mAh g⁻¹ under current density with 100 mA g⁻¹, it could be operated for 100 and 200 cycles under current densities of 500 mA g⁻¹ and 1000 mA g⁻¹, leading to reversible capacities of 1070 mA g⁻¹ and 948 mAh g⁻¹, separately. If current density was up to 5000 mA g⁻¹, it still reversibly presents a decent capacity of more than 530 mAh g⁻¹ after 400 cycles, exhibiting a high rate of retention of 84.4% in terms of capacity. It is

considered that the excellent electrochemical output is due to the perfect bond of an extremely conductive platform (graphene), high-level doping of nitrogen (defect-rich) and hierarchically porous structure.

Secondly, via interface engineering, solid edge-on heterostructures between few-layered MoS₂ and TiO₂ were produced on large scale through a facile two-step, which realized the idea that layered MoS₂ can be welded laterally to photocatalysts via edges to enhance the catalytic activity toward water splitting owing to the efficient transport of photoexcited electrons along the highly conductive edges and basal planes of MoS₂. The unusual photocatalytic activity is attributed to the improved electronic contact and the optimized electron transport pathways between TiO₂ and MoS₂, where the recombination of photoexcited electron-hole pairs is effectively suppressed. This work represents a strategy, which marries low-cost layered transition-metal dichalcogenides with backbone photocatalyst as a promising heterostructure for high-efficiency water splitting.

Lastly, a facile and large-scale approach has been developed to prepare platinum-based binary alloy nanosheets by stacking engineering target platinum-based alloy foil with aluminum foil, in which asymmetric mechanical rolling technique was employed to repeat the folding and rolling process. With the assistance of sodium hydroxide, aluminum metal layers were selectively etched and removed completely. Combining theoretical calculations, rational material design with optimal compositions of Pt₃M (M: Ni, Fe, Co, Ir, Y, Au, Pb) was proposed for electrocatalytic oxygen reduction reactions (ORR). Through a series of characterization techniques, the sheet-like morphology was observed with lateral size of 2-3 μm and the thickness ranges from 5.5 nm to 9.7 nm. The activity and stability of ORR were greatly improved. It is widely believed that altered electronic properties by alloying and changed surface by 2D materials induce a variation for adsorption behavior, which were considered to be the origin of the high ORR activity.

Lay Summary

Nanoscience and nanotechnology could revolutionarily bring about dramatic change in terms of material properties and electronic structure at nanoscale due to quantum confinement effect (1-100 nm), which indeed provide much access to understanding and manipulating fundamental phenomena. The great success of zero-dimensional (0D) quantum dots/nanoparticles, one-dimensional (1D) nanowire/nanotube and three dimensional (3D) nanostructures in a large variety of research fields have demonstrated their substantial potential. In this regard, the startling discovery of two-dimensional (2D) materials, which are new forms of nanomaterials, emerges as remarkable platform for future clean energy applications, aiming to address the environmental and energy issues faced with the whole humanity. The intrinsic layered structure with expanded spacing is conducive to lithium storage because the expanded structure can store more ions. On the other hand, due to the ultrathin surface structure, catalytic reactions, which are recognized as surface-involved chemical reactions, may probably seek more opportunities in 2D materials. These are two simplest aspects and also two basic ideas for this thesis.

This thesis is mainly concerned about how to address then energy and environmental issues by virtue of the novel 2D materials, emphasizing the engineering strategies to further enhance, improve and boost the efficiency and durability of the energy storage and conversion processes. The major contribution of this thesis lies in controlled synthesis of edge-on heterostructures that could hardly be achieved previously, developing new preparation method for non-layered 2D materials and elucidating the role of defect for lithium storage.

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Before I started my PhD journey during the short stay at home, I have read a book titled "PhD grind: a PhD student Memoir", which is the first known detailed account of entire PhD experience. Actually, I imagine conducting cutting-edge research in the lab and was ready for challenges ahead. But during the past two years, I am fully aware of what "grind" means. There are so many persons I should mention during the tough 4-year process.

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Table of Contents

Abstract	i
Lay Summary	iii
Acknowledgements	v
Table of Contents	vii
Table Captions	xi
Figure Captions	xiii
Abbreviations	xvii
Chapter 1 Introduction.....	1
1.1 Hypothesis/Problem Statement	2
1.2 Objectives and Scope	3
1.3 Dissertation Overview.....	4
1.4 Findings and Outcomes/Originality	6
References.....	7
Chapter 2 Literature Review	11
2.1 Overview	12
2.1.1 Energy Storage and Conversion.....	12
2.1.2 The Appearance of 2D materials	16
2.1.3 Engineering 2D Materials for Energy Applications	21

2.2	Questions to Answer Based on Literature.....	24
2.3	PhD in Context of Literature.....	26
	References.....	27
Chapter 3 Experimental Methodology.....		33
3.1	Rationale for Selection.....	34
3.2	Synthesis.....	35
3.2.1	Chemicals.....	35
3.2.2	Synthesis of Nitrogen-doped Hierarchical Graphene Networks	36
3.2.3	Synthesis of Edge-on MoS ₂ /TiO ₂ Heterostructure	37
3.2.4	Preparation of Binary Platinum-based Alloy Nanosheets	37
3.3	Characterization	38
3.3.1	Scanning Electron Microscopy (SEM)	39
3.3.2	Transmission Electron Microscopy (TEM)	38
3.3.3	Scanning Transmission Electron Microscopy (STEM)	39
3.3.4	Atomic Force Microscopy (AFM)	40
3.3.5	X-ray Diffraction (XRD)	41
3.3.6	X-ray Photoelectron Spectroscopy (XPS)	43
3.3.7	Raman Spectroscopy and Photoluminescence (PL)	44
3.3.8	Brunauer–Emmett–Teller Measurements (BET).....	45
3.4	Applications	45
3.4.1	Fabrication and Performance of Lithium Ion Battery.....	45
3.4.2	Fabrication and Performance of Photocatalytic HER.....	46
3.4.3	Fabrication and Performance of Electrocatalytic ORR	46
	References.....	48

Chapter 4 Defect Engineering of Nitrogen-doped Hierarchical Graphene Networks	51
4.1 Introduction	52
4.2 Results and Discussion.....	53
4.2.1 Synthesis and Characterization of Nitrogen-doped Hierarchical Graphene Networks	53
4.2.2 Lithium Ion Battery Based on Nitrogen-doped Hierarchical Graphene Networks	59
4.3 Conclusions	62
References	64
 Chapter 5 Interface Engineering of Edge-on MoS₂/TiO₂ Heterostructure	67
5.1 Introduction	68
5.2 Results and Discussion.....	69
5.2.1 Synthesis and Characterization of Edge-on MoS ₂ /TiO ₂ Heterostructure	69
5.2.2 Enhanced Photocatalytic HER of Edge-on MoS ₂ /TiO ₂ Heterostructure	74
5.3 Conclusions	75
References	76
 Chapter 6 Stack Engineering of Platinum-based Alloy Nanosheets	79
6.1 Introduction	80
6.2 Results and Discussion.....	81
6.2.1 Synthesis and Characterization of Platinum-based Alloy Nanosheets	81
6.2.2 Boosted Electrocatalytic ORR of Platinum-based Alloy Nanosheets	86
6.3 Conclusions	88
References	88

Chapter 7	Implications/Impact/Outstanding Questions.....	91
7.1	General Discussion.....	92
7.2	Reconnaissance Work not Included in Main Chapters	93
7.3	Outcomes Reflected in the Original Hypothesis	95
References.....		97

Table Captions

Table 4.1 Comparisons of electrochemical performance of the designed PNCs@Gr sample in our work with those of formerly published carbon-based negative electrodes when used in LIBs63

Table 4.2 Comparisons of electrochemical performance of the designed PNCs@Gr sample in our work with those of previously reported other MOF negative electrodes for LIBs.....63

Figure Captions

Figure 2.1	Schematic of working principle of lithium ion battery	13
Figure 2.2	Schematic of photocatalytic water splitting.....	14
Figure 2.3	Working principle of fuel cells	15
Figure 2.4	Two-dimensional materials family. (a) graphene. (b) boron nitride. (c) MoS ₂ . (d) phosphene, (e) MXenes	18
Figure 2.5	Sonication-assistant exfoliation of graphite to graphene in water	19
Figure 2.6	Chemical-assistant exfoliation method of MoS ₂	20
Figure 2.7	Schematic of Li-intercalation method.....	20
Figure 2.8	Colloidal Synthesis of 1T-WS ₂ and 2H-WS ₂ Nanosheets	21
Figure 2.9	Electrochemical performance of MoS ₂ as the electrode material for LIBs	22
Figure 2.10	Electrochemical performance of pure MoS ₂ as an electrocatalyst.....	24
Figure 3.1	Working principle of scanning electron microscopy	40
Figure 3.2	Comparison of light microscope and transmission electron microscope	41
Figure 3.3	Equivalence in between conventional TEM and bright-field STEM.....	42
Figure 3.4	Schematic of working principle in AFM.....	43

Figure 3.5	Schematic of XRD principle and corresponding patterns.....	44
Figure 3.6	Schematic of XPS working principle.....	45
Figure 3.7	Signals from Raman effect.....	46
Figure 4.1	Schematic of the process of synthesis of the pre-designed PNCs@Gr sandwich-like nanostructure	54
Figure 4.2	XRD data of (a) ZIF and ZIF-8@GO without carbonization procedure and (b) as-prepared PNCs@Gr nanostructure and bare PNCs with the procedure of carbonization.....	56
Figure 4.3	SEM images with different resolution of (a, b) pure PNCs, (c, d) ZIF-8@GO sample and (e, f) PNCs@Gr nanostructure	57
Figure 4.4	(a, b) TEM images with different resolution of ZIF-8@GO, and (c) High-resolution TEM of ZIF-8@GO. (d, e) TEM at different resolution of the PNCs@Gr nanostructure, and (f) High-resolution TEM of sandwich-like PNCs@Gr nanostructure	58
Figure 4.5	Raman Spectra corresponding to PNCs@Gr, ZIF-8@GO and ZIF-8	58
Figure 4.6	Cyclic voltammetry (CV) profiles of PNCs@Gr (a) and pure PNCs (b) using the same scanning rate of 0.1 mVs ⁻¹	59
Figure 4.7	Discharge/charge characteristics of PNCs@Gr anode operated (a) with 100 mA g ⁻¹ during first 3 cycles and (b) with a variety of current densities	60
Figure 4.8	Electrochemical measurements of PNCs@Gr and pure PNCs based anodes. (a, b) Cycling performance of PNCs@Gr and pure PNCs based anodes under current densities of 500 mA g ⁻¹ and 1A g ⁻¹ . (c, d) Cycling test of PNCs@Gr based electrode	

under the current density of 5 A g⁻¹ cycled for four hundred cycles and corresponding result of Columbic efficiency. (e) Rate performance of PNCs@Gr and bare PNCs based electrodes operated under a variety of specific current densities from 100 mA g⁻¹ to 6 A g⁻¹. (f) Nyquist of pure PNCs and PNCs@Gr..... 61

Figure 5.1 Schematic illustration of preparing TiO₂/MoS₂ nanostructures. a) Wet chemical approach fabricating TiO₂/MoO₃/(B), in which MoS₂ plates combine with TiO₂ planes with basal surface; b) CVD method to synthesize TiO₂/MoS₂(E) heterostructure, in which MoS₂ plates combine TiO₂ plane with highly conductive surfaces; c) Synthesis illustration of the final sulfurization in the CVD system.....71

Figure 5.2 Morphologies of TiO₂/MoS₂(E) composites. a) and b) SEM of as-obtained TiO₂/MoS₂(E)3%; c) TEM of TiO₂/MoS₂(E)3%, exhibiting MoS₂ nanoplate stands onto TiO₂ plane; d) high-magnification TEM of TiO₂/MoS₂(E)3%. I MoS₂ nanoplate clearly combines TiO₂ through the edges. Fast Fourier transform (FFT) patterns are in the inset from the area which is marked with green rectangular box 72

Figure 5.3 (a) XRD patterns and (b) Raman spectra of TiO₂ and TiO₂/MoS₂(E) 3% heterostructures; (c) UV-Vis spectra of TiO₂, TiO₂/MoS₂(E) 3%, TiO₂/MoS₂(B) 3% and TiO₂/MoS₂(E) 5% heterostructures; and (d) XPS spectrum of the sample..... 73

Figure 5.4 a) The rate of H₂ evolution over TiO₂/MoS₂(E) using all kinds of amount MoS₂; b) demonstration of H₂ evolution rate using TiO₂, TiO₂/MoS₂(E)3% and TiO₂/MoS₂(B)3%; c) H₂ evolution measurement with recycling photocatalytic process on the sample of TiO₂/MoS₂(E)3%; d) transport pathway of photo-excited electrons on TiO₂/MoS₂(E) by schematic illustration 75

Figure 6.1 Volcano plots of Pt-based binary systems for ORR 81

Figure 6.2 Schematic of asymmetric mechanical rolling approach and corresponding optical images of Pt-Ni sheets after different repeating times 82

- Figure 6.3** Characterization of the variation of thickness with increasing number of folding and rolling repeating. (a) Pure Al metal foil with 0.1 mm, pure PtNi foil with 0.1 mm, stacking sheets alternate Al layer and PtNi layer after 20 times repeating. (b-c) Cross-section SEM images of Al-PtNi stacking layers after 20 times repeating..... 83
- Figure 6.4** Characterization of as-prepared samples. (a) low-magnitude SEM image, scale bar 1 μm (b) high-magnitude SEM image, scale bar 300 nm; (c) TEM image (d) SAED pattern of the as-prepared sample 84
- Figure 6.5** AFM images of sample-5.5nm (a), sample-6.7nm 2 (b), sample-8.6nm (c), sample-9.7 (d), and the corresponding line depth profiles below. The insets in a-d are photographs of each sample suspensions..... 85
- Figure 6.6** XRD patterns of Pt₃Ni with different thickness 86
- Figure 6.7** (a) Cyclic voltammograms in N₂-protected 0.1 M and (b) corresponding ORR polarization curves in O₂-saturated 0.1 M of the Pt₃Ni/C nanosheets with different thickness..... 87
- Figure 7.1** Schematic of preparation of graphene encapsulated E-GaIn alloy 94
- Figure 7.2** CVD grown samples with different morphology and orientation 95

Abbreviations

0D	Zero-Dimension
1D	One-Dimension
2D	Two-Dimension
3D	Three-Dimension
TMDCs	Transition Metal Dichalcogenides
hBN	Hexagonal Boron Nitride
BP	Black Phosphorous
AFM	Atomic Force Microscopy
PXRD	Powder X-ray Diffraction
SAED	Selected Area Electron Diffraction
SEM	Scanning Electron Microscopy
TEM	Transmission Electron Microscopy
STEM	Scanning Transmission Electron Microscopy
XRD	X-ray Diffraction
XPS	X-ray Photoelectron Spectroscopy
PL	Photoluminescence
LIBs	Lithium Ion Batteries
HER	Hydrogen Evolution Reaction
ORR	Oxygen Reduction Reaction
OER	Oxygen Evolution Reaction
PVDF	Poly (vinylidene fluoride)
PVP	Polyvinylpyrrolidone
VdWs	Powder X-ray Diffraction
DFT	Density Functional Theory
EIS	Electrochemical Impedance Spectroscopy
EDS	Energy Dispersive X-ray Spectroscopy
GO	Graphene Oxide
rGO	reduced Graphene Oxide
PET	Polyethylene Terephthalate Film

PCEs	Power Conversion Efficiencies
NMP	N-methyl-pyrrolidone
NPs	Nanoparticles
PNCs	Porous Nitrogen-doped Carbon

Chapter 1

Introduction

In this Chapter, a brief introduction of the thesis is presented. Firstly, the hypotheses relating to how to further optimize the electronic structure and improve catalytic properties are tentatively proposed as well as their potential applications such as lithium ion batteries, photocatalytic hydrogen evolution and electrocatalytic oxygen reduction reaction. Based on the hypotheses, the objectives and scopes of the thesis including three projects are then elaborated. Thirdly, the dissertation overview for each chapter was also introduced. Finally, in light of the whole content, the main findings and outcomes of the thesis are summarized.

1.1 Hypothesis/Problem Statement

The startling discovery of graphene in 2004 opened a new window for various research areas owing to the intriguing and novel physicochemical properties, such as electronics, optoelectronics, supercapacitors, batteries, catalysis, and sensing to name a few and so on.[1-5] Inspired by pioneering two-dimensional (2D) graphene with varied success, extensive efforts have been devoted to active search for novel 2D crystals with the expectation of unprecedented properties, which therefore provides much access to a large variety of available 2D materials beyond elemental graphene in the last decade, e.g. hexagonal boron nitride (h-BN),[6] graphitic carbon nitride (g-C₃N₄),[7] layered metal chalcogenides (MoS₂, ReS₂, NbSe₂, WTe₂, ZnIn₂S₄),[8-12] layered metal oxides/hydroxides,[13-15] black phosphorous,[16] and MXenes.[17] Apart from the intrinsically (van der Waals gapped) 2D materials, a distinct type of non-layered 2D material is also emerging. Compositionally, these new types of 2D materials can be metal, oxides, chalcogenides or any 3D crystal structures that are made into 2D nanosheets through clever engineering of the bottom up synthesis, such as Au,[18] Ag,[19] CdS,[20] CoSe₂,[21] CoP,[22] and MoP etc.[23]

Being electronically and electrochemically active, ultrathin two-dimensional (2D) materials—that is, the thickness down to single- or few-atom limit (typically less than 5 nm)—emerge as favorable platforms for electrochemical energy storage and electrocatalysis.[24] Different from their bulk counterparts, 2D materials with atomic thickness show distinct and unique behaviors, which herald great prospect especially in energy-related field. When the dimension along Z-direction, e.g. the thickness of bulk materials, is dramatically decreased to atomic thickness scale, the most direct and clear consequence is large specific surface area and high ratio of surface atoms to entire atoms, which are of considerable benefits to facilitating surface-related electrochemical reactions.

Moreover, for non-van der Waals solids and in materials without intrinsically 2D structures, new and fascinating properties tied to the variations of the local atomic arrangement have been observed if the thickness of the target materials is decreased to

atom-thin limit. Furthermore, the local atomic arrangements will experience remarkable variations including coordination number, disorder degree of the surface atoms, bond length, and bond angle and probably even lead to the formation of a large amount of surface defects.[25] More importantly, the appearance of intrinsic quantum confinement effect in ultrathin 2D materials will definitely result in variation of the electronic structure. Therefore, the resulting ultrathin 2D materials not only can show enhanced intrinsic characteristics inherited from the bulk parental materials to some extent but also always give rise to novel unique physicochemical properties beyond their bulk counterparts including electronic anisotropy, planar conductivity, high surface activity and tunable energy band structure.

Based on the aforementioned discussions, the hypotheses tested here in this thesis are that there are possibilities to further improve the desirable properties of 2D materials for energy applications in LIBs and energy conversion process. Doping strategy has been proven to boost lithium storage through altering the electronic conductivity and shortening the ion pathway. On the other hand, energy conversion processes such as photocatalytic HER are surface-involved reactions. Therefore, interface and surface could be of essential importance for boosting the photocatalytic HER performance. Lastly, alloying with other transition metals should be a suitable way to heavily reduce the reliance on precious metal, platinum, which is the state-of-the-art electrocatalyst for ORR. In addition, preparation of 2D Pt-based alloy nanosheets via facile and scale-up techniques holds great promise for enhanced electrocatalytic ORR activity.

1.2 Objectives and Scope

On basis of the discussions above in the hypotheses part, the objectives of this thesis as well as research scope are presented in the following, which hopefully address three aspects of two dimensional materials in clean energy applications. The aim of the thesis and problems expected to solve in this thesis lie in constructing novel nanostructures (sandwich hierarchical structures and edge-on heterostructures) using two typical/representative two dimensional materials (graphene oxide and MoS₂) by defect

engineering and interface engineering respectively as well as developing a new mechanical rolling method to fabricate 2D platinum-based alloy nanosheets for enhanced oxygen reduction reactions. The scope of the thesis always emphasizes on how to further improve or boost clean energy applications based on two dimensional materials.

Firstly, highly nitrogen-doped and defect-rich porous nanocarbon has been synthesized by in-situ simple pyrolysis of zeolitic imidazolate framework (ZIF) nanoparticles grown on graphene oxide as negative electrode in lithium ion batteries (LIBs). It is considered that the excellent electrochemical output is due to the perfect bond of an extremely conductive platform (graphene), high-level doping of nitrogen (defect-rich) and hierarchically porous structure.

Secondly, via interface engineering, solid edge-on heterostructures between few-layered MoS_2 and TiO_2 were produced on large scale through a facile two-step, which enhanced the catalytic activity toward water splitting owing to the efficient transport of photoexcited electrons along the highly conductive edges and basal planes of MoS_2 . The unusual photocatalytic activity is attributed to the improved electronic contact and the optimized electron transport pathways between TiO_2 and MoS_2 .

Lastly, a facile and large-scale approach has been developed to prepare platinum-based binary alloy nanosheets by stacking platinum-based alloy foil with aluminum foil. Combining theoretical calculations, rational material design with optimal compositions of Pt3M was proposed for electrocatalytic oxygen reduction reactions (ORR). It is widely believed that altered electronic properties by alloying and changed surface by 2D materials induce a variation for adsorption behavior, which was considered as the origin of the high ORR activity.

1.3 Dissertation Overview

The thesis in general addresses developing three engineering/tuning strategies for further modifying two dimensional materials and fabricate novel two-dimensional materials

towards further optimizing and improving the electronic structure and catalytic properties for energy storage and conversion processes. Specifically, the thesis aim at understanding how defecting/doping strategy of 2D materials can boost lithium storage through altering the electronic conductivity and shortening the ion pathway as well providing more available active sites for lithium storage, and how novel edge-on heterostructure different from previous ones can dramatically enhance photocatalytic HER of traditional photocatalysts TiO_2 by co-catalyst of MoS_2 via precise interface engineering, and how to boost electrocatalytic ORR of Pt-based binary nanosheets and finally demonstrates the proof-of-concept applications of these strategies in 2D materials in a larger variety of energy applications including LIBs, photocatalytic HER and electrocatalytic ORR.

Chapter 1 provides a rationale for the research and outlines the goals and scope.

Chapter 2 reviews the literature concerning the background, motivation and research progress of 2D materials for energy applications addressing the environmental and energy issues. Especially, various preparation methods of 2D materials developed will be introduced. Moreover, 2D materials for energy storage (LIBs) and energy conversion (HER, ORR) will also reviewed as well as the advantages and potential of 2D materials in energy applications.

Chapter 3 discusses the principles of the methods and characterization techniques employed to synthesize and probe 2D materials and elucidate the mechanism behind. A detailed explanation of why these techniques are suitable for the projects in the thesis.

Chapter 4 elaborates highly nitrogen-doped and defect-rich porous nanocarbon has been synthesized by in-situ simple pyrolysis of zeolitic imidazolate framework (ZIF) nanoparticles grown on graphene oxide as negative electrode in lithium ion batteries (LIBs). It is considered that the excellent electrochemical output is due to the perfect bond of an extremely conductive platform (graphene), high-level doping of nitrogen (defect-rich) and hierarchically porous structure.

Chapter 5 elaborates via interface engineering, solid edge-on heterostructures between

few-layered MoS₂ and TiO₂ were produced on large scale through a facile two-step, which enhanced the catalytic activity toward water splitting owing to the efficient transport of photoexcited electrons along the highly conductive edges and basal planes of MoS₂. The unusual photocatalytic activity is attributed to the improved electronic contact and the optimized electron transport pathways between TiO₂ and MoS₂.

Chapter 6 elaborates a facile and large-scale approach has been developed to prepare platinum-based binary alloy nanosheets by stacking platinum-based alloy foil with aluminum foil. Combining theoretical calculations, rational material design with optimal compositions of Pt₃M was proposed for electrocatalytic oxygen reduction reactions (ORR). It is widely believed that altered electronic properties by alloying and changed surface by 2D materials induce a variation for adsorption behavior, which was considered as the origin of the high ORR activity.

Chapter 7 presents the conclusions and also demonstrates the reconnaissance studies that could be carried out in near future. Specifically, the correlations between the results of this thesis and the hypotheses will be highlighted as well as the implications of the research for future work.

1.4 Findings and Outcomes/Originality

This research led to several novel outcomes by:

1. Designing a novel hierarchically porous structure with highly nitrogen-doped and defect-rich porous nanocarbon by in-situ simple pyrolysis of zeolitic imidazolate framework (ZIF) nanoparticles grown on graphene oxide as negative electrode in lithium ion batteries (LIBs), surpassing carbon-based electrodes in literature and most of metal oxide-based anodes from metal organic frameworks (MOFs). With an impressive initial capacity of 1378 m Ah g⁻¹ under current density of 100 mA g⁻¹, it could be operated for 100 and 200 cycles under current densities of 500 mA g⁻¹ and 1000 mA g⁻¹, leading to reversible capacities of 1070 mA g⁻¹ and 948 m

Ah g⁻¹, separately. If the current density was up to 5000 mA g⁻¹, it still reversibly presents a decent capacity of more than 530 m Ah g⁻¹ after 400 cycles, exhibiting a high rate of retention of 84.4% in terms of capacity.

2. Synthesizing solid edge-on heterostructures between few-layered MoS₂ and TiO₂ via interface engineering on large scale through a facile two-step, which realized the idea that layered MoS₂ can be welded laterally to photocatalysts via edges to enhance the catalytic activity toward water splitting due to the efficient transport of photoexcited electrons along the highly conductive edges and basal planes of MoS₂. The unusual photocatalytic activity is attributed to the improved electronic contact and the optimized electron transport pathways between TiO₂ and MoS₂, where the recombination of photoexcited electron-hole pairs is effectively suppressed.
3. Developing a facile and large-scale approach to prepare platinum-based binary alloy nanosheets by stacking engineering target platinum-based alloy foil with aluminum foil, in which asymmetric mechanical rolling technique was employed to repeat the folding and rolling process. With the assistance of sodium hydroxide, aluminum metal layers were selectively etched and removed completely. Combining theoretical calculations, rational material design with optimal compositions of Pt₃M (M: Ni, Fe, Co, Ir, Y, Au, Pb) was proposed for electrocatalytic oxygen reduction reactions (ORR). Through a series of characterization techniques, the sheet-like morphology was observed with lateral size of 2-3 μm and the thickness ranges from 5.5 nm to 9.7 nm. The activity and stability of ORR were greatly improved. It is widely believed that altered electronic properties by alloying and changed surface by 2D materials induce a variation for adsorption behavior.

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Chapter 2

Literature Review

This chapter presents and reviews the literature concerning the background, motivation and research progress of 2D materials for energy-related applications, targeting at addressing the environmental and energy issues. Firstly, a brief introduction of current energy status is given. Especially, various preparation methods and strategies developed of numerous 2D materials are also introduced, which provide much access to solve the energy issue. Moreover, 2D materials for energy storage (LIBs) and energy conversion (HER, ORR) are also be reviewed as well as the advantages and potential of 2D materials in energy applications, with the emphasis of available tuning and engineering strategies of 2D materials for clean energy applications.

2.1 Overview

The ever-growing demand for global-scale energy supply due to the rising worldwide population, which still depends heavily on the consumption of unrenewable fossil fuels including petroleum, coal and natural gas, will inevitably bring about more severe energy crisis and environmental issues in the foreseeable future, thus imminently requiring the exploration of next-generation renewable energy.[1-5] To alleviate the challenge and reduce our strong reliance on fossil fuels, it is highly desirable and imperative to explore and develop clean and sustainable technologies as new driving force toward efficient, fossil-free and smart future. Therefore, various clean technologies and devices emerge, such as lithium ion batteries (LIBs),[6-7] water electrolyzer,[8-9] fuel cells,[10-12] metal-air batteries.[13]

Among the components of these aforementioned energy devices, electrode materials are recognized to play a central role in determining the resulting performance [14-18]. In this regard, the continuous exploration of advanced electrode materials with high electrochemical activity and satisfactory cost is, to large content, of essential importance in enhancing the performance of the devices, aiming to efficient and maximum utilization of energy sources.

2.1.1 Energy Storage and Conversion

Batteries: Renewable energy storage and conversion systems, as promising alternatives to fossil powers, have emerged and aroused tremendous research and technological interests in recent years due to their vast potential in future applications. Among various energy storage devices, rechargeable lithium-ion batteries (LIBs) currently dominate the market of portable and wearable electronic devices owing to the competitive cost, wide-range operation temperature, relatively high energy density and no “memory effect”. [6] Therefore, developing high-capacity, fast-charging, and durable LIBs/SIBs is extremely desirable but still a formidable challenge. Currently, mainly dominating the research market are metal oxides as negative electrode materials, and Sn, Si and graphite as the

anode materials. However, there are some problems existing to be solved to meet the increasing demand. For example, a dramatic change in volume usually happens in the host of these active electrode materials (metals oxides and metal) during the cycle process, causing pulverization of the electrode materials and rapid capacity degradation. To overcome these shortcomings, carbon-based materials with excellent strength, good flexibility and extraordinary electrical conductivity have widely been used as soft matrices for the traditional materials including metal oxides and metals to boost the cycling performance.

Figure 2.1 Schematic of working principle of lithium ion battery.[5]

Energy conversions: Energy conversion systems, compared with energy storage devices, usually involve various electrocatalytic processes, such as hydrogen evolution reaction (HER), oxygen evolution reaction (OER) and oxygen reduction reaction (ORR), which provide an ideal avenue for renewable energy circle. To date, extensive studies have focused on water electrolyzer (HER and OER), fuel cells (ORR) and metal-air batteries (OER and ORR). Specifically, photocatalytic/electrocatalytic water splitting coupled with solar cells (or wind, hydric) is one of the most promising pathways toward sustainability

for harvesting renewable energy into clean hydrogen energy.[8-9] High-efficiency fuel cells, which are powered by hydrogen fuel with zero emission and water byproduct, typically depend on electrocatalytic ORR process.[10, 13] ORR and OER are critical for rechargeable metal–air batteries.[13] Notably, the state-of-the-art electrocatalysts for these dominant reactions are scarce noble metals or noble-metal based materials (e.g., Pt,[10] IrO₂,[11] RuO₂,[12] etc.), which will undoubtedly hinder their practical utilizations on large scale. From the high school textbook, the famous but simple chemical reaction of $\text{H}_2\text{O}=\text{H}_2+\text{O}_2$ can theoretically produce hydrogen gas by electrochemically splitting water. On the other hand, a hydrogen fuel cell which is considered to be a promising electricity generator, can provide an output voltage of 1.23 V. More interestingly, the voltage can be reversible, demonstrating the lowest voltage required to make electrochemically splitting water happen is also 1.23 V. The voltage of 1.23 V is based on the thermodynamic calculations. But in reality from the point of view of kinetics, to make this reaction occur needs higher voltage depending upon the electrode materials used, which can also be attributed to their acting as a catalyst for the hydrogen evolution reaction.

Figure 2.2 Schematic of photocatalytic water splitting.[7]

Typically, the electrocatalytic HER process can mainly be described as follows: firstly, the protons originated from the acid environment are attracted by the electrode, namely the catalytic part of the electrode. Then the electrons provided by the outside voltage through the outside circuit to the electrode are combined with these protons forming H atoms. Two H atoms then combine generating H_2 . This is the absorption step. Then the desorption process occurs meaning that many hydrogen molecules leaving from the electrode surface. Tafel behavior must be discussed in electrochemistry in order to explain it more clearly. For electrocatalytic water splitting, there are normally two kinds of electrolyte environment. Specifically, when used in acid, the reaction rate is measured based on the current from the outside circuit. From the process, we can obviously observe that the current dramatically increases in terms of over-potential, which is called Tafel behavior. Based on this clear phenomena or behavior, we can obtain two important indicators, namely Tafel slope and exchange current through fitting the linear relationship with the measured data, which are believed to be the criteria for evaluating electrocatalytic performance of the as-prepared catalysts. Better electrocatalyst towards HER process should show a smaller Tafel slope and larger exchange current.

Figure 2.3 Working principle of fuel cells. [11]

As known to us, the noble metal platinum currently is considered to be the best candidate for this procedure. But due to its scarcity and high price, searching for earth-abundant and low-cost materials, which are at the same time relatively comparable to Pt, is a hot topic. MoS₂ seems to be a promising candidate. For the case of bulk MoS₂, however, it is actually inactive for hydrogen evolution reaction. Firstly, bulk MoS₂ possesses a hexagonal crystal structure in which three atomic layers are covalently bonded forming S-Mo-S and along the z direction between S-Mo-S is dependent of Van der Waals interactions. Theoretical calculation indicates that the edges, which are exposed just along one line, especially Mo edges, are supposed to play a part in HER instead of the basal planes. So the above descriptions can explain why bulk MoS₂ crystal is considered to be a bad electrocatalyst in hydrogen evolution reaction since exposure edge sites are so few. Depending on the calculations about MoS₂ above, many groups started to figure out all kinds of ways to improve the edge density in MoS₂ by synthesizing different structures, including nanowires, nanoparticles and amorphous MoS₂ and so on.

2.1.2 The Appearance of 2D Materials

The startling discovery of graphene in 2004 opened up a new window for various research areas owing to the intriguing and novel physicochemical properties, such as electronics,[19] optoelectronics,[20] supercapacitors,[21] batteries,[22] catalysis,[23] and sensing and others.[24] Inspired by pioneering two-dimensional (2D) graphene with varied success, extensive efforts have been devoted to active search for novel 2D crystals with the expectation of unprecedented properties, which therefore provides much access to a large variety of available 2D materials beyond elemental graphene in the last decade, e.g hexagonal boron nitride (h-BN),[25] graphitic carbon nitride (g-C₃N₄),[26] layered metal chalcogenides (MoS₂, ReS₂, NbSe₂, WTe₂, ZnIn₂S₄),[27-31] layered metal oxides/hydroxides,[32-33] black phosphorous,[34] and MXenes.[35] Apart from the intrinsically (van der Waals gapped) 2D materials, a distinct type of non-layered 2D material is also emerging. Compositionally, these new types of 2D materials can be metal, oxides, chalcogenides or any 3D crystal structures that are made into 2D nanosheets

through clever engineering of the bottom up synthesis, such as Au, Ag, CdS, CoSe₂, CoP and MoP etc.[36-41]

Elemental 2D materials: As the first reported and well-studied two-dimensional materials, graphene, which is just one-atom thick carbon sheet, was mechanically exfoliated by scotch tape method in 2004 and then manually transferred to a silicon wafer.[42] As one kind of crystalline allotrope of carbon, graphene is visibly transparent and are of the strongest materials known to us. It was reported to have the highest electrical and thermal conductivity. The current densities are 1,000,000 times that of copper. [43] Ever since, many groups across the globe from almost any disciplines have been devoted to this research field. Phosphene, discovered by a research group based in China Fudan University, is the other single element 2D material. And phosphene is really an intrinsic semiconductor with a direct small bandgap.[44]

Boron nitride: Single layer h-BN shares the totally same atomic structure with graphene, which is therefore called “white graphene” with boron atoms and nitrogen atoms replacing carbon atoms alternatively. It has an atomically smooth surface and strong bonding, which is complementary to graphene. In terms of stability, h-BN has excellent thermal and chemical stability that can resist degradation up to 1000°C in air, 1400°C in vacuum and 2800°C in an inert atmosphere (graphene degrades at about 500°C).[45] Intrinsically, wide-bandgap h-BN is an electrical insulator which may be used in insulating coatings and as a far ultra-violet light source.[46]

Transition metal dichalcogenides: As the two-component 2D materials prototype, layer-structured transition metal dichalcogenides, previously used for lubricants, have in recent years attracted the research attention mainly due to the wonderful optoelectronic and electronic properties, which have drawn wide range of fundamental-level as well as practical-level attention including applications such as field effect transistors, photodetectors, energy conversion etc.[47-52]

MXene: Firstly discovered in 2011, MXenes, as an emerging class of inorganic two-dimensional compounds, cover transition metal nitrides, transition metal carbides and transition metal carbonitrides with few-atom thickness. MXenes are metallic in terms of conductivity and are prepared via selectively etching aluminum layers, resulting in a hydrophilic nature due to the hydroxyl or oxygen terminated surfaces.

Figure 2.4 Two-dimensional materials family. (a) graphene. (b) boron nitride. (c) MoS2. (d) phosphene, (e) MXenes. [12-15]

Preparation of 2D materials: Two-dimensional layered structure materials, especially the first example, graphene, have attracted enormous attention and demonstrated great promise for a broad range of practical applications. Stimulated by the huge success of graphene-based projects in the last ten years,[31] many promising graphene analogs have been discovered, such as two dimensional transition metal dichalcogenides (TMDs), representing a large group of layered compounds which could be indicated by the general chemical formula of MX_2 . [32]

Figure 2.5 Sonication-assistant exfoliation of graphite to graphene in water.[17]

Though the intrinsic nature of semiconducting properties of two dimensional TMDs make them strong candidates for optoelectronics and electronics applications, their quite bad electrical conductivity would limit their use in clean energy applications including energy storage and conversion process, where the electrical conductivity is considered to be one of the major factors to achieve good output. On the other hand, recent progress has showed that phase engineering (e.g., in MoS_2 and WS_2) in which the semiconducting 2H phase can be changed partially or fully into a metastable metallic 1T phase can significantly improve the electrical conductivity, rendering these 2D materials promising in energy-related applications, including low-resistance contact transistors,[33] electrocatalytic hydrogen evolution,[34] electrochemical supercapacitors.[35]

The appealing properties associated with so many potential practical applications of two dimensional TMDs strongly pushed the progress into different types of ways to obtain 2D TMDs with different size, thickness and chemical properties.[36] Currently, 2D TMDs of mono- or oligo-layers in thickness can be obtained through a variety of methods for example mechanical scotch-tape exfoliation, chemical vapor deposition (CVD), chemical synthesis [37] and liquid exfoliation. Among these approaches, the solution-based approaches (liquid exfoliation and chemical synthesis), specially including sonication-assisted exfoliation, colloidal synthesis or hydrothermal (solvothermal) synthesis, Li-intercalation and exfoliation (electrochemical), can synthesize 2D TMDs not only on a

large scale but also in high yield, which are of great importance for energy-related applications where lots of samples are needed for the electrode preparation.

Figure 2.6 Chemical-assistant exfoliation method of MoS₂. [22]

Figure 2.7 Schematic of Li-intercalation method. [25]

Specifically, the basic principle can be summarized as follows: the metal foil which is coated by layered structure bulk parent TMDs is used for negative electrode while lithium metal foil for positive electrode constructing the simple battery, which subsequently

undergoes the procedure of discharging to insert lithium ions in the layered TMDs crystals to produce Li-intercalated compounds. So high-yield monolayer two dimensional TMDs could be achieved followed through the following sonication-assist operation.

Figure 2.8 Colloidal Synthesis of 1T-WS₂ and 2H-WS₂ Nanosheets.[30]

Of particular interest is that the solution-based 2D TMDs obtained by aforementioned methods can be used as templates or building blocks to prepare various 2D TMDs-based composites so as to further improve their chemical and physical properties, therefore achieving better performance in specific energy-related applications, such as supercapacitors, secondary (rechargeable) batteries, electrocatalytic and photocatalytic hydrogen generation (HER) and electrocatalytic oxygen reduction reaction (ORR).

2.1.3 Engineering 2D Materials for Energy Applications

Because of the ultrathin morphology (single-or few-layer thickness), 2D TMDs (two-dimensional transition metal dichalcogenides) have demonstrated some extraordinary and unique properties compared to their bulk counterparts, meaning they hold great promise for future applications. Firstly, all the 2D TMDs show a bandgap transition when thinning down to single layer. And their bandgaps can be tuned depending on the number of layers. For instance, an indirect bandgap of 1.3 eV for bulk MoS₂ crystals can be converted into

a 1.8 eV direct bandgap for monolayer MoS₂, which paves the way towards optoelectronics applications. [14] Secondly, the well-known graphene has achieved great success in surface-active applications due to its ultra-high specific surface area. Similarly, 2D TMDs with the ultrathin thickness and 2D morphology make themselves very promising for energy related applications, such as electrocatalysis and supercapacitors. What is more, 2D TMDs are considered to be highly flexible and to possess excellent mechanical strength compared to the bulk single crystals in view of their extraordinary 2D structural characteristics. Because of these extraordinary properties, 2D TMDs have been explored potentially for a number of applications like optoelectronic and electronic devices, biomedicine industry and gas sensors. [15] Notably, the attractive characteristics of two dimensional TMDs such as high specific surface area, many active edge sites with large exposure and ease to be inserted with another guest molecule or ions enable them suitable for energy-related applications such as supercapacitors, secondary batteries, catalytic hydrogen production and solar cells. [16]

Figure 2.9 Electrochemical performance of MoS₂ as the electrode material for LIBs.[33]

Being electronically and electrochemically active, ultrathin two-dimensional (2D) materials—that is, the thickness down to single- or few-atom limit (typically less than 5

nm)—emerge as favorable platforms for electrochemical energy storage and electrocatalysis.[42] Different from their bulk counterparts, 2D materials with atomic thickness show distinct and unique behaviors, which herald great prospect especially in energy-related applications. When the dimension along Z-direction, e.g. the thickness of bulk materials, is dramatically decreased to an atomic thickness scale, the most direct and clear consequence is a large specific surface area and a high ratio of surface atoms to entire atoms, which are of considerable benefit to facilitating surface-related electrochemical reactions.

Moreover, for non-vdW solids and in materials without intrinsically 2D structures, new and fascinating properties tied to the variations of the local atomic arrangement have been observed if the thickness of the target materials is decreased to atom-thin. Furthermore, the local atomic arrangements will experience remarkable variations such as coordination number, disorder degree of the surface atoms, bond length and bond angle and probably even lead to the formation of a large amount of surface defects.[43] More importantly, the appearance of intrinsic quantum confinement effects in ultrathin 2D materials will definitely result in variation of their electronic structure. Therefore, the resulting ultrathin 2D materials not only can show enhanced intrinsic characteristics inherited from the bulk parental materials to some extent but also give rise to novel unique physicochemical properties beyond their bulk counterparts including high surface activity, electronic anisotropy, planar conductivity, and tunable energy band structure[44, 45]

Furthermore, it can be further improvement via various tuning and engineering strategies to make full utilization of this emerging class of novel materials. The discovery of single-layer graphene has triggered extensive research fanaticism regarding other two-dimensional (2D) materials with similar ultrathin structure. Numerous materials with 2D structure have been successful explored including metals, oxides, nitrides, dichalcogenides and so on. Due to the unique structure feature and outstanding physicochemical property, these 2D materials beyond graphene have widely been studied for use in a large variety of applications, including electronics, energy storage, biology, catalysis and sensing. Compared to their bulk counterparts, the 2D materials with

ultrathin configuration could supply many advantages, such as ultra-lightweight, mechanical flexibility, large specific surface area, high charge migration rate, good and diverse electronic properties and can be combined via stacking, which undoubtedly ensure 2D materials with promising application prospect especially in energy storage and conversion.

Figure 2.10 Electrochemical performance of pure MoS₂ as an electrocatalyst.[41]

2.2 Questions to Answer Based on Literature

As discussed in the literature review above, in despite of tremendous progress made in the past years about the synthesis of a large variety of 2D functional materials and their electrochemical storage and conversion utilizations, many aspects still remain unexplored such as engineering 2D materials for boosted energy applications beyond their intrinsic

properties. Herein, some interesting questions to answer in this thesis are presented as follows:

Firstly, lithium-ion batteries have been commonly used as power sources in portable electronics, such as laptops and mobile phones. Nevertheless, the ever-increasing demands for emerging applications in portable electronics and electric vehicles are pushing the development of the lithium ion batteries technologies with higher energy density (longer usage or drive-miles) as well as high rate capability (fast charging). In this regard, currently available graphite anode (372 m Ah/g) with poor rate capability (hours to fully charged) is far from the expected target. Thus, it is imperative to explore alternative electrode materials with highly reversible capacity, enhanced cycling stability, better rate performance as well as the potential for industrial scale production. To develop high-performance carbonaceous electrode materials for new-generation LIBs, one strategy is to design and synthesize a novel nanostructure with the following features: (i) large surface area with abundant active sites to facilitate Li-ion storage capacity, (ii) high porosity for enhanced charge transport, thereby resulting in improved rate capability, (iii) excellent structural stability and electronic conductivity to promote rapid charge transfer with prolonged cycle life, and (iv) heteroatom N or S doping to manipulate electronic and electrochemical properties and increase number of available active sites for Li-ion storage. To achieve these, many new carbonaceous anode materials with various nanostructures have been evaluated for lithium storage and demonstrated notably improved battery performance compared to commercial graphite anodes, such as heteroatom-doped graphene sheets, micro/nanoporous carbon, hollow carbon spheres, carbon nanofibers, and carbon nanobeads. In spite of these efforts, few have sought to satisfy all the aforementioned features simultaneously since most carbonaceous materials have low electrical conductivity and poor structural stability when cycled at high charge/discharge rates as well as limited active sites for effective Li-ion storage. Therefore, the lithium storage capability and rate performance of carbonaceous anodes still need improvement. By introducing more available active sites for lithium storage, incorporation of nitrogen into carbon has proven to significantly enhance both electronic conductivity and electrochemical reactivity of carbon-based anode materials, resulting in improved

performance in LIBs and other energy applications. However, the synthesis of N-rich carbonaceous nanostructures reported previously usually involve tedious processes such as complex chemical reactions, chemical vapor deposition (CVD), thermal annealing with ammonia, and/or various template-based approaches, which are costly and tedious, and thus hamper their practical applications for industrial scale production. Because of these trade-offs, design and synthesis of highly porous N-rich carbonaceous anode materials with superior electrical conductivity remain a big challenge.

Secondly, converting solar energy into chemical fuels has been considered as one of the major strategies to solve the energy crisis. Since Fujishima and co-workers for the firstly time split water on TiO_2 electrode in 1972, tremendous progress has been achieved in TiO_2 photocatalysis, especially solar water splitting. Generally, photocatalysts are composed by semiconductor and co-catalyst. Previous studies show that the hydrogen evolution, a key step in water splitting, depends on the properties of the co-catalysts and efficient charge transfer between the semiconductor and the co-catalysts. The co-catalysts not only assist in accelerating the separation of photoexcited electron-hole pairs in the semiconductors, but also supply active sites for hydrogen evolution. It is well known that noble metal and its oxides are effective co-catalysts. However, they are costly. Therefore, it is valuable to explore alternative low-cost co-catalysts to replace the noble metals for such application. Recently, the low-cost layered molybdenum disulfide (MoS_2) has been extensively investigated as a potential electrocatalyst for hydrogen evolution, with the goal to replace the costly noble metals. Moreover, several reports demonstrated that MoS_2 could also be used as a potential co-catalyst for photocatalytic hydrogen evolution. For instance, the photocatalytic activity of CdS can be improved by loading MoS_2 as co-catalyst. Liu et al. reported that integration of a certain quantity of MoS_2 with TiO_2 can effectively enhance the photocatalytic hydrogen production. The catalytic efficiency of the systems decorated with MoS_2 as a co-catalyst, however, is still not comparable with those loaded with noble metals. The low efficiency of such MoS_2 co-catalyst systems may own to the unoptimized geometrical configuration of MoS_2 on the semiconductor surface. It is commonly believed that layered MoS_2 prefers to grow along its basal plane on the semiconductor surface to minimize surface energy (surface energy at the edges is

100 time higher than basal plane). Such configuration leads to a low exposure of the active edge sites. Furthermore, in such lay-down configuration of MoS₂ flakes, the photoexcited electrons in the semiconductor have to hop through each layer to reach the active edge sites in the MoS₂ flakes, resulting in a much higher electron resistance ($\approx$ 2200 times higher than the electron moving in the same layer). According to the fact that edges of MoS₂ is more conductive than its basal plane, making MoS₂ standing on the semiconductor surface, e.g., connecting the edges of few-layered MoS₂ flakes with the semiconductor, serves as a promising heterostructures for improving the efficiency of the hydrogen evolution, owing to a better electronic contact and an optimized electron transport pathway. However, to the best of our knowledge, few strategies have been reported to realize such configuration of MoS₂ on the semiconductor surface, such as TiO₂, in large scale.

Thirdly, platinum represents the essential element for catalyzing the oxygen reduction reaction. However, its sluggish ORR rate and the limited reserves on earth are becoming the primary limiting factor in the commercialization of fuel cell devices. Extensive efforts have been devoted to both improving the intrinsic activity of Pt-based electrocatalyst and reducing the Pt usage for ORR without compromising the fuel cell performance. The combined experimental and theoretical studies provide the important clues for revealing the structure-function relationship and achieving the enhanced ORR performance. In order to facilitate the maximized catalytic activity of ORR, the adsorption energies of reactive intermediates and surface coverage by spectator oxygenated species as well as specifically adsorbed anions on the catalyst surface should be well balanced. The better ORR catalysts should bind oxygen more weakly than that of Pt, and more strongly than that of Pt₃V or Pt₃Ti. In this regard, Ni, Co and Fe are found to be the effective alloying elements with Pt for enhancing ORR intrinsic activity. The intrinsic activity enhancement is originated from the downshift of the d-band center of Pt in the alloyed Pt₃M (M = Fe, Co, Ni) structure, resulting in a decrease of the bonding strength between Pt and the spectator oxygenated species. Therefore, alloying Pt with some transition metals (e.g., Cu, Fe, Co, Ni) or forming a less expensive core/Pt shell structure has become the attractive strategy to reduce the required usage of Pt, and meantime achieve much enhanced ORR

electrocatalytic activity and durability over the state-of-the-art carbon supported platinum (Pt/C) catalyst. Besides multimetallic composition, ultrathin Pt-based multimetallic nanostructures are recently attracting more extensive attention. In comparison with solid or bulk counterparts, ultrathin size can lead to more exposed surface atoms with more active sites. These important features of multimetallic nanomaterials with the characteristic of ultrathin sizes make them very promising catalysts for high efficient ORR catalytic applications. However, despite the obvious advantages of ultrathin Pt based multimetallic nanostructures, the key challenge has been the generation of active ultrathin Pt based nanostructure using reliable synthetic techniques. It is not an easy task to synchronously control the nucleation and growth of diverse metals with especially big differences in redox potentials, which makes ultrathin Pt-based multimetallic nanostructures hard to be synthesized. So how to fabricate ultrathin Pt-based nanosheets toward enhanced ORR activity is an intriguing challenge.

2.3 PhD in Context of Literature

In this thesis, the controlled synthesis of nitrogen-doped hierarchical graphene networks, solid MoS₂/TiO₂ edge-on heterostructure and binary Pt-based alloy nanosheets were demonstrated. The characterizations of the as-obtained 2D materials with desired functionalities were conducted. Then, their potential applications in lithium ion batteries, photocatalytic water splitting and electrocatalytic oxygen reduction reaction were explored to demonstrate the superiority of the strategies in energy applications. The main contributions of this thesis were summarized as follows:

Firstly, highly nitrogen-doped and defect-rich porous nanocarbon has been synthesized by in-situ simple pyrolysis of zeolitic imidazolate framework (ZIF) nanoparticles grown on graphene oxide as negative electrode in lithium ion batteries (LIBs), which demonstrates extraordinary capacities, remarkable cycling performances and rate capability and surpasses carbon-based electrodes in literature and most of metal oxide-based anodes from metal organic frameworks (MOFs). With an impressive initial capacity of 1378 m Ah g⁻¹ under current density of 100 mA g⁻¹, it could be operated for

100 and 200 cycles under current densities of 500 mA g^{-1} and 1000 mA g^{-1} , leading to reversible capacities of 1070 mA g^{-1} and 948 m Ah g^{-1} , separately. When the current density was 5000 mA g^{-1} , it still reversibly presents a decent capacity of more than 530 m Ah g^{-1} after 400 cycles, exhibiting a high rate of retention of 84.4% in terms of capacity. It is considered that the excellent electrochemical output is due to the perfect bond of an extremely conductive platform (graphene), high-level doping of nitrogen (defect-rich) and hierarchically porous structure.

Secondly, via interface engineering, solid edge-on heterostructures between few-layered MoS_2 and TiO_2 were produced on large scale through a facile two-step, which realized the idea that layered MoS_2 can be welded laterally to photocatalysts via edges to enhance the catalytic activity toward water splitting due to the efficient transport of photoexcited electrons along the highly conductive edges and basal planes of MoS_2 . The unusual photocatalytic activity is attributed to the improved electronic contact and the optimized electron transport pathways between TiO_2 and MoS_2 , where the recombination of photoexcited electron-hole pairs is effectively suppressed. This work represents a strategy, which marries low-cost layered transition-metal dichalcogenides with backbone photocatalyst as a promising heterostructure for high-efficiency water splitting.

Thirdly, a facile and large-scale approach has been developed to prepare platinum-based binary alloy nanosheets by stacking engineering target platinum-based alloy foil with aluminum foil, in which asymmetric mechanical rolling technique was employed to repeat the folding and rolling process. With the assistance of sodium hydroxide, aluminum metal layers were selectively etched and removed completely. Combining theoretical calculations, rational material design with optimal compositions of Pt_3M (M: Ni, Fe, Co, Ir, Y, Au, Pb) was proposed for electrocatalytic oxygen reduction reactions (ORR). Through a series of characterization techniques, the sheet-like morphology was observed with lateral size of $2\text{-}3 \mu\text{m}$ and the thickness ranges from 5.5 nm to 9.7 nm . The activity and stability of ORR were greatly improved. It is widely believed that altered electronic properties by alloying and changed surface by 2D materials induce a variation for adsorption behavior, which were considered to be the origin of the high ORR activity.

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Chapter 3

Experimental Methodology

In this Chapter, the preparation approaches, characterization techniques and the applications of 2D materials are summarized. Particularly, this chapter emphasizes the rationale of the whole thesis, which summarizes how to choose/select the materials system and the motivation of proceeding the projects covered in the thesis. Moreover, this chapter is the foundation of the whole thesis, ranging from selection of materials to characterization of the as-prepared samples to the measurements of the electrochemical devices. Specifically, the rationale for selection of approaches and chemicals is firstly presented. Then, the used experimental approaches and materials for the controlled synthesis of two-dimensional materials are introduced, followed by the detailed discussions of the characterization techniques employed in this projects. Lastly, the potential applications of the as-obtained 2D nanostructures are presented.

3.1 Rationale for Selection

In the first part of the thesis, graphene oxide was selected as the template for the synthesis of highly doped and defect-rich carbon nanospheres by simple in situ pyrolysis of zeolitic imidazolate framework (ZIF) nanoparticles for negative electrode in lithium ion batteries (LIBs). The reasons are summarized as follows: (i) high porosity, which could enhance charge transport and lead to enhanced rate capability, (ii) large surface area, which provide sufficient active sites to improve storage capacity for lithium ions, (iii) heteroatom N or S doping, which can therefore manipulate the electronic structure and increase more active sites for Li-ion storage, (iv) excellent structural stability and electronic conductivity, which come from graphene network and could facilitate charge transfer. On the other hand, metal organic frameworks (MOFs) have been chosen in lithium ion batteries (LIBs) owing to large surface area and the intrinsic high porosity since they have been successfully demonstrated as exceptional precursors for numerous nanostructured electrodes. However, the previous MOFs-derived nitrogen-doped carbon materials still possess bad structural stability and poor electronic conductivity, even severe capacity degradation during long-term cycling in LIBs because of the inevitable breaking inside MOFs and large crystal size from 200 to 500 nm.

In the second part of the thesis, layered molybdenum disulfide (MoS_2) with very competitive cost has been selected as a potential extraordinary co-catalyst of TiO_2 , the most studied photocatalyst for hydrogen evolution, aiming to hopefully replace highly efficient but costly noble metals. Nevertheless, the photocatalytic efficiency of this structure loaded with MoS_2 , is still far from satisfactory, which is much lower than those with precious metals. The previous investigations revealed that the geometrical configuration of such MoS_2 co-catalyst structure might lead to the low efficiency on the semiconductor surface, in which layered MoS_2 , to minimize the surface energy, preferentially grows along its basal direction onto the semiconductor surface (surface energy of basal plane is 100 folds lower than the edges). Such configuration, however, results in a low edge exposure, which are commonly believed as active site of MoS_2 . Moreover, this lay-down geometrical configuration of layered MoS_2 would make the

photoexcited electrons in the TiO_2 photocatalyst to hop through layered MoS_2 flakes to reach the active edge sites, eventually bringing about extremely higher resistance (~ 2200 times through the layers higher than in the same MoS_2 layer). Bearing the fact that MoS_2 edge is more conductive than the basal plane in mind, it can be reasonably expected that enabling MoS_2 erecting onto the semiconductor surface, that is to say, the MoS_2 flakes edges contacting with the semiconductor, will greatly improve the efficiency of the hydrogen evolution, which could be ascribed to an optimized electronic connection with better electron transfer pathway. Nevertheless, such geometrical configuration of MoS_2 onto a semiconductor surface, for instance TiO_2 , has rarely been reported in large scale.

In the third part of the thesis, inspired by repeated mechanical folding and rolling and the aim of reducing the reliance on precious metal in commercial fuel cells, a facile and large-scale approach has been developed to prepare platinum-based binary alloy nanosheets by stacking engineering target platinum-based alloy foil with aluminum foil, in which asymmetric mechanical rolling technique was employed to repeat the folding and rolling process. With the assistance of sodium hydroxide, aluminum metal layers were selectively etched and removed completely. Combining theoretical calculations, rational material design with optimal compositions of Pt_3M (M: Ni, Fe, Co, Ir, Y, Au, Pb) was proposed for electrocatalytic oxygen reduction reactions (ORR). Through a series of characterization techniques, the sheet-like morphology was observed with lateral size of 2-3 μm and the thickness ranges from 5.5 nm to 9.7 nm. The activity and stability of ORR were greatly improved. It is widely believed that altered electronic properties by alloying and changed surface by 2D materials induce a variation for adsorption behavior to boost ORR activities.

3.2 Synthesis

3.2.1 Chemicals

The methanol (absolute, 99.8%), tetrahydrofuran (THF, 99.8%), graphene oxide (GO), $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 2-methylimidazole, acetylene black (conductive carbon, Alfa Aesar,

99.5%), acetone and N-methylpyrrolidone (NMP) were purchased from Sigma-Aldrich (Singapore). 1 M of LiPF_6 in a mixture of ethyl carbonate and dimethyl carbonate (v:v = 1:1) was obtained from Sigma-Aldrich (Singapore). Poly(vinylidene fluoride) (PVDF), copper foil and lithium foil were purchased from. TiO_2 powder, MoO_3 powder, HCl solution, NaOH solution, hexaammonium molybdate, and thioacetamide were acquired from Sigma-Aldrich (Singapore). The platinum-nickel alloy foil (99.9%, weight ratio=3:1, 0.1 mm) and all other platinum-based binary alloy foils (weight ratio=3:1) and aluminum foils (99.9%, 0.1 mm) were purchased from Jiangsu Metal Ltd, China.

3.2.2 Synthesis of Nitrogen-doped Hierarchical Graphene Networks

Firstly, 2-methylimidazole with the weight of 0.81 g is coupled with methanol of 25 ml. When the materials were completely dissolved with methanol solvent, 0.7 g of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ associated with 25 ml methanol was then poured into as-obtained solution. Subsequently, the mixture was intensively stirred as long as for five hours. Afterwards, the product was then obtained through centrifugation for ten minutes under the speed of 3000 rpm and then washed using methanol for 3 times or more. The as-obtained final product was subsequently processed at 750 °C the whole night before further usage. By sonication and stirring, 1 g of graphene oxide solution (8 mg mL⁻¹) could be uniformly mixed to methanol which contains fifty milli-gram of PVP. In the following step, 5 ml of 2-methylimidazole and 5 ml of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ of methanol were respectively poured into the aforementioned PVP/GO solution (40 ml) and then sonicated as long as for four hours. Afterwards, the dispersion was held for 5 hours under room temperature. Then the sample was obtained through centrifugation for ten minutes at the speed of 3000 rpm and cleaned using methanol at least for 3 times. The resulting target sample (ZIF-8@GO) can be achieved after freeze drying treatment. Similarly, the as-prepared ZIF-8@GO mentioned above was heated at 700 °C for five hours with N_2 atmosphere protection by the heating rate of 2 °C min⁻¹. For the purpose of comparison and tests, pure PNCs was also synthesized through direct heating and carbonization of as-prepared ZIF-8 crystal with the same treatment conditions.

3.2.3 Synthesis of Edge-on MoS₂/TiO₂ Heterostructure

Molybdenum disulfide was synthesized through hydrothermal approach. Specifically, 0.1 g, 1 ml 12 mol/L HCl acid and PVP with the weight of 0.5 g were mixed to 30 ml solvent at room temperature in which H₂O and CH₃CH₂OH are mixed with the ration of 2:1. After stirring for two hours to ensure the uniformity, the solution was then poured into 100 ml autoclave and kept at 180 °C for twelve hours. After that, the as-obtained solution with MoO₂ were then diluted into the concentration of 1 mg/l. As for TiO₂, the hydrothermal approach which is similar to the description in the reference was employed to prepare the TiO₂ nanofibre. Typically, the commercial TiO₂ powder of 6 g was uniformly mixed with NaOH (80 ml, 10 mol/L). The mixed solution was then processed by stirring for half an hour. The next step is doing hydrothermal treatment under 180 °C for forty-eight hours. The final product was then annealed at 700C for two hours. MoO₂ nanoparticle and TiO₂ nanorod with certain weight ratio were uniformly mixed with diluted water. Then the mixed solution was processed by stirring for complete mixture under 60 °C for twelve hours. Afterwards, the as-obtained sample was filtrated and dried under 80 °C under the vacuum atmosphere. The as-obtained TiO₂/MoO₂ was placed in the central position of the furnace while the S powder inside the boat was put in the position of upstream. Finally, TiO₂/MoS₂(E) was obtained by heating at 400 °C for one hour. TiO₂ nanofibers were uniformly mixed with diluted water by the operation of ultrasonic. Then hexaammonium molybdate and thioacetamide were respectively put inside the as-prepared TiO₂ nanofiber solution by strong stirring. Lastly, the solution was poured to the autoclave, then heated for ten hours at 200 °C. After typical heat treatment, the final products can be obtained by filtration and washing with DI water.

3.2.4 Preparation of Binary Platinum-based Alloy Nanosheets

Preparation of free-standing PtNi nanosheets: Ultrathin PtNi nanosheets were prepared, following the developed asymmetric mechanical rolling method, as shown in Figure 6.2. Specifically, in this process, PtNi foil (purity 99%, 0.1 mm in thickness and Pt:Ni=3:1) and aluminum foil (purity 99.9%, 0.1 mm in thickness) were firstly stacked together

forming a PtNi-Al layer structure. Then PtNi and Al foils with similar size and thicknesses (overall thicknesses of 0.2mm, 2 layers) were pressed together by the roll squeezer machine, resulting in a thickness of about 0.1 mm. The resulting 0.1mm PtNi-Al foil (2 layers) was then completely folded (0.2mm, 4 layers) followed by mechanical rolling again to 0.1mm (4 layers). In this regard, the thickness of each layer was approximately decreased to half of its previous thickness, while the final sample thickness of PtNi-Al plate always remained about 0.1 mm after folding and rolling, which is the basic principle of this preparation idea. As expected, with the folding and rolling process continuing, the thickness of each layer gradually reduced since the numbers of PtNi and Al layers increase steadily to keep the overall thickness the same. From the theoretical viewpoint, when the folding and rolling repeats for 20 times, the total number of the layers (half PtNi and half Al) will eventually achieve 1 million, which means the thickness of each layer will be thinned down to the scale of 0.1nm. Even though the repeating process lasts for 20 times, however, the theoretical thickness is extremely difficult to reach due to unavoidable useless folding and intrinsic limited ductility. Subsequently, free-standing 2D Pt-based binary nanosheets were prepared through selectively etching the Al metal layer, which indeed is a very simple chemistry removal process. Specifically, 2.5 mol/L sodium hydroxide (NaOH) dilute solution was employed to completely etch all Al metal layers, aiming to expose pure individual Pt-based nanosheets. When the sample was soaking in the prepared NaOH solution for the whole day (24 h), the resulting suspension solution containing PtNi nanosheets was then vigorously ultrasonicated. Finally, the suspension was centrifuged at the speed of 10,00 rpm for fifteen minutes and cleaned using sufficient DI water for at least 10 times. In this case, a suspension of ultrathin 2D PtNi nanosheets was eventually obtained. Moreover, the suspension containing PtNi nanosheets showed reasonable stability not only in water but also in ethanol.

3.3 Characterization

After the preparation of highly nitrogen-doped hierarchical graphene networks, edge-on MoS₂/TiO₂ heterostructure and Pt-based alloy nanosheets, how to characterize them with

the help of proper characterization techniques is of essential importance as well to prove, verify and confirm the details including crystal phase, surface morphology, compositions, optical properties and electrochemical properties. Different techniques will give different aspects of information of samples. To make a full understanding of the as-prepared samples, a series of powerful characterization techniques were employed. However, every technique actually has its own advantages as well as limitations. Therefore, before using these powerful techniques, it is also of great importance to have a good understanding of the principles in order to get reliable and useful data. In this section, different techniques employed to test, measure and characterize the as-synthesized two-dimensional nanomaterials in the projects were introduced.

3.3.1 Scanning Electron Microscopy (SEM)

Among all electron microscopes, scanning electron microscope (SEM) can give images and surface morphology of a sample. The principle is as follows: the incident electron beam firstly interacts with surface atoms of the sample, thus generating many signals which include data about surface information of the sample, such as composition and topography. SEM can reach the excellent resolution of one nanometer. Secondary electron mode is the most commonly used SEM mode in the experiment. Secondary electrons are emitted from sample atoms which interacted with the incident electron beam. Through fully scanning the specimen and collecting the secondary electrons with the help of a unique detector, a surface morphology image of the sample can be generated.

In the experiment, SEM characterization is employed to observe the morphology of the as-obtained sample. For example, in the first project, ZIF8@GO, PNCs@Gr and pure PNCs were characterized by SEM to show their morphologies for comparison under different resolutions. In the second project, FE-SEM images of MoS₂/TiO₂ (E) were obtained to show the edge-on structure. In the last project, the nanosheet-structure of platinum-nickel alloy was confirmed by SEM.

Figure 3.1 Working principle of scanning electron microscopy. [1]

3.3.2 Transmission Electron Microscopy (TEM)

Transmission electron microscope is one of the most powerful microscopy techniques that often used to test the crystal. When electrons are transmitted through the thin specimen such as crystal, they will interact with the sample as they pass through it. At this time, the image will be produced due to the interaction between the sample and the transmitted electrons. Then the collected image can be magnified to focus onto an imaging device which often are detected by a CCD camera. The capable of images obtained by TEM has a higher resolution than others such as the light microscopes, which is caused by the small de Broglie wavelength of electrons. This will help us detect the fine detail in the samples.

In the experiment, TEM characterization is employed to confirm the layered structure of 2D materials. TEM images were shown with different resolutions of ZIF-8@GO, and High-resolution TEM of ZIF-8@GO, TEM of the PNCs@Gr at different resolutions, and high-resolution TEM of sandwich-like PNCs@Gr nanostructure. High resolution TEM (HRTEM) has been performed to present the existence of MoS₂ nanoplates. And the fact

that few-layer MoS₂ nanosheet is well connected to TiO₂ nanorod outside surface along with the MoS₂ edge sites was revealed by TEM. Lattice obtained from HRTEM of the (002) crystal plane of hexagonal MoS₂ helps verify the presence of MoS₂.

Figure 3.2 Comparison of light microscope and transmission electron microscope. [2]

3.3.3 Scanning Transmission Electron Microscopy (STEM)

STEM can be classified as one of most powerful technique to characterize atomic structure of 2D materials. As the same the TEM, STEM image is also generated with the incident electrons through extremely thin samples. However, under STEM mode, the electron beam can be more focused on a finer spot with the electrons beam scanning across the sample in a raster. Another significant aspect of STEM is the Z-contrast annular dark-field imaging, which can analyze in detail the sample. Moreover, electron energy loss spectroscopy (EELS) can be attached in STEM, which is more suitable for light elements mapping compared with energy dispersive X-ray (EDX) spectroscopy. In all, these signals can be collected simultaneously, allowing for direct relationship between image information and spectroscopic data. A schematic diagram of a STEM instrument is shown in Figure 3.3

Figure 3.3 Equivalence in between conventional TEM and bright-field STEM. [3]

In the experiment, the edge-on MoS₂/TiO₂ structure can be clearly revealed by STEM, in which the atomic bonding was obviously observed and confirmed.

3.3.4 Atomic Force Microscopy (AFM)

Atomic force microscopy is usually employed to measure the thickness of the samples and image samples, which is an advanced characterization tool in 2D research. Normally, the forces between the probe and the samples were measured to give relevant information such as thickness. In terms of imaging function, the interaction will appear when the AFM probe gets close to the sample surface, then the three-dimensional topography image of the sample surface will be acquired through the computer. On the other hand, when the probe scans along specific line across the sample, then the height of this position in the sample will be recorded by raster in terms of the tip on basis of the constant probe-sample interactions.

When the preparation of 2D materials was completed, AFM technique was then employed to measure the thickness and check the surface morphology, which is of great importance to 2D materials research. In terms of morphology, the uniformity of the

sample could be clearly observed on basis of the obtained AFM images. In the experiments, the real thickness as-prepared platinum-nickel alloy nanosheets was confirmed by AFM.

Figure 3.4 Schematic of working principle in AFM.[4]

3.3.5 X-ray Diffraction (XRD)

X-ray diffraction (XRD) is considered to be one of the fastest analytical method used for phase determination of any unknown crystalline materials. The interaction between the incident X-rays and the sample generates feedback when conditions exactly match Bragg's Law, namely $n\lambda=2d\sin\theta$. The satisfied diffracted X-rays are subsequently observed, processed and collected. Through scanning the specimen, all satisfied diffraction pathways of the crystal lattice would be detected because of the randomly orientated lattice of the polycrystalline powder sample. Then the as-obtained diffraction peaks are converted to d-spacings allowing identification of the sample because each

crystal possesses its specific d-spacings set. Generally, this is completed through the comparison between the as-obtained d-spacings and standard database.

Figure 3.5 Schematic of XRD principle and corresponding patterns.[5]

In the experiment, XRD is employed to determine the crystal structure to help confirm the structure of materials. In the first project, X-ray diffraction (XRD) will help to confirm the crystal structures of the as-synthesized ZIF-8, pure PNCs, ZIF-8@GO, and PNCs@Gr nanostructures respectively. And in the second project, X-ray diffraction (XRD) was performed to identify $\text{TiO}_2/\text{MoS}_2$ (E) heterojunctions and pure TiO_2 . For the last project, XRD was employed to characterize the binary platinum-nickel nanosheets.

3.3.6 X-ray Photoelectron Spectroscopy (XPS)

As a powerful surface-sensitive spectroscopic approach, X-ray photoelectron spectroscopy (XPS) can quantitatively measures the electronic state, elemental composition, and chemical state of the elements of the sample. For the detail, with the

help of the X-ray irradiating the given sample while simultaneously characterizing the kinetic energy and collecting the number of electrons that originated from the surface of the sample (0-10nm), XPS spectra are therefore created. Theoretically, XPS technique can measure all the elements. However, with the typical X-ray sources used in the lab, XPS can only effectively detect an atomic number more than 3.

Figure 3.6 Schematic of XPS working principle.[6]

In the experiment, XPS measurement would be employed to confirm the bonding state to help determine chemical states of my samples. The electrochemical activity of carbon materials for negative electrode in LIBs extremely relies on the type of doped nitrogen and the content, which could be quickly and precisely analyzed via XPS technique.

3.3.7 Raman Spectroscopy and Photoluminescence (PL)

Raman spectroscopy is probably one of most popular spectroscopic approaches that often is employed to investigate rotational, vibrational and other low-frequency transitions in samples. Generally, Raman spectroscopy is usually employed to offer unique evidence to confirm the material structures. The principle depends on Raman scattering and in elastic scattering. The procedure is that interaction between the laser light and phonons (other

excitations) from the sample, leading to the shift (up or down) of energy from the photons. The change in terms of energy offers information about the sample. The fundamental Raman effect can be found in **Figure 3.7**.

Figure 3.7 Signals from Raman effect.[7]

In the experiment, here we can use Raman spectra to confirm the 2D materials. With the excitation laser of 532 nm were carried out with a WITEC alpha 300R Confocal Raman system. Before Raman characterization, the system was calibrated with the Raman peak of Si at 520 cm^{-1} . The Raman and PL mapping was performed on a Renishaw in Via microscope with a laser of 514.5 nm. The laser powers are less than 1mW.

3.3.8 Brunauer–Emmett–Teller Measurements (BET)

BET technique offers accurate specific surface area calculation of sample based on nitrogen adsorption and relative pressure with a completely automatic analyser. The method makes use of pore area and external area assessments to confirm the specific surface area causing significant output in investigating the effects of particle size and porosity of the surface. This approach demonstrates the distribution of pore size despite of external area because of particle size of the materials.

In the experiment, BET is employed for measuring the specific surface area and porosity of the samples. BET was used to obtain isotherms of N₂ adsorption-desorption corresponding to PNCs@Gr nanostructure and bare PNCs as well as the pore size distribution of sandwich-like PNCs@Gr.

3.4 Applications

3.4.1 Fabrication and Performance Measurements of Lithium Ion Battery

The electrochemical performances of the as-prepared electrode were assessed through constructing into 2032-type coin cells for LIBs. Normally, to obtain the electrodes, it involves uniform coating of 10 wt% acetylene black, a homogeneous slurry of 80 wt% active material powders, polyvinylidene fluoride (10 wt%, Alfa Aesar) binder in 1-methyl-3-pyrrolidone (NMP) solvent on copper foils, and subsequently dried in the condition of vacuum under one hundred and twenty degrees for twenty-four hours. The employed electrolyte was 1 M LiPF₆ which is mixed with diethyl carbonate (DEC), ethylene carbonate (EG) and dimethyl carbonate (DMC) based on the ratio of 1:1:1 in terms of volume. The electrochemical property of coin cells was measured under a variety of current rates for the voltage ranging from 0.01 to 3.0 V vs. Li/Li⁺. Furthermore, cyclic voltammetric (CV) was performed with a CHI605C-type electrochemical workstation under 0.1 mV/s scan rate from 0.01 V to 3.0 V vs. Li/Li⁺. It should be noted that all the electrochemical tests were carried out under room temperature.

3.4.2 Fabrication and Performance Measurements of Photocatalytic Hydrogen Evolution Reaction

The photocatalytic hydrogen production measurements were carried out in a quartz reactor with 50 mL. Specifically, the as-prepared photocatalysts of 10 mg was uniformly mixed with 10 mL solution which is consisted of ethanol and diluted water with the ratio of 2:8 in volume. Then the as-obtained dispersion of photocatalyst was subsequently sealed into 50 mL-size quartz reactor with a tight rubber plug. To totally remove the air

dissolved inside the solution, argon gas was used to get bubbled for 30 min. In the following step, the quartz reactor slightly was placed under the Xe lamp with 300 W, which can be exposed. The gas product, originating from the above space, was continuously collected and periodically analyzed with the help of a gas chromatograph (GC), equipping with a detector for thermal conductivity to help the analysis.

3.4.3 Fabrication and Performance Measurements of Electrocatalytic Oxygen Reduction Reaction

In this project, all the powder electrocatalysts were dispersed onto the 1x1 cm² carbon paper to fabricate electrodes. The as-prepared PtNi nanosheets with different thickness (5.5nm-9.1nm) were firstly associated with 50 mL Naon, 350 mL ethyl alcohol, 650 mL DI water, and 8 mL N, N-dimethylformamide (DMF) to obtain the uniform ink. Subsequently, the as-obtained carbon electrodes had been intensively dried under 65 °C inside the oven for one hour to totally clear ethanol, and to completely remove the DMF, the as-obtained electrode materials were again moved to the vacuum drying oven for another one hour at 130°C. During the electrochemical measurements, the electrochemical tests were conducted with the assistance of CHI 660E electrochemical workstation with a standard three-electrode system, using 1 M KOH or 6 M KOH as the environment. Subsequently, linear sweep voltammetry (LSV) was carried out under the scanning rate of 5 mV/s using a Pt mesh as the counter electrode and an Ag/AgCl as the reference electrode. Finally, long-term cyclic voltammetry (CV) was carried out ranging from 0.3 V to 0.75 V under the scan rate of 5 mV/s. All of the LSV curves were carried out using the iR compensation method and then be plotted out in figures.

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Chapter 4*

Defect Engineering of Nitrogen-doped Hierarchical Graphene Networks

In this Chapter, the controlled synthesis of highly nitrogen-doped and defect-rich hierarchical graphene networks via in-situ simple pyrolysis of zeolitic imidazolate framework (ZIF) nanoparticles grown on graphene oxide are presented. The as-synthesized 2D materials were characterized in detail by XRD, TEM, SEM, XPS and Raman spectroscopy. In addition, a high-performance lithium ion battery based on the as-prepared materials was constructed and demonstrated using the as-prepared materials as negative electrode. This novel hierarchical structure as well as graphene support is considered to be the contributors to the excellent rate capability and good capacity.

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4.1 Introduction

Secondary lithium-ion batteries (LIBs) have been broadly employed for various portable electronic devices as energy carrier.[1,2] However, the ever-growing requirements of higher-performance LIBs toward electric vehicles (EVs) utilization, which hold great promise to revolutionize the automobile industry, require power density, higher energy density and longer cycling life. The current commercial graphite anode encounters several shortcomings including worse electrochemical activities under higher charge-discharge rates and poor theoretical capacity of 372 m Ah g⁻¹, which, as a consequence, cannot satisfy the demands in the industry with high power and high-energy LIBs.[3,4] In this regard, it is desirable to develop other promising carbon materials as anode with better rate capability, longer cycle life, improved Li-ion storage capacity, and also competitive expense for large-scale applications.

To explore satisfactory carbon materials as alternative anode toward new-generation LIBs, the previous studies indicated that the required characteristics are summarized as follows: (i) high porosity, which could enhance charge transport and lead to enhanced rate capability, (ii) large surface area, which provide sufficient active sites to improve storage capacity for lithium ions, (iii) heteroatom N or S doping, which can therefore manipulate the electronic structure and increase more active sites for Li-ion storage, (iv) excellent structural stability and electronic conductivity, which come from graphene network and could facilitate charge transfer. Guided by these design principles, various carbon materials have already been tested as anodes in lithium ion batteries, demonstrating remarkably enhanced lithium storage in contrast with commercially available graphite, including carbon nanofibers,[19] hollow carbon spheres,[18] micro/nanoporous carbon,[17] heteroatom-doped graphene sheets,[16] and carbon nanobeads.[20] Regardless of the tremendous progress mentioned above, satisfying all of the characteristics summarized above at the same time still remained unexplored due to the fact that bad structural stability and poor electrical conductivity of carbon materials when cycling under high charge-discharge rates. From this, it clear that there is much scope for improvement.

On the other hand, metal organic frameworks (MOFs) have been chosen in lithium ion batteries (LIBs) owing to large surface area and the intrinsic high porosity since they have been successfully demonstrated as exceptional precursors for numerous nanostructured electrodes. However, the previous MOFs-derived nitrogen-doped carbon materials still possess bad structural stability and poor electronic conductivity, even severe capacity degradation during long-term cycling in LIBs because of the inevitable breaking inside MOFs and large crystal size from 200 to 500 nm, these MOFs-derive N-doped carbon matrices still exhibit poor structural stability and low electronic conductivity, and thus result in significant capacity fading over prolonged cycling in LIBs. Therefore, to achieve a carbonaceous anode material with all the merits of hierarchically porous structure, superior excellent conductivity, and high-level nitrogen doping, we present an in-situ synthesis approach to obtain sandwich-like, graphene-based porous nitrogen-doped carbons (PNCs@Gr) via facile pyrolysis of zeolitic imidazolate framework (ZIF-8) nanocrystals grown on graphene oxide (GO) (ZIF-8@GO), for application as a high-performance anode material in LIBs. We selected ZIF-8 as a suitable carbon precursor to yield in situ N-doped porous carbon due to its high N content of ~34 wt %, large porosity, and high specific surface area, and meanwhile GO serves as a structure-directing agent and potential platform for nucleation, growth, and stabilization of ZIF-8 nanocrystals. Due to insufficient surface functional groups of GO, the amide carbonyl groups of poly(vinylpyrrolidone) (PVP) can be utilized to enrich the functional groups of GO, which might be beneficial for the uniform growth of ZIF-8 nanocrystals on the GO sheets. During a subsequent carbonization process, ZIF-8 nanoparticles are transformed to N-rich porous carbon nanospheres, meanwhile GO is thermally reduced to highly conductive graphene. Finally, the sandwich-like PNCs@Gr nanostructure with high porosity, superior electrical conductivity, and rich nitrogen content is successfully synthesized and will thus boost electrochemical performance in LIBs, due to synergic effects of the highly desirable properties. As a result, the sandwich-like PNCs@Gr electrode demonstrates remarkable capacities, outstanding rate performances, as well as cycling stability that are better than most carbonaceous anode materials reported previously.

4.2 Results and Discussion

4.2.1 Synthesis and Characterization of Nitrogen-doped Hierarchical Graphene Networks

Preparation of ZIF-8: ZIF-8 crystals were synthesized by mixing 0.81 g of 2-methylimidazole with 25 mL of methanol. To this solution, 0.7 g of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 25 mL of methanol were added. Afterward, the mixed solution was stirred for 5 h. Finally, the solid was collected by centrifuging the mixture at 3000 rpm for 10 min, followed by washing with methanol three times. The collected solid was dried at 75 °C overnight before using.

Synthesis of ZIF-8@GO: Synthesis of ZIF-8@GO was carried out based on a modified approach from literature. Typically, 1 g of the as-prepared graphene oxide solution (8 mg mL^{-1}) was dispersed in methanol solution containing 50 mg of PVP, by sonication and stirring. Then 5 mL of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ of methanol solution was first added into GO/PVP solution (40 mL) followed by adding 5 mL of 2-methylimidazole. Then the mixed solution was kept for 5 h at room temperature. Afterward, the product was collected by centrifuging at 3000 rpm for 10 min followed by washing with methanol three times. After freeze-drying, the final product (ZIF-8@GO) was obtained.

Synthesis of PNCs@Gr: The as-synthesized ZIF-8@GO was heated at 700 °C for 5 h under N_2 using a ramp rate of 2 °C/min. For comparison purposes, bare PNCs were prepared by facile pyrolysis of the as-synthesized ZIF-8 sample under the same condition.

Figure 4.1 demonstrates the synthesis schematic presenting the synthesis pathway to preparing PNCs@Gr used for active materials in LIBs in this project. Graphene oxide (GO) was firstly processed with PVP, and then mixed with 2-methylimidazole and zinc nitrate respectively, so as to grow ZIF-8 nanoparticles in situ graphene oxide. For the next step, the ZIF-8@GO nanosheet would be changed to PNCs@Gr through a process of direct carbonization under nitrogen gas atmosphere at 700 °C.

Figure 4.1 Schematic of the synthesis procedures of the pre-designed PNCs@Gr sandwich-like nanostructure.

In Figure 4.2, the X-ray diffraction (XRD) data and measurements of the as-synthesized ZIF-8, ZIF-8@GO, pure PNCs and PNCs@Gr nanostructures are presented respectively. It can be clearly observed that all major peaks before pyrolysis can be assigned to the pattern of ZIF-8. Also, there is no clear difference in terms of the XRD data between ZIF-8 and ZIF-8@GO. However, it should be noted that ZIF-8 and ZIF-8@GO are respectively changed into PNCs and PNCs@Gr after carbonization. At the same time, their XRD patterns have significant changes, which can be concluded by the main peak at about 25° which corresponds to the graphite carbon reflection (002) interplane. Moreover, the wide peaks and low intensity show as-obtained PNCs@Gr and PNCs samples possess low degree of graphitization. It should be also noted that characteristic zinc peaks were not observed in both XRD profiles of PNCs@Gr and pure PNCs, exhibiting zinc metal with low melting point (419.5°C) which is reduced in the reaction may have been vaporized out during the process at 700°C .

Moreover, the wide peaks and low intensity show as-obtained PNCs@Gr and PNCs samples possess low degree of graphitization. It should be also noted that characteristic zinc peaks were not observed in both XRD profiles of PNCs@Gr and pure PNCs,

exhibiting zinc metal with low melting point (419.5 °C) which is reduced in the reaction may have been vaporized out during the process at 700 °C.

Figure 4.2 XRD data of (a) ZIF and ZIF-8@GO without carbonization procedure and (b) as-prepared PNCs@Gr nanostructure and bare PNCs with the procedure of carbonization. XPS peaks of N 1s corresponding to (c) pure ZIF-8 and (d) bare PNCs. (e) Isotherms of N adsorption-desorption corresponding to bare PNCs and PNCs@Gr nanostructure. (f) Pore size distribution of sandwich-like PNCs@Gr.

The electrochemical performance, as well-known, of carbon materials as negative electrode in LIBs is heavily dependent on the type of doped nitrogen and the content in the carbon materials, which could be precisely analyzed using X-ray photoelectron spectroscopy (XPS) as demonstrated in Figure 4.2c-d. As can be seen, N 1s spectrum

could be indexed to 3 kinds of peaks after carbonization, namely quaternary N (400.8 ± 0.3 eV), pyridinic N (398.3 ± 0.2 eV) and pyrrolic N (399.8 ± 0.2 eV). On the other hand, it has previously been discovered that the nitrogen doping strategy could improve the intrinsic conductivity in carbon materials and also be conducive to charge transfer at the interface between two phases, which could be extremely helpful when used as anode in LIBs.

Figure 4.3 presents the SEM morphology of as-prepared samples, namely ZIF-8@GO, PNCs@Gr and pure PNCs. As seen from Figure 4.3 a and b, many nanoparticles (~ 100 nm in terms of diameter) with relatively rough surfaces are observed in bare PNCs and strong agglomeration can also be seen. However, Figure 4.3c and d display ZIF-8@GO specimen keeps typical GO surface morphology, where nanoparticles of ZIF-8 are evenly attached onto the graphene oxide surface. What is more, the typical morphology of GO is exactly kept when experiencing direct pyrolysis of ZIF-8@GO under 700°C in the sample of PNCs@Gr, as shown in Figure 3e and f.

Figure 4.3 SEM images with different resolution of (a, b) pure PNCs, (c, d) ZIF-8@GO sample and (e, f) PNCs@Gr nanostructure

TEM characterization is also carried out for better understanding the nanostructures of as-synthesized PNCs@Gr and ZIF-8@GO samples demonstrated in Figure 4.4. For example, Figure 4.4 a and b reveal that ZIF-8 nanoparticles were evenly attached onto the graphene oxide surface matching with the results of SEM. Additionally, the in Figure 4.4c demonstrates the high-resolution TEM of ZIF-8@GO, revealing a quiet small domain of graphene oxide on the edges, determining the existence evidence of graphene oxide within the specimen and further confirming the crystal structure of ZIF-8@GO with sandwich like morphology. Figure 5d-e shows that PNCs@Gr sample obtained by direct process of carbonization of ZIF-8@GO has a clearly porous characteristic and keep the morphology of precursor of ZIF-8@GO. Selected area electron diffraction (SAED) of PNCs@Gr sample was demonstrated in the inset in Figure 5d, showing the non-crystalline feature of PNCs@Gr sample, which is also in agreement with the above XRD result. Last but not least, the HR-TEM image of Figure 5f can help confirm the presence of graphene in the sample.

Figure 4.4 (a, b) TEM images with different resolution of ZIF-8@GO, and (c) High-resolution TEM of ZIF-8@GO. (d, e) TEM at different resolution of the PNCs@Gr nanostructure, and (f) High-resolution TEM of sandwich-like PNCs@Gr nanostructure.

Figure 4.5 Raman Spectra corresponding to PNCs@Gr, ZIF-8@GO and ZIF-8.

Moreover, Raman spectroscopy was carried out to further confirm our assumption. As can be seen from Figure 4.5, Raman spectra of PNCs@Gr and ZIF-8@GO presents two main peaks located at 1590 cm^{-1} and 1352 cm^{-1} , which can be assigned to G band and D band in graphitic carbon materials, but these peaks do not occur in the Raman spectra of ZIF-8. Furthermore, in terms of ZIF-8@GO, it can be concluded that all the Raman peaks, which are marked with aster, should be attributed to the part of ZIF-8.

4.2.2 Lithium Ion Battery Based on Nitrogen-doped Hierarchical Graphene Networks

In order to assess the as-synthesized bare/pure PNCs and PNCs@Gr specimens as negative electrode for LIBs, a variety of electrochemical tests (CV, cycling performance, charge/discharge profile) are carried out, as all results are showed in Figure 4.6, 4.7 and

4.8. Figure 4.6a and 4.6b shows the cycling voltammetry characteristic curves of PNCs@Gr and bare PNCs which are tested from 0.01 to 3.0 V (versus Li/Li+) respectively. As can be seen from the figure, typical CV features of carbon materials anodes could be clearly identified from both of them. But the specific currents in which the redox reactions happen in the sample of PNCs@Gr are higher than those of bare PNCs.

Figure 4.6 Cyclic voltammetry (CV) profiles of PNCs@Gr (a) and pure PNCs (b) using the same scanning rate of 0.1 mVs⁻¹.

Figure 4.6 presents the first 3-cycle characteristic of PNCs@Gr based anode under the specific current density of 100 mA g⁻¹. What's more, the discharge/charge curves are matched with those published for nitrogen-doped carbon-based negative electrode in LIBs. Also, a huge irreversible capacity degradation is detected, probably due to SEI film formation and decomposition of the liquid organic electrolyte. In all, these data are pretty matched with the CV data shown in Figure 4.6, where the cathodic peaks are demonstrated for 1st cycle but do not occur in the following 2nd and 3rd cycles. The cycling properties of PNCs@Gr and PNCs as negative materials for LIBs are recorded respectively under specific current densities of 500 mA g⁻¹ and 1 mA g⁻¹ in Figure 4.7. As presented in Figure 4.7a-b, the sample of PNCs@Gr based electrode exhibits the excellent cycling stability with the highly reversible capacity. Typically, when applied a specific current density of more than 500 mA g⁻¹, negative electrode based on the

PNCs@Gr preserve a good capacity of 1070 mAh g^{-1} even cycled one hundred cycles, which could be far better than pure/bare PNCs.

Figure 4.7 Discharge/charge characteristics of PNCs@Gr anode operated (a) with 100 mA g^{-1} during first 3 cycles and (b) with a variety of current densities.

Under the 1 A g^{-1} specific current density, the electrode from PNCs@Gr could demonstrate the capacity of 948 mAh g^{-1} after having experienced 200 cycles, 97.7% retention of the 4th cycle, while under the same conditions the value for pure/bare PNCs is about 291 mAh g^{-1} . On the other, if the current density rises up to 6 A g^{-1} , as shown in Figure 4.7c, PNCs@Gr electrode preserves an acceptable capacity of as good as 530 mAh g^{-1} when cycled four hundred cycles, demonstrating as high as 84.4% capacity retention rate. Additionally, Figure 6d, the ultra-long cycling performance in Figure 4.8d demonstrates its excellent reversibility.

Figure 4.8 Electrochemical measurements of PNCs@Gr and pure PNCs based anodes. (a, b) Cycling performance of PNCs@Gr and pure PNCs based anodes under current densities of 500 mA g⁻¹ and 1 A g⁻¹. (c, d) Long-cycling test of PNCs@Gr based electrode under the current density of 5 A g⁻¹ cycled for four hundred cycles and the corresponding result of Coulombic efficiency. (e) Rate performance of PNCs@Gr and bare PNCs based electrodes operated under a variety of specific current densities from 100 mA g⁻¹ to 5 A g⁻¹. (f) Nyquist of PNCs@Gr and pure PNCs.

Moreover, the reversible capacities of the PNCs@Gr anode are calculated to be 1378, 1228, 1070, 984, 915, 854 and 647 mAh g⁻¹ associated with the specific current density which is 100, 200, 400, 600, 800, 2000 and 4000 mA g⁻¹, separately, shown in Figure 4.8e. What's more, under ultra-high specific current density of 6000 mA g⁻¹, the pretty good reversible capacity of 412 mAh g⁻¹ is still achieved. Moreover, the capacity could be returned back to 1432 mAh g⁻¹, if the current density is tuned to 100 mA g⁻¹, showing its excellent cycling performance and reversibility. To further investigate the nature of ultrahigh rate performance of PNCs@Gr negative electrode, electrochemical impedance spectra (EIS) was performed for exploring the processes. As can be seen in Figure 4.8f, the Nyquist of pure PNCs and PNCs@Gr are listed. It is clearly noted that the sample of electrode of PNCs@Gr demonstrates much lower resistance of 30 Ω in terms of charge transfer compared to bare PNCs (100 Ω), which also supports the results in Figure 5 above.

4.3 Conclusion

The excellent cycling stability, superior rate performance and ultra-high capacity of sandwich-like hierarchical PNCs@Gr nanostructure could be due to high-content nitrogen doping and the novel hierarchical structure. Specifically, in situ synthesis of ultra-small highly porous and nitrogen-doped nanoparticles attached onto graphene network could further decrease the agglomeration effect in contrast with pure/bare PNCs, as a consequence, leading to enough electrolyte/electrode interface and shorter transportation distance for lithium ions, eventually facilitating fast charge transfer. Moreover, graphene network support, which is mechanically strong and conductive, offers a perfect route for electron transportation and enables the structure stable even for ultra-long cycling. Additionally, it is previously proved that high-content nitrogen-doping level could further improve the electrochemical reactivity and electronic conductivity, which is also conducive to the resulting electrochemical activity when used for LIBs.

Table 1 Comparisons of electrochemical activities of the designed PNCs@Gr sample in our work with those formerly published carbon-based negative electrodes when used in LIBs

Anode materials	Current density (mA g ⁻¹)	Cycle number	Specific capacity (mAh g ⁻¹)	Ref.
PNCs@Gr	500	100	1070	Our work
	1000	200	948	
	5000	400	530	
N-doped graphene sheets	50	30	872	Ref.1
Hollow carbon nanospheres (HCNS)	37	50	630	Ref.2
Micro-sized porous carbon spheres	100	100	507	Ref.3
N-rich porous carbon (OHC)	100	100	1178	Ref.4
	1000	100	591	
Porous carbon	100	70	660	Ref.5
Porous carbon microspheres (HPCM)	50	70	480	Ref.6
CNT-CNF	100	70	1150	Ref.7
N-doped graphene	50	50	1136	Ref.8
HN-CNT	100	100	397	Ref.9
PMC-650	100	100	1365	Ref.10

Table 2 Comparisons of electrochemical activities of the designed PNCs@Gr sample in our work with those formerly published other MOF negative electrodes for LIBs.

Anode materials	Current density (mA g ⁻¹)	Cycle number	Specific capacity (mAh g ⁻¹)	Ref.
PNCs@Gr	500	100	1070	Our work
	1000	200	948	
	5000	400	530	
Co-doped ZnO@C (CZO@C)	100	50	725	Ref.11
ZIF-8@chitosan	50	50	750	Ref.12
Co ₃ O ₄ /N-PC	100	100	892	Ref.13
MWCNTs/Co ₃ O ₄	100	100	813	Ref.14
ZnO@ZnO/C NRAs on carbon cloth	500	100	699	Ref.15
CuO nanostructure derived from Cu-MOF	100	40	538	Ref.16
ZnO QDs@porous carbon	75	50	1200	Ref.17
Spindle-like mesoporous Fe ₂ O ₃	200	50	911	Ref.18
Porous TiO ₂ derived from MIL-125	840	200	155	Ref.19

In conclusion, a hierarchical sandwich-like, nitrogen-doped graphene-based porous carbon structure (PNCs@Gr) has been synthesized via direct simple in-situ pyrolysis of zeolitic imidazolate framework nanoparticles grown on graphene oxide (GO) (ZIF-

8@GO), which was then used as a promising negative electrode material for high-performance LIBs. The following electrochemical measurements suggested that the as-designed nanostructure exhibited superior rate capability, optimized cycling stability and remarkably enhanced capacity in comparison with pure/bare PNCs. A detailed series of characterization and analysis indicated that the extraordinary electrochemical activities of the as-obtained PNCs@Gr negative electrode materials could be attributed to its novel hierarchical sandwich-like structure and the high-content nitrogen-doping level. In all, the as-prepared PNCs@Gr holds great promise to be a competitive alternative negative electrode material toward high-power and high-energy LIBs. Furthermore, this novel sandwich-like PNCs@Gr structure could also have some insightful implications for other energy applications such as supercapacitors.

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Chapter 5*

Interface Engineering of Edge-on MoS₂/TiO₂ Heterostructure

In this Chapter, via interface engineering, solid edge-on heterostructures between few-layered MoS₂ and TiO₂ have been produced on large scale through a facile two-step vapor phase approach, which realized the idea that layered MoS₂ can be welded laterally to photocatalysts via edges to enhance the catalytic activities toward water splitting due to the efficient transport of photoexcited electrons along the highly conductive edges and basal planes of MoS₂. This work represents a strategy, which marries low-cost layered transition-metal dichalcogenides with backbone photocatalyst as a promising heterostructure for high-efficiency water splitting.

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5.1 Introduction

Harvesting solar energy from nature into useful chemical fuels (chemical energy) by sustainable and cost-effective pathways has been extensively recognized as one of the most promising pathways to address the increasingly pressing energy issues.[1-4] Since Honda and Fujishima for the first time split water using TiO_2 photoelectrodes, opening a new field in photocatalysis.[5,6] Typically, a complete photocatalysts are usually consisted of a semiconductor and a co-catalyst.[7-9] Extensive efforts previously demonstrate that hydrogen evolution, the half reaction of overall water splitting, relies heavily on the performances of the co-catalysts and efficient electron-hole transfer in between the co-catalysts and the semiconductor, which was required to prevent the electron-hole recombination as much as possible. It is unambiguously believed that the co-catalysts not only help to accelerate the efficient separation of photoexcited electron-hole pairs which are produced in the semiconductors, but also can provide other active sites which are beneficial to hydrogen evolution.[10-12] As well-known, precious metals and their oxides are traditionally important co-catalysts. The scarcity and expensive cost, however, hinder their large-scale applications in photocatalysis, as a consequence, pushing the research to explore/search for other earth-abundant and low-cost alternative to supersede them in these applications.

Recently, layered molybdenum disulfide (MoS_2) with very competitive cost has been selected as a potential extraordinary co-catalyst of TiO_2 , the most studied photocatalyst for hydrogen evolution, aiming to hopefully replace highly efficient but costly noble metals. Nevertheless, the photocatalytic efficiency of this structure loaded with MoS_2 , is still far from satisfactory, and is much lower than those with precious metals. The previous investigations revealed that the geometrical configuration of such MoS_2 co-catalyst structure might lead to the low efficiency on the semiconductor surface, in which layered MoS_2 , to minimize the surface energy, preferentially grows along its basal direction onto the semiconductor surface (surface energy of basal plane is 100-fold lower than the edges). Such configuration, however, results in a low edge exposure, which are commonly believed as active site of MoS_2 . Moreover, this lay-down geometrical

configuration of layered MoS₂ would make the photoexcited electrons in the TiO₂ photocatalyst to hop through layered MoS₂ flakes to reach the active edge sites, eventually bringing about extremely higher resistance (~2200 times through the layers higher than in the same MoS₂ layer). Bearing the fact that MoS₂ edge is more conductive than the basal plane in mind, it can be reasonably expected that enabling MoS₂ to lie erecting onto the semiconductor surface, that is to say, the MoS₂ flakes edges contacting with the semiconductor, will greatly improve the efficiency of the hydrogen evolution, which could be ascribed to a optimized electronic connection with better electron transfer pathway. Nevertheless, such geometrical configuration of MoS₂ onto a semiconductor surface, for instance TiO₂, has rarely been reported on a large scale.

5.2 Results and Discussion

5.2.1 Synthesis and Characterization of Edge-on MoS₂/TiO₂ Heterostructure

Molybdenum disulfide was synthesized through hydrothermal approach. Specifically, 0.1g, 1 ml of 12 mol/L HCl acid and PVP (0.5 g) were added to 30 ml solvent at room temperature (H₂O:CH₃CH₂OH=2:1). After stirring for two hours to ensure the uniformity, the solution was then poured into 100 ml autoclave and kept at 180 °C for twelve hours. After that, the as-obtained solution of MoO₂ was then diluted to a concentration of 1 mg/L. For TiO₂, a hydrothermal approach which is similar to that in the literature was employed to prepare the TiO₂ nanofibres. Typically, the commercial TiO₂ powder of 6 g was uniformly mixed with NaOH (80 ml, 10 mol/L). The mixed solution was then processed by stirring for half an hour. The next step is doing hydrothermal treatment at 180 °C for forty-eight hours. The final product was then annealed at 700 °C for two hours. MoO₂ nanoparticle and TiO₂ nanorod with certain weight ratio were uniformly mixed with diluted water. Then the mixed solution was processed by stirring for complete mixture at 60 °C for twelve hours. Afterwards, the as-obtained sample was filtrated and dried at 80 °C under vacuum. Subsequently, the as-obtained TiO₂/MoO₂ was placed in the central position of the furnace while the S powder inside the boat was put in the upstream position. Finally, TiO₂/MoS₂(E) was obtained by treating at 400 °C for one hour. TiO₂

nanofibers were uniformly mixed with diluted water by the operation of ultrasonic. Then hexaammonium molybdate and thioacetamide were respectively put inside the as-prepared TiO_2 nanofiber solution by strong stirring. Last solution was poured to the autoclave, then left for ten hours under 200 °C. After the typical heat treatment, the final products can be obtained by filtration and washing with DI water.

Figure 5.1 shows the conventional (a) and the new method (b) for synthesis of $\text{TiO}_2/\text{MoS}_2$ heterostructure. It can be concluded from previous reports that MoS_2 tends to form flat structure on the TiO_2 template so as to lower surface energy when synthesizing the MoS_2 using TiO_2 nanorod as template (Figure 1a). [19,25] When this case occurs, the MoS_2 nanoplates are usually associated with TiO_2 nanorods along with the basal planes that we call $\text{TiO}_2/\text{MoS}_2$ (B) in the following part. But as the early studies show that this type of nanostructure would have low catalytical activity in photocatalytic water splitting. [77]

In order to suppress the flat structure and obtain the vertical heterostructure with the edge side of MoS_2 connecting with TiO_2 (here this heterostructure is called as $\text{TiO}_2/\text{MoS}_2$ (E)), a two-step approach was adopted to tune the growth direction of MoS_2 nanoplates onto TiO_2 nanorods surface for synthesizing the so called vertical heterostructures in which MoS_2 stands on TiO_2 along with the edge side. Specifically, MoO_3 nanoparticles were firstly attached to the titanium dioxide surface forming $\text{TiO}_2/\text{MoO}_3$ composite, which was then sulfurized in a home-made system by chemical vapor deposition (CVD) method as illustrated in Figure 5.1b.

The next step focuses on the morphologies and structure characterization of the as synthesized $\text{TiO}_2/\text{MoS}_2$ (E) which can be seen in Figure 5.2. Specifically, Figure 5.2a,b shows FE-SEM images of $\text{MoS}_2/\text{TiO}_2$ (E). But the MoS_2 nanoplates cannot be observed from the SEM images probably owing to their small size. So to prove the existence of MoS_2 nanoplates, high resolution TEM (HRTEM) has been performed. Figure 5.2c and d shows the HRTEM images of the obtained heterostructure sample with the 3% mass content of MoS_2 . It can be obviously seen that the few-layer MoS_2 nanosheet is well

connected to the TiO_2 nanorod outside surface along with the MoS_2 edge sites, demonstrating the viability of this method.

Figure 5.1 Schematic illustration of synthesizing $\text{TiO}_2/\text{MoS}_2$ nanostructures. a) Wet chemical approach fabricating $\text{TiO}_2/\text{MoO}_2$ (B), in which MoS_2 plates combine with TiO_2 planes with basal surface; b) CVD method to synthesize $\text{TiO}_2/\text{MoS}_2$ (E) heterostructure, in which MoS_2 plates combine TiO_2 plane with highly conductive surfaces; c) Synthesis illustration of the final sulfurization in the CVD system.

Moreover, as shown in Figure 5.2d, fringes highlighted with red with lattice spacing of ≈ 6.1 are in good agreement with the (002) crystal plane of hexagonal MoS_2 to help verify the presence of MoS_2 . As for TiO_2 characterization, the lattice spacing information which is extracted, as presented in the inset of Figure 5.2d, from the selected area marked by green rectangle are well consistent with the value for anatase TiO_2 in the literature [12].

Figure 5.3 shows other characterization techniques used in this project to help characterize the nanostructure and more information to support our hypotheses. The X-ray diffraction (XRD) was performed to identify $\text{TiO}_2/\text{MoS}_2$ (E) heterojunctions. As can be seen from the morphologies of as-synthesized TiO_2 nanorods and as-obtained $\text{TiO}_2/\text{MoS}_2$ (E) heterostructure, these two patterns show almost no difference, which could be both assigned to the phase of anatase (JCPDS file No. 21-1272), implying the

good preservation of the basic structure of TiO_2 after sulfurization process, namely the intrinsic properties.

Figure 5.2 Morphologies of $\text{TiO}_2/\text{MoS}_2(\text{E})$ composites. a) and b) SEM of as-obtained $\text{TiO}_2/\text{MoS}_2(\text{E})3\%$; c) TEM of $\text{TiO}_2/\text{MoS}_2(\text{E})3\%$, exhibiting MoS_2 nanoplate stands onto TiO_2 plane; d) high-magnification TEM of $\text{TiO}_2/\text{MoS}_2(\text{E})3\%$. I MoS_2 nanoplate clearly combines to TiO_2 through the edges. Fast Fourier transform (FFT) patterns are in the inset from the area which is marked with green rectangular box.

To further characterize the MoS_2 of the as-prepared $\text{TiO}_2/\text{MoS}_2(\text{E})$ heterostructure samples, Raman spectroscopy was used to identify the phonon vibration modes which can be obtained from the Raman signals. The Raman spectra of the as-prepared samples exhibit some typical peaks located at 639, 518, 399, and 148 cm^{-1} , which could be attributed to the $\text{E}_g(2)$, $\text{A}_{1g}+\text{B}_{1g}(2)$, $\text{B}_{1g}(1)$, and $\text{E}_g(1)$ modes of anatase phase TiO_2 , separately. Based on the data obtained above, it is noted that identifying signals and peaks that belongs to molybdenum disulfide in both XRD patterns and Raman spectra, is a challenging job mainly due to quite low content (only 3%) of MoS_2 . [12]

Figure 5.3 (a) XRD patterns and (b) Raman spectra of TiO₂ and TiO₂/MoS₂(E) 3% heterostructures; (c) UV-Vis spectra of TiO₂, TiO₂/MoS₂(E) 3%, TiO₂/MoS₂(B) 3% and TiO₂/MoS₂(E) 5% heterostructures; and (d) XPS spectrum of the sample.

Therefore, the UV-vis absorption spectrum was employed to further characterize the as-prepared TiO₂/MoS₂ (E) sample in Figure S. As is well known, the bandgap of anatase TiO₂ is about 3.2 eV. So from the Figure, the absorption bands that are centred under 400 nm could be considered to be contributed by the intrinsic anatase TiO₂. In contrast with TiO₂ nanorods, the heterostructure composite TiO₂/MoS₂ (E) shows obvious absorption bands located at 423 and 605 nm, indicating the presence of few-layer MoS₂. What's more, X-ray photoelectron spectroscopy (XPS) was carried out to explore chemical states of the as-prepared heterostructure sample. From XPS measurement of Mo 3d, those XPS peaks located at 232.3 and 229.0 eV indicate existence of 2H phase MoS₂. Besides, the other elements detected: S, O and Ti, are consistent with presence of TiO₂ and MoS₂.

5.2.2 Enhanced Photocatalytic HER of Edge-on MoS₂/TiO₂ Heterostructure

To assess the photocatalytic property for hydrogen production of the as-obtained heterostructure sample, a series of experiments were carried out as can be seen in Figure 5.4. Figure 5.4a demonstrates hydrogen generation rate with a range of 0 to 5% in terms of the percentage of MoS₂ in mass. It can be clearly observed that with 0 percentage of MoS₂, the sample shows not so good photocatalytic activity for H₂ evolution with pretty low reaction rate centred about 120 $\mu\text{mol h}^{-1} \text{g}^{-1}$. When the content of MoS₂ is increased to 0.5%, the reaction rate to produce hydrogen gas also increases to the value which is almost four times higher than that obtained from pure TiO₂. Furthermore, the reaction rate reaches its maximum value with the content of MoS₂ being 3%, which is almost thirty-six times higher than TiO₂, achieving 4300 $\mu\text{mol h}^{-1} \text{g}^{-1}$. Then when the loading of MoS₂ is further increased, the reaction rate of the heterostructure also begins to further decrease. As a more convincing evidence, the conventional heterostructure with 3% mass percentage of MoS₂ shows much lower reaction rate as can be seen in Figure 5.4b. It is noted that the stability is a quite important aspect when evaluating the performance of the catalyst. Therefore, the long time reaction was carried out for twelve hours. As shown in Figure 4c, the stability of hydrogen evolution reaction was pretty good from the very beginning and there is almost no obvious decay in the following repeating cycles, demonstrating excellent stability of the as-obtained heterostructure.

A mechanism was tentatively developed to hopefully make the explanation of the origin of better photocatalytic performance from the as-obtained heterostructure sample, as the illustration is shown in Figure 5.4d. Specifically, when UV light lamp is on, the photoexcited holes and electrons are produced in the position of the valance band and conduction band of the semiconductor, namely TiO₂ nanorod, respectively. Then the photoexcited electrons will transfer to the MoS₂ side and further transport into conducting sites. Former research has demonstrated that resistance in the junction and the speed of electron transport in MoS₂ cocatalyst would have a significant effect on the electron-hole

pair separation efficiency, thus causing a dramatic change to the photocatalytic performance of the hydrogen evolution.

Figure 5.4 a) The rate of hydrogen evolution on TiO₂/MoS₂(E) using all kinds of amount MoS₂; b) demonstration of hydrogen evolution rate using TiO₂, TiO₂/MoS₂(E)3% and TiO₂/MoS₂(B)3%; c) Hydrogen evolution measurement with recycling photocatalytic process on the sample of TiO₂/MoS₂(E)3%; d) transport pathway of photo-excited electrons from TiO₂/MoS₂(E) by schematic illustration

5.3 Conclusion

In conclusion, TiO₂/MoS₂(E) photocatalysts, via interface engineering and controlled synthesis of the MoS₂ growth, with optimized electron transportation pathway were prepared. The as-obtained TiO₂/MoS₂(E) photocatalysts exhibited greatly enhanced photocatalytic hydrogen evolution performance with a rate of 4300 μmolh⁻¹g⁻¹ in terms of the best sample with the loading of 3% MoS₂, which is 36 folds higher than the traditional photocatalyst pure TiO₂. A detailed characterization and analysis suggested that the higher conductivity from edge site of MoS₂ could remarkably enhance the interfacial conductivity and further prevent the electron-hole recombination. In addition, the novel design could modulate the electron transportation pathway to the direction of

basal plane once the separation with TiO₂, thus facilitating photoexcited electrons to the active edge site of MoS₂. The findings in this project offer a new avenue for understanding and realizing the rational material design for optimized electronic contact between semiconductor TiO₂ and TMD materials, which is of essential importance to the improvement of electron-hole separation and the acquirement of boosted photocatalytic performance.

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Chapter 6*

Stack Engineering of Binary Platinum-based Alloy Nanosheets

In this Chapter, a facile and large-scale approach has been developed to prepare platinum-based binary alloy nanosheets by stacking engineering target platinum-based alloy foil with aluminum foil, in which asymmetric mechanical rolling technique was employed to repeat the folding and rolling process. With the assistance of sodium hydroxide, aluminum metal layers were selectively etched and removed completely. Combining theoretical calculations, rational material design with optimal compositions of Pt_3M (M: Ni, Fe, Co, Ir, Y, Au, Pb) is proposed for electrocatalytic oxygen reduction reactions (ORR).

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6.1 Introduction

Oxygen reduction reaction (ORR) is widely recognized as the cornerstone yet challenge of diverse clean energy conversion technologies shaping a sustainable, smart and efficient future.[1-3] As the half reaction on the cathode of various metal-air batteries and fuel cells,[4-5] oxygen reduction electrocatalysis in general significantly suffers from serious issues, such as complicated electron transfer pathway[6], sluggish kinetics[7], high overpotential[8] and low stability[9], thus greatly hindering the further development of these devices with high energy efficiency. To address this challenge, extensive efforts have been devoted to exploring and developing highly active ORR electrocatalysts. With comparable activity, inexpensive cost, have aroused substantial research interest due to their great potential/promise as the competitive /promising alternative/substitutes to/for precious metals which have long been identified as state-of-the-art oxygen electrocatalysts.

ORR is critical reaction, currently noble metal is the state-of-the-art electrocatalysts,[10-15] although various non-precious electrocatalysis have been developed. However, the most practical way is still to use PGM-based catalyst. To further reduce the reliance on noble metal Pt, alloying with other transition metals emerges as a promising and effective strategy to achieve higher ORR activity and more competitive durability. Moreover, previous density function theory calculations have demonstrated that Pt₃M alloy may hold great potential for ORR, which can be clearly seen in the volcano plot in Figure 6.1.[16] Moreover, nanoparticle, nano-frame have been synthesized, with not excellent durability.

Therefore, a facile and scale-up approach has been developed to prepare different Pt-based binary alloy nanosheets with using foils as starting materials, as a consequence, realizing boosted ORR activities.

Figure 6.1 Volcano plots of Pt-based binary systems for ORR

6.2 Results and Discussion

6.2.1 Synthesis and Characterization of Platinum-based Alloy Nanosheets

Preparation of free-standing PtNi nanosheets: Ultrathin PtNi nanosheets were prepared, following the developed asymmetric mechanical rolling method, as shown in Figure 6.2. Specifically, in this process, PtNi foil (purity 99%, 0.1 mm in thickness and Pt:Ni=3:1) and Al foil (purity 99.95%, 0.1 mm in thickness) were firstly stacked together forming a PtNi-Al layer structure. Then PtNi and Al foils with similar size and thicknesses (overall thickness of 0.2mm, 2 layers) were pressed together by the roll squeezer machine, resulting in the thickness of about 0.1 mm. The resulting 0.1mm PtNi-Al foil (2 layers) was then completely folded (0.2mm, 4 layers) followed by mechanical rolling again to 0.1mm (4 layers). In this regard, the thickness of each layer was approximately decreased

to half of its previous thickness, while the final sample thickness of PtNi-Al plate always remained about 0.1mm after folding and rolling, which is the basic principle of this preparation idea. As expected, with the folding and rolling process continuing, the thickness of each layer gradually reduced since the numbers of PtNi and Al layers increase steadily to keep the overall thickness the same. From the theoretical viewpoint, when the folding and rolling repeats for 20 times, the total number of the layers (half PtNi and half Al) will eventually achieve 1 million, which means the thickness of each layer will be thinned down to the scale of 0.1nm. Even though the repeating process lasts for 20 times, however, the theoretical thickness is extremely difficult to reach due to unavoidable useless folding and intrinsic limited ductility.

Figure 6.2 Schematic of asymmetric mechanical rolling approach and corresponding optical images of Pt-Ni sheets after different repeating times.

Three photographs of starting Al foil, starting PtNi foil and cross-section SEM images of the resulting PtNi-Al plate with 10 times continuous folding and rolling were demonstrated in Figure 6.3 a, b-c, respectively. It should be noted that the thickness of each layer in the final sample plate could be easily controlled just by changing the repeating times of folding and rolling process.

Figure 6.3 Characterization of the variation of thickness with increasing number of folding and rolling repeating. (a) Pure Al metal foil with 0.1 mm, pure PtNi foil with 0.1 mm, stacking sheets alternate Al layer and PtNi layer after 20 times repeating. (b-c) Cross-section SEM images of Al-PtNi stacking layers after 20 times repeating.

Subsequently, free-standing 2D Pt-based binary nanosheets were prepared through selectively etching the Al metal layer, which indeed is a very simple chemistry removal process. Specifically, 2.5 mol/L sodium hydroxide (NaOH) dilute solution was employed to completely etch all Al metal layers, aiming to expose pure individual Pt-based nanosheets. When the sample was soaking in the prepared NaOH solution for the whole day (24 h), the resulting suspension solution containing PtNi nanosheets was then vigorously ultrasonicated. Finally, the suspension was centrifuged at the speed of 10,000 rpm for 15 min and washed using sufficient deionized water at least 10 times. In this case, a suspension of ultrathin 2D PtNi nanosheets was eventually obtained. Moreover, the suspension containing PtNi nanosheets showed reasonable stability not only in water but also in ethanol.

The as-prepared PtNi nanosheets were firstly characterized by field emission scanning electron microscopy (SEM, MERLIN VP Compact, ZEISS, Germany) and transmission electron microscopy (TEM, JEOL-2100 TEM) with selected area electron diffraction in Figure 6.4. It can be clearly observed that the sheet-morphology structure was formed. Moreover, the lateral size in Figure 6.4b should be 2-3 μm , which is also consistent with TEM observations in Figure 6.4c and the following AFM measurements.

Figure 6.4 Characterization of as-prepared samples. (a) low-magnitude SEM image, scale bar 1 μm (b) high-magnitude SEM image, scale bar 300 nm; (c) TEM image (d) SAED pattern of the as-prepared sample.

Atomic force microscopy (AFM) is considered as the one of most powerful techniques to characterize two dimensional nanostructures, including morphology and thickness which can directly measure the thickness of the nanosheet. Thus, the as-prepared PtNi nanosheet was carefully measured under atomic force microscopy to assess the thickness and roughness on the surface using the tapping mode. Fig. 6.5 demonstrates the AFM images

of different batches of PtNi nanosheets and the corresponding line depth profiles. The first batch PtNi sample was measured to be 5.5 nm thick with few wrinkles (Fig. 6.5a).

Figure 6.5 AFM images of sample-5.5nm (a), sample-6.7nm 2 (b), sample-8.6nm (c), sample-9.7 (d), and the corresponding line depth profiles below. The insets in a-d are photographs of each sample suspensions.

To further confirm the fact that there is no alloying effect during the repeating folding and rolling process, X-ray diffraction (XRD) was carried out and dispersed on the Si substrates for collecting patterns with Cu Ka radiation. The as-prepared PtNi samples were tested by powder X-ray diffraction to obtain basic structural information, as shown in Fig. 6.6. Three other peaks can be indexed to (111), (200), and (220) planes of a face-

centered cubic (fcc) structure, thus confirming an alloy phase of the Pt–Ni, which further suggests thick nanosheets and in consistent with the TEM observations.

Figure 6.6 XRD patterns of Pt₃Ni with different thickness

6.2.2 Boosted Electrocatalytic ORR of Platinum-based Alloy Nanosheets

Preparation of electrode: all the electrocatalysts were firstly dispersed onto 1x1cm² carbon paper electrodes and the PtNi nanosheets with different thickness samples were associated with 8 mL N,N-dimethylformamide (DMF), 650 mL DI water and 150 mL alcohol forming a homogeneous ink, which was subsequently loaded with the same amount. In this case, each of the samples possesses a loading amount of 1 mg/cm². To evaluate the robust repeatability, the as-obtained carbon electrodes should be then dried in the oven under 70 °C lasting for sixty minutes in order to clear the removal of the ethanol, and moved to a vacuum drying oven under 140 °C for one more hour to remove DMF by evaporation completely.

Electrochemical measurements and analysis: During the electrochemical measurements, the electrochemical tests were conducted with the assistance of CHI 660E electrochemical work station with a standard three-electrode system, using 1 M KOH or 6 M KOH as the environment. Subsequently, linear sweep voltammetry (LSV) was carried out under the scanning rate of 5 mV/s using a Pt mesh as the counter electrode and an

Ag/AgCl as the reference electrode. Finally, long-term cyclic voltammetry (CV) was carried out ranging from 0.3 V to 0.75 V under the scan rate of 5 mV/s. All of the LSV curves were carried out using the iR compensation method and then be plotted out in figures.

Figure 6.7 (a) Cyclic voltammograms in N₂-protected 0.1 M and (b) corresponding ORR polarization curves in O₂-saturated 0.1 M of the Pt₃Ni/C nanosheets with different thickness.

The electrochemical properties of the as-prepared Pt₃Ni alloy nanosheets with different thickness are presented in Fig. 6.7. As exhibited in Fig. 6.7A, the cyclic voltammograms (CV) of the as-prepared catalysts were collected in N₂-protected 0.1 M HClO₄. The oxygen reduction reaction performance of the as-obtained electrocatalysts were measured through carrying out linear sweep voltammetry (LSV). As can be seen in Figure 6.7a, the

half-wave potential changed positively due to an increase in the octahedral Pt₃Ni nanosheet thickness, further suggesting thinner nanosheets should be more active in terms of ORR performance. The area-specific kinetic current density of pre-activated and as-prepared electrocatalysts at 0.90 V vs. RHE was obtained by applying the Koutecky–Levich equation and normalizing with the help of the electrochemically active surface areas. The 8.1 nm-Pt₃Ni nanosheets exhibited the highest $i_{area,0}$ of 4.06 mA cm⁻² Pt, which is over sixty percentage higher than 4.5 nm-Pt₃Ni nanosheets, which indicates that 8.1 nm-Pt₃Ni nanosheets is top among these samples, as the most active ORR electrocatalyst. The exciting value suggests a twenty times improvement for the intrinsic ORR performance activity in comparison with the commonly used Pt/C which are commercial and tested in a large variety of previous studies.

6.3 Conclusion

The facile approach inspired by simple rolling was further modified via asymmetric rolling, as a consequence, resulting in considerably ultrathin Pt-based binary alloy nanosheets with lateral size of 2-3 μ m. With the assistance of sodium hydroxide, aluminum metal layers were selectively etched and removed completely. Combining theoretical calculations, rational material design with optimal compositions of Pt₃M (M: Ni, Fe, Co, Ir, Y, Au, Pb) was proposed for electrocatalytic oxygen reduction reactions (ORR). Through a series of characterization techniques, the sheet-like morphology was observed with lateral size of 2-3 μ m and the thickness ranges from 5.5 nm to 9.7 nm. The activity and stability of ORR were greatly improved. It is widely believed that altered electronic properties by alloying and changed surface by 2D materials induce a variation for adsorption behavior, which were considered to be the origin of the high ORR activity.

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Chapter 7

Implications/Impact/Outstanding Questions

This concluding chapter presents a general discussion of the whole thesis, including implications of the thesis, the impact of the thesis, and also some outstanding questions triggered in the thesis which may be addressed in the near future. The originality of the projects completed in the thesis is also discussed. On basis of current research progress in the field, some suggestions for possible future work that can be conducted in the near future are given from the author's point of view. Especially, the significance of this thesis is also highlighted, aiming to developing novel ideas in 2D materials toward efficient clean energy applications.

7.1 General Discussion

The thesis addresses how to further optimize and improve the electronic structure and catalytic properties for energy storage and conversion processes. Specifically, the thesis aim at understanding how defecting/doping strategy of 2D materials can boost lithium storage through altering the electronic conductivity and shortening the ion pathway, and how to dramatically enhance photocatalytic HER of MoS₂ via precise interface engineering, and how to boost electrocatalytic ORR of Pt-based binary nanosheets and finally demonstrates the proof-of-concept applications of these strategies in 2D materials in a larger variety of energy applications including LIBs, photocatalytic HER and electrocatalytic ORR.

Firstly, highly nitrogen-doped and defect-rich porous nanocarbon has been synthesized by simple in-situ pyrolysis of zeolitic imidazolate framework nanoparticles (ZIF) grown on graphene oxide as negative electrode in lithium ion batteries (LIBs), which demonstrates extraordinary capacities, remarkable cycling performances and rate capability and surpasses carbon-based electrodes in literature and most of metal oxide-based anodes from metal organic frameworks (MOFs). With an impressive initial capacity of 1378 m Ah g⁻¹ at current density of 100 mA g⁻¹, it could be operated for 100 and 200 cycles under current densities of 500 mA g⁻¹ and 1000 mA g⁻¹, leading to reversible capacities of 1070 mA g⁻¹ and 948 m Ah g⁻¹, separately. When the current density was 5000 mA g⁻¹, it still reversibly presented a decent capacity of more than 530 m Ah g⁻¹ after four hundred cycles, exhibiting a high rate of retention of 84.4% in terms of capacity. It is considered that the excellent electrochemical output is due to the perfect bond of an extremely conductive platform (graphene), high-level doping of nitrogen (defect-rich) and hierarchically porous structure.

Secondly, via interface engineering, solid edge-on heterostructures between few-layered MoS₂ and were produced on large scale through a facile two-step, which realized the idea that layered MoS₂ can be welded laterally to photocatalysts via edges to enhance the catalytic activity toward water splitting due to the efficient transport of photoexcited

electrons along the highly conductive edges and basal planes of MoS₂. The unusual photocatalytic activity is attributed to the improved electronic contact and the optimized electron transport pathways between TiO₂ and MoS₂, where the recombination of photoexcited electron-hole pairs is effectively suppressed. This work represents a strategy, which marries low-cost layered transition-metal dichalcogenides with backboned photocatalyst as a promising heterostructure for high-efficiency water splitting.

Lastly, a facile and large-scale approach has been developed to prepare platinum-based binary alloy nanosheets by stacking engineering target platinum-based alloy foil with aluminum foil, in which asymmetric mechanical rolling technique was employed to repeat the folding and rolling process. With the assistance of sodium hydroxide, aluminum metal layers were selectively etched and removed completely. Combining theoretical calculations, rational material design with optimal compositions of Pt₃M (M: Ni, Fe, Co, Ir, Y, Au, Pb) was proposed for electrocatalytic oxygen reduction reactions (ORR). Through a series of characterization techniques, the sheet-like morphology was observed with lateral size of 2-3 μm and the thickness ranges from 5.5 nm to 9.7 nm. The activity and stability of ORR were greatly improved. It is widely believed that altered electronic properties by alloying and changed surface by 2D materials induce a variation for adsorption behavior, which were considered to be the origin of the high ORR activity.

7.2 Reconnaissance Work not Included in Main Chapters

The above three interesting aspects including defect engineering, interface engineering and stack engineering were explored in detail for energy applications covering energy storage and conversions. Some exciting results were achieved. However, these were just preliminary results and extensive efforts should be made into this emerging field in which 2D materials can offer great opportunities in energy-related issues.

Firstly, alloys as an ancient class of materials which has been developed since at least 3000 years ago, have attracted more and more attention when we are in the nano energy era, due to their good conductivity, plasticity, energy density and electrical catalyst

performance. Although alloy anodes have been investigated since 1990s, the large volume change and poor cycling performance has hindered their commercial use in Li-ion batteries. Figure 7.1 demonstrates a schematic of the synthesis pathway for obtaining E-GaIn encapsulated by reduced graphene oxide used for anode materials of LIBs. But aforementioned research all needs expensive pre-treatment methods to artificially make some porous structure to resist large volume change, which is not favourable for large-scale production and commercialization.[1] Fortunately, recent research in self-healing materials has opened another door for solving this question. Bao's group in Stanford has developed a new spontaneous self-healing polymer and used to encapsulate Si micro-particles, which has attained a cycle life ten times longer than state-of-art anodes made from Si micro-particles and still retaining a high capacity (up to 3,000 mA h g⁻¹). Gallium (melting point, 29.8) and its alloys, such as eutectic gallium indium (EGaIn, 15.5) and gallium indium tin (GaInSn, -19) are liquid at room temperature, which are notable for having fluidity and metallic conductivity, and without toxicity like mercury. The unique liquid nature makes itself as a promising active material candidate for Li-ion battery anode.

Figure 7.1 Schematic of preparation of graphene encapsulated E-GaIn alloy

Secondly, Since the strong capability in the CVD synthesis in monolayer and few-layer TMDs (up to 40 kinds of TMDs), another aspect that could be done in the near future is to explore the possibility in catalytic properties of these CVD-grown samples since currently most studies focus on the solution-based methods. And the problem is that we should expose as many edge sites as possible since it is reported that the edge sites are responsible for the HER activity. So many grain boundaries or defects and vertical morphology are demanded, as demonstrated in Fig.7.2.[2-3] This kind of design provides not only maximum density of edge sites, but also ensure efficient and fast charge migration between the active surface sites and conductive support to because of the excellent intra-layer conductivity.

Figure 7.2 CVD grown samples with different morphology and orientation

In addition to morphology engineering in CVD-grown two-dimensional materials discussed above, there are several emergent tuning (engineering) concepts which hold enormous promise in clean energy applications. Various engineering strategies developed to modify the microstructure, tailor electronic structure and tune local atomic configuration of ultrathin 2D materials, with the aim of pushing the efficiency limit beyond their intrinsic performances, are particularly highlighted. For example, for MoS₂, the most available phase is 2H semiconducting phase which is extremely popular in field effect transistors in semiconductor electronic devices. However, the metastable phase, 1T or 1T' MoS₂ is metallic, meaning that it is of great importance to enhance their electrocatalytic reactions. Therefore, how to efficiently convert the 2H to 1T (1T') MoS₂,

called as phase engineering, could be an appealing research direction as well as other layered 2D materials possessing similar characteristics.[4-5] Recently, Guo and Huang et al. reported biaxial strain could help to greatly boost oxygen reduction catalysis in PtPb/Pt core/shell nanoplates.[6] Actually, strain-induced hydrogen evolution enhancement was previously reported in sulfur-vacancy MoS₂. [7] Strain engineering in ultrathin 2D materials plays an important role for energy conversion, especially in electrocatalytic hydrogen evolution and oxygen reduction. Electric-field effect has been demonstrated as an effective strategy to boost the lithium storage due to lithium ion transfer dynamics.[8-9] Moreover, electric effect was reported to enhance the electrocatalytic hydrogen evolution catalysis.[10] In this respect, electric or electric field effect engineering could provide some insights into hydrogen evolution and battery research. Very recently, in electrocatalysis field, atomically dispersed metal catalyst was deposited on graphene support to maximize the full potential of their catalytic activities characterized with the powerful 3D probing techniques.[11] Hence, single atom engineering in 2D materials could be proposed for future research work.

7.3 Outcomes Reflected in the Original Hypothesis

The thesis addresses how to further optimize and improve the electronic structure and catalytic properties for energy storage and conversion processes. Specifically, the thesis aim at understanding how defecting/doping strategy of 2D materials can boost lithium storage through altering the electronic conductivity and shortening the ion pathway, and how to dramatically enhance photocatalytic HER of MoS₂ via precise interface engineering, and how to boost electrocatalytic ORR of Pt-based binary nanosheets and finally demonstrates the proof-of-concept applications of these strategies in 2D materials in a larger variety of energy applications including LIBs, photocatalytic HER and electrocatalytic ORR.

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surpassing carbon-based electrodes in literature and most of metal oxide-based anodes from metal organic frameworks (MOFs). With an impressive initial capacity of 1378 m Ah g⁻¹ under current density of 100 mA g⁻¹, it could be operated for 100 and 200 cycles under current densities of 500 mA g⁻¹ and 1000 mA g⁻¹, leading to reversible capacities of 1070 mA g⁻¹ and 948 m Ah g⁻¹, separately. When the current density was 5000 mA g⁻¹, it still reversibly presents a decent capacity of more than 530 m Ah g⁻¹ after four hundred cycles, exhibiting a high rate of retention of 84.4% in terms of capacity.

Synthesizing solid edge-on heterostructures between few-layered MoS₂ and TiO₂ via interface engineering on large scale through a facile two-step, which realized the idea that layered MoS₂ can be welded laterally to photocatalysts via edges to enhance the catalytic activity toward water splitting due to the efficient transport of photoexcited electrons along the highly conductive edges and basal planes of MoS₂. The unusual photocatalytic activity is attributed to the improved electronic contact and the optimized electron transport pathways between TiO₂ and MoS₂, where the recombination of photoexcited electron-hole pairs is effectively suppressed.

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