Noble metal nanomaterials with novel crystal phase : syntheses and catalytic applications

Chen, Ye

2018

Chen, Y. (2018). Noble metal nanomaterials with novel crystal phase : syntheses and catalytic applications. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/83263>

<https://doi.org/10.32657/10220/48007>

**NANYANG
TECHNOLOGICAL
UNIVERSITY**

SINGAPORE

**NOBLE METAL NANOMATERIALS WITH NOVEL CRYSTAL
PHASE: SYNTHESSES AND CATALYTIC APPLICATIONS**

CHEN YE

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2018

METAL NANOMATERIALS WITH NOVEL CRYSTAL PHASE: SYNTHESES AND CATALYTIC APPLICATIONS

CHEN YE

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.

17 Dec 2018
.....

Date

.....

Chen Ye

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.

17 Dec 2018

.....
Date

.....
Prof. ZHANG Hua

Authorship Attribution Statement

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

Chapter 4 is published as Z. Fan, Y. Chen (co-first author), Y. Zhu, J. Wang, B. Li, Y. Zong, H. Zhang. Epitaxial growth of unusual 4H hexagonal Ir, Rh, Os, Ru and Cu nanostructures on 4H Au nanoribbons. *Chemical Science* **8**, 795 (2017). DOI: 10.1039/C6SC02953A.

The contributions of the co-authors are as follows:

- Prof. Zhang provided the initial project direction and revised the manuscript drafts. Prof. Zong and Dr. Zhu helped to revise the manuscript.
- I co-designed the study with Dr. Fan and performed all the laboratory work together at the School of Materials Science and Engineering.
- Dr. Fan prepared the manuscript drafts.
- All microscopy, including sample preparation, was conducted by Dr. Fan and me in the Facility for Analysis, Characterization, Testing and Simulation.

Chapter 5 is published as Y. Chen, Z. Fan, Z. Luo, X. Liu, Z. Lai, B. Li, Y. Zong, L. Gu, H. Zhang. High-Yield Synthesis of Crystal-Phase-Heterostructured 4H/*fcc* Au@Pd Core-Shell Nanorods for Electrocatalytic Ethanol Oxidation. *Advanced Materials* **29**, 1701331 (2017). DOI:10.1002/adma.201701331.

The contributions of the co-authors are as follows:

- Prof Zhang provided the initial project direction and revised the manuscript drafts.
- I prepared the manuscript draft. The manuscript was revised by Prof Gu and Dr. Zong.
- I co-designed the study with Dr. Fan and performed all the laboratory work at the School of Materials Science and Engineering. I also analyzed the data.

- The high-resolution spherical-aberration-corrected transmission electron microscopy and the corresponding energy dispersive X-ray spectroscopy images were taken by Mr. Liu and Prof. Gu.
- Dr. Lai conducted the scanning electron microscopy test of the nanomaterials.
- All the other transmission electron microscopy images and the X-ray diffraction characterization were conducted by me in the Facility for Analysis, Characterization, Testing and Simulation.
- Dr. Li conducted the X-ray photoelectron microscopy characterization of the nanomaterials.

Chapter 6 is submitted as Y. Chen, J. Wang, Z. Fan, X. Liu, Z. Huang, Z. Lai, B. Li, B. Chen, Y. Zong, L. Gu, X. Wang, H. Zhang. Crystal Phase Heterostructured 4H/fcc Au@Cu Core-Shell Nanorods for Electrocatalytic CO₂ Reduction.

The contributions of the co-authors are as follows:

- Prof Zhang suggested the research direction and edited the manuscript drafts.
- I wrote the drafts of the manuscript. The manuscript was revised together with Dr. Fan, Prof. Wang, Dr. Zong and Prof. Zhang.
- I performed all the materials synthesis, collected low-magnification transmission electron microscopy images, X-ray diffraction patterns, and conducted data analyses.
- Dr. Wang performed the electrochemical CO₂RR tests of the nanomaterials. Dr. Huang provided guidance and helped analyzed the test results.
- Mr. Liu helped to take the high-resolution spherical aberration-corrected scanning transmission electron microscopy image of the nanomaterials.
- Dr. Lai conducted the scanning electron microscopy test of the nanomaterials.
- Dr. Li conducted the X-ray photoelectron microscopy characterization of the nanomaterials.
- Dr. Chen conducted the inductively coupled plasma mass spectroscopy characterization of the nanomaterials.

- Dr. Huang provided guidance and advices for the performance analyses in the CO₂RR tests.

17 Dec 2018
.....
Date

.....
Chen Ye

Abstract

Noble metal nanomaterials possess outstanding catalytic properties in a wide range of reactions. In the past decades, controlled synthesis to fine tune the size, shape, architecture, and composition of noble metal nanocrystals to boost their catalytic performances has been intensively investigated. The crystal structure represents another important parameter of nanocrystals. However, to date, most studies on crystal phase engineering of noble metal nanocrystals rely on extreme conditions such as high pressure and high temperature. It is still relatively difficult to prepare large-scale, free-standing metal nanostructures with unusual crystal structures under ambient condition, hindering a comprehensive study on their phase-dependent physicochemical properties. Moreover, the effects of crystal structure on the catalytic properties of noble metal nanomaterials and the strategies to further improve the catalytic performances via crystal phase control are yet to be explored.

The first project introduces the epitaxial growth of a series of metals, namely Ru, Rh, Ir, Os, Cu, with novel 4H crystal phase under mild conditions. By simply reducing the metal precursors in the solution of 4H Au nanoribbons, free standing Au@metal nanostructures are obtained under room temperature. Importantly, Ru, Rh, Ir, Os, Cu shells with 4H crystal phase are obtained for the first time. The general approach can be readily applied to a wide range of other metals.

Compared to the Au NRBs with pure 4H crystal phase, Au nanostructures with a mixture of different crystal phases may be more suitable for the template of nanocatalysts, due to the high density of active sites generated at the phase boundaries. To explore the possibility of preparing new Au substrates, the second project first introduces the synthesis of crystal-phase-heterostructured 4H/*fcc* Au nanorods with high yield. Then, the subsequent epitaxial growth of 4H/*fcc* Pd shell for electrochemical oxidation of ethanol is carried out. For the first time, crystal-phase-heterostructured 4H/*fcc* Au nanorods with alternating 4H and *fcc* crystal phases grown on each single nanorod are prepared with yield approaching 100%. The 4H/*fcc* Au nanorods serve as excellent template to grow other metals with 4H/*fcc* crystal phase heterostructures. As a proof of concept, a Pd shell is grown epitaxially on the

Au nanorods. The resultant Au@Pd nanorods demonstrate impressive performance in the ethanol oxidation reaction with mass activity 6.2 times those of commercial Pd catalyst.

Based on the general method developed by the first project and the crystal-phase-heterostructured 4H/*fcc* Au NRs discovered in the second project, it is possible to further extend the crystal phase library of metals by preparing crystal-phase-heterostructured 4H/*fcc* non-noble metals. The third work introduces the epitaxial growth of a transition metal, Cu, on the crystal-phase-heterostructured 4H/*fcc* Au nanorods and the superior performance of the crystal-phase-heterostructured 4H/*fcc* Au@Cu nanorods in electrocatalytic CO₂ reduction reaction. The high yield of the 4H/*fcc* Au@Cu nanorods allows a relatively fair comparison between heterophased 4H/*fcc* Au@Cu and *fcc* Cu nanoparticles, which suggests that the 4H/*fcc* heterophased Cu exhibit better selectivity of C₂H₄ and activity than *fcc* Cu CPS in the CO₂RR catalysis.

Lay Summary

The way we consume energy has evolved rapidly into a diverse yet coherent system in the past decade, standing as an indicator of the expanding global economy. On the one hand, oil & gas still accounts for more than half of global energy consumption. The crude oil is exploited directly from nature, refined and reformed for various downstream industries. On the other hand, multiple forms of renewable and clean energy sources have been utilized and infiltrated successfully in our daily lives. In both aspects, chemists and materials scientist played a critical role to catalyze the energy harvesting process. This statement is true literally, as the performance of catalysts is one of the key limiting factors in energy industries.

Specifically, in conventional oil and gas industries, heterogeneous catalysts are the heroes to produce high-purity fuels and many important chemical products related to packaging, furnishing and automotive industries, such as ethylene and propylene. Meanwhile, a huge market is growing in future industries related to renewable energy resources. For example, electrocatalytic water splitting converts water into hydrogen and oxygen, which can be directly used in fuel cells to power electric vehicles. In this reaction cycle, electrocatalysts play key roles in the hydrogen evolution reaction, oxygen evolution reaction, and oxygen reduction reaction. However, current commercial catalysts generally suffer from the low cost efficiency and relatively low durability, hindering their wide applications as practical catalysts. Therefore, developing new noble metal catalysts to overcome these problems is fundamentally and practically important.

Noble metal and transition metal nanomaterials, such as Pt, Pd, Ir, Ru and Cu, possess distinctive catalytic properties. They are widely used in many catalytic reactions applications related to heterogeneous catalysis, electrocatalysis, and photocatalysis. However, the worldwide implementation of metal nanomaterials has been limited due to the finite proven reserves, cost of beneficiation and extraction, and durability concerns in some reactions. An effective mitigation strategy is to boost their catalytic activities so that the overall consumption of metals can be reduced.

Besides the well-established size, composition, shape and architecture-control, the crystal phase engineering emerges as a new strategy to tune the physicochemical properties of metal nanomaterials. For instance, the *fcc* FePt nanoparticle has been reported to be a superior electrocatalyst with substantial stability towards the oxygen reduction reaction compared to its *fcc* counterpart. Conventionally, the crystal phase control of noble metal nanomaterials is realized under extreme conditions, e.g. high temperature and high pressure, which cause the aggregation or degradation of ultras-small nanostructures and thus cannot be widely used. Therefore, great potential lies in the development of new metal nanocatalysts with novel crystal phases via facile methods, in fulfilling their wide demands in practical catalytic applications.

Acknowledgements

I would like to thank my university, Nanyang Technological University, for providing the generous scholarship and the research platform for my graduate study at School of Materials Science and Engineering.

I would like to express my sincerest gratitude to my supervisor Prof. Zhang Hua, on his inspiring guidance and full support to my research work and many more. He has been dedicated in offering timely advice with enthusiasm and encouragement, which greatly affected my attitude and confidence towards responsible and meaningful scientific research. His openness to science, excellent writing skills, and sharp detection of research direction have made my PhD life not only fulfilling, but also full of excitement. I also must thank my mentor Dr. Fan Zhanxi, who taught me patiently how to conduct experiments, characterizations and literature reviews. His expertise and valuable experience have greatly encouraged me in pursuing my project goals.

I would also like to thank my thesis committee, Prof. Xue Can and Prof. Zhang Qichun. Through their examples, I have learned how strong character is successfully expressed in science, teaching, and leadership.

Most key data during my PhD study were collected at laboratories in School of Materials Science and Engineering at the Nanyang Technological University by myself. I want to thank the staff scientist in Facility of Analysis, Characterization, Testing and Simulation as well as the Organic Service lab, on providing thoughtful trainings and guidance before/during the characterizations and tests.

I also want to thank my important collaborator from School of Chemical and Biomedical Engineering, Prof. Wang Xin and Dr. Wang Jiong, on their kind guidance and help in the characterization of my nanomaterials in the electrocatalytic CO₂ reduction reaction.

In addition to my gratitude to the faculty at Nanyang Technological University, I would also like to thank Dr. Li Bing and Dr. Zong Yun from Institute of Materials Research and Engineering under Agency for Science, Technology and Research, Singapore, who have been given continuous supports and had numerous collaborations with me in the X-ray photoelectron spectroscopy study of various nanomaterials I synthesized.

Moreover, there have been many kind helps from the past and current members from Zhang Research Group, especially Dr. Luo Zhimin, Dr. Chen Bo, Dr. Yang Nailiang, Dr. Zhang Zhicheng, Dr. Niu Wenxin, Dr. Li Cuiling, Dr. Wu Xuejun, Dr. Zhang Xiao, Dr. Lai zhuangchai, Ms. Tran Thu Ha, and Mr. Yun Qinbai. With their expertise in various areas and generous guidance, I have been equipped with the specialties needed for a qualified PhD candidate. We have spent numerous hours together discussing ideas, sharing opinions, having memorial gathering events and happy lunch hours. Outside lab, we also play sports and go shopping together. The have made my PhD life much more fruitful and joyful.

Lastly, I would like to thank my family for their understanding and support. Particularly, my mom and dad have put great belief in me, the only child in the family, by providing me with great freedom and letting me choose my career. I must also thank my wonderful cousin Tao, who has been given me crucial suggestions when I make momentous decisions in my PhD study.

Table of Contents

Abstract	ii
Lay Summary	vi
Acknowledgements	ix
Table of Contents	xi
Table Captions	xvii
Figure Captions	xix
Abbreviations	xxv
 Chapter 1 Introduction.....	 1
1.1 Hypothesis	2
1.2 Objectives and Scope	3
1.3 Dissertation Overview.....	3
1.4 Findings and Outcomes.....	5
References.....	5
 Chapter 2 Literature Review	 7
2.1 Noble Metal Nanomaterials	8
2.1.1 Historical Development and Basic Information	8
2.1.2 General Strategies in Wet-chemical Synthesis of Metal Nanomaterials ...	10
2.1.2.1 Case Study on the Au-Oleylamine System	11

2.1.3	Crystal Phase Control in Metal Nanomaterials.....	14
2.1.3.1	The Importance of Crystal Phase	14
2.1.3.2	Crystal Phase Based Epitaxial Growth.....	15
2.2	Characterization Techniques for Noble Metal Nanomaterials.....	16
2.2.1	Atomic Force Microscopy	16
2.2.2	Scanning Electron Microscopy	17
2.2.3	Transmission Electron Microscopy	18
2.2.4	X-ray Diffraction	21
2.2.5	Energy-Dispersive X-ray Spectroscopy.....	21
2.2.6	X-ray Photoelectron Spectroscopy	22
2.2.7	X-ray Absorption Structure Analysis.....	23
2.3	Catalytic Applications	26
2.4	Questions to Answer Based on Literature.....	29
	References	30
Chapter 3	Experimental Methodology	37
3.1	Rationale for selection	38
3.2	Materials and Chemicals	38
3.2.1	Chemicals.....	38
3.2.2	Materials	39
3.3	Synthesis Methods.....	39
3.3.1	Synthesis of 4H Au NRBs	39
3.3.2	Synthesis of 4H/ <i>fcc</i> Au@Ir core-shell NRBs	39
3.3.3	Synthesis of 4H/ <i>fcc</i> Au@Rh core-shell NRBs	40
3.3.4	Synthesis of 4H/ <i>fcc</i> Au@Os core-shell NRBs	40

3.3.5	Synthesis of 4H/ <i>fcc</i> Au@Ru core-shell NRBs	41
3.3.6	Synthesis of 4H/ <i>fcc</i> Au@Cu core-shell NRBs	41
3.3.7	Synthesis of crystal-phase-heterostructured 4H/ <i>fcc</i> Au NRs	42
3.3.8	Synthesis of crystal-phase-heterostructured 4H/ <i>fcc</i> Au@Pd core-shell NRs	42
3.3.9	Synthesis of crystal-phase-heterostructured 4H/ <i>fcc</i> Au@Cu core-shell NRs	43
3.4	Materials Characterization	44
3.4.1	SEM	44
3.4.2	TEM, EF-STEM, and STEM-EDS	44
3.4.3	XRD	44
3.4.4	XPS	45
3.5	Electrocatalytic Applications	45
3.5.1	EOR Measurement of Au@Pd NRs	45
3.5.2	CO ₂ RR Measurement of Au@Cu NRs	46
	References	46
 Chapter 4 Epitaxial Growth of Unusual 4H Ir, Rh, Os, Ru and Cu Nanostructures on 4H Au Nanoribbons		47
4.1	Introduction	48
4.2	Results and Discussion	49
4.3	Conclusions	65
	References	66
 Chapter 5 High-Yield Synthesis of Crystal-Phase-Heterostructured 4H/<i>fcc</i> Au@Pd Core-Shell Nanorods for Electrocatalytic Ethanol Oxidation		69

5.1	Introduction	70
5.2	Results and Discussion.....	71
5.2.1	Exploration of Novel Au Nanostructures	71
5.2.2	Crystal-phase-heterostructured 4H/ <i>fcc</i> Au NRs.....	75
5.2.3	Crystal-phase-heterostructured 4H/ <i>fcc</i> Au@Pd NRs via Epitaxial Growth	79
5.2.4	Electrocatalytic Performance of 4H/ <i>fcc</i> Au@Pd NRs in EOR	80
5.3	Conclusions	83
	References	84
 Chapter 6 Crystal Phase Heterostructured 4H/<i>fcc</i> Au@Cu Core-Shell Nanorods for Electrocatalytic CO₂ Reduction		87
6.1	Introduction	88
6.2	Results and Discussion.....	89
6.2.1	High-yield Epitaxial Growth of 4H/ <i>fcc</i> Au@Cu NRs	89
6.2.2	Electrocatalytic CO ₂ RR by 4H/ <i>fcc</i> Au@Cu NRs	95
6.3	Conclusions	100
	References	100
 Chapter 7 Discussion and Future Work		103
7.1	General Discussion.....	104
7.1.1	Discussion on the Epitaxial Growth of 4H/ <i>fcc</i> Au@M NRBs	104
7.1.2	Discussion on the High-yield Synthesis of 4H/ <i>fcc</i> Au NRs and Epitaxial Growth of 4H/ <i>fcc</i> Au@Pd NRs	104
7.1.3	Discussion on the High-yield Epitaxial Growth of 4H/ <i>fcc</i> Au@Cu NRs..	105
7.2	Reconnaissance Work not Included in Main Chapters	105
7.3	Outstanding Questions and Future Works	106

References	107
------------------	-----

Publication List	109
-------------------------------	-----

Table Captions

Table 2.1 Reduction potentials of half-reactions of selected metals.

Table 2.2 Crystal structures of noble metals in bulk.

Table 5.1 Comparison of 4H Au NRBs and 4H/*fcc* crystal phase heterostructured Au NRBs.

Figure Captions

Figure 2.1 The eight elements of noble metal in the periodic table.

Figure 2.2 Preparation of ultrathin Au nanowires with oleylamine as surface ligand, the comparison of three works.

Figure 2.3 Formation mechanism of 1D Au nanowires.

Figure 2.4 Preparation of 4H Au NRBs and 2H Au SSs.

Figure 2.5 Crystal phase-controlled synthesis of noble metal nanomaterials.

Figure 2.6 Template synthesis of noble metal nanocrystals with unusual crystal structures.

Figure 2.7 Case studies of AFM characterizations on noble metal nanomaterials.

Figure 2.8 Case studies of SEM characterizations on noble metal nanomaterials.

Figure 2.9 Case studies of TEM characterizations on noble metal nanomaterials.

Figure 2.10 Case studies of XRD, EDS, and XPS characterizations on noble metal nanomaterials.

Figure 2.11 Case studies of XAS characterizations on noble metal nanomaterials.

Figure 2.12 Phase-dependent electrocatalytic performances of noble metal nanomaterials.

Figure 2.13 The superior catalytic activity of polytypic 4H/*fcc* Au@PdAg core-shell

NRBs towards the hydrogen evolution reaction.

Figure 4.1 TEM characterizations of 4H Au NRBs.

Figure 4.2 Schematic illustration of the solution-phase epitaxial growth of 4H Ir, Rh, Os, Ru and Cu shells on 4H Au NRBs.

Figure 4.3 TEM and EDS characterizations of 4H/*fcc* Au@Ir NRBs.

Figure 4.4 XPS spectra of 4H/*fcc* Au@Ir core-shell NRB.

Figure 4.5 STEM-EDS spectrum of the as-synthesized 4H/*fcc* bimetallic Au@Ir NRBs,

Figure 4.6 HAADF-STEM image and corresponding STEM-EDS line scanning profile of a representative 4H/*fcc* bimetallic Au@Ir NRB.

Figure 4.7 A typical XRD pattern of the synthesized 4H/*fcc* bimetallic Au@Ir NRBs.

Figure 4.8 TEM and EDS characterizations of 4H/*fcc* Au@Rh, 4H/*fcc* Au@Os, and 4H/*fcc* Au@Ru NRBs.

Figure 4.9 STEM-EDS spectrum of the synthesized 4H/*fcc* bimetallic Au@Rh NRBs.

Figure 4.10 HAADF-STEM image and corresponding STEM-EDS line scanning profile of a representative 4H/*fcc* bimetallic Au@Rh NRB.

Figure 4.11 STEM-EDS spectrum of the synthesized 4H/*fcc* bimetallic Au@Os NRBs.

Figure 4.12 HAADF-STEM image and corresponding STEM-EDS line scanning profile of a representative 4H/*fcc* bimetallic Au@Os NRB.

Figure 4.13 STEM-EDS spectrum of the synthesized 4H/*fcc* bimetallic Au@Ru NRBs.

Figure 4.14 HAADF-STEM image and corresponding STEM-EDS line scanning profile of a representative 4H/*fcc* bimetallic Au@Ru NRB.

Figure 4.15 XPS spectra of 4H/*fcc* Au@Rh, Au@Os, and Au@Ru core-shell NRBs.

Figure 4.16 Representative XRD patterns of the synthesized 4H/*fcc* bimetallic Au@Rh, Au@Os, and Au@Ru NRBs.

Figure 4.17 TEM and EDS characterizations of 4H/*fcc* Au@Cu NRBs.

Figure 4.18 XPS spectra of alternating 4H/*fcc* Au@Cu core-shell NRBs.

Figure 4.19 STEM-EDS spectrum of the synthesized 4H/*fcc* bimetallic Au@Cu NRBs.

Figure 4.20 HAADF-STEM image and corresponding STEM-EDS line scanning profile of a representative 4H/*fcc* bimetallic Au@Cu NRB.

Figure 4.21 A representative XRD pattern of the synthesized 4H/*fcc* bimetallic Au@Cu NRBs.

Figure 5.1 Chemical formulas of common alcohol molecules used in the synthesis.

Figure 5.2 Exploration of the effects of various alcohol molecules on the yield and morphology of Au nanostructures.

Figure 5.3 Optimization of synthetic conditions for high-yield 4H/*fcc* Au NRs.

Figure 5.4 Comparison of reaction set-ups between syntheses of 4H Au NRBs and 4H/*fcc* Au NRs.

Figure 5.5 Removal of byproducts to further purify the as-obtained 4H/*fcc* Au NRs.

Figure 5.6 Schematic illustration of the synthesis of 4H/*fcc* Au NR and epitaxial growth of Pd on 4H/*fcc* Au NR to form 4H/*fcc* Au@Pd core-shell NR.

Figure 5.7 Morphological and crystallographic characterization of crystal-phase-heterostructured 4H/*fcc* Au NRs.

Figure 5.8 XRD pattern of crystal phase heterostructured 4H/*fcc* Au NRs collected in the $\theta/2\theta$ mode.

Figure 5.9 XPS spectra of 4H/*fcc* Au NRs and 4H/*fcc* Au@Pd NRs,

Figure 5.10 Low-magnification TEM images of 4H/*fcc* Au NRs obtained at different reaction times and different H₂AuCl₄ concentrations.

Figure 5.11 High-magnification TEM, C_s-corrected TEM, and EDS characterizations of crystal-phase-heterostructured 4H/*fcc* Au@Pd NRs.

Figure 5.12 Electrocatalytic EOR performance of 4H/*fcc* Au@Pd NRs.

Figure 6.1 Schematic illustration of the synthesis of 4H/*fcc* crystal-phase-heterostructured Au@Cu NR and its application in electrocatalytic CO₂RR.

Figure 6.2 SEM and TEM characterization of the crystal-phase-heterostructured 4H/*fcc* Au NRs.

Figure 6.3 SEM and TEM characterization of the crystal-phase-heterostructured 4H/*fcc* Au@Cu NRs.

Figure 6.4 High-magnification TEM, C_s -corrected TEM, and EDS characterizations of crystal-phase-heterostructured 4H/*fcc* Au@Cu NRs.

Figure 6.5 Thickness control of epitaxially grown Cu shell.

Figure 6.6 XPS spectra of 4H/*fcc* Au NRs and 4H/*fcc* Au@Cu NRs.

Figure 6.7 C_s -corrected STEM image of one Au@Cu nanorod with a thin layer of Cu oxide.

Figure 6.8 Optimization of loading density for CO₂RR performance in terms of Faradaic efficiency of C₂H₄.

Figure 6.9 Electrocatalytic CO₂RR performance of 4H/*fcc* Au@Cu NRs.

Figure 6.10 Characterizations of *fcc* Cu nanoparticles.

Figure 6.11 Comparison of CO₂RR performance between 4H/*fcc* Au@Cu NRs and *fcc* Cu NPs.

Figure 6.12 SEM images of 4H/*fcc* Au@Cu NRs loaded on carbon paper electrode before and after the CO₂RR test.

Figure 6.13 Post-test TEM characterizations of 4H/*fcc* Au@Cu NRs.

Abbreviations

0D	Zero-dimensional
1D	One-dimensional
2D	Two-dimensional
AA	L-ascorbic acid
AFM	Atomic force microscopy
<i>bcc</i>	Body-centered cubic
BF	Bright Field
CV	Cyclic voltammetry
CO ₂ RR	Carbon Dioxide Reduction Reaction
DF	Dark Field
ECSA	Electrochemical active surface area
EDS	Energy Dispersive X-ray Spectroscopy
EOR	Ethanol Oxidation Reaction
FAOR	Formic Acid Oxidation Reaction
FE	Faradaic efficiency
FFT	Fast Fourier Transformation
<i>fcc</i>	Face-centered Cubic
<i>ftc</i>	Face-centered Tetragonal
GCE	Glassy Carbon Electrode
HAADF	High-Angle Annual Dark-Field
<i>hcp</i>	Hexagonal Close-packed
HRTEM	High Resolution Transmission Electron Microscopy
ICP-OES	Inductive Coupled Plasma-optical Emission Spectroscopy
MOR	Methanol Oxidation Reaction
NPs	Nanoparticles
NRs	Nanorods
NRBs	Nanoribbons
OAm	Oleylamine
PTFE	Polytetrafluorethylene
RHE	Reversible Hydrogen Electrode

SAED	Selected Area Electron Diffraction
SCE	Saturated Calomel Electrode
SEM	Scanning Electron Microscopy
SSs	Square Sheets
STEM	Scanning Transmission Electron Microscopy
TEM	Transmission Electron Microscopy
XAS	X-ray Absorption Structure
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction

Chapter 1

Introduction

This chapter gives the brief introduction to this thesis. First, the hypotheses and research background of this thesis are introduced. Second, based on the hypotheses, the objectives and scope of this thesis are described in details. Then, the dissertation overview for each chapter in the whole thesis is also briefly presented. Finally, based on the achieved research results, the findings and outcomes of this thesis are summarized comprehensively.

1.1 Hypothesis

Normally, noble metal materials crystalize in its thermodynamically stable phase. The crystal structure of bulk noble metal materials are very stable under ambient condition. However, noble metal nanomaterials may possess more than one type of crystal phase.

At nanoscale, the surface to volume ratio of metal nanostructures greatly increases. As a result, the total free energy of a nanostructure could be largely influenced by its surface energy. In wet-chemical synthesis, the surface energy of a nanocrystal can be well controlled. Extrinsically, the nanocrystal can be stabilized or destabilized by varying the solvent, surfactant, temperature, etc. Intrinsically, the surface energy of a nanocrystal can be tuned by different exposed crystal facets,¹ different dimensions,² different crystal types, etc. Recently, unusual crystal phases of metal nanomaterials that are different from their bulk crystal phases have been observed. With fine tuning strategies in the wet-chemical synthesis of noble metal nanostructures, it is believed that a variety of abnormal crystal structures can be obtained.

Moreover, the as-obtained unusual crystal phase of noble metal nanomaterials can be stabilized to some extent, so that a subsequent reaction or treatment is possible to further study the properties of the new crystal phase. The stability, or meta-stability, of the obtained nanostructures may also be optimized to achieve a boost of catalytic performances compared to the commercial noble metal based catalysts and their counterparts with normal crystal phase.

Epitaxial growth is one type of the seeded growth method to obtain hybrid nanomaterials. Using the noble metal nanostructures with novel crystal phase as the seed, epitaxial growth of a secondary metal layer on the surface of the noble metal nanostructures can be achieved, in which the metal shell can well adopt the novel crystal phase of the metal core. With this strategy, a library of metals that can adopt certain new crystal phase can be efficiently established. Furthermore, catalytically active metals with new crystal phase that may not be able to obtain via direct bottom-up synthesis could possibly be obtained via the epitaxial

growth.³ In addition, the synergistic effect between the different metal components and the lattice strain generated by the lattice mismatch between the core and shell may provide more active sites for further enhancement in catalytic performances.⁴

1.2 Objectives and Scope

Based on the hypotheses proposed above, the objectives and scope of this thesis are listed as follows:

- Explore and expand the crystal structure library of noble metal nanomaterials.
- Explore novel noble metal nanostructures with new crystal phase
- Study the crystal phase dependency of noble metal nanomaterials on catalytic performances.

1.3 Dissertation Overview

This thesis demonstrates the preparation of novel noble metal nanomaterials with unusual crystal phases by synthesizing Au nanostructures with unusual crystal phase and using them as the template for epitaxial growth of catalytically active noble metals, to enhance their performance in catalysis. The thesis also addresses how to use suitable and useful analytical techniques to investigate the as-synthesized noble metal nanomaterials. The potentials of the obtained noble metal nanocatalysts in electrocatalytic applications is investigated and demonstrated.

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

Chapter 2 reviews the literatures regarding the historical development, the current research progress, and the general strategies on the preparation of noble metal nanomaterials, with a special focus on the crystal phase control in wet-chemical synthesis. This chapter also

gives a detailed study on the Au-OAm system to provide a general background for the results discussed in the 4, 5, and 6, and then introduces the catalytic applications of noble metal nanomaterials, with a focus in electrocatalysis.

Chapter 3 elaborates the rational design and selection of experimental methods and target materials, the detailed preparation procedures, characterization techniques, calculation models and principles, as well as the potential applications.

Chapter 3 discusses the principles underlying the synthesis/characterization/modeling techniques employed and the methods of data analysis, including errors. An explanation of why particular methods are appropriate is required. This is an important chapter that demonstrates your understanding of the techniques and approach used.

Chapter 4 elaborates the preparation of a series of 4H/*fcc* noble metal and transition metal shells via an epitaxial growth on the surface of 4H Au NRBs under ambient condition. The developed strategy is universal and readily applicable for large-scale synthesis.

Chapter 5 demonstrates the first-time synthesis of crystal-phase-heterostructured 4H/*fcc* Au NRs, which can be readily used as the seed for the epitaxial growth of crystal-phase-heterostructured Pd. The as-obtained 4H/*fcc* Au@Pd NRs demonstrated superior mass activity in EOR, which is 6.2 and 4.9 times those of commercial Pd black and Pt/C catalysts, respectively.

Chapter 6 demonstrates the facile synthesis of crystal-phase-heterostructured 4H/*fcc* Au@Cu NRs and their superior catalytic performance in electrochemical CO₂RR, with a much higher selectivity of C₂ product and enhanced catalytic activity as compared to *fcc* Cu NPs.

Chapter 7 summarizes the whole thesis and discusses the research directions that can be further explored in the near future.

1.4 Findings and Outcomes

This research led to several novel outcomes by:

1. Developing a general method to obtain 4H phase metals via the epitaxial growth on the 4H Au nanostructure.
2. Introducing a facile synthetic method to obtain crystal-phase-heterostructured 4H/*fcc* Au NRs with high yield.
3. Realizing the epitaxial growth of noble metal Pd and transition metal Cu with 4H/*fcc* crystal phase heterostructures on 4H/*fcc* Au NRs.
4. Demonstrating the superior electrocatalytic performances of 4H/*fcc* Au@Pd NRs in EOR and 4H/*fcc* Au@Cu NRs in CO₂RR compared to their *fcc* counterparts, respectively.

References

- (1) Chen, C.; Kang, Y.; Huo, Z.; Zhu, Z.; Huang, W.; Xin, H. L.; Snyder, J. D.; Li, D.; Herron, J. A.; Mavrikakis, M. et al. Highly Crystalline Multimetallic Nanoframes with Three-Dimensional Electrocatalytic Surfaces. *Science* **2014**, *343*, 1339-1343.
- (2) Chen, Y.; Fan, Z.; Zhang, Z.; Niu, W.; Li, C.; Yang, N.; Chen, B.; Zhang, H. Two-Dimensional Metal Nanomaterials: Synthesis, Properties, and Applications. *Chem. Rev.* **2018**, *118*, 6409-6455.
- (3) Fan, Z.; Zhang, H. Template Synthesis of Noble Metal Nanocrystals with Unusual Crystal Structures and Their Catalytic Applications. *Acc. Chem. Res.* **2016**, *49*, 2841-2850.
- (4) Gilroy, K. D.; Ruditskiy, A.; Peng, H.-C.; Qin, D.; Xia, Y. Bimetallic Nanocrystals: Syntheses, Properties, and Applications. *Chem. Rev.* **2016**, *116*, 10414-10472.

Chapter 2

Literature Review

This chapter gives a comprehensive literature review on the related research and knowledge on the noble metal nanomaterials, with a focus on the historical development of noble metal nanomaterials, the wet-chemical strategies for crystal phase control, and the advancement in characterization techniques. A detailed case study will be given to understand the state-of-the-art research progress made in the wet-chemical synthesis of Au nanostructures using the Au-OAm system, which is the basis of the results presented in the later chapters. Then, the utilization of noble metal materials in catalytic applications will be summarized, with an emphasis on electrocatalysis for clean energy applications. Finally, the questions related to the thesis based on literature review are discussed.

2.1 Noble Metal Nanomaterials

2.1.1 Historical Development and Basic Information

In this context, noble metals are referred as the family of eight elements, namely Silver (Ag), Gold (Au), Palladium (Pd), Platinum (Pt), Rhodium (Rh), Iridium (Ir), Ruthenium (Ru), and Osmium (Os). Although some other literatures also include one or more elements like Copper (Cu), Mercury (Hg), and Rhenium (Re), this report follows the definition from “Lehrbuch der Anorganischen Chemie” here.¹ The relative positions in the periodic table and the electronic configurations of the eight noble metal elements are shown in Figure 2.1. Normally, noble metals are more chemically resistant to corrosion compared to other metal and non-metal materials.

7 / VIIb	8 / VIIIb	9 / VIIIb	10 / VIIIb	11 / Ib	12 / IIb
25 Mn Manganese [Ar]4s ² 3d ⁵	26 Fe Iron [Ar]4s ² 3d ⁶	27 Co Cobalt [Ar]4s ² 3d ⁷	28 Ni Nickel [Ar]4s ² 3d ⁸	29 Cu Copper [Ar]4s ¹ 3d ¹⁰	30 Zn Zinc [Ar]4s ² 3d ¹⁰
43 Tc Technetium [Kr]5s ² 4d ⁵	44 Ru Ruthenium [Kr]5s ¹ 4d ⁷	45 Rh Rhodium [Kr]5s ¹ 4d ⁸	46 Pd Palladium [Kr]4d ¹⁰	47 Ag Silver [Kr]5s ¹ 4d ¹⁰	48 Cd Cadmium [Kr]5s ² 4d ¹⁰
75 Re Rhenium [Xe]6s ² 4f ¹⁴ 5d ⁵	76 Os Osmium [Xe]6s ² 4f ¹⁴ 5d ⁶	77 Ir Iridium [Xe]6s ² 4f ¹⁴ 5d ⁶	78 Pt Platinum [Xe]6s ¹ 4f ¹⁴ 5d ⁹	79 Au Gold [Xe]6s ¹ 4f ¹⁴ 5d ¹⁰	80 Hg Mercury [Xe]6s ² 4f ¹⁴ 5d ¹⁰

Figure 2.1 The eight elements of noble metal in the periodic table.

The development of noble metal nanomaterials dated from the very beginning of nanoscience. Noble metal nanomaterials, especially gold and silver nanomaterials, has been playing pioneering part in the realization and understanding of nanosized materials. In 4th-century, on the Lycurgus Cup made from Roman glass, people observed the different color appearance of the cup when the light source changes from inside the cup to outside. This phenomenon reveals a classic property of metal nanoparticle colloid, where the local surface Plasmon resonance effect influence the observed color of the particles. At that time, the implementation of Au and Ag nanomaterials was not well controlled. In fact, the discovery of such properties was likely due to an unexpected contamination of Au and Ag dusts.

The modern society knows noble metals more from jewelry and chemistry industries. The word “noble” tells the importance and rareness of such type of materials. Although noble metals are superior catalysts in a wide range of industrial reactions, the implementation of noble metals in the chemical industry must be carefully designed to minimize the usage of noble metals and reduce the cost. Many strategies have been investigated to improve the utilization efficiency of noble metal nanocatalysts, including increasing their surface-to-volume ratio and improving their intrinsic catalytic activities. Therefore, it is of particular importance to understand the structure-property relationship of noble metal nanomaterials, so that well-controlled noble metal nanostructures can be synthesized with optimal catalytic performance.

While ancient workers breakdown bulk noble metals into nanosize, modern synthetic chemical methods build up nanostructures from molecular level precursors. The positive reduction potentials of noble metal precursors (Table 2.1) make bottom-up methods preferable for designing noble metal nanostructures. Generally, all noble metal ions can be easily reduced to metallic states under room temperature. In a typical wet-chemical approach, noble metal salt is dissolved in a solution containing surface ligands and reducing agents, and is controllably reduced to grow into desired nanostructures. The competitive mechanism between the stabilization effect from surface ligand and the reducing capability of the reducing agent is carefully tuned to realize a controlled growth rate of the noble metal nanocrystals.² Many additive species, such as polymeric molecules, small ions and gas molecules, have also been introduced to aid in the controlled synthesis.³

Table 2.1 Reduction potentials of half-reactions of selected metals.⁴

Metal	Reduction reaction	E_0 (V vs SHE)
Au	$Au^{3+} + 3e^- \rightarrow Au$	1.50
Pt	$Pt^{2+} + 2e^- \rightarrow Pt$	1.18
Ir	$Ir^{2+} + 2e^- \rightarrow Ir$	1.16
Pd	$Pd^{2+} + 2e^- \rightarrow Pd$	0.95
Rh	$Rh^{2+} + 2e^- \rightarrow Rh$	0.76
Ag	$Ag^+ + e^- \rightarrow Ag$	0.80
Ru	$Ru^{2+} + 2e^- \rightarrow Ru$	0.45
Cu	$Cu^{2+} + 2e^- \rightarrow Cu$	0.34
Ni	$Ni^{2+} + 2e^- \rightarrow Ni$	-0.25
Co	$Co^{2+} + 2e^- \rightarrow Co$	-0.28
Fe	$Fe^{2+} + 2e^- \rightarrow Fe$	-0.44

Noble metals are well-crystallized materials. Noble metal atoms, which are often modeled as spherical hard balls, are packed densely by the strong and non-directional metallic bonds. The different ways of ordered packing are recognized as different crystal phases (or crystal structures). The thermodynamically stable crystal phases of noble metals in bulk are summarized in Table 2.2. All noble metals adopt the most closely packed crystal structures, namely either cubic close-packing (*ccp*) or hexagonal close-packing (*hcp*). Note that cubic close-packing (*ccp*) is more often known as the face-centered cubic (*fcc*) crystal structure.

Table 2.2 Crystal structures of noble metals in bulk.

Noble metal	Au	Ag	Pt	Pd	Ir	Rh	Os	Ru
Crystal structure in bulk	<i>fcc</i>						<i>hcp</i>	
Unit Cell Structure

2.1.2 General Strategies in Wet-chemical Synthesis of Metal Nanomaterials

Since the citrate reduction method for colloidal gold nanoparticles was developed in the 1950s,^{5,6} scientists have put great efforts in controlling the parameters of colloidal

nanocrystals via wet-chemical approach and revealing their structure-property dependence. There are three stages in the formation of colloidal nanostructures, namely nucleation, growth and coarsening/agglomeration. To fine tune the physiochemical properties of noble metal nanomaterials, numerous synthetic methods have been developed to control their shapes,^{2,7-10} sizes,¹¹ and composition.¹² In solution-based synthesis, many factors could affect the formation of final products by interfering one or more of the three stages.^{2,4} These factors include type of metal precursor,¹³ surface ligand,¹⁴ solvent,¹⁵ reducing agent,¹⁶ as well as reaction temperature,¹⁷ reaction time,¹⁸ reaction atmosphere,¹⁹ etc. The classification of synthetic methods for noble metal materials can be based on one of or a combination of these factors. For example, in terms of the growth directing species, the synthetic methods for noble metal nanostructures can be categorized into (i) surfactant/molecule directed growth,^{20,21} (ii) template-assisted growth,²² (iii) seed-mediated growth,²³ and (iv) external energy induced growth.²⁴⁻²⁶ The vast library of synthetic methods will not be introduced in details as they are not within the scope of this report. Instead, one type of synthetic method for Au nanomaterials is adequately described here.

2.1.2.1 Case Study on the Au-Oleylamine System

In May 2008, three reports were published almost simultaneously by Xia's, Yang's, and Sun's group, reporting the preparation of ultrathin Au nanowires using OAm as the surface ligand.²⁷⁻²⁹ Interestingly, they used different strategy to promote the formation of Au nanowires and obtained very similar morphologies. Xia's group introduced Ag nanoparticles in the mixture of [(OAm)AuCl] and claimed that Ag nanoparticles can alter the reduction rate of Au^I to Au⁰ and direct the formation of 1D Au nanowires.²⁹ The yield of Au nanowires, apart from the nanoparticle byproduct, was increased from ~20 % to ~70 % (Figure 2.2A-D). In the work from Sun et al, the formation of ultrathin Au nanowires was realized in the homogenous mixture of HAuCl₄, OAm, and OA.²⁷ The diameter of the nanowires can be tuned between 3 nm to 9 nm by controlling the OAm/OA ratio (Figure 2.2E, F). Yang et al reported a third approach to synthesize Au nanowires by simply leaving the sonicated mixture of HAuCl₄ and OAm in the room temperature for days. The aging

process of OAm will lead to the gradual reduction of $\text{Au}^{3+} \rightarrow \text{Au}^+ \rightarrow \text{Au}$ and formation of single crystal Au nanowires (Figure 2.2G-I).

Figure 2.2 Preparation of ultrathin Au nanowires with oleylamine as surface ligand, the comparison of three works. (A-B) TEM images of 3 nm and 9 nm Au nanowires synthesized by Sun's group, and corresponding (C-D) high resolution TEM images.²⁷ (E-F) Au nanowires obtained by Xia et al using Ag nanoparticles as aiding agents, with an average diameter of ~ 2 nm.²⁹ (G) Low and (H-I) high magnification images of ultrathin Au nanowires reported by Yang et al.²⁸

Figure 2.3 Formation mechanism of 1D Au nanowires.

Although different strategies are applied in the three reports, all of them emphasized the important role of OAm in the formation of ultrathin, ultralong, and single-crystal Au nanowires. OAm is an aurophilic long-chain molecule that can act as a surfactant, solvent, and reducing agent to form various nanostructures.³⁰ In the case of Au, the self-assembly of OAm-Au complex directly results in the 1D architecture. As described in Figure 2.3, during the step-by-step reduction of Au, OAm molecules form wire-shape micelles and cap the $\text{Au}^{[1+]}$ species inside the micelles. The complete reduction of Au into single crystal $\text{Au}^{[0]}$ nanowire is then achieved by an aging process.

Importantly, based on the HRTEM images, X-ray diffraction patterns, and other characterization techniques, all the aforementioned works claimed the formation of *fcc* Au nanowires, with the (111) planes perpendicular to the wire axis. Besides the thermodynamically stable *fcc* crystal phase, noble metal nanomaterials with unusual metastable crystal phases have been realized via wet-chemical synthesis recently,³¹⁻³⁴ leading to intriguing findings of crystal phase-dependent catalytic properties.^{35,36} For instance, it is found that under slightly different synthesis conditions, Au nanostructures with hexagonal-closely packed (2H type, Figure 2.4A,B) and 4H crystal phases (Figure 2.4C) can be achieved.^{21,22} Moreover, the crystal structure transformation of Au SSs from 2H to *fcc* and Au NRBs from 4H to *fcc* have been realized under mild conditions, by surface modification of the obtained 2H and 4H Au structures.^{21,37} Specifically, the formation of 4H Au NRBs is believed to be promoted by the addition of 1,2-dichloropropane, while the formation of 2H Au SSs is aided by the graphene template.

Figure 2.4 Preparation of 4H Au NRBs and 2H Au SSs. (A) TEM image of 4H Au NRBs and (B) the unit cell model and crystallographic model of 4H Au crystal structure.²¹ (C) TEM image of AuSSs on GO surface. (Inset: simulated crystal structural models for a typical AuSS.²² The black dots in (A) and (C) are nanoparticle byproducts.

Notably, theoretical calculations suggest that the energy difference between 4H and *fcc* phases of Au nanostructures is relatively small.^{38,39} Therefore, it is thermodynamically feasible to obtain Au nanostructures in polymorphs in a one-step synthesis method.⁴⁰ The

example of Au nanostructure polymorph has greatly inspired the exploration of novel crystal phases of noble metals.

2.1.3 Crystal Phase Control in Metal Nanomaterials

2.1.3.1 The Importance of Crystal Phase

Crystal structure of materials can have great impact on their physicochemical properties. The most famous example would be the two allotropes of carbon, namely diamond and graphite. The cubic diamond is super-hard, transparent, and an insulator, while hexagonal graphite is soft, opaque, and conductive. In the case of noble metals, nanosized noble metals have demonstrated distinctive physical and chemical properties compared to their bulk counterparts. Among the various parameters, including shape, size, composition and architecture, crystal phase has emerged as another important parameter to introduce fascinating properties of noble metal nanocrystals.^{31,32} Some of the representative crystal phases observed in noble metal nanomaterials are summarized in Figure 2.5.

Figure 2.5 Crystal phase-controlled synthesis of noble metal nanomaterials.³¹

Conventionally, the crystal phase control over materials have been achieved under high pressure or high temperature.^{34,41} However, these extreme conditions are not suitable to produce large-scale, free-standing noble metal nanocatalysts, which is essential for practical applications in catalysis. At nanoscale, the surface energy of a nanocrystal often dominates the total systemic energy.⁴² Therefore, colloidal synthesis using protective surface ligands is often applied to produce stable and well-dispersed nanocrystals.

Meanwhile, direct synthesis of noble metal nanomaterials with novel crystal phase via a bottom-up approach is still difficult, and it is often achieved by a long-term screening of “phase-directing” agents. To date, strategies of phase control over solution-based noble metal nanomaterials has been focusing on either reduction of size, or surface modification of pre-synthesized novel-phase nanostructures via ligand exchange or metal coating.⁴³

2.1.3.2 Crystal Phase Based Epitaxial Growth

One promising strategy to obtain a library of materials with new crystal phases is to realize their epitaxial growth on a crystal phase template. Figure 2.6a demonstrates the simple principle of epitaxial growth. Specifically, a pre-synthesized noble metal nanostructure with either unusual or crystal phase is used as the template to induce the lattice-matching growth of unusual crystal structures of other noble metals. This strategy is straightforward and general to obtain a variety of other metals, which may not be easily obtained from direct bottom-up synthesis. The relatively small lattice mismatch between the noble metals (Figure 2.6b) makes it feasible to grow a layer of another metal with certain thickness that can follow the exact crystal lattice of the template metal, i.e. achieve an epitaxial growth. For example, the crystal phase-based template growth can be applied to the polymorphic Au substrates, resulting in polymorphic bimetallic core-shell nanostructures.³³

Figure 2.6 Template synthesis of noble metal nanocrystals with unusual crystal structures. (a) Principle of the template synthesis. (b) The crystal lattice constant of noble metal crystals in bulk.³³

With the grown shell fully adopting the heterostructured crystal phase of core, the polymorphic bimetallic nanostructures could combine advantages from both the novel crystal phase and the synergistic effect between different metal components.⁴⁴

2.2 Characterization Techniques for Noble Metal Nanomaterials

The development of characterization techniques has been one of the major driving forces pushing the advancement of nanoscience. In this section, some important characterization tools and techniques commonly used on metal nanomaterials are briefly introduced. Some of the techniques, such as AFM, SEM, and TEM, are often used to determine the thickness, size, shape, and crystal structure of nano-sized metals, while some other techniques such as EDS, XPS, and XAS are applied to give chemical information like composition, chemical state, and chemical environment. Case studies will be given for each technique with highlights of its contribution to determining the various features of metal nanomaterials.

2.2.1 Atomic Force Microscopy

AFM, a high-resolution scanning probe microscopy technique, can detect the topography information of samples by measuring the atomic force between the surface atoms of samples and a cantilever tip.⁴⁵ Theoretically, AFM can detect topological variations with a vertical resolution of 0.1 nm and a lateral resolution of 3 nm.⁴⁶ In the case of noble metal nanomaterials, AFM is able to provide direct evidences on the thickness of ultrathin nanosheets and 3D morphology information of complicated 2D nanostructures. Figure 2.7 demonstrates two typical cases in which AFM played critical roles in determining sample morphologies. In Figure 2.7a, an AFM image of a single-atom-thick Rh nanosheet was shown.⁴⁷ The height profiles taken at three edge regions revealed that the thickness of the nanosheet is *ca.* 0.4 nm. As the atomic radius of Rh is 0.173 nm, the nanosheet was deduced to possess only single atomic layer of Rh. In another work, the thickness of a Hanoi tower-like architecture composed of Pd nanosheets was measured with AFM.⁴⁸ A 3D AFM topography image of the architecture is shown in Figure 2.7b, exhibiting a direct visualization of the nanosheet morphology. The height profile across several layers shown in Figure 2.7c revealed that the thickness of each Pd nanosheet layer varied from 0.26 to 1.1 nm.

Figure 2.7 Case studies of AFM characterizations on noble metal nanomaterials. (a) AFM image and the corresponding height profiles of a bare Rh nanosheet. (b) AFM 3D topography and (c) height profile of multilayer Pd nanosheets.

2.2.2 Scanning Electron Microscopy

SEM is a type of electron microscopy technique that scans the sample surface with a focused electron beam and collects the various signals generated from the interactions between electron beam and sample atoms. The most frequently used SEM mode, secondary electron imaging (SEI), which detects the secondary electrons generated during the inelastic scattering of incident electrons by the sample atoms and produces an image based on the intensities of the collected secondary electrons. SEM, or SEI, has been widely used to characterize noble metal nanostructures, especially to obtain microscale image and topological information, such as cross-section thickness. Three typical examples are shown in Figure 2.8. The high-yield and entangled flexible Au nanobelts were characterized with low-magnification SEM (Figure 2.8a), while their thickness of ~ 10 nm and tip morphology were clearly observed in the high-magnification SEM images (Figure 2.8b,c).⁴⁹ Figure 2.8d

is the low-magnification SEM image of a hexagonal multi-layered Au spirangle, showing a completely loop-shaped, star-like geometry.⁵⁰ Figure 2.8e demonstrates the SEM image of bilayer Ag-Al metal plates after repeated mechanical compression and folding, from which ultrathin Ag nanosheets (Figure 2.8f) could be obtained by simply etching away the sacrificial Al layer.⁵¹ In this work, SEM is a critical tool to examine the thickness reduction during multiple times of compression and the morphology change after etching by viewing directly from the cross sections.

Figure 2.8 Case studies of SEM characterizations on noble metal nanomaterials. (a) Low-magnification and (b,c) high-magnification SEM images of Au nanobelts. (d) SEM image of a typical Au spirangle, showing the unique multi-layered structure. (e) Cross-sectional SEM image of Ag-Al metal plate with the folding and calendaring process repeated for 20 times. (f) Cross-sectional SEM images of the obtained Ag nanosheet film after etching away Al followed by a suction filtration process.

2.2.3 Transmission Electron Microscopy

As the most frequently employed electron microscopy technique, TEM is often used to determine the size, shape, crystal structure, and dispersity of metal nanostructures.

Different from SEM, TEM uses a high-energy electron beam that is able to penetrate through samples. Therefore, TEM is usually used to observe the morphologies of relatively thin metallic nanostructures. Particularly, HRTEM imaging mode allows the direct observation of atomic level structures and defects of sample, giving critical crystallographic information like lattice distance and atom arrangement. Besides the normal functions, TEM images can also be used to estimate the thickness of ultrathin metal nanosheets by measuring the width of the folded edges. Figure 2.9a,d show two typical cases where ~2.4 nm-thick Au square sheets and ~3.6 nm-thick Au nanosheets were measured.^{22,52} As shown in Figure 2.9b,c, when an ultrathin nanosheet folds on itself, the top view of the folded edge will exhibit a darker strip, the width of which corresponds to its thickness. This strategy can effectively estimate the “naked” thickness of metal nanomaterials without the influence from surface capping ligands. Meanwhile, TEM images are often accompanied with corresponding SAED pattern, which can reveal crystallographic information of samples in a selected region. A typical SAED pattern can determine the crystallinity, crystal phase, and crystal orientation of metal nanomaterials. In particular, for ultrathin metal nanostructures, the quantitative intensity profile of the diffracted pattern can be used to estimate the number of atomic layers. Figure 2.9e shows a typical example of an SAED pattern of an individual single Rh nanosheet. The intensities of the diffracted points observed from a single nanosheet were compared quantitatively with simulated diffraction patterns of Rh nanosheets with different number of atomic layers and stacking sequences (Figure 2.9f-i).⁴⁷ By comparing the intensity profiles of (10) and (11) directions between the experimental SAED pattern and simulated ones, only single-layered Rh matched the experimentally observed intensity profile.

Figure 2.9 Case studies of TEM characterizations on noble metal nanomaterials. (a) TEM image of a folded Au square sheet with an average width of the folded edges of ~ 2.4 nm. (b) Schematic illustration showing how the Au square sheet folded in (a). (c) The section view of line S-S' in (b), showing how the thickness can be measured from the top view. (d) TEM image and (inset) HRTEM image taken at the folded edge of a typical Au nanosheet where the thickness was measured to be 3.6 nm. (e) SAED pattern and corresponding intensity profiles of the ultrathin Rh nanosheets. (f-i) Simulated SAED pattern and corresponding intensity profiles of Rh nanosheets with (f) single layer, (g) double layer, (h) triple layers with an *hcp* ABA stacking, and (i) triple layers in an *fcc* ABC stacking, respectively.

Importantly, the spatial resolution of conventional TEM is still far from its theoretical limit, *i.e.* the wavelength of the incident electrons. Recently, spherical aberration corrected (C_s -corrected) TEM has become increasingly popular due to its sub- $\text{\AA}$ resolution feature, and have been widely used in characterizing atomic level lattice structure and defects.⁵³ For heterostructured noble metal nanomaterials, C_s -corrected TEM is critically helpful in visualizing the atomic arrangements at the interfaces and thus understanding the crystallographic feature of the heterostructures.

2.2.4 X-ray Diffraction

XRD is a non-destructive technique commonly used to provide crystallographic information of crystalline materials. XRD technique records the intensity of scattered X-ray beams generated by emitting a filtered X-ray beam with known wavelength on the sample surface at different incident angles. A plot of the incident angle between X-ray beam and detector (2θ) vs. detected X-ray intensity is generally obtained for subsequent data analysis. Based on the crystal structure, size, composition, and orientation of the noble metal nanomaterials, characteristic sets of peaks can be observed. For example, in the XRD spectrum of 4H Au nanoribbons, the characteristic peaks at $2\theta = 36.2^\circ$, 37.4° , 40.9° and 79.7° were observed, corresponding to the $(100)_{4H}$, $(101)_{4H}$, $(102)_{4H}$ and $(202)_{4H}$ planes of 4H Au, respectively, confirming the 4H hexagonal structure of the obtained Au nanoribbons (Figure 2.10a,b).⁵⁴ Due to the preferred orientation of $[110]_{4H}$ for 4H Au nanoribbons deposited on the substrate, the XRD spectra of the 4H Au nanoribbons at different scan mode exhibited different peak densities. As a result, the peak at $2\theta = 64.8^\circ$ relative intensity obtained in the 2θ mode is much weaker compared to that in the $\theta/2\theta$ model. Significantly, XRD not only can provide qualitative information like type of crystal structure and degree of crystallinity, but also support quantitative analysis like estimating chemical composition and ratio of different crystal phases. Unlike AFM, SEM, and TEM, XRD measures samples in a large scale (millimeter/centimeter scale), and only gathers the accumulated signals from a considerable amount of metal nanomaterials. Therefore, XRD is particularly effective in identifying the purity of samples with known crystal phase, or the existence of trace amount of samples with unknown crystal phase.

2.2.5 Energy-Dispersive X-ray Spectroscopy

EDS, also called EDX, is an elemental analysis technique commonly used to determine elemental composition and distribution in nanomaterials. EDS is often coupled with SEM and TEM systems, in which it harvests the characteristic X-ray signals generated during the e-beam irradiation on nanomaterials. The interaction between the incident e-beam and

atoms can knock out an inner shell electron from the nanomaterials. When electrons migrate from higher states to the vacant site, the energy difference is released in the form of X-ray, which is unique for each element. The EDS spectrum is plotted by recording the X-ray intensities against different X-ray energy, and used to identify the composition and relative quantity of each element in the nanomaterials. Usually, with the corresponding SEM or TEM images of nanomaterials, EDS elemental analysis can be conducted on a selected region of samples in various forms, such as a linear scan of element, an elemental mapping of selected area, or a simple spectrum showing the atomic/mass ratio of different elements. As a typical example, Figure 2.10c-h demonstrate the different EDS modes applied to the elemental analysis of 4H/*fcc* Au@PdAg nanoribbons, giving the Au/Ag/Pd ratios and elemental distributions in the core-shell nanoribbons.⁵⁵

2.2.6 X-ray Photoelectron Spectroscopy

XPS is a surface characterization technique that irradiate sample surface with monochromatic X-ray beam to probe the chemical state and chemical composition of certain elements. In a typical XPS measurement, the incident X-ray beam induces the emission of photoelectrons from the surface atoms, and the intensities of the emitted photoelectrons are recorded and plotted against the incident X-ray energy. As the energy required for photoelectrons to escape from the sample atoms, *i.e.* the binding energy, is dependent on both the element and its chemical states, the peak shapes and positions in XPS spectrum can be used to determine the chemical states or change of electronic states of elements. For noble metal nanomaterials, XPS is often used to determine the metallic states of metals and to detect the change of electronic structures of certain metals in alloys or heterostructures. For example, Figure 2.10i-k show the XPS spectra of Pd in pure Pd nanosheets and the XPS spectra of Pd and Ru in Pd@Ru nanosheets, respectively.⁵⁶ While Figure 2.10k proved the metallic states of the Ru sub-monolayer, Figure 2.10i,j demonstrated a positive peak shift of Pd 3d from Pd nanosheets to Pd@Ru nanosheets. These XPS results indicated that the coating of metallic Ru layer had changed the electronic structure of Pd.

Figure 2.10 Case studies of XRD, EDS, and XPS characterizations on noble metal nanomaterials. (a,b) XRD patterns of 4H Au nanoribbons collected in the $\theta/2\theta$ and 2θ modes, respectively. (c) HAADF-STEM image and (d-f) STEM-EDS element mappings of a single 4H/fcc trimetallic Au@PdAg nanoribbon. (g) STEM-EDS spectrum of 4H/fcc Au@PdAg nanoribbons, showing the average atomic ratio of Au/Ag/Pd to be around 1.00/1.94/1.06. (h) STEM-EDS line scanning profile of a single 4H/fcc Au@PdAg nanoribbon. Inset: HAADF-STEM image of the corresponding Au@PdAg nanoribbon. (i) Pd 3d XPS spectrum of Pd nanosheets. (j) Pd 3d and (k) Ru 3p XPS spectra of Pd@Ru nanosheets.

2.2.7 X-ray Absorption Structure Analysis

XAS is a powerful technique to determine the local electronic structure of materials by measuring the X-ray absorption coefficient of a material as a function of the energy of incident X-ray. XAS-related analysis is particularly persuasive in determining the coordination environment of metal element in the ultra-small metal nanostructures or metal nanostructure based hybrids. XAS spectra are usually obtained using X-ray sources from synchrotron radiation to achieve desired X-ray intensity. Benefiting from the synchrotron X-ray sources with fine-tuned energy, the detection limit of element concentration is down to ppm level. The XAS analysis of solid-state nanomaterials is usually divided in different energy regions. X-ray absorption fine structure (XAFS), for example, is a specific structure observed in XAS that can be used to analyze the coordination environment of elements in samples. As a typical example, in the identification of single layer Rh nanosheets, XAFS was used to determine the coordination environment of Rh (Figure 2.11a-d).⁴⁷ The extended XAFS (EXAFS) spectra (Figure 2.11a) and k-space spectra (Figure 2.11b) of the PVP-capped Rh nanoparticles and the PVP-capped Rh nanosheets showed closely resembled pattern compared to that of Rh foil, indicating that Rh in the nanoparticles and nanosheets have identical chemical states as the Rh in the Rh foil. However, the reduced oscillations of PVP-capped Rh nanosheets and PVP-capped Rh nanoparticles in the k-space spectra (Figure 2.11b) showed that their Rh atoms had different coordination environment. This result was more clearly observed in the Fourier-transformed EXAFS spectra (Figure 2.11c), in which the peak intensities at 2.37 Å, representing the first shell Rh-Rh scattering, decreased in the order Rh foil > PVP-capped Rh nanoparticles >> PVP-capped Rh nanosheets. Curve fittings could then be carried out to obtain the coordination numbers (CNs) and Rh-Rh bond lengths in the three samples. CN of Rh in Rh foil, Rh nanoparticles, and Rh-nanosheets were 12, ~10.4, and ~6.4, with similar average bond lengths of ~2.687 Å, ~2.687 Å, and ~2.692 Å, respectively. The similar Rh-Rh bond lengths suggest that all Rh atoms were closely packed in all three samples, while the CN of ~6.4 in Rh nanosheet indicated that the Rh nanosheet is most likely to be single layer, to match the theoretical CN value of 6 for single layer Rh nanosheet (Figure 2.11d). In another study of ultrathin Au nanosheet, XAFS was used to determine the coordination environment of Au in Au/LDH hybrid.⁵⁷ The Fourier-transformed spectra of filtered k^3 -weighted Au L-edge EXAFS spectra and filtered k^3 -weighted Au L-edge EXAFS spectra of Au foil, Au/LDH

hybrid and SiO₂-supported Au nanoparticles are shown in Figure 2.11e,f, respectively. The less intense peak of Au/LDH compared to that in Au foil and SiO₂ supported Au nanoparticles indicated that the Au-Au first shell coordination in Au/LDH hybrid was different from the others. The CN of Au and bond length of Au-Au in Au foil, Au/LDH hybrid, and SiO₂ supported Au nanoparticles, derived from the curve fitting, were ~6.9 and ~2.80 Å, ~11.2 and 2.85 Å, 10.1 and 2.86 Å, respectively. The lower CN and slightly shorter Au-Au bond length of Au in Au/LDH provided evidences of the atomic thickness of 2D Au nanostructures in the Au/LDH hybrid.

Figure 2.11 Case studies of XAS characterizations on noble metal nanomaterials. (a) Normalized Rh K-edge EXAFS spectra, (b) k^3 -weighted Rh K-edge k-space oscillations, and (c)

Fourier-transformed spectra of k^3 -weighted Rh K-edge EXAFS (solid lines) and corresponding curve-fitting results (dotted lines) of Rh foil, PVP-capped Rh nanoparticles, and PVP-capped Rh nanosheets. (d) Schematic illustration of the coordination states with coordination number of Rh nanosheets in single, double, triple, and multiple layered structure exposing Rh (111) crystal plane. (e) Fourier-transformed spectra of $k^3 \cdot \chi(k)$ -filtered R-space EXAFS spectra (red dashed lines: curve-fitting results). (f) Filtered $k^3 \cdot \chi(k)$ -filtered EXAFS spectra (red dotted lines: curve-fitting results).

2.3 Catalytic Applications

The unique physiochemical properties of noble metal nanomaterials make them irreplaceable catalysts in a wide range reactions such as electrochemical reactions, photocatalytic reactions, and heterogeneous reactions.⁵⁸⁻⁶⁰ Among the promising applications of noble metal nanomaterials, the electrochemical catalytic reactions, including organic reactions,⁵⁶ hydrogen evolution reaction,³⁵ oxygen reduction reaction,² EOR,^{61,62} FAOR,²⁰ and CO₂RR⁶³⁻⁶⁵, have been intensively investigated. To fine-tune the catalytic properties of noble metal nanomaterials, numerous synthetic methods have been developed to control the shape,^{2,7} size,¹¹ and architecture.¹² However, the aforementioned studies are based on the thermodynamically stable crystal phase of noble metals. The crystal phase-dependent study of the electrocatalytic performance of noble metal nanocatalysts is still in an infant stage.

The electrocatalytic performance of metal nanocatalysts is highly dependent on their surface properties such as surface atom arrangement and ligand environment.^{66,67} To date, the current crystal phase-controlled synthesis of noble metal-based nanocatalysts is still difficult to produce perfect models, which hinders the investigation on how the novel polymorphs/allotropes lead to novel electrocatalytic properties towards key reactions in this domain and beyond. For example, one of the most important applications of noble metal nanomaterials in electrocatalysis is the low-temperature fuel cell, which is a promising power source for next-generation automotive vehicles and portable electronic devices. Unfortunately, commercial electrocatalysts still suffer from both low catalytic activity and poor durability.^{68,69}

As a typical example, systematically studies on the electrocatalytic performances of Pt/Pd-based electrocatalysts with different sizes, compositions and shapes towards the methanol oxidation reaction,^{70,71} oxygen reduction reaction,^{72,73} FAOR⁷⁴ and glycerol oxidation reaction⁷⁵ have been an intensive research direction in decades. Notably, these Pt/Pd-based electrocatalysts often exhibit superior performance compared to the commercial Pt/C and Pd/C catalysts. The electrocatalytic oxidation of various liquids, such as methanol and ethanol, represents a critical anodic reaction in the proton exchange membrane fuel cells. Although noble metal nanomaterials stands as the best candidates for the reactions, their implementation is hindered by the relatively low stability during the cycling, in which they may be deactivated by the reaction intermediates such as CO radicals.⁷⁶ A recent report showed that with rational design of the composition and structure, the catalytic activity and durability of Pt-based nanocatalysts can be enhanced.⁷⁶ Specifically, when the crystal phase of the FePtAu NPs changes from the disordered *fcc* to ordered *fct* phases, the durability in FAOR can be greatly promoted (Figure 2.12a,b). The improved stability of the *fct* FePtAu NPs was probably caused by the synergistic effect from the formation of ordered *fct* phase and the doping effect from the Au atoms. Besides FAOR, the phase-dependent behaviour of FePtAu NPs also appeared in MOR, in which the ordered *fct* FePtAu NPs demonstrated superior tolerance to CO compared to the commercial Pt, ordered *fct* FePt, and disordered *fcc* FePtAu NPs (Figure 2.12c).

Figure 2.12 Phase-dependent electrocatalytic performances of noble metal nanomaterials.³¹ (a) FAOR performances of $\text{Fe}_{43}\text{Pt}_{37}\text{Au}_{20}$ NPs obtained at different annealing temperatures. (b) Stability test of ordered *fct* FePtAu NPs for FAOR. (c) CV curves of the ordered *fct* $\text{Fe}_{43}\text{Pt}_{37}\text{Au}_{20}$, disordered *fcc* $\text{Fe}_{43}\text{Pt}_{37}\text{Au}_{20}$, ordered *fct* $\text{Fe}_{55}\text{Pt}_{45}$ and commercial Pt NPs for MOR. (d) The 50% conversion-temperature of CO to CO_2 conversion for *fcc* and *hcp* Ru NPs as a function of particle size.

Another important reaction is the oxidation of CO, which is a widely used catalytic reaction in industries.⁷⁷ For this typical reaction, Ru nanocatalysts stand out as one of most promising candidates due to their excellent intrinsic activity.⁷⁸ Interestingly, a very recent report suggest that the crystal phase of Ru NPs can greatly alter their behavior in the catalytic CO oxidation reaction.⁷⁸ When the Ru NPs adopt the uncommon *fcc* crystal structure, the catalytic activity of CO oxidation increases with the particle size, while when they adopt the common *hcp* crystal structure, their catalytic activity decreases with the particle size (Figure 2.12d). Specifically, at particle size less than 3 nm, *hcp* Ru NPs are more catalytically active compared to the *fcc* Ru NPs; at particle size bigger than 3 nm, *hcp* Ru NPs exhibit lower catalytic activity than the *fcc* Ru NPs.

Particularly, this thesis focuses on two electrocatalytic reactions, i.e., ethanol oxidation reaction and CO_2 reduction reaction.

EOR. Electrochemical ethanol oxidation reaction converts ethanol to acetic acid under applied potential. As an important type of half reaction in alkaline direct alcohol fuel cells, EOR has several advantages compared to other fuel cells, such as the ease of fuel storage and transportation, the relatively high mass energy density, and the wide range of catalyst candidates. Metal nanomaterials, such as Pd- and Pt-based nanocatalysts, are one of the most promising candidates for ethanol oxidation, due to their high catalytic activity and relatively good durability.⁷⁹

CO₂RR. CO₂ reduction reaction converts the greenhouse gas, CO₂, to fuels or value-added products such as CO, CH₄ and C₂H₄. It is considered a prospective pathway for the recycling of carbon resource and the generation of sustainable fuels through clean and economical chemical processes. In particular, transition metal-based nanocatalysts are known to produce a variety of CO₂RR products at different test conditions.⁸⁰ Different structural parameters, such as the size, shape, and oxidation state, of various metal nanostructures have been investigated toward efficient and selective electrocatalytic CO₂RR.⁸⁰

2.4 Questions to Answer Based on Literature

As discussed in the aforementioned literature review, great research progress has been made on the preparation, characterization and applications of noble metal nanomaterials. However, except some very recent reports, most of the studies focus on the noble metal nanomaterials with the common crystal phase, i.e., the same crystal phase as their bulk counterparts. Taking into account that the crystal phase may great affect the physicochemical behavior of noble metal nanomaterials, there are plenty of questions remaining unanswered and requiring deeper investigations.

First, more novel allotropes of noble metal nanomaterials, including Au, and catalytically active metals such as Pd are yet to be explored. This concept should also be further extended to transition metals such as Cu. The expansion of the library of metal

nanomaterials with novel crystal phases is fundamentally important. Yet a general and low-cost method is desired.

Second, the relationship between electrocatalytic properties and crystal structures should be established. A recent report demonstrated the superior catalytic activity of polytypic 4H/*fcc* Au@PdAg core-shell NRBs towards the hydrogen evolution reaction compared to the commercial Pd/C catalysts, which is even competitive with commercial Pt/C catalyst (Figure 2.13).⁴⁴

Figure 2.13 The superior catalytic activity of polytypic 4H/*fcc* Au@PdAg core-shell NRBs towards the hydrogen evolution reaction. (a) Polarization curves of 4H/*fcc* trimetallic Au@PdAg NRBs, Pd black and Pt black. The current density is denoted as “ J ”. (b) Onset potentials and overpotentials at current density of 10.0 mA/cm² of 4H/*fcc* trimetallic Au@PdAg NRBs, Pd black, and Pt black.

Inspired by this work, further investigation of novel allotropes of other noble metal nanomaterials, especially for the bi-/multi-metallic nanostructures, in various electrocatalytic reactions should be carried out. Note that the synergistic effect of different metal elements will also improve the electrocatalytic activity and stability of these nanomaterials.⁷⁶

References

- (1) A. Holleman, N. W. *Lehrbuch Der Anorganischen Chemie*; 33 ed., 1985.

- (2) Xia, Y.; Xiong, Y.; Lim, B.; Skrabalak, S. E. Shape-Controlled Synthesis of Metal Nanocrystals: Simple Chemistry Meets Complex Physics? *Angew. Chem. Int. Ed.* **2009**, *48*, 60-103.
- (3) Chen, Y.; Fan, Z.; Zhang, Z.; Niu, W.; Li, C.; Yang, N.; Chen, B.; Zhang, H. Two-Dimensional Metal Nanomaterials: Synthesis, Properties, and Applications. *Chem. Rev.* **2018**, *118*, 6409-6455.
- (4) Gilroy, K. D.; Ruditskiy, A.; Peng, H.-C.; Qin, D.; Xia, Y. Bimetallic Nanocrystals: Syntheses, Properties, and Applications. *Chem. Rev.* **2016**, *116*, 10414-10472.
- (5) Turkevich, J.; Stevenson, P. C.; Hillier, J. A Study of the Nucleation and Growth Processes in the Synthesis of Colloidal Gold. *Discuss. Faraday Soc.* **1951**, *11*, 55-75.
- (6) Turkevich, J.; Garton, G.; Stevenson, P. C. The Color of Colloidal Gold. *J. Colloid Sci.* **1954**, *9*, 26-35.
- (7) Sun, Y.; Xia, Y. Shape-Controlled Synthesis of Gold and Silver Nanoparticles. *Science* **2002**, *298*, 2176-2179.
- (8) Jana, N. R.; Gearheart, L.; Murphy, C. J. Wet Chemical Synthesis of High Aspect Ratio Cylindrical Gold Nanorods. *J. Phys. Chem. B* **2001**, *105*, 4065-4067.
- (9) Jana, N. R.; Gearheart, L.; Murphy, C. J. Wet Chemical Synthesis of Silver Nanorods and Nanowires of Controllable Aspect Ratio. *Chem. Comm.* **2001**, DOI:10.1039/B100521I 10.1039/B100521I617-618.
- (10) Ahmadi, T. S.; Wang, Z. L.; Green, T. C.; Henglein, A.; El-Sayed, M. A. Shape-Controlled Synthesis of Colloidal Platinum Nanoparticles. *Science* **1996**, *272*, 1924-1925.
- (11) El-Sayed, M. A. Small Is Different: Shape-, Size-, and Composition-Dependent Properties of Some Colloidal Semiconductor Nanocrystals. *Acc. Chem. Res.* **2004**, *37*, 326-333.
- (12) Yu, Y.; Zhang, Q.; Yao, Q.; Xie, J.; Lee, J. Y. Architectural Design of Heterogeneous Metallic Nanocrystals—Principles and Processes. *Acc. Chem. Res.* **2014**, *47*, 3530-3540.
- (13) Kozlov, A. I.; Kozlova, A. P.; Asakura, K.; Matsui, Y.; Kogure, T.; Shido, T.; Iwasawa, Y. Supported Gold Catalysts Prepared from a Gold Phosphine Precursor and as-Precipitated Metal-Hydroxide Precursors: Effect of Preparation Conditions on the Catalytic Performance. *J. Cat.* **2000**, *196*, 56-65.
- (14) Gorin, D. J.; Sherry, B. D.; Toste, F. D. Ligand Effects in Homogeneous Au Catalysis. *Chem. Rev.* **2008**, *108*, 3351-3378.
- (15) Cason, J. P.; Miller, M. E.; Thompson, J. B.; Roberts, C. B. Solvent Effects on Copper Nanoparticle Growth Behavior in Aot Reverse Micelle Systems. *J. Phys. Chem. B* **2001**, *105*, 2297-2302.
- (16) Zhang, L.; Lee, K.; Zhang, J. Effect of Synthetic Reducing Agents on Morphology and Orr Activity of Carbon-Supported Nano-Pd-Co Alloy Electrocatalysts. *Electrochim. Acta* **2007**, *52*, 7964-7971.
- (17) Li, C.; Shuford, K. L.; Park, Q. H.; Cai, W.; Li, Y.; Lee, E. J.; Cho, S. O. High-Yield Synthesis of Single-Crystalline Gold Nano-Octahedra. *Angew. Chem. Int. Ed.* **2007**, *119*, 3328-3332.
- (18) Peng, Z.; Yang, H. Ptau Bimetallic Heteronanostructures Made by Post-Synthesis Modification of Pt-on-Au Nanoparticles. *Nano Research* **2009**, *2*, 406-415.

- (19) Meng, X.; Li, B.; Ren, X.; Tan, L.; Huang, Z.; Tang, F. One-Pot Gradient Solvothermal Synthesis of Au-Fe₃O₄ Hybrid Nanoparticles for Magnetically Recyclable Catalytic Applications. *J. Mater. Chem. A* **2013**, *1*, 10513-10517.
- (20) Huang, X.; Tang, S.; Mu, X.; Dai, Y.; Chen, G.; Zhou, Z.; Ruan, F.; Yang, Z.; Zheng, N. Freestanding Palladium Nanosheets with Plasmonic and Catalytic Properties. *Nat. Nanotechnol.* **2011**, *6*, 28-32.
- (21) Fan, Z.; Bosman, M.; Huang, X.; Huang, D.; Yu, Y.; Ong, K. P.; Akimov, Y. A.; Wu, L.; Li, B.; Wu, J. et al. Stabilization of 4h Hexagonal Phase in Gold Nanoribbons. *Nat. Commun.* **2015**, *6*, 7684.
- (22) Huang, X.; Li, S.; Huang, Y.; Wu, S.; Zhou, X.; Li, S.; Gan, C. L.; Boey, F.; Mirkin, C. A.; Zhang, H. Synthesis of Hexagonal Close-Packed Gold Nanostructures. *Nat. Commun.* **2011**, *2*, 292.
- (23) Nikoobakht, B.; El-Sayed, M. A. Preparation and Growth Mechanism of Gold Nanorods (Nrs) Using Seed-Mediated Growth Method. *Chem. Mater.* **2003**, *15*, 1957-1962.
- (24) Tsuji, M.; Hashimoto, M.; Nishizawa, Y.; Kubokawa, M.; Tsuji, T. Microwave-Assisted Synthesis of Metallic Nanostructures in Solution. *Chem. Eur. J* **2005**, *11*, 440-452.
- (25) Pérez-Juste, J.; Liz-Marzán, L. M.; Carnie, S.; Chan, D. Y. C.; Mulvaney, P. Electric-Field-Directed Growth of Gold Nanorods in Aqueous Surfactant Solutions. *Adv. Func. Mater.* **2004**, *14*, 571-579.
- (26) Huang, X.; Qi, X.; Huang, Y.; Li, S.; Xue, C.; Gan, C. L.; Boey, F.; Zhang, H. Photochemically Controlled Synthesis of Anisotropic Au Nanostructures: Platelet-Like Au Nanorods and Six-Star Au Nanoparticles. *ACS Nano* **2010**, *4*, 6196-6202.
- (27) Wang, C.; Hu, Y.; Lieber, C. M.; Sun, S. Ultrathin Au Nanowires and Their Transport Properties. *J. Am. Chem. Soc.* **2008**, *130*, 8902-8903.
- (28) Huo, Z.; Tsung, C.-k.; Huang, W.; Zhang, X.; Yang, P. Sub-Two Nanometer Single Crystal Au Nanowires. *Nano Lett.* **2008**, *8*, 2041-2044.
- (29) Lu, X.; Yavuz, M. S.; Tuan, H.-Y.; Korgel, B. A.; Xia, Y. Ultrathin Gold Nanowires Can Be Obtained by Reducing Polymeric Strands of Oleylamine–AuCl Complexes Formed Via Auophilic Interaction. *J. Am. Chem. Soc.* **2008**, *130*, 8900-8901.
- (30) Mourdikoudis, S.; Liz-Marzán, L. M. Oleylamine in Nanoparticle Synthesis. *Chem. Mater.* **2013**, *25*, 1465-1476.
- (31) Fan, Z.; Zhang, H. Crystal Phase-Controlled Synthesis, Properties and Applications of Noble Metal Nanomaterials. *Chem. Soc. Rev.* **2016**, *45*, 63-82.
- (32) Kusada, K.; Kitagawa, H. A Route for Phase Control in Metal Nanoparticles: A Potential Strategy to Create Advanced Materials. *Adv. Mater.* **2016**, *28*, 1129-1142.
- (33) Fan, Z.; Zhang, H. Template Synthesis of Noble Metal Nanocrystals with Unusual Crystal Structures and Their Catalytic Applications. *Acc. Chem. Res.* **2016**, *49*, 2841-2850.
- (34) Sun, S.; Murray, C. B.; Weller, D.; Folks, L.; Moser, A. Monodisperse FePt Nanoparticles and Ferromagnetic FePt Nanocrystal Superlattices. *Science* **2000**, *287*, 1989-1992.
- (35) Fan, Z.; Luo, Z.; Chen, Y.; Wang, J.; Li, B.; Zong, Y.; Zhang, H. Synthesis of 4h/Fcc-Au@M (M = Ir, Os, Iros) Core-Shell Nanoribbons for Electrocatalytic Oxygen Evolution Reaction. *Small* **2016**, *12*, 3908-3913.

- (36) Gu, J.; Guo, Y.; Jiang, Y.-Y.; Zhu, W.; Xu, Y.-S.; Zhao, Z.-Q.; Liu, J.-X.; Li, W.-X.; Jin, C.-H.; Yan, C.-H. et al. Robust Phase Control through Hetero-Seeded Epitaxial Growth for Face-Centered Cubic Pt@Ru Nanotetrahedrons with Superior Hydrogen Electro-Oxidation Activity. *J. Phys. Chem. C* **2015**, *119*, 17697-17706.
- (37) Fan, Z.; Huang, X.; Han, Y.; Bosman, M.; Wang, Q.; Zhu, Y.; Liu, Q.; Li, B.; Zeng, Z.; Wu, J. et al. Surface Modification-Induced Phase Transformation of Hexagonal Close-Packed Gold Square Sheets. *Nat. Commun.* **2015**, *6*, 6571.
- (38) Indrani, C.; Daniel, C.; Sharmila, N. S.; Sandeep, L.; Somnath, B.; Rajarshi, B.; Umesh, W.; Pushan, A. Novel Hexagonal Polytypes of Silver: Growth, Characterization and First-Principles Calculations. *J. Phys. Condens. Matter* **2011**, *23*, 325401.
- (39) Benaissa, H.; Ferhat, M. Polytypism-Induced Stabilization of Hexagonal 2h, 4h and 6h Phases of Gold. *Superlattices and Microstruct.* **2017**, *109*, 170-175.
- (40) Huang, X.; Li, H.; Li, S.; Wu, S.; Boey, F.; Ma, J.; Zhang, H. Synthesis of Gold Square-Like Plates from Ultrathin Gold Square Sheets: The Evolution of Structure Phase and Shape. *Angew. Chem. Int. Ed.* **2011**, *50*, 12245-12248.
- (41) Lin, J.-F.; Degtyareva, O.; Prewitt, C. T.; Dera, P.; Sata, N.; Gregoryanz, E.; Mao, H.-k.; Hemley, R. J. Crystal Structure of a High-Pressure/High-Temperature Phase of Alumina by in Situ X-Ray Diffraction. *Nat. Mater.* **2004**, *3*, 389.
- (42) Liu, X.; Luo, J.; Zhu, J. Size Effect on the Crystal Structure of Silver Nanowires. *Nano Lett.* **2006**, *6*, 408-412.
- (43) Jialiang, W.; Yang, W.; Hai, L.; Xiao, H.; Hua, Z. Crystal Phase Control in Two-Dimensional Materials. *SCI. CHINA Chem.* **2018**, *61*, 1227.
- (44) Fan, Z.; Luo, Z.; Huang, X.; Li, B.; Chen, Y.; Wang, J.; Hu, Y.; Zhang, H. Synthesis of 4h/Fcc Noble Multimetallc Nanoribbons for Electrocatalytic Hydrogen Evolution Reaction. *J. Am. Chem. Soc.* **2016**, *138*, 1414-1419.
- (45) Haugstad, G. *Atomic Force Microscopy: Understanding Basic Modes and Advanced Applications*, 2012.
- (46) Binnig, G.; Quate, C. F.; Gerber, C. Atomic Force Microscope. *Phys. Rev. Lett.* **1986**, *56*, 930-933.
- (47) Duan, H.; Yan, N.; Yu, R.; Chang, C.-R.; Zhou, G.; Hu, H.-S.; Rong, H.; Niu, Z.; Mao, J.; Asakura, H. et al. Ultrathin Rhodium Nanosheets. *Nat. Commun.* **2014**, *5*, 3093.
- (48) Yin, X.; Liu, X.; Pan, Y. T.; Walsh, K. A.; Yang, H. Hanoi Tower-Like Multilayered Ultrathin Palladium Nanosheets. *Nano Lett.* **2014**, *14*, 7188-7194.
- (49) Zhang, J. L.; Du, J. M.; Han, B. X.; Liu, Z. M.; Jiang, T.; Zhang, Z. F. Sonochemical Formation of Single-Crystalline Gold Nanobelts. *Angew. Chem. Int. Ed.* **2006**, *45*, 1116-1119.
- (50) Jang, M. H.; Kim, J. K.; Tak, H.; Yoo, H. Controllable Synthesis of Multi-Layered Gold Spirangles. *J. Mater. Chem.* **2011**, *21*, 17606-17608.
- (51) Liu, H.; Tang, H.; Fang, M.; Si, W.; Zhang, Q.; Huang, Z.; Gu, L.; Pan, W.; Yao, J.; Nan, C. et al. 2d Metals by Repeated Size Reduction. *Adv. Mater.* **2016**, *28*, 8170-8176.
- (52) Niu, J.; Wang, D.; Qin, H.; Xiong, X.; Tan, P.; Li, Y.; Liu, R.; Lu, X.; Wu, J.; Zhang, T. et al. Novel Polymer-Free Iridescent Lamellar Hydrogel for Two-Dimensional Confined Growth of Ultrathin Gold Membranes. *Nat. Commun.* **2014**, *5*, 3313.

- (53) Batson, P. E.; Dellby, N.; Krivanek, O. L. Sub-Angstrom Resolution Using Aberration Corrected Electron Optics. *Nature* **2002**, *418*, 617-620.
- (54) Fan, Z.; Bosman, M.; Huang, X.; Huang, D.; Yu, Y.; Ong, K. P.; Akimov, Y. A.; Wu, L.; Li, B.; Wu, J. et al. Stabilization of 4h Hexagonal Phase in Gold Nanoribbons. *Nat. Commun.* **2015**, *6*, 7684.
- (55) Fan, Z.; Luo, Z.; Huang, X.; Li, B.; Chen, Y.; Wang, J.; Hu, Y.; Zhang, H. Synthesis of 4h/Fcc Noble Multimetallic Nanoribbons for Electrocatalytic Hydrogen Evolution Reaction. *J. Am. Chem. Soc.* **2016**, *138*, 1414-1419.
- (56) Zhang, Z.; Liu, Y.; Chen, B.; Gong, Y.; Gu, L.; Fan, Z.; Yang, N.; Lai, Z.; Chen, Y.; Wang, J. et al. Submonolayered Ru Deposited on Ultrathin Pd Nanosheets Used for Enhanced Catalytic Applications. *Adv. Mater.* **2016**, *28*, 10282-10286.
- (57) Wang, L.; Zhu, Y.; Wang, J.-Q.; Liu, F.; Huang, J.; Meng, X.; Basset, J.-M.; Han, Y.; Xiao, F.-S. Two-Dimensional Gold Nanostructures with High Activity for Selective Oxidation of Carbon-Hydrogen Bonds. *Nat. Commun.* **2015**, *6*, 6957.
- (58) Tian, N.; Zhou, Z.-Y.; Sun, S.-G.; Ding, Y.; Wang, Z. L. Synthesis of Tetrahexahedral Platinum Nanocrystals with High-Index Facets and High Electro-Oxidation Activity. *Science* **2007**, *316*, 732-735.
- (59) Chen, C.; Kang, Y.; Huo, Z.; Zhu, Z.; Huang, W.; Xin, H. L.; Snyder, J. D.; Li, D.; Herron, J. A.; Mavrikakis, M. et al. Highly Crystalline Multimetallic Nanoframes with Three-Dimensional Electrocatalytic Surfaces. *Science* **2014**, *343*, 1339-1343.
- (60) Huang, X.; Zhao, Z.; Cao, L.; Chen, Y.; Zhu, E.; Lin, Z.; Li, M.; Yan, A.; Zettl, A.; Wang, Y. M. et al. High-Performance Transition Metal-Doped Pt₃Ni Octahedra for Oxygen Reduction Reaction. *Science* **2015**, *348*, 1230-1234.
- (61) Chen, L.; Lu, L.; Zhu, H.; Chen, Y.; Huang, Y.; Li, Y.; Wang, L. Improved Ethanol Electrooxidation Performance by Shortening Pd-Ni Active Site Distance in Pd-Ni-P Nanocatalysts. *Nat. Commun.* **2017**, *8*, 14136.
- (62) Jiang, K.; Wang, P.; Guo, S.; Zhang, X.; Shen, X.; Lu, G.; Su, D.; Huang, X. Ordered PdCu-Based Nanoparticles as Bifunctional Oxygen-Reduction and Ethanol-Oxidation Electrocatalysts. *Angew. Chem. Int. Ed.* **2016**, *55*, 9030-9035.
- (63) Kim, D.; Resasco, J.; Yu, Y.; Asiri, A. M.; Yang, P. Synergistic Geometric and Electronic Effects for Electrochemical Reduction of Carbon Dioxide Using Gold-Copper Bimetallic Nanoparticles. *Nat. Commun.* **2014**, *5*, 4948.
- (64) Sun, K.; Cheng, T.; Wu, L.; Hu, Y.; Zhou, J.; MacLennan, A.; Jiang, Z.; Gao, Y.; Goddard, W. A.; Wang, Z. Ultrahigh Mass Activity for Carbon Dioxide Reduction Enabled by Gold-Iron Core-Shell Nanoparticles. *J. Am. Chem. Soc.* **2017**, *139*, 15608-15611.
- (65) Liu, S.; Wang, X.-Z.; Tao, H.; Li, T.; Liu, Q.; Xu, Z.; Fu, X.-Z.; Luo, J.-L. Ultrathin 5-Fold Twinned Sub-25nm Silver Nanowires Enable Highly Selective Electroreduction of CO₂ to CO. *Nano Energy* **2018**, *45*, 456-462.
- (66) Wu, B.; Zheng, N. Surface and Interface Control of Noble Metal Nanocrystals for Catalytic and Electrocatalytic Applications. *Nano Today* **2013**, *8*, 168-197.
- (67) Chao, T.; Hu, Y.; Hong, X.; Li, Y. Design of Noble Metal Electrocatalysts on an Atomic Level. *ChemElectroChem* *0*.
- (68) Borup, R.; Meyers, J.; Pivovar, B.; Kim, Y. S.; Mukundan, R.; Garland, N.; Myers, D.; Wilson, M.; Garzon, F.; Wood, D. et al. Scientific Aspects of Polymer Electrolyte Fuel Cell Durability and Degradation. *Chem. Rev.* **2007**, *107*, 3904-3951.

- (69) Zhang, J.; Sasaki, K.; Sutter, E.; Adzic, R. R. Stabilization of Platinum Oxygen-Reduction Electrocatalysts Using Gold Clusters. *Science* **2007**, *315*, 220-222.
- (70) Xia, B. Y.; Wu, H. B.; Li, N.; Yan, Y.; Lou, X. W.; Wang, X. One-Pot Synthesis of Pt-Co Alloy Nanowire Assemblies with Tunable Composition and Enhanced Electrocatalytic Properties. *Angew. Chem. Int. Ed.* **2015**, *54*, 3797-3801.
- (71) Xia, B. Y.; Wu, H. B.; Wang, X.; Lou, X. W. One-Pot Synthesis of Cubic PtCu₃ Nanocages with Enhanced Electrocatalytic Activity for the Methanol Oxidation Reaction. *J. Am. Chem. Soc.* **2012**, *134*, 13934-13937.
- (72) Xia, B. Y.; Ng, W. T.; Wu, H. B.; Wang, X.; Lou, X. W. Self-Supported Interconnected Pt Nanoassemblies as Highly Stable Electrocatalysts for Low-Temperature Fuel Cells. *Angew. Chem. Int. Ed.* **2012**, *51*, 7213-7216.
- (73) Xia, B. Y.; Wu, H. B.; Wang, X.; Lou, X. W. Highly Concave Platinum Nanoframes with High-Index Facets and Enhanced Electrocatalytic Properties. *Angew. Chem. Int. Ed.* **2013**, *52*, 12337-12340.
- (74) Xia, B. Y.; Wu, H. B.; Yan, Y.; Lou, X. W.; Wang, X. Ultrathin and Ultralong Single-Crystal Platinum Nanowire Assemblies with Highly Stable Electrocatalytic Activity. *J. Am. Chem. Soc.* **2013**, *135*, 9480-9485.
- (75) Wang, H.; Thiaß, L.; Li, N.; Ge, X.; Liu, Z.; Wang, X. Pd Nanoparticles on Carbon Nitride-Graphene for the Selective Electro-Oxidation of Glycerol in Alkaline Solution. *ACS Catal.* **2015**, *5*, 3174-3180.
- (76) Zhang, S.; Guo, S.; Zhu, H.; Su, D.; Sun, S. Structure-Induced Enhancement in Electrooxidation of Trimetallic FePtAu Nanoparticles. *J. Am. Chem. Soc.* **2012**, *134*, 5060-5063.
- (77) Joo, S. H.; Park, J. Y.; Renzas, J. R.; Butcher, D. R.; Huang, W.; Somorjai, G. A. Size Effect of Ruthenium Nanoparticles in Catalytic Carbon Monoxide Oxidation. *Nano Lett.* **2010**, *10*, 2709-2713.
- (78) Kusada, K.; Kobayashi, H.; Yamamoto, T.; Matsumura, S.; Sumi, N.; Sato, K.; Nagaoka, K.; Kubota, Y.; Kitagawa, H. Discovery of Face-Centered-Cubic Ruthenium Nanoparticles: Facile Size-Controlled Synthesis Using the Chemical Reduction Method. *J. Am. Chem. Soc.* **2013**, *135*, 5493-5496.
- (79) Brouzgou, A.; Podias, A.; Tsiakaras, P. PEMFCs and AEMFCs Directly Fed with Ethanol: a Current Status Comparative Review. *J. Appl. Electrochem.* **2013**, *43*, 119-136.
- (80) Zhang, W.; Hu, Y.; Ma, L.; Zhu, G.; Wang, Y.; Xue, X.; Chen, R.; Yang, S.; Jin, Z. Progress and Perspective of Electrocatalytic CO₂ Reduction for Renewable Carbonaceous Fuels and Chemicals. *Adv. Sci.* **2018**, *5*, 1700275.

Chapter 3

Experimental Methodology

In this chapter, the rational selection of synthetic methods and target materials is first discussed. Then, the chemicals used in the experiments and the experimental procedures for the syntheses of epitaxially growth 4H/fcc Au@Ir, Au@Rh, Au@Os, Au@Ru, Au@Cu core-shell NRBs, the high-yield crystal-phase-heterostructured 4H/fcc Au NRs, and the epitaxially growth 4H/fcc Au@Pd, Au@Cu core-shell NRs are presented in detail. After that, the techniques and equipment used for SEM, TEM, XRD and XPS characterizations are described. Lastly, the details of the electrode preparation and performance measurements using the as-synthesized nanocatalysts are elaborated.

3.1 Rationale for selection

In the first part of the thesis, the previously reported 4H Au NRB is used as the crystal phase-based template for the epitaxial growth of other noble metals and transition metals. The reason to choose this material is due to its metastability and the fact that the required energy to heterogeneously grow noble metal nanocrystals on a template is much smaller than the direct homogeneous nucleation of noble metal nanocrystals with the uncommon phase. It is important to prove that the metastable phase of other metals can exist stably in the presence of a crystal phase template. This work provides the fundamental support and pre-investigation on the feasibility of further exploring the catalytic properties of the as-synthesized noble metals with novel crystal phases.

In the second and third work, a novel crystal structure of Au with high yield was first synthesized. The rationale lies in the systematic study of Au-OAm system, in which Au nanostructures with novel crystal structures have been frequently reported. This heterophased Au is then chosen as the crystal phase template to further extension of the crystal phase library of more metal nanostructures. Another critical reason to choose this 4H/*fcc* Au NR instead of the 4H Au NRB is the yield, which is the precondition to study the phase-dependent property of the as-synthesized nanostructures such as the 4H/*fcc* Au@Pd NR and 4H/*fcc* Au@Cu NR. With the purification technique developed in the second work, the yield of the final nanocatalysts, i.e. the 4H/*fcc* Au@Pd NR and 4H/*fcc* Au@Cu NR, can reach almost 100%, while the proof-of-concept epitaxial growth of five metals in the first work is always accompanied with a ~30-40 % of NPs as byproduct.

3.2 Materials and Chemicals

3.2.1 Chemicals

Gold(III) chloride hydrate ($\text{HAuCl}_4 \cdot x\text{H}_2\text{O}$, ~50% Au basis), iridium(III) chloride hydrate ($\text{IrCl}_3 \cdot \chi\text{H}_2\text{O}$, reagent grade), rhodium(III) chloride hydrate ($\text{RhCl}_3 \cdot \chi\text{H}_2\text{O}$, crystalline, $\geq 99.9\%$ trace metal basis), osmium(III) chloride hydrate ($\text{OsCl}_3 \cdot \chi\text{H}_2\text{O}$, reagent grade),

ruthenium(III) chloride hydrate ($\text{RuCl}_3 \cdot x\text{H}_2\text{O}$, 99.98% trace metal basis), copper(II) nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$), palladium chloride (PdCl_2 , $\geq 99.9\%$), AA (anhydrous, $\geq 99\%$), commercial Pt/C (10 wt.% loading), potassium iodide (KI, ACS reagent, $\geq 99\%$), sodium iodide (NaI, ACS reagent, $\geq 99.5\%$), sodium bromide (NaBr, ACS reagent, $\geq 99\%$), OAm (technique grade, 70%), 1,2-dichloropropane (99%), chloroform ($\geq 99.5\%$), hexane (technical grade, $\geq 99\%$), and Nafion solution (117 solution, $\sim 5\%$) used in the experiments without special mention were purchased from Sigma-Aldrich (Saint Louis, Missouri, USA). Ethanol (absolute, 99.9%), and isopropanol (technical grade, $\geq 99\%$) were bought from Merck (Nordic European Centre, Singapore). Deionized water was obtained from the Milli-Q Water Purification. All the chemical reagents were used as received without further purification.

3.2.2 Materials

Carbon fiber paper (AvCarb MGL 190) was purchased from Fuel Cell Store. Carbon black (XC-72) was purchased from Gashub. Isopropanol alcohol swabs were used as purchased from BD Alcohol Swabs.

3.3 Synthesis Methods

3.3.1 Synthesis of 4H Au NRBs

The 4H Au NRBs were synthesized according to the previously reported method with a slight modification.¹ Briefly, 330 μL of OAm, 5.31 mL of hexane, and 375 μL of 1,2-dichloropropane were successively added into a glass vial containing 6.12 mg of $\text{HAuCl}_4 \cdot x\text{H}_2\text{O}$. The glass vial was then tightly sealed with PTFE tape, transferred to a water bath at 58 $^\circ\text{C}$, and left undisturbed for 16 h. The resulting product was collected by centrifugation (5,000 rpm, 1 min), washed four times with hexane, and then re-dispersed in 6 mL of hexane.

3.3.2 Synthesis of 4H/fcc Au@Ir core-shell NRBs

The epitaxially grown 4H/*fcc* Au@Ir NRBs were prepared by reducing the Ir precursor in the presence of the 4H Au NRBs. First, 125 μL of the 4H Au NRBs in hexane were washed with a mixture of hexane/ethanol ($v/v = 1/2$) and re-dispersed in 250 μL of ethanol. Then, 100 μL of freshly prepared IrCl_3 aqueous solution (2 mM) and 50 μL of KI aqueous solution (400 mM) were mixed and preheated at 95 $^\circ\text{C}$ for 20 min in an oil bath. After that, the mixture containing dissolved IrCl_3 was added into 250 μL of the as-prepared 4H Au NRB solution (in ethanol). The reducing agent, 120 μL of freshly prepared NaBH_4 solution (20 mM, in ethanol), was then rapidly added to the mixture. The reaction was sealed in a glass vial and kept undisturbed at ambient conditions for 1 h. The resultant product was collected by centrifugation (7,000 rpm, 1 min), washed twice with ethanol, and then re-dispersed in 250 μL ethanol.

3.3.3 Synthesis of 4H/*fcc* Au@Rh core-shell NRBs

The epitaxially grown 4H/*fcc* Au@Rh NRBs were prepared by reducing the Rh precursor in the presence of the 4H Au NRBs. First, 250 μL the 4H Au NRBs in hexane were washed with a mixture of hexane/ethanol ($v/v = 1/2$) and then re-dispersed in 250 μL of ethanol. Meanwhile, 100 μL of freshly prepared RhCl_3 solution (2 mM, in ethanol), 100 μL of NaBr solution (100 mM, in ethanol) and 10 μL of NaI solution (2 mM, in ethanol) were mixed and then heated at 70 $^\circ\text{C}$ for 30 min in an oil bath. After that, the mixture with dissolved RhCl_3 was added into 250 μL of the as-prepared 4H Au NRB solution (in ethanol). The reducing agent, 120 μL of freshly prepared NaBH_4 solution (20 mM, in ethanol), was then rapidly added to the mixture. The reaction was sealed in a glass vial and kept undisturbed at ambient conditions for 1 h. The resultant product was collected by centrifugation (7,000 rpm, 1 min), washed twice with ethanol, and then re-dispersed in 250 μL ethanol.

3.3.4 Synthesis of 4H/*fcc* Au@Os core-shell NRBs

The epitaxially grown 4H/*fcc* Au@Os NRBs were by reducing the Os precursor in the presence of the 4H Au NRBs. First, 250 μL of the 4H Au NRBs in hexane were washed with a mixture of hexane/ethanol ($v/v = 1/2$) and re-dispersed in 250 μL of ethanol. After

that, 100 μL of freshly prepared OsCl_3 aqueous solution (4 mM), 50 μL of H_2O and 120 μL of freshly prepared NaBH_4 solution (40 mM, in ethanol) were successively added into 250 μL of the as-prepared 4H Au NRB solution (in ethanol). The reaction was sealed in a glass vial and kept undisturbed at ambient conditions for 1 h. The resultant product was collected by centrifugation (7,000 rpm, 1 min), washed twice with ethanol, and then re-dispersed in 250 μL ethanol.

3.3.5 Synthesis of 4H/*fcc* Au@Ru core-shell NRBs

The epitaxially grown 4H/*fcc* Au@Ru NRBs were by reducing the Ru precursor in the presence of the 4H Au NRBs. First, 500 μL of the 4H Au NRBs in hexane were washed with a mixture of hexane/ethanol ($v/v = 1/2$) and re-dispersed in 250 μL of ethanol. After that, 100 μL of freshly prepared RuCl_3 solution (4 mM, in ethanol) and 120 μL of freshly prepared NaBH_4 solution (20 mM, in ethanol) were successively added into 250 μL of the as-prepared 4H Au NRB solution (in ethanol). The reaction was sealed in a glass vial and kept undisturbed at ambient conditions for 1 h. The resultant product was collected by centrifugation (7,000 rpm, 1 min), washed twice with ethanol, and then re-dispersed in 250 μL ethanol.

3.3.6 Synthesis of 4H/*fcc* Au@Cu core-shell NRBs

The epitaxially grown 4H/*fcc* Au@Cu NRBs were by reducing the Cu precursor in the presence of the 4H Au NRBs. First, 500 μL of the 4H Au NRBs in hexane were washed once with a mixture of hexane/ethanol ($v/v = 1/1$) then re-dispersed in 250 μL of chloroform. After that, 250 μL of chloroform, 280 μL of ethanol, 100 μL of freshly prepared $\text{Cu}(\text{NO}_3)_2$ solution (8 mM, in ethanol) and 120 μL of freshly prepared NaBH_4 solution (40 mM, in ethanol) were successively added into the as-prepared 250 μL 4H Au NRB solution in chloroform. The reaction was sealed in a glass vial and kept undisturbed at ambient conditions for 1 h. The resulting product was collected by centrifugation (7,000 rpm, 1 min), washed with a mixture of chloroform/ethanol ($v/v = 1/1$) and then re-dispersed in 250 μL ethanol.

3.3.7 Synthesis of crystal-phase-heterostructured 4H/*fcc* Au NRs

In the finally optimized synthesis, 6 mg of $\text{HAuCl}_4 \cdot x\text{H}_2\text{O}$ was first dissolved in 1 mL of OAm via vortexing. The resultant transparent orange solution was diluted by adding more OAm to reach a final HAuCl_4 concentration of 3.6 mM. The homogeneous solution was then transferred into a 10 ml glass vial sealed with PTFE tape and parafilm. The vial was then immersed in an oil bath at 70 °C and kept undisturbed for 17 h, during which the solution gradually turns into semi-transparent, dark reddish brown. The reaction is stopped by letting the vial cool down to room temperature naturally. The final product was precipitated by diluting the solution with a mixture of hexane and ethanol (v/v = 10/1) to twice of its original volume. The mixture is then fully sonicated and centrifuged at 4,000 rpm for 5 min. The product was washed twice by a mixture of hexane and ethanol (v/v = 10/1) with reduced centrifugation time to 3 min and 1 min, respectively. The purified product was re-dispersed into 2 mL of hexane or ethanol for storage or further reaction. It is worth mentioning that mass production is readily applicable for this synthesis by simply amplify the amount of all reactants proportionally.

3.3.8 Synthesis of crystal-phase-heterostructured 4H/*fcc* Au@Pd core-shell NRs

The stock H_2PdCl_4 aqueous solution was prepared by gradually dissolving PdCl_2 in a mixture of concentrated HCl and H_2O . Then, in a typical synthesis of Au@Pd NRs, 250 μL of the obtained Au NRs in ethanol was fully sonicated and transferred to a 3 ml glass vial under ambient condition. 100 μL of H_2PdCl_4 solution (2 mM, H_2O) was added into the vial and fully mixed with the Au NR solution. After that, 120 μL of AA solution (1 mM, H_2O) was rapidly added into the vial and fully mixed with the solution. It is critical to obtain a homogeneous colloidal solution at this stage to realize the uniform epitaxial growth of Pd on Au NRs. The resultant mixture was left undisturbed under room temperature for 10 min. The final product was collected by centrifugation at 6,000 rpm for

1 min, washed with ethanol twice at the same centrifugation speed, and re-dispersed in 250 μL of ethanol.

3.3.9 Synthesis of crystal-phase-heterostructured 4H/*fcc* Au@Cu core-shell NRs

First, fresh crystal-phase-heterostructured 4H/*fcc* Au NRs were synthesized using a slightly modified method described in section 3.3.7. In brief, 10 mg of $\text{HAuCl}_4 \cdot x\text{H}_2\text{O}$ were dissolved in 4 mL of oleylamine via sonication. The resultant reddish orange solution was transferred into a 10 mL glass vial sealed with PTFE tape and parafilm. Then, the vial was kept undisturbed in an oven preheated at 68 $^{\circ}\text{C}$. Note that it is important to avoid water contamination throughout the synthesis, which can result in the formation of nanoparticle byproduct. After 18 hr of reaction, the resultant reddish brown solution was cooled down to room temperature naturally and diluted with 8 mL of hexane. The final products were collected by fully sonicating the solution for 3 min and then centrifuging at 7,000 rpm for 5 min. The precipitated sample is re-dispersed into 4 mL of hexane as the stock solution for further reaction.

Second, 900 μL of the Au NR stock solution were taken out and washed twice with hexane at a centrifugation speed of 5,000 rpm to remove excess OAm molecules. After the second wash, a mixture of hexane/ethanol ($v/v=1/1$) were added to the precipitated Au NRs and fully sonicated. This step is to ensure a good dispersion of Au NRs in ethanol later. The resultant brownish suspension is centrifuged at 7,000 rpm for 2 min, re-dispersed in 1.8 mL of ethanol, and transferred to a 4 mL glass vial. Then, 150 μL of fresh $\text{Cu}(\text{NO}_3)_2$ solution (20 mM in ethanol) were added into the vial and mixed with the Au NR solution. After that, 720 μL of NaOH solution (250 mM in ethanol) were rapidly added into the vial and mixed with the aforementioned solution. Lastly, 330 μL of N_2H_4 /ethanol mixture ($v/v=1/10$) were rapidly injected to the solution. Note that throughout the addition of different reacting species, the solution should stay transparent without any aggregation. The resultant mixture was kept undisturbed for 10 min. The final product was collected by centrifugation at 6,000

rpm for 1 min. The product was then washed twice with ethanol at the same centrifugation speed and re-dispersed in 900 μL of ethanol.

3.4 Materials Characterization

3.4.1 SEM

The SEM sample of crystal-phase-heterostructured 4H/*fcc* Au NRs NRs was prepared by dropping 20 μL of Au NR solution (hexane) on a 0.5 cm $\times$ 0.5 cm silicon substrate. The SEM sample of crystal-phase-heterostructured 4H/*fcc* Au@Cu NRs was prepared by dropping 10 μL of Au@Cu NR solution (ethanol) on a 0.5 cm $\times$ 0.5 cm silicon substrate. All SEM samples were naturally dried under ambient condition.

3.4.2 TEM, DF-STEM, and STEM-EDS

TEM samples of 4H/*fcc* Au@Ir, Au@Rh, Au@Os and Au@Ru NRBs were prepared by dropping 5.0 μL of the corresponding sample solutions onto a carbon-coated copper grid (200 mesh). TEM samples of 4H/*fcc* Au@Cu NRBs were prepared by dropping 5.0 μL of the corresponding sample solutions onto a carbon coated nickel grid (200 mesh).

The TEM samples of 4H/*fcc* Au NRs and 4H/*fcc* Au@Pd NRs were prepared by dropping 2.0 μL of sample solution onto the 200-mesh full-carbon copper grids. The TEM samples of 4H/*fcc* Au@Cu NRs and *fcc* Cu NPs were prepared by dropping 2.0 μL of sample solution onto a 200-mesh full-carbon molybdenum grid. After the loaded TEM grids were dried at ambient condition, TEM, HRTEM and DF-STEM images, SAED patterns, and STEM-EDS data were collected on a JEOL JEM-2100F transmission electron microscopy operated at 200 kV. The DF-STEM images of 4H/*fcc* Au@Pd NR and 4H/*fcc* Au@Cu NR were acquired from the high-resolution aberration-corrected TEM (JEOL JEM-ARM200F) operated at 200 kV.

3.4.3 XRD

The XRD samples of 4H/*fcc* Au NRs and *fcc* Cu NPs were prepared by dropping 30 μL concentrated sample solution (originally 500 μL) onto the center of 1.5 cm* 1.5 cm glass slices. The XRD patterns of 4H/*fcc* Au NRs and *fcc* Cu NPs was obtained using the X-ray diffractometer (Shimadzu, XRD-6000) operated at 40 kV and 30 mA.

3.4.4 XPS

The XPS samples were prepared using the same method preparing SEM samples. The XPS data were acquired with a Theta Probe electron spectrometer (ESCA-Lab-200i-XL, Thermo Scientific).

3.5 Electrocatalytic Applications

3.5.1 EOR Measurement of Au@Pd NRs

GCE with diameter of 3 mm was polished and cleaned according to the previous report.² Before the electrochemical characterization, the obtained Au@Pd NRs were centrifuged and re-dispersed in a mixture of acetic acid and ethanol ($v/v = 1/1$), which was stirred at room temperature for 12 h to partially remove the surfactant molecules. The treated sample was then washed with ethanol twice and concentrated in a mixed solution of ethanol and water ($v/v = 7/3$) containing 0.17 wt% Nafion solution. Then, 5.0 μL of Au@Pd NR solution with concentration of Pd, 0.865 $\text{mg}\cdot\text{mL}^{-1}$, determined by the ICP-OES, was dropped onto the surface of cleaned GCE. After drying at room temperature for 2 h, the Au@Pd NR-modified GCE was irradiated by UV light (wavelength = 254 nm) for 6 h to remove the surfactant on the surface of Au@Pd NRs. The CV curves of Au@Pd NR-modified GCE for the EOR were measured in N_2 -saturated 1.0 M KOH solution containing 1.0 M ethanol at a scan rate of 50 $\text{mV}\cdot\text{s}^{-1}$ with SCE and Pt wire as reference and counter electrodes, respectively. Amperometric measurements were carried out at the work potential of 0.77 V (vs. RHE) to evaluate electrocatalytic stability of Au@Pd NR for EOR. The GCEs modified with commercial Pd black and Pt/C catalysts were prepared according

to the aforementioned method, in which the Au@Pd NRs were replaced with the Pd black and Pt/C, respectively.

3.5.2 CO₂RR Measurement of Au@Cu NRs

1 mL of the as-prepared Au@Cu NR solution was precipitated by centrifugation at 6,000 rpm for 1 min and re-dispersed in a mixture of Nafion/ethanol (v/v=1/30) containing 70 wt% of carbon black. The mixture is fully sonicated for 10 min. Carbon fiber paper is cut into 0.5 cm width of strips and gently wiped with isopropanol swab on both sides of surface to remove dust. Then, the mixture is evenly pasted on the carbon paper on both sides. The final effective area is carefully measured, which is typically around $1\text{ cm} \times 0.5\text{ cm} \times 2 = 1\text{ cm}^2$.

References

- (1) Fan, Z.; Bosman, M.; Huang, X.; Huang, D.; Yu, Y.; Ong, K. P.; Akimov, Y. A.; Wu, L.; Li, B.; Wu, J. et al. Stabilization of 4h Hexagonal Phase in Gold Nanoribbons. *Nat. Commun.* **2015**, *6*, 7684.
- (2) Fan, Z.; Luo, Z.; Huang, X.; Li, B.; Chen, Y.; Wang, J.; Hu, Y.; Zhang, H. Synthesis of 4h/Fcc Noble Multimetallic Nanoribbons for Electrocatalytic Hydrogen Evolution Reaction. *J. Am. Chem. Soc.* **2016**, *138*, 1414-1419.

Chapter 4*

Epitaxial Growth of Unusual 4H Ir, Rh, Os, Ru and Cu Nanostructures on 4H Au Nanoribbons

Metal nanomaterials normally adopt the crystal structure same as their bulk counterparts. In this work, via a solution-based epitaxial growth based on the previously developed 4H Au NRBs, Ir, Rh, Os, Ru and Cu nanostructures with the unusual 4H crystal phase were successfully obtained for the first time. Moreover, during the metal coating process, partial phase transformation of Au NRB from 4H to fcc takes. As a result, a series of polytypic 4H/fcc bimetallic Au@M (M = Ir, Rh, Os, Ru and Cu) core-shell NRBs has been prepared. The rational crystal structure-controlled synthesis of metal nanomaterials will bring new opportunities for exploring their phase-dependent physicochemical properties and promising applications.

*This section published substantially as (Z. Fan, Y. Chen (*co-first author*), Y. Zhu, J. Wang, B. Li, Y. Zong, H. Zhang. Epitaxial growth of unusual 4H hexagonal Ir, Rh, Os, Ru and Cu nanostructures on 4H Au nanoribbons. *Chemical Science* 2017, 8, 795).

4.1 Introduction

The exceptional optical, magnetic, electronic, and catalytic properties of metal nanomaterials have made them promising candidates in a wide range of applications including energy conversion, surface-enhanced Raman scattering, bio-sensing, photo-thermal therapy, and catalysis.¹⁻⁶ The physicochemical properties of metal nanomaterials have been found closely related to their morphology and chemical component.³ Very recent studies suggest that besides architecture and composition, crystal phases of metal nanomaterials may also have remarkable impact on their various functional properties.^{7,8} For example, when the crystal structure of FePt nanoparticles change from the common *fcc* phase to the unusual *fcc* phase, their magnetic properties change from superparamagnetic to ferromagnetic.⁹ Another work found that at a size larger than 3 nm, *fcc* Ru nanoparticles exhibit higher catalytic activity in CO oxidation compared to the *hcp* Ru nanoparticles.¹⁰ Therefore, as another important parameter of metal nanomaterials, the crystal phase control of metal nanomaterials may provide a new strategy to fine-tune their various properties and broaden their applications. Meanwhile, it remains a great challenge to realize crystal structure-controlled synthesis of metal nanomaterials under ambient condition.

Epitaxial growth refers to the oriented deposition of a crystalline material over a crystalline substrate, which has been applied to obtain new crystal structures of the deposited material.^{11,12} Conventionally, vapor-phase epitaxial growth has been widely used to prepare metastable crystal structures of thin metal films on different substrates, such as *bcc* Cu on Fe,¹³ *fcc* Co on Cu,¹⁴ and *bcc* Pd on W.¹⁵ However, the vapor-phase epitaxial growth always involves harsh experimental conditions like ultra-high vacuum and high temperature,¹³⁻¹⁵ which can induce the aggregation/degradation of ultrathin anisotropic metal nanomaterials and becomes not suitable for the crystal structure-controlled synthesis. In the past decades, solution-phase epitaxial growth, which can be carried out under mild experimental conditions, has been developed for the size-, shape- and composition-controlled synthesis of bimetallic core-shell nanomaterials, such as Pt@Pd,¹⁶ Au@Pd,^{17,18} Pd@Pt,¹⁹ Au@Ag,^{17,20} Pd@Ir,²¹ Au@Rh,²² and Au@Ni.²³ All the aforementioned epitaxially grown metal shells possess the same crystal phases as their bulk

counterparts, *i.e.* *fcc* phase. To date, the development of the solution-phase epitaxial growth of new crystal structures of metal nanomaterials remains primitive.

Recently, solution-based synthesis of ultrathin *hcp* Au square sheets²⁴ and the 4H hexagonal Au NRBs²⁵ has been demonstrated. By using these Au nanostructures as seeds, the *hcp* Ag,²⁶ and 4H hexagonal Ag, Pd and Pt have been successfully synthesized via the epitaxial growth strategy.²⁵ Moreover, the 4H hexagonal PtAg, PdAg and PtPdAg alloy nanostructures have also been prepared via a galvanic reaction method.²⁷ Note that the lattice mismatch between the Au core and Ag, Pd or Pt shells is usually less than 5%.^{17,18,20} However, due to the relatively large lattice mismatch between Au and some other metals, such as Ir, Rh, Os, Ru and Cu, their epitaxial growth on non-*fcc* Au nanostructures has not been achieved. Here, for the first time, the solution-based epitaxial growth of 4H hexagonal Ir, Rh, Os, Ru and Cu on 4H Au NRBs under ambient condition is demonstrated. Importantly, a partial phase transition from 4H to *fcc* phases is observed in the Au NRBs after the metal coating. As a result, the corresponding bimetallic core-shell NRBs possess an unusual 4H/*fcc* crystal structure.

4.2 Results and Discussions

In this work, the 4H Au NRBs were first synthesized using a previously reported method with slight modifications (see section 3.3.1 for details).²⁵ The typical TEM images and corresponding SAED pattern show that Au NRBs with the characteristic “ABCB” 4H stacking were successfully prepared (Figure 4.1a-c). The 4H crystal structure of Au NRBs was further confirmed by the representative HRTEM image (Figure 4.1d), which is consistent with the previous result.²⁵

Figure 4.1 TEM characterizations of 4H Au NRBs. (a) Low- and (b) high-magnification TEM images of the as-synthesized 4H Au NRBs. (c) SAED pattern of a typical 4H Au NRB taken along the $[110]_{4H}$ zone axis. (d) A representative HRTEM image of the 4H Au NRB.

The obtained 4H Au NRBs were then used as crystal-phase templates for the solution-phase epitaxial growth of 4H structures of Ir, Rh, Os, Ru and Cu. During the growth of secondary metal, partial 4H-to-*fcc* crystal phase transition took place, leading to the formation of polytypic 4H/*fcc* bimetallic Au@M (M = Ir, Rh, Os, Ru and Cu) core-shell NRBs, as illustrated in Figure 4.2.

Figure 4.2 Schematic illustration of the solution-phase epitaxial growth of 4H hexagonal Ir, Rh, Os, Ru and Cu nanostructures on 4H Au NRBs.

Taking Ir as an example, the solution-phase epitaxial growth of 4H hexagonal Ir was achieved by reducing IrCl_3 with NaBH_4 in the presence of 4H Au NRBs and iodide ions under ambient condition (see section 3.3.2 for details). After the reduction reaction, the NRBs becomes wider with a rougher thickness, indicating the successful coating of Ir on Au NRBs (Figure 4.3a,b).

Figure 4.3 TEM and EDS characterizations of 4H/fcc Au@Ir NRBs. (a) Low-magnification TEM image of 4H/fcc bimetallic Au@Ir core-shell NRBs. (b) High-magnification TEM image and (c) the corresponding SAED pattern of a representative Au@Ir NRB. (d) A representative HRTEM image of Au@Ir NRBs. Inset: the corresponding FFT pattern of the selected region, *i.e.* the magenta dashed rectangle in (d). (e) HAADF-STEM image, and (f–h) corresponding STEM-EDS element maps of a representative Au@Ir NRB.

In addition, the XPS confirmed the metallic states of Au(0) and Ir(0) in the Au@Ir NRBs (Figure 4.4).

Figure 4.4 XPS spectra of alternating 4H/fcc Au@Ir core-shell NRs showing the core level peaks of (a) Au 4f and (b) Ir 4f.

The elemental composition of Au@Ir NRs was revealed by STEM-EDS, revealing an average Au/Ir molar ratio of approximately 1.00/0.99 (Figure 4.5).

Figure 4.5 STEM-EDS spectrum of the as-synthesized 4H/fcc bimetallic Au@Ir NRs, giving an average Au/Ir atomic ratio of approximately 1.00/0.99.

A typical HAADF-STEM image (Figure 4.3e) and corresponding STEM-EDS element maps (Figure 4.3f-h) demonstrate that the Ir shell was continuously formed on the Au core, which is also verified by the STEM-EDS line scan profile (Figure 4.6).

Figure 4.6 (a) HAADF-STEM image and (b) corresponding STEM-EDS line scanning profile of a representative 4H/*fcc* bimetallic Au@Ir NRB.

These results suggest that the Ir coating on the 4H Au NRBs may follow the Stranski-Krastanov (S-K) mode of growth.²⁸ The average thickness of the Ir shell is measured to be around 3.9 nm (Figure 4.3b). A representative SAED pattern of the obtained Au@Ir NRB shows a characteristic diffraction pattern along $[110]_{4H}$ zone axis, along with some diffraction streaks along the $[001]_{4H}$ close-packed direction (Figure 4.3c). The presence of diffraction streaks in the SAED pattern indicates the formation of *fcc* domains and stacking faults in the $[001]_{4H}/[111]_f$ directions (Figure 4.3c). Such a partial phase transition, *i.e.* from $(110)_{4H}$ -oriented 4H phase to $(101)_f$ -oriented *fcc* phase, can be realized *via* the relative movement of partial dislocations on close-packed planes.²⁹ During the phase transition of Au NRBs from 4H to *fcc* structures, the close-packed directions, *i.e.* $[001]_{4H}$ and $[111]_f$ directions, are preserved. The partial phase change of Au NRBs from the 4H to *fcc* phases may be caused by the strain generated between Au and Ir at the core-shell interface.^{11,25,26,30-32} Importantly, the Ir shell is epitaxially grown on the Au core as no other diffraction spot is observed (Figure 4.3c). To further investigate the crystal structure of Au@Ir NRBs, a HRTEM image was also collected, which clearly reveals the alternating intergrowth of 4H and *fcc* structures (Figure 4.3d). An inter-planar distance of 2.4 Å is assigned to the lattice spacing of close-packed planes in $[001]_{4H}/[111]_f$ directions (Figure 4.3d). Meanwhile, it can be clearly seen that the lattice fringe coherently extends from the inside Au core to the outside Ir shell, indicating the epitaxial relation between them (Figure 4.3d). Furthermore, the corresponding selected-area FFT of the HRTEM image shows a typical $[110]_{4H}$ -zone diffraction pattern, indicating the successful synthesis of the 4H

hexagonal structure of Ir (inset in Figure 4.3d). The lattice spacings of 2.2 Å and 2.4 Å can be attributed to the (004)_{4H} and (1 $\bar{1}$ 0)_{4H} planes of 4H Ir, respectively (Figure 4.3d).

The coexistence of 4H and *fcc* phases in Au@Ir NRBs is also confirmed by the XRD pattern (Figure 4.7).

Figure 4.7 A typical XRD pattern of the synthesized 4H/*fcc* bimetallic Au@Ir NRBs.

It should be noted that bulk Ir crystals normally adopt the *fcc* phase.³³ This is the first time that an Ir nanostructure with an uncommon 4H hexagonal crystal phase has been synthesized and observed.

Impressively, by using similar synthetic strategy and replacing the metal precursor of IrCl₃ with RhCl₃, OsCl₃ or RuCl₃, the unusual 4H structure of Rh, Os or Ru can also be obtained by the epitaxial growth (see the section 3.3.3, 3.3.4, 3.3.5 for details). Note that the bulk crystals of Rh, Os and Ru crystallize in the *fcc*, *hcp* and *hcp* phases, respectively.³³ Figure 4.8a shows the TEM image of a representative Au@Rh NRB. The Rh shell, with an average thickness of around 2.8 nm, epitaxially grows on the Au core (Figure 4.8b and c). The SAED pattern and HRTEM image of bimetallic Au@Rh NRBs suggest an alternating intergrowth of 4H and *fcc* structures along the close-packed directions of [001]_{4H}/[111]_f (Figure 4.8b and c). The selected-area FFT pattern of the HRTEM image confirms the successful formation of 4H Rh (Figure 4.8d). The lattice distances of 2.2 Å and 2.4 Å can be attributed to the (004)_{4H} and (1 $\bar{1}$ 0)_{4H} planes of 4H Rh, respectively (Figure 4.8 c).

Figure 4.8 TEM and STEM-EDS characterizations of 4H/*fcc* Au@Rh, 4H/*fcc* Au@Os, and 4H/*fcc* Au@Ru NRBs. (a) TEM image, (b) SAED pattern, and (c) HRTEM image of a representative 4H/*fcc* bimetallic Au@Rh core-shell NRB. (d) The corresponding FFT pattern of the selected region, i.e. the magenta dashed rectangle in (c). (e) HAADF-STEM image, and (f–h) corresponding STEM-EDS element maps of a representative Au@Rh NRB. (i) TEM image, (j) SAED pattern, and (k) HRTEM image of a representative 4H/*fcc* Au@Os core-shell NRB. (l) The corresponding FFT pattern of the selected region, i.e. the magenta dashed rectangle in (k). (m) HAADF-STEM image, and (n–p) corresponding STEM-EDS element maps of a representative Au@Os NRB. (q) TEM image, (r) SAED pattern, and (s) HRTEM image of a representative 4H/*fcc* Au@Ru core-shell NRB. (t) The corresponding FFT pattern of the selected region, i.e. the magenta dashed rectangle in (s). (u) HAADF-STEM image, and (v–x) corresponding STEM-EDS element maps of a representative Au@Ru NRB.

The average Au/Rh molar ratio is estimated to be 1.00/0.75 (Figure 4.9).

Figure 4.9 STEM-EDS spectrum of the synthesized 4H/*fcc* bimetallic Au@Rh NRBs, giving an average Au/Rh atomic ratio of approximately 1.00/0.75.

The HAADF-STEM image and corresponding STEM-EDS element maps and line scan curves further identify the successful formation of the Rh shell on the Au core (Figure 4.8e-h and Figure 4.10).

Figure 4.10 (a) HAADF-STEM image and (b) corresponding STEM-EDS line scanning profile of a representative 4H/*fcc* bimetallic Au@Rh NRB.

Figure 4.8i shows a typical TEM image of an Au@Os NRB. The average thickness of the Os shell is around 3.0 nm. The epitaxial relation between Au and Os, and the coexistence of 4H and *fcc* phases in Au@Os NRBs are further confirmed by the SAED pattern and HRTEM image (Figure 4.8j,k). The successful formation of 4H hexagonal Os is confirmed by the selected-area FFT pattern of the HRTEM image (Figure 4.8l). The inter-plane spacings of 2.2 Å and 2.4 Å

can be assigned to the (004)_{4H} and (1 $\bar{1}$ 0)_{4H} planes of 4H Os, respectively (Figure 4.8k). The average Au/Os molar ratio is approximately 1.00/0.81 (Figure 4.11).

Figure 4.11 STEM-EDS spectrum of the synthesized 4H/*fcc* Au@Os NRs, giving an average Au/Os atomic ratio of approximately 1.00/0.81.

The homogeneous growth of Os on Au NRs is further proved by the HAADF-STEM image and STEM-EDS analysis (Figure 4.8m-p and Figure 4.12).

Figure 4.12 (a) HAADF-STEM image and (b) corresponding STEM-EDS line scanning profile of a representative 4H/*fcc* bimetallic Au@Os NR.

Figure 4.8q shows a representative TEM image of an Au@Ru NR. The average thickness of the Ru shell is around 2.7 nm. Similarly, the Ru shell is also epitaxially grown on the Au core, and Au@Ru NRs also exhibit the alternating 4H/*fcc* structures (Figure 4.8r and s). Meanwhile, the 4H hexagonal structure of Ru has also been observed (Figure 4.8t). The lattice distances of

2.2 Å and 2.4 Å can be attributed to the (004)_{4H} and (1 $\bar{1}$ 0)_{4H} planes of 4H Ru, respectively (Figure 4.8s). The average Au/Ru molar ratio is approximately 1.00/0.71 (Figure 4.13).

Figure 4.13 STEM-EDS spectrum of the synthesized 4H/*fcc* bimetallic Au@Ru NRBs, giving an average Au/Ru atomic ratio of approximately 1.00/0.71.

The HAADF-STEM image and corresponding STEM-EDS analysis further confirm the uniform deposition of Ru on Au NRBs (Figure 4.8u-x and Figure 4.14).

Figure 4.14 (a) HAADF-STEM image and (b) corresponding STEM-EDS line scanning profile of a representative 4H/*fcc* bimetallic Au@Ru NRB.

Additionally, the metallic states of Au(0) and Rh(0), Au(0) and Os(0), and Au(0) and Ru(0) in the as-synthesized Au@Rh, Au@Os, and Au@Ru NRBs, respectively, were confirmed by XPS (Figure 4.15).

Figure 4.15 XPS spectra of alternating 4H/*fcc* Au@Rh, Au@Os, and Au@Ru core-shell NRBs showing the core level peaks of (a) Au 4f and (b) Rh 3d, (c) Au 4f and (d) Os 4f, and (e) Au 4f and (f) Ru 3d_{5/2}, respectively.

The coexistence of 4H and *fcc* phases in Au@Rh, Au@Os and Au@Ru NRBs is confirmed by the XRD pattern (Figure 4.16).

Figure 4.16 Representative XRD patterns of the synthesized 4H/fcc bimetallic (a) Au@Rh, (b) Au@Os and (c) Au@Ru NRBs.

Remarkably, besides the aforementioned four noble metals, this solution-phase epitaxial growth strategy can also be extended to synthesize the 4H structure of common transition metals. As a representative, Cu was deposited on Au NRB with 4H phase in this experiment. Briefly, the epitaxial growth of 4H hexagonal Cu was achieved by reducing $\text{Cu}(\text{NO}_3)_2$ with NaBH_4 in the

presence of 4H Au NRBs under ambient condition (see section 3.3.6 for details). Figure 4.17a shows a typical TEM image of Au@Cu core-shell NRBs. The Cu shell shows a relatively smooth surface and has an average thickness of around 2.0 nm (Figure 4.17b).

Figure 4.17 TEM and EDS characterizations of 4H/fcc Au@Cu NRBs. (a) Low-magnification TEM image of alternating 4H/fcc bimetallic Au@Cu core-shell NRBs. (b) High-magnification TEM image and (c) corresponding SAED pattern of a representative Au@Cu NRB. (d) A representative HRTEM image of Au@Cu NRBs. Inset: the corresponding FFT pattern of the selected region, *i.e.* the magenta dashed rectangle in (d). (e) HAADF-STEM image, and (f–h) corresponding STEM-EDS element maps of a representative Au@Cu NRB.

The metallic states of Au(0) and Cu(0) in the obtained Au@Cu NRBs are revealed by XPS.(Figure 4.18).

Figure 4.18 XPS spectra of alternating 4H/fcc Au@Cu core-shell NRBs showing the core level peaks of (a) Au 4f and (b) Cu 2p_{3/2}.

The elemental composition of as-prepared Au@Cu NRBs was investigated by STEM-EDS, exhibiting an average Au/Cu molar ratio of approximately 1.00/0.45 (Figure 4.19).

Figure 4.19 STEM-EDS spectrum of the synthesized 4H/fcc bimetallic Au@Cu NRBs, giving an average Au/Cu atomic ratio of approximately 1.00/0.45.

The typical HAADF-STEM image (Figure 4.20) and corresponding STEM-EDS element maps (Figure 4.17e-h) of an Au@Cu NRB show the continuous coating of Cu on Au NRBs, which is also identified by STEM-EDS line scan curves (Figure 4.20).

Figure 4.20 (a) HAADF-STEM image and (b) corresponding STEM-EDS line scanning profile of a representative 4H/*fcc* bimetallic Au@Cu NRB.

These results indicate that the coating of Cu on the surface of 4H Au NRBs might proceed *via* layered growth, *i.e.* the Frank-van der Merwe (F-M) mode.²⁸ Notably, the SAED pattern of a representative Au@Cu NRB reveals the coexistence of 4H/*fcc* structures and the epitaxial relation between Au and Cu (Figure 4.17c), which has been further confirmed by a representative HRTEM image (Figure 4.17d). The coexistence of 4H and *fcc* phases in Au@Cu NRBs is also identified by the XRD pattern (Figure 4.21).

Figure 4.21 A representative XRD pattern of the synthesized 4H/*fcc* bimetallic Au@Cu NRBs.

A lattice distance of 2.4 Å is assigned to close-packed planes in the $[001]_{4H}/[111]_f$ directions (Figure 4.17d). Significantly, the selected-area FFT pattern demonstrates a characteristic diffraction pattern in the $[110]_{4H}$ zone, suggesting that the 4H structure of Cu is successfully formed (inset in Figure 4.17d). The lattice spacings of 2.2 Å and 2.4 Å can be attributed to the $(004)_{4H}$ and $(1\bar{1}0)_{4H}$ planes of 4H Cu, respectively (Figure 4.17d). Note that bulk Cu crystals demonstrate the common high-symmetry *fcc* phase.³³ This is the first time a Cu nanostructure with a unique 4H hexagonal phase has been synthesized.

4.3 Conclusions

In summary, by using the 4H Au NRB as a crystal-phase template, unusual 4H crystal structures of Ir, Rh, Os, Ru and Cu are successfully obtained via a facile solution-based epitaxial growth strategy under ambient condition. During the metal coating, a partial 4H-to-*fcc* phase transition in the 4H Au NRBs is observed. As a result, a library of bimetallic core-shell NRBs with alternating 4H/*fcc* phases, *i.e.* Au@Ir, Au@Rh, Au@Os, Au@Ru and Au@Cu NRBs, has been prepared. It is expected that the as-prepared metal nanomaterials with novel crystal structures might have some promising applications in electrocatalysis^{5,6,19,34} and energy conversion.² Importantly, our findings suggest that the solution-based templated growth of novel nanostructures with new crystal phases provides a general strategy for the crystal-phase controlled synthesis of various multimetallic heterostructures.^{25-27,32} Impressively, this universal template strategy can also be extended for the preparation of metal-semiconductor³⁵ and semiconductor-semiconductor heterostructures.³⁶⁻³⁸

Meanwhile, it is worth mentioning that the 4H Au NRBs applied in this project still suffer from low yield (usually less than 70%). The existence of NP byproduct greatly hinders the further electrocatalytic characterization of the as-obtained 4H/*fcc* Au@M nanocatalysts, as it will be difficult to distinguish the catalytic performances from the unusual 4H phase and the usual *fcc* phase. In addition, the partial 4H-to-*fcc* phase transition is always observed after the coating of a secondary metal. This interesting phenomena suggests that the coexistence of 4H and *fcc* phases may be a more stable state of Au@M core-shell nanostructures as compared to that of pure 4H phase. The mixture of crystal phases, or heterophase, could also possibly introduce more catalytically active sites at the phase boundaries. Therefore, the next project aims to develop a method to produce Au nanostructures with heterophase in high yield, so that the general method introduced here can be applied to prepare relatively stable and catalytically active Au@M nanocatalysts for electrocatalytic characterizations.

References

- (1) Puentes, V. F.; Gorostiza, P.; Aruguete, D. M.; Bastus, N. G.; Alivisatos, A. P. Collective Behaviour in Two-Dimensional Cobalt Nanoparticle Assemblies Observed by Magnetic Force Microscopy. *Nat. Mater.* **2004**, *3*, 263.
- (2) Linic, S.; Christopher, P.; Ingram, D. B. Plasmonic-Metal Nanostructures for Efficient Conversion of Solar to Chemical Energy. *Nat. Mater.* **2011**, *10*, 911.
- (3) Xia, Y.; Xiong, Y.; Lim, B.; Skrabalak, S. E. Shape-Controlled Synthesis of Metal Nanocrystals: Simple Chemistry Meets Complex Physics? *Angew. Chem. Int. Ed.* **2009**, *48*, 60-103.
- (4) Fan, Z.; Huang, X.; Tan, C.; Zhang, H. Thin Metal Nanostructures: Synthesis, Properties and Applications. *Chem. Sci.* **2015**, *6*, 95-111.
- (5) Huang, X.; Zhao, Z.; Cao, L.; Chen, Y.; Zhu, E.; Lin, Z.; Li, M.; Yan, A.; Zettl, A.; Wang, Y. M. et al. High-Performance Transition Metal-Doped Pt₃Ni Octahedra for Oxygen Reduction Reaction. *Science* **2015**, *348*, 1230-1234.
- (6) Tian, N.; Zhou, Z.-Y.; Sun, S.-G.; Ding, Y.; Wang, Z. L. Synthesis of Tetrahedral Platinum Nanocrystals with High-Index Facets and High Electro-Oxidation Activity. *Science* **2007**, *316*, 732-735.
- (7) Fan, Z.; Zhang, H. Crystal Phase-Controlled Synthesis, Properties and Applications of Noble Metal Nanomaterials. *Chem. Soc. Rev.* **2016**, *45*, 63-82.
- (8) Sun, Y.; Ren, Y.; Liu, Y.; Wen, J.; Okasinski, J. S.; Miller, D. J. Ambient-Stable Tetragonal Phase in Silver Nanostructures. *Nat. Commun.* **2012**, *3*, 971.
- (9) Li, Q.; Wu, L.; Wu, G.; Su, D.; Lv, H.; Zhang, S.; Zhu, W.; Casimir, A.; Zhu, H.; Mendoza-Garcia, A. et al. New Approach to Fully Ordered Fct-FePt Nanoparticles for Much Enhanced Electrocatalysis in Acid. *Nano Lett.* **2015**, *15*, 2468-2473.
- (10) Kusada, K.; Kobayashi, H.; Yamamoto, T.; Matsumura, S.; Sumi, N.; Sato, K.; Nagaoka, K.; Kubota, Y.; Kitagawa, H. Discovery of Face-Centered-Cubic Ruthenium Nanoparticles: Facile Size-Controlled Synthesis Using the Chemical Reduction Method. *J. Am. Chem. Soc.* **2013**, *135*, 5493-5496.
- (11) Flynn, C. P. Strain-Assisted Epitaxial Growth of New Ordered Compounds. *Phys. Rev. Lett.* **1986**, *57*, 599-602.
- (12) Copel, M.; Reuter, M. C.; Kaxiras, E.; Tromp, R. M. Surfactants in Epitaxial Growth. *Phys. Rev. Lett.* **1989**, *63*, 632-635.
- (13) Wang, Z. Q.; Lu, S. H.; Li, Y. S.; Jona, F.; Marcus, P. M. Epitaxial Growth of a Metastable Modification of Copper with Body-Centered-Cubic Structure. *Phys. Rev. B* **1987**, *35*, 9322-9325.
- (14) Li, H.; Tonner, B. P. Structure and Growth Mode of Metastable Fcc Cobalt Ultrathin Films on Cu(001) as Determined by Angle-Resolved X-Ray Photoemission Scattering. *Surface Sci.* **1990**, *237*, 141-152.
- (15) Wormeester, H.; Hüger, E.; Bauer, E. Hcp and Bcc Cu and Pd Films. *Phys. Rev. Lett.* **1996**, *77*, 1540-1543.
- (16) Habas, S. E.; Lee, H.; Radmilovic, V.; Somorjai, G. A.; Yang, P. Shaping Binary Metal Nanocrystals through Epitaxial Seeded Growth. *Nat. Mater.* **2007**, *6*, 692.
- (17) Fan, F.-R.; Liu, D.-Y.; Wu, Y.-F.; Duan, S.; Xie, Z.-X.; Jiang, Z.-Y.; Tian, Z.-Q. Epitaxial Growth of Heterogeneous Metal Nanocrystals: From Gold Nano-

- Octahedra to Palladium and Silver Nanocubes. *J. Am. Chem. Soc.* **2008**, *130*, 6949-6951.
- (18) Wang, F.; Li, C.; Sun, L.-D.; Wu, H.; Ming, T.; Wang, J.; Yu, J. C.; Yan, C.-H. Heteroepitaxial Growth of High-Index-Faceted Palladium Nanoshells and Their Catalytic Performance. *J. Am. Chem. Soc.* **2011**, *133*, 1106-1111.
- (19) Lim, B.; Jiang, M.; Camargo, P. H. C.; Cho, E. C.; Tao, J.; Lu, X.; Zhu, Y.; Xia, Y. Pd-Pt Bimetallic Nanodendrites with High Activity for Oxygen Reduction. *Science* **2009**, *324*, 1302-1305.
- (20) Langille, M. R.; Zhang, J.; Personick, M. L.; Li, S.; Mirkin, C. A. Stepwise Evolution of Spherical Seeds into 20-Fold Twinned Icosahedra. *Science* **2012**, *337*, 954-957.
- (21) Xia, X.; Figueroa-Cosme, L.; Tao, J.; Peng, H.-C.; Niu, G.; Zhu, Y.; Xia, Y. Facile Synthesis of Iridium Nanocrystals with Well-Controlled Facets Using Seed-Mediated Growth. *J. Am. Chem. Soc.* **2014**, *136*, 10878-10881.
- (22) Sneed, B. T.; Kuo, C.-H.; Brodsky, C. N.; Tsung, C.-K. Iodide-Mediated Control of Rhodium Epitaxial Growth on Well-Defined Noble Metal Nanocrystals: Synthesis, Characterization, and Structure-Dependent Catalytic Properties. *J. Am. Chem. Soc.* **2012**, *134*, 18417-18426.
- (23) Grzelczak, M.; Rodríguez-González, B.; Pérez-Juste, J.; Liz-Marzán, L. M. Quasi-Epitaxial Growth of Ni Nanoshells on Au Nanorods. *Adv. Mater.* **2007**, *19*, 2262-2266.
- (24) Huang, X.; Li, S.; Huang, Y.; Wu, S.; Zhou, X.; Li, S.; Gan, C. L.; Boey, F.; Mirkin, C. A.; Zhang, H. Synthesis of Hexagonal Close-Packed Gold Nanostructures. *Nat. Commun.* **2011**, *2*, 292.
- (25) Fan, Z.; Bosman, M.; Huang, X.; Huang, D.; Yu, Y.; Ong, K. P.; Akimov, Y. A.; Wu, L.; Li, B.; Wu, J. et al. Stabilization of 4h Hexagonal Phase in Gold Nanoribbons. *Nat. Commun.* **2015**, *6*, 7684.
- (26) Fan, Z.; Huang, X.; Han, Y.; Bosman, M.; Wang, Q.; Zhu, Y.; Liu, Q.; Li, B.; Zeng, Z.; Wu, J. et al. Surface Modification-Induced Phase Transformation of Hexagonal Close-Packed Gold Square Sheets. *Nat. Commun.* **2015**, *6*, 6571.
- (27) Fan, Z.; Luo, Z.; Huang, X.; Li, B.; Chen, Y.; Wang, J.; Hu, Y.; Zhang, H. Synthesis of 4h/Fcc Noble Multimetallic Nanoribbons for Electrocatalytic Hydrogen Evolution Reaction. *J. Am. Chem. Soc.* **2016**, *138*, 1414-1419.
- (28) Peng, Z.; Yang, H. Designer Platinum Nanoparticles: Control of Shape, Composition in Alloy, Nanostructure and Electrocatalytic Property. *Nano Today* **2009**, *4*, 143-164.
- (29) Bauer, R.; Jägle, E. A.; Baumann, W.; Mittemeijer, E. J. Kinetics of the Allotropic Hcp-Fcc Phase Transformation in Cobalt. *Philos. Mag.* **2011**, *91*, 437-457.
- (30) Ithurria, S.; Guyot-Sionnest, P.; Mahler, B.; Dubertret, B. Mn²⁺ as a Radial Pressure Gauge in Colloidal Core/Shell Nanocrystals. *Phys. Rev. Lett.* **2007**, *99*, 265501.
- (31) Jain, S. C.; Harker, A. H.; Cowley, R. A. Misfit Strain and Misfit Dislocations in Lattice Mismatched Epitaxial Layers and Other Systems. *Philos. Mag.* **1997**, *75*, 1461-1515.
- (32) Fan, Z.; Zhu, Y.; Huang, X.; Han, Y.; Wang, Q.; Liu, Q.; Huang, Y.; Gan, C. L.; Zhang, H. Synthesis of Ultrathin Face-Centered-Cubic Au@Pt and Au@Pd Core-

- Shell Nanoplates from Hexagonal-Close-Packed Au Square Sheets. *Angew. Chem. Int. Ed.* **2015**, *54*, 5672-5676.
- (33) Skriver, H. L. Crystal Structure from One-Electron Theory. *Phy. Rev. B* **1985**, *31*, 1909-1923.
- (34) Gu, J.; Guo, Y.; Jiang, Y.-Y.; Zhu, W.; Xu, Y.-S.; Zhao, Z.-Q.; Liu, J.-X.; Li, W.-X.; Jin, C.-H.; Yan, C.-H. et al. Robust Phase Control through Hetero-Seeded Epitaxial Growth for Face-Centered Cubic Pt@Ru Nanotetrahedrons with Superior Hydrogen Electro-Oxidation Activity. *J. Phy. Chem. C* **2015**, *119*, 17697-17706.
- (35) Huang, X.; Zeng, Z.; Bao, S.; Wang, M.; Qi, X.; Fan, Z.; Zhang, H. Solution-Phase Epitaxial Growth of Noble Metal Nanostructures on Dispersible Single-Layer Molybdenum Disulfide Nanosheets. *Nat. Commun.* **2013**, *4*, 1444.
- (36) Tan, C.; Zeng, Z.; Huang, X.; Rui, X.; Wu, X.-J.; Li, B.; Luo, Z.; Chen, J.; Chen, B.; Yan, Q. et al. Liquid-Phase Epitaxial Growth of Two-Dimensional Semiconductor Hetero-Nanostructures. *Angew. Chem. Int. Ed.* **2015**, *54*, 1841-1845.
- (37) Tan, C.; Zhang, H. Epitaxial Growth of Hetero-Nanostructures Based on Ultrathin Two-Dimensional Nanosheets. *J. Am. Chem. Soc.* **2015**, *137*, 12162-12174.
- (38) Wu, X.-J.; Chen, J.; Tan, C.; Zhu, Y.; Han, Y.; Zhang, H. Controlled Growth of High-Density Cds and Cdse Nanorod Arrays on Selective Facets of Two-Dimensional Semiconductor Nanoplates. *Nat. Chem.* **2016**, *8*, 470.

Chapter 5*

High-Yield Synthesis of Crystal-Phase-Heterostructured 4H/fcc Au@Pd Core–Shell Nanorods for Electrocatalytic Ethanol Oxidation

Noble metal nanomaterials are attracting increasing research interest due to their wide range of promising applications in plasmonics and catalysis. In the past decades, great progress has been made in controlling the size, shape, and architecture of noble metal nanomaterials. However, the crystal phase-controlled synthesis is still in its infant stage. In this chapter, for the first time, high-yield synthesis of Au NRs with alternating 4H/fcc crystal-phase heterostructures via a one-pot wet-chemical method is realized. The 4H and fcc phases coexist in single NR and are relatively stable. Importantly, the 4H/fcc Au NRs can serve as the template for epitaxial growth of other metals with 4H/fcc crystal-phase heterostructure. As an example, bimetallic 4H/fcc Au@Pd core-shell NRs are synthesized via the epitaxial growth of Pd on 4H/fcc Au NRs. Moreover, the 4H/fcc Au@Pd NRs show superior mass activity toward the ethanol oxidation reaction, i.e., 6.2 and 4.9 times those of commercial Pd black and Pt/C catalysts, respectively. This new synthetic strategy can be further applied to prepare a series of other novel hybrid nanostructures for various kinds of catalytic reactions.

*This section is published substantially as (Y. Chen, Z. Fan, Z. Luo, X. Liu, Z. Lai, B. Li, Y. Zong, L. Gu, H. Zhang. High-Yield Synthesis of Crystal-Phase-Heterostructured 4H/fcc Au@Pd Core–Shell Nanorods for Electrocatalytic Ethanol Oxidation. *Advanced Materials* 2017 29, 1701331).

5.1 Introduction

Noble metal nanomaterials possess unique physicochemical properties and have proven critical in a wide range of potential applications.¹⁻³ Particularly, the performance of noble metal based nanocatalysts in electrochemical catalysis for various chemical reactions, such as organic reactions,⁴ hydrogen evolution reaction,⁵ oxygen reduction reaction,⁶ EOR^{7,8} and FAOR,⁹ has been intensively studied. To fine tune the catalytic properties of noble metal nanomaterials, numerous synthetic methods have been developed to control their shapes,^{10,11} sizes,¹² and architectures.¹³ For instance, controlling the exposed facets of Pt nanocrystals are found effective to tune their electrocatalytic activity for EOR and FAOR.¹ These reported nanostructures, however, are all based on the thermodynamically stable crystal phases of noble metals, which is identical to their bulk counterparts.

Besides the thermodynamically stable crystal phases, noble metal nanomaterials with unusual metastable crystal phases have also been realized via wet-chemical synthesis,¹⁴⁻¹⁷ leading to the discovery of crystal phase-dependent catalytic properties.^{5,18} Au nanostructures, for example, normally crystallize in *fcc* phase. Until very recently, the wet-chemical synthesis of Au nanostructures with *hcp* (2H) and 4H crystal structures is reported.^{19,20} The unusual crystal phases of Au are also found to be metastable, as the crystal phase transformations from 2H to *fcc* phases and from 4H to *fcc* phases have been achieved under ambient conditions after the surface modification.^{19,21} Specifically, after a secondary growth of Au on the 2H Au square sheets, relatively stable Au nanoplates with alternating 2H/*fcc* crystal phase were obtained.²² These reports suggest that the crystal phase-based templated growth strategy can be used to prepare polymorphic bimetallic core-shell nanostructures,¹⁶ which are not only more stable, but also intriguing in applications such as catalysis, owing to the unique crystal phase heterostructures and the synergistic effect between different metal components.

In this chapter, a high-yield synthesis of crystal phase heterostructured 4H/*fcc* Au NRs with alternating 4H and *fcc* crystal phases via a mild wet-chemical method is introduced. By simply heating the homogeneous mixture of Au precursor and OAm at 70 °C, 1D Au NRs

in one pot can be obtained, which could only been realized via seeded growth in previous studies. Importantly, the obtained 4H/*fcc* Au NRs can be used as templates for the epitaxial growth of crystal phase heterostructured 4H/*fcc* Au@Pd core-shell NRs. Significantly, the 4H/*fcc* Au@Pd NRs show excellent electrocatalytic activity towards EOR, which is 6.2 and 5.0 times those of the commercial Pd black and Pt/C, respectively.

5.2 Results and Discussions

5.2.1 Exploration of Novel Au Nanostructures

This work starts with the exploration of novel Au nanostructures based on the synthetic conditions developed previously for 2H Au SSs and 4H Au NRBs. It was noted that the two syntheses have very similar conditions, but yield very different products, i.e. ultrathin square-shape 2H Au and ribbon-like ultralong 4H Au. A systematic comparison was carried out by changing/removing each of the reacting species involved.

In the synthesis of 2H Au SSs, a solvent mixture of hexane/ethanol is used, while in the synthesis of 4H Au NRBs, a mixture of hexane/DCP is applied. To explore if the presence of ethanol has influence on the shape and crystal phase of Au nanostructures, the effect of the presence of -OH group in various alcohol molecules (as listed in Figure 5.1) is investigated.

Figure 5.1 Chemical formulas of common alcohol molecules used in the synthesis.

Low-magnification TEM images in Figure 5.2 show the morphologies and yields of 1D Au nanostructures when a small amount of -OH containing molecules is mixed with the solvent. The short molecules can be considered additives to the growth system, while the longer ones are expected to act as ligands, which can modify the OAm-Au interactions. However, although 1D Au nanostructures can be obtained with all the selected molecules except benzyl alcohol, the yields of Au nanostructures as compared to the unwanted Au nanoparticles are not very high.

Figure 5.2 Exploration of the effects of various alcohol molecules on the yield and morphology of Au nanostructures.

Therefore, it is believed that the presence of ethanol, or other alcohol molecules is not favored to increase the yield of 1D Au nanostructures. Meanwhile, when exploring the feasibility to increase the yield of 4H Au NRBs, a simplification of reaction species is carried out (Figure 5.3).

Figure 5.3 Optimization of synthetic conditions for high-yield 4H/*fcc* Au NRs.

Surprisingly, as the solvent (hexane) and DCP are removed from the synthesis stepwise, uniform 1D Au nanostructures were obtained, with very low amount of byproducts. An optimized condition was achieved with proper purification procedure.

With the optimized synthesis condition for 4H/*fcc* Au NRs, a comparison of the synthesis set-up between 4H NRBs and 4H/*fcc* NRs is illustrated in the Figure 5.4 below.

Figure 5.4 Comparison of reaction set-ups between syntheses of 4H Au NRBs and 4H/*fcc* Au NRs.

Compared with the original set-up to produce NRBs, the experimental set-up for Au NRs is very similar. The reaction temperature is slightly increased from 58 °C to 70 °C and the final product became uniform suspension of Au nanorods instead of entangled precipitates of Au NRBs. A detailed comparison is elaborated in the Table 5.1 below on the final products obtained from the two different set-ups.

Table 5.1 Comparison of 4H Au NRBs and 4H/fcc crystal-phase-heterostructured Au NRs.

	HRTEM	SAED	Dominant phase	Main byproduct
4H Gold Nanoribbons			4H
4H/fcc Gold Nanorods			Stacking faults originated from random stacking of fcc (111) and 4H (0001)

The newly developed synthesis set-up is also similar to those reported in 2008 for ultrathin gold nanowires. In fact, the byproduct produced using this method is ultrathin nanowires. Furthermore, chloroform is found a very effective solvent to remove the nanowire byproduct during centrifugation of NRs. The purification process is illustrated in Figure 5.5.

Figure 5.5 Removal of byproducts to further purify the as-obtained 4H/fcc Au NRs.

It is believed that by removing hexane, ethanol, and DCP, this optimized experimental set-up dramatically increases the viscosity of the reaction solution. OAm can be considered to serve as the surface ligand, solvent, and reducing agent at the same time, which promotes

the formation of well-dispersed 1D Au-OAM assemblies and subsequent uniform growth toward Au NRs.

5.2.2 Crystal-phase-heterostructured 4H/*fcc* Au NRs

Figure 5.6 summarizes the optimized procedures for the one-pot synthesis of crystal-phase-heterostructured 4H/*fcc* Au NRs and the subsequent growth of 4H/*fcc* Au@Pd core-shell NRs. Briefly, after heating $\text{HAuCl}_4 \cdot x\text{H}_2\text{O}$ dissolved in OAm at 70 °C for 17 h, crystal-phase-heterostructured 4H/*fcc* Au NRs were prepared (Step a, see section 3.3.7 for details). After reduction of H_2PdCl_4 with AA in the presence of 4H/*fcc* Au NRs, crystal phase heterostructured 4H/*fcc* Au@Pd core-shell NRs were obtained (Step b, see section 3.3.8 for details).

Figure 5.6 Schematic illustration of the (a) synthesis of 4H/*fcc* Au NR and (b) epitaxial growth of Pd on 4H/*fcc* Au NR to form 4H/*fcc* Au@Pd core-shell NR.

SEM and TEM were used to confirm the morphology and crystal phase of the obtained Au NRs (Step a in Figure 5.1). Figure 5.6a,b show the high yield of Au NRs (> 98%) with diameters of ~11-27 nm and lengths of ~200-1000 nm. HRTEM image of a typical Au NR reveals the coexistence of 4H and *fcc* crystal phases, forming 4H/*fcc* crystal phase heterostructures (Figure 5.6c). The SAED pattern taken on a single Au NR shows the characteristic $[101]_{4\text{H}}$ and $[110]_{\text{f}}$ zone diffraction patterns of 4H and *fcc* phases (Figure 5.6d).¹⁹

Figure 5.7 Morphological and crystallographic characterization of crystal-phase-heterostructured 4H/*fcc* Au NRs. (a) SEM and (b) TEM images of crystal phase heterostructured 4H/*fcc* Au NRs. (c) High-magnification TEM image of a representative 4H/*fcc* Au NR showing alternating 4H and *fcc* crystal phases. (d) Typical SAED pattern of a single 4H/*fcc* Au NR acquired from the zone axes of $[110]_{4H}/[101]_f$.

The coexistence of 4H and *fcc* phases can be told from the XRD pattern. In Figure 5.8, the XRD pattern of Au NRs clearly shows two sets of peaks that can be well assigned to the two phases. Specifically, the peaks at 36.2° , 37.4° , 40.9° and 79.7° correspond to $(100)_{4H}$, $(101)_{4H}$, $(102)_{4H}$ and $(202)_{4H}$ planes, while the peaks located at 38.1° , 44.4° , 77.6° and 81.7° correspond to $(111)_f$, $(200)_f$, $(311)_f$, and $(222)_f$ planes, further confirming the co-existence of 4H and *fcc* crystal phases in the obtained Au NRs. Note that the $(110)_{4H}$ and $(220)_f$ peaks are overlapped with each other due to their equal lattice spacing.

Figure 5.8 XRD pattern of crystal phase heterostructured 4H/*fcc* Au NRs collected in the $\theta/2\theta$ mode. (110)_{4H} and (220)_f peaks are overlapped due to their equal lattice spacing. The four peaks at 36.2°, 37.4°, 40.9° and 79.7° are attributed to the (100)_{4H}, (101)_{4H}, (102)_{4H} and (202)_{4H} planes of 4H Au, respectively, whereas the four peaks at 38.1°, 44.4°, 77.6° and 81.7° correspond to the (111)_f, (200)_f, (311)_f, and (222)_f planes of *fcc* Au, respectively

Moreover, the metallic state of Au in Au NRs was confirmed by the XPS analysis, as shown in Figure 5.9a.

Figure 5.9 XPS spectra of 4H/*fcc* Au NRs and 4H/*fcc* Au@Pd NRs, showing the core level peaks of (a) Au4f of 4H/*fcc* Au NRs, (b) Au4f of 4H/*fcc* Au@Pd NRs, and (c) Pd3d of 4H/*fcc* Au@Pd NRs.

The growth mechanism of such alternating crystal phases is believed to be related to the small energy difference between 4H and *fcc* phases.^{23,24} The time-dependent experiments were conducted by taking samples from the growth solution at the reaction time of 8 and 12 h, respectively (Figure 5.10a,b). After reaction for 8 h, ultrathin Au nanowires with

diameter of ~ 3 nm formed (Figure 5.10a), which is consistent with the previous report about the formation of ultrathin Au nanowires with *fcc* crystal phase.²⁵ However, as the reaction continues at 70 °C, the ultrathin Au nanowires start to reform into wider and shorter NRs (Figure 5.10b). Notably, it is observed that 4H phase appears as the widening of nanowires takes place (Figure 5.10c). This widening mechanism from nanowires has been observed in the synthesis of 4H Au NRBs, where the addition of DCP and the lower reaction temperature of 58 °C allow a slow and steady growth of 4H phase in the system.²⁶ In this work, the absence of DCP and the higher reaction temperature of 70 °C make the formation of 4H phase faster and less steady. Thus, *fcc* and 4H phases grow competitively by each other and coexist on individual NRs.

Figure 5.10 Low-magnification TEM images of 4H/*fcc* Au NRs obtained at reaction time of (a) 8 h and (b) 12 h. (c) High magnification TEM image of Au NRs obtained at reaction time of 12 h (Inset: FFT pattern of (c), showing typical 4H/*fcc* crystal structure), (d,e) Low-magnification TEM images of 4H/*fcc* Au NRs synthesized at different H₂AuCl₄ concentrations: (d) [C₀] and (e) 12[C₀].

Moreover, by using pure OAm as the only solvent, the assembly of one-dimensional OAm-AuCl complexes is favorable and thus promotes the formation of Au nanowires at the early stage.²⁷ In this way, the formation of Au nanoparticle byproducts is effectively suppressed, resulting in the high product yield of crystal phase heterostructured 4H/*fcc* Au NRs.

Importantly, the length of Au NRs can be varied when the concentration of Au precursor in OAm is changed. Figures 5.10d,e demonstrate the elongation of NRs when the concentration of H₂AuCl₄ increased from 3.6 mM ($[C_0]$) to 43.2 mM ($12[C_0]$).

5.2.3 Crystal-phase-heterostructured 4H/*fcc* Au@Pd NRs via Epitaxial Growth

Inspired by the work introduced in chapter 4, the crystal-phase-heterostructured Au NRs can act as active templates for epitaxial growth of other crystal-phase-heterostructured noble metal nanostructures (e.g. Pd, Ag and Pt). Compared to 4H Au NRs, the alternating 4H and *fcc* phases could generate rich lattice strain at interfaces.²⁸ As a typical example, in this work, the crystal-phase-heterostructured 4H/*fcc* Au@Pd core-shell NRs were prepared via the epitaxial growth of Pd on Au NRs (Step b in Figure 5.1, see section 3.3.8 for details). The Pd shell with thickness of ~2-7 nm was observed to be thoroughly coated on the surface of Au NRs (Figure 5.11a,b). The metallic states of Au and Pd in Au@Pd NRs were confirmed by XPS (Figure 5.9b,c). A typical aberration-corrected HAADF-STEM image of Au@Pd NR proved the epitaxial growth of 4H and *fcc* Pd on the 4H and *fcc* phases of Au NRs, respectively. The continuous lattice alignment from the Au backbone to the Pd shell (Figure 5.11c) can be clearly identified by the selected-area FFT patterns (Figure 5.11d-g). In addition, the STEM-EDS linear scan revealed the core-shell architecture of Au@Pd NRs. (Figure 5.11h,i). Meanwhile, the Pd shell completely covered the surface of Au NRs, as evidenced by the TEM images (Figure 5.10b,c) and STEM-EDS element mappings (Figure 5.11j-l).

Figure 5.11 High-magnification TEM, Cs-corrected TEM, and EDS characterizations of crystal-phase-heterostructured 4H/*fcc* Au@Pd NRs. (a) Low and (b) high magnification TEM images of crystal phase heterostructured 4H/*fcc* Au@Pd core-shell NRs. (c) Aberration-corrected high-resolution HAADF-STEM image of a representative 4H/*fcc* Au@Pd NR. (d-g) Selected-area FFT patterns of a 4H Pd island (d) and its 4H Au backbone (e), and an *fcc* Pd island (f) and its *fcc* Au backbone (g), as marked in (c). (h) High magnification HAADF-STEM image of a representative 4H/*fcc* Au@Pd NR with (i) corresponding line-scanning profiles and (j-m) aberration-corrected HAADF-STEM image and the corresponding STEM-EDS element mapping and overlapping images of Au and Pd of a typical 4H/*fcc* Au@Pd NR.

The aforementioned results suggest that the heterogeneous growth of Pd on 4H/*fcc* Au NRs may follow the Stranski-Krastanov mode,²⁹ i.e. a mixed growth mode in which the deposition initially takes place layer-by-layer to form a uniform coverage, and then continues by forming island-like morphology.

5.2.4 Electrocatalytic Performance of 4H/*fcc* Au@Pd NRs in EOR

Pd-based bimetallic nanocatalysts are known to be promising in substituting the precious Pt catalysts in many electrochemical reactions, including oxidation of alcohols to aldehydes.³⁰ As a proof-of-concept application, the obtained crystal-phase-heterostructured 4H/*fcc* bimetallic Au@Pd core-shell NRs were tested as electrocatalysts toward the EOR. The electrocatalytic performance of Au@Pd NRs for EOR was measured by CV at a scan rate of 50 mV·s⁻¹. The CV curve of Au@Pd NRs shows much stronger hydrogen absorption peak compared to the commercial Pd black and Pt/C catalysts in N₂-saturated 1.0 M KOH aqueous solution (Figure 5.12a), indicating their larger ECSA compared to the commercial Pd black and Pt/C catalysts. The EOR CV scans were carried out in N₂-saturated 1.0 M KOH aqueous solution containing 1.0 M CH₃CH₂OH. As shown in Figure 5.12b, the CV curve of Au@Pd NRs show higher current for EOR at the same work potential in the range of 0.6 to 0.9 V (vs. RHE) compared to those of commercial Pd black and Pt/C catalysts. Specifically, the mass activity of Au@Pd NRs for EOR at peak potential is calculated to be 2.921 A·mg⁻¹_{Pd}, around 6.2 times that of commercial Pd black and 5.0 times that of commercial Pt/C catalyst (Figure 5.12c).

The electrocatalytic stability of Au@Pd NRs was also evaluated by the amperometric measurement at the work potential of 0.77 V (vs. RHE) (Figure 5.12d). After the electrocatalytic EOR proceeded for 1200 s, the response current of commercial Pd black and Pt/C dropped to zero, while Au@Pd NRs still maintained 32% of their initial response current, suggesting the higher electrocatalytic stability of Au@Pd NRs compared to the commercial Pd black and Pt/C under the alkaline condition.

Figure 5.12 Electrocatalytic EOR performance of 4H/*fcc* Au@Pd NRs. (a) CV measurements of crystal-phase-heterostructured 4H/*fcc* Au@Pd core-shell NRs, commercial Pd black and Pt/C in N₂-saturated 1.0 M KOH aqueous solution at scan rate of 50 mV·s⁻¹. (b) CV measurements of 4H/*fcc* Au@Pd core-shell NRs, Pd black and Pt/C in N₂-saturated aqueous solution containing 1.0 M CH₃CH₂OH and 1.0 M KOH at scan rate of 50 mV·s⁻¹. (c) Mass activities of 4H/*fcc* Au@Pd NRs, Pd black and Pt/C at their corresponding peak potentials in the CV curves in (b). (d) J - t curves of 4H/*fcc* Au@Pd NRs, Pd black and Pt/C at 0.77 V (vs RHE). “ J ” represents the mass current density.

The excellent electrocatalytic activity and enhanced stability of crystal phase heterostructured 4H/*fcc* Au@Pd core-shell NRs could be attributed to the following reasons. First, at crystal phase boundaries, the change of coordination environment and chemical bonding could lead to the altering electron band structure and enhancement in catalytic activity.³¹ In this work, the crystal phase heterostructured 4H/*fcc* Pd nanostructure contains large amounts of crystal phase boundaries (Figure 5.11c), which could increase its electrocatalytic activity. Second, previous studies have identified that the atomic contact of different metal elements could change their electronic structures and thus enhance the

catalytic activity, resulting in a synergistic effect.³² In this work, the Pd shells were epitaxially grown and fully covered on the Au NRs to form the Au@Pd NR heterostructure (Figure 5.11c-g), which could be another cause in enhancing in the electrocatalytic activity. Third, atomic surface roughness of catalysts could largely increase the exposed area of catalytically active sites. The dendritic morphology of our Pd shells are rich of atomic steps/kinks, as evidenced by the aberration-corrected high-resolution HAADF-STEM image (Figure 5.11c). Last, Au is found to have stabilization effect on the electrocatalytic stability of its coordinated catalyst.³³ As a unique template, the Au NR can stabilize the grown Pd shell, and thus greatly help the realization of phase-boundary induced active sites and maintenance of the polymorphic structure.

5.3 Conclusions

To conclude, a wet-chemical method for the high-yield synthesis of crystal-phase-heterostructured 4H/*fcc* Au NRs is reported. The 4H and *fcc* crystal phases appear alternatively with random length in every single Au NR. Importantly, via the epitaxial growth of Pd on Au NRs, crystal-phase-heterostructured 4H/*fcc* bimetallic Au@Pd core-shell NRs were obtained, which showed much higher electrocatalytic activity and stability toward the EOR as compared to the commercial catalysts, i.e. Pd black and Pt/C. This chapter provides a new template to engineer the crystal phase of noble metal nanostructures to enhance their catalytic performances. It is believed that the crystal-phase-heterostructured 4H/*fcc* Au NRs can serve as a universal template for the growth of other novel crystal-phase-heterostructured bi-/multi-metallic nanostructures or metal-semiconductor hybrids for various promising applications.

Specifically, to further extend the crystal phase library of metals, this method can also be used to deposit non-noble metals such as transition metals. By carefully choosing the type of transition metals, the relatively larger lattice mismatch between noble metals and transition metals can be overcome by the coherent alloying effect or the introduction of ordered defects. As a proof of concept, the feasibility of depositing Cu on the crystal-phase-heterostructured 4H/*fcc* Au NRs is explored in the next project.

References

- (1) Tian, N.; Zhou, Z.-Y.; Sun, S.-G.; Ding, Y.; Wang, Z. L. Synthesis of Tetrahedral Platinum Nanocrystals with High-Index Facets and High Electro-Oxidation Activity. *Science* **2007**, *316*, 732-735.
- (2) Chen, C.; Kang, Y.; Huo, Z.; Zhu, Z.; Huang, W.; Xin, H. L.; Snyder, J. D.; Li, D.; Herron, J. A.; Mavrikakis, M. et al. Highly Crystalline Multimetallic Nanoframes with Three-Dimensional Electrocatalytic Surfaces. *Science* **2014**, *343*, 1339-1343.
- (3) Huang, X.; Zhao, Z.; Cao, L.; Chen, Y.; Zhu, E.; Lin, Z.; Li, M.; Yan, A.; Zettl, A.; Wang, Y. M. et al. High-Performance Transition Metal-Doped Pt₃Ni Octahedra for Oxygen Reduction Reaction. *Science* **2015**, *348*, 1230-1234.
- (4) Zhang, Z.; Liu, Y.; Chen, B.; Gong, Y.; Gu, L.; Fan, Z.; Yang, N.; Lai, Z.; Chen, Y.; Wang, J. et al. Submonolayered Ru Deposited on Ultrathin Pd Nanosheets Used for Enhanced Catalytic Applications. *Adv. Mater.* **2016**, *28*, 10282-10286.
- (5) Fan, Z.; Luo, Z.; Huang, X.; Li, B.; Chen, Y.; Wang, J.; Hu, Y.; Zhang, H. Synthesis of 4h/fcc Noble Multimetallic Nanoribbons for Electrocatalytic Hydrogen Evolution Reaction. *J. Am. Chem. Soc.* **2016**, *138*, 1414-1419.
- (6) Lim, B.; Jiang, M.; Camargo, P. H. C.; Cho, E. C.; Tao, J.; Lu, X.; Zhu, Y.; Xia, Y. Pd-Pt Bimetallic Nanodendrites with High Activity for Oxygen Reduction. *Science* **2009**, *324*, 1302-1305.
- (7) Chen, L.; Lu, L.; Zhu, H.; Chen, Y.; Huang, Y.; Li, Y.; Wang, L. Improved Ethanol Electrooxidation Performance by Shortening Pd-Ni Active Site Distance in Pd-Ni-P Nanocatalysts. *Nat. Commun.* **2017**, *8*, 14136.
- (8) Jiang, K.; Wang, P.; Guo, S.; Zhang, X.; Shen, X.; Lu, G.; Su, D.; Huang, X. Ordered PdCu-Based Nanoparticles as Bifunctional Oxygen-Reduction and Ethanol-Oxidation Electrocatalysts. *Angew. Chem. Int. Ed.* **2016**, *55*, 9030-9035.
- (9) Huang, X.; Tang, S.; Mu, X.; Dai, Y.; Chen, G.; Zhou, Z.; Ruan, F.; Yang, Z.; Zheng, N. Freestanding Palladium Nanosheets with Plasmonic and Catalytic Properties. *Nat. Nanotechnol.* **2011**, *6*, 28-32.
- (10) Xia, Y.; Xiong, Y.; Lim, B.; Skrabalak, S. E. Shape-Controlled Synthesis of Metal Nanocrystals: Simple Chemistry Meets Complex Physics? *Angew. Chem. Int. Ed.* **2009**, *48*, 60-103.
- (11) Sun, Y.; Xia, Y. Shape-Controlled Synthesis of Gold and Silver Nanoparticles. *Science* **2002**, *298*, 2176-2179.
- (12) El-Sayed, M. A. Small Is Different: Shape-, Size-, and Composition-Dependent Properties of Some Colloidal Semiconductor Nanocrystals. *Acc. Chem. Res.* **2004**, *37*, 326-333.
- (13) Yu, Y.; Zhang, Q.; Yao, Q.; Xie, J.; Lee, J. Y. Architectural Design of Heterogeneous Metallic Nanocrystals—Principles and Processes. *Acc. Chem. Res.* **2014**, *47*, 3530-3540.
- (14) Fan, Z.; Zhang, H. Crystal Phase-Controlled Synthesis, Properties and Applications of Noble Metal Nanomaterials. *Chem. Soc. Rev.* **2016**, *45*, 63-82.
- (15) Kusada, K.; Kitagawa, H. A Route for Phase Control in Metal Nanoparticles: A Potential Strategy to Create Advanced Materials. *Adv. Mater.* **2016**, *28*, 1129-1142.

- (16) Fan, Z.; Zhang, H. Template Synthesis of Noble Metal Nanocrystals with Unusual Crystal Structures and Their Catalytic Applications. *Acc. Chem. Res.* **2016**, *49*, 2841-2850.
- (17) Sun, S.; Murray, C. B.; Weller, D.; Folks, L.; Moser, A. Monodisperse FePt Nanoparticles and Ferromagnetic FePt Nanocrystal Superlattices. *Science* **2000**, *287*, 1989-1992.
- (18) Gu, J.; Guo, Y.; Jiang, Y.-Y.; Zhu, W.; Xu, Y.-S.; Zhao, Z.-Q.; Liu, J.-X.; Li, W.-X.; Jin, C.-H.; Yan, C.-H. et al. Robust Phase Control through Hetero-Seeded Epitaxial Growth for Face-Centered Cubic Pt@Ru Nanotetrahedrons with Superior Hydrogen Electro-Oxidation Activity. *J. Phys. Chem. C* **2015**, *119*, 17697-17706.
- (19) Fan, Z.; Bosman, M.; Huang, X.; Huang, D.; Yu, Y.; Ong, K. P.; Akimov, Y. A.; Wu, L.; Li, B.; Wu, J. et al. Stabilization of 4h Hexagonal Phase in Gold Nanoribbons. *Nat. Commun.* **2015**, *6*, 7684.
- (20) Huang, X.; Li, S.; Huang, Y.; Wu, S.; Zhou, X.; Li, S.; Gan, C. L.; Boey, F.; Mirkin, C. A.; Zhang, H. Synthesis of Hexagonal Close-Packed Gold Nanostructures. *Nat. Commun.* **2011**, *2*, 292.
- (21) Fan, Z.; Huang, X.; Han, Y.; Bosman, M.; Wang, Q.; Zhu, Y.; Liu, Q.; Li, B.; Zeng, Z.; Wu, J. et al. Surface Modification-Induced Phase Transformation of Hexagonal Close-Packed Gold Square Sheets. *Nat. Commun.* **2015**, *6*, 6571.
- (22) Huang, X.; Li, H.; Li, S.; Wu, S.; Boey, F.; Ma, J.; Zhang, H. Synthesis of Gold Square-Like Plates from Ultrathin Gold Square Sheets: The Evolution of Structure Phase and Shape. *Angew. Chem. Int. Ed.* **2011**, *50*, 12245-12248.
- (23) Wu, C.-H.; Aruguete, D. M.; Reynolds, W. T.; Murayama, M. The Role of Twin Boundary and Surface Energies in Periodically Twinned $\langle 111 \rangle$ Nanowires. *Acta Mater.* **2014**, *75*, 180-187.
- (24) Indrani, C.; Daniel, C.; Sharmila, N. S.; Sandeep, L.; Somnath, B.; Rajarshi, B.; Umesh, W.; Pushan, A. Novel Hexagonal Polytypes of Silver: Growth, Characterization and First-Principles Calculations. *J. Phys. Condens. Matter* **2011**, *23*, 325401.
- (25) Wang, C.; Hu, Y.; Lieber, C. M.; Sun, S. Ultrathin Au Nanowires and Their Transport Properties. *J. Am. Chem. Soc.* **2008**, *130*, 8902-8903.
- (26) Fan, Z.; Bosman, M.; Huang, X.; Huang, D.; Yu, Y.; Ong, K. P.; Akimov, Y. A.; Wu, L.; Li, B.; Wu, J. et al. Stabilization of 4h Hexagonal Phase in Gold Nanoribbons. *Nat. Commun.* **2015**, *6*, 7684.
- (27) Huo, Z.; Tsung, C.-k.; Huang, W.; Zhang, X.; Yang, P. Sub-Two Nanometer Single Crystal Au Nanowires. *Nano Lett.* **2008**, *8*, 2041-2044.
- (28) Wu, J.; Li, P.; Pan, Y.-T.; Warren, S.; Yin, X.; Yang, H. Surface Lattice-Engineered Bimetallic Nanoparticles and Their Catalytic Properties. *Chem. Soc. Rev.* **2012**, *41*, 8066-8074.
- (29) Casavola, M.; Buonsanti, R.; Caputo, G.; Cozzoli, P. D. Colloidal Strategies for Preparing Oxide-Based Hybrid Nanocrystals. *Eur. J. Inorg. Chem.* **2008**, *2008*, 837-854.
- (30) Zhang, L.; Xie, Z.; Gong, J. Shape-Controlled Synthesis of Au-Pd Bimetallic Nanocrystals for Catalytic Applications. *Chem. Soc. Rev.* **2016**, *45*, 3916-3934.

- (31) Scanlon, D. O.; Dunnill, C. W.; Buckeridge, J.; Shevlin, S. A.; Logsdail, A. J.; Woodley, S. M.; Catlow, C. R. A.; Powell, M. J.; Palgrave, R. G.; Parkin, I. P. et al. Band Alignment of Rutile and Anatase TiO₂. *Nat Mater* **2013**, *12*, 798-801.
- (32) Strasser, P.; Koh, S.; Anniyev, T.; Greeley, J.; More, K.; Yu, C.; Liu, Z.; Kaya, S.; Nordlund, D.; Ogasawara, H. et al. Lattice-Strain Control of the Activity in Dealloyed Core-Shell Fuel Cell Catalysts. *Nat. Chem.* **2010**, *2*, 454-460.
- (33) Zhang, J.; Sasaki, K.; Sutter, E.; Adzic, R. R. Stabilization of Platinum Oxygen-Reduction Electrocatalysts Using Gold Clusters. *Science* **2007**, *315*, 220-222.

Chapter 6*

Crystal-Phase-Heterostructured 4H/fcc Au@Cu Core-Shell Nanorods for Electrocatalytic CO₂ Reduction

Copper-based nanomaterials are promising electrocatalysts for carbon CO₂RR owing to its ability of producing various C1 and C2 products. Although numerous efforts have been made to study the effect of size, shape, and composition of Cu-based nanocatalysts on their CO₂RR performance, to date, these reports are limited to the fcc crystal phase of Cu. Here, crystal-phase-heterostructured 4H/fcc Cu in high yield is successfully prepared via the epitaxial growth of Cu on the crystal-phase-heterostructured 4H/fcc Au NRs. For the first time, the CO₂RR performance of 4H/fcc Cu is investigated. Importantly, the crystal-phase-heterostructured 4H/fcc Au@Cu NRs exhibit better CO₂RR performance compared to fcc Cu nanoparticles in terms of significantly higher specific current density and C₂/C₁ product ratio, indicating the preference of utilizing 4H/fcc Cu for C₂H₄ production. It is believed that this synthetic strategy can be further extended to prepare other novel catalysts for various promising applications.

*This section submitted substantially as (Y. Chen, J. Wang, Z. Fan, X. Liu, Z. Huang, Z. Lai, B. Li, B. Chen, Y. Zong, L. Gu, X. Wang, H. Zhang. Crystal Phase Heterostructured 4H/fcc Au@Cu Core-Shell Nanorods for Electrocatalytic CO₂ Reduction).

6.1 Introduction

Metal based nanostructures possess superior intrinsic catalytic activity in a wide range of electrochemical reactions for future clean energy solutions.¹ Among the many critical reactions, electrochemical reduction of CO₂ emerges as an efficient strategy to utilize the excess atmospheric CO₂ for valuable chemical products.² Cu-based electrocatalysts are the most excellent candidates for CO₂RR owing to their high energy density and wide spectrum of useful products including carbon monoxide, formic acid, as well as C₁, C₂ and C₃ hydrocarbon products such as methane and ethylene.³ However, the development of Cu-based CO₂RR catalysts is still facing several challenges, often suffering from low selectivity, low production rates and relatively poor energy efficiencies.⁴

In the past decade, various types of Cu-based nanocatalysts have been investigated to understand the structure-property relationship in CO₂RR application. Many efforts have been devoted to realize morphology-,⁵⁻⁷ composition-,^{4,8} and chemical state-controlled^{9,10} syntheses of Cu-based nanostructures for enhanced CO₂RR performances. One promising strategy is to prepare Cu-based bimetallic or alloy nanocrystals.^{11,12} For example, the synergistic geometric and electronic effects are found responsible for the tunable catalytic activity in Cu-Au bimetallic nanoparticles.^{4,8} Importantly, recent studies suggest that the atomic arrangement of Cu can affect the catalytic performance in CO₂RR. For instance, a very recent work reported that amorphous Cu nanoparticles possess much higher catalytic activity and selectivity of CO₂ reduction to liquid-form fuels compared to crystalline Cu nanoparticles.¹³

However, the aforementioned results are all based on the face-centered cubic (*fcc*) Cu, which is the thermodynamically stable crystal phase. As another important parameter, the crystal phase of metal nanostructures could have great impact on their catalytic behaviors.¹⁴⁻¹⁶ In section 4, we have developed a universal wet-chemical method to obtain unusual crystal phase of metal nanostructures via the epitaxial growth on Au nanostructure template,¹⁷ while in section 5, we successfully obtained crystal-phase-heterostructured 4H/*fcc* Au nanorods (NRs) with high-yield.¹⁸ By combining these two works, it is probable

to obtain high-yield Au@Cu NRs with the unusual crystal phase of 4H/*fcc* Cu, which allows the further study on the crystal phase-dependent CO₂RR performance of nanostructured Cu.

In this chapter, a high-yield approach to synthesize crystal-phase-heterostructured 4H/*fcc* Au@Cu core-shell NRs is realized under ambient condition. In brief, the solution-phase epitaxial growth of 4H/*fcc* crystal-phase-heterostructured Cu was achieved by reducing Cu(NO₃)₂ with N₂H₄·H₂O in the presence of pre-synthesized Au NRs and NaOH under ambient condition (see section 3.3.9 for details). The uniform and epitaxial coating of 4H/*fcc* Cu shell allows the further exploration on its CO₂RR performance. Compared to *fcc* Cu NPs, the crystal-phase-heterostructured 4H/*fcc* Cu demonstrated much higher catalytic activity and a significantly improvement of C₂/C₁ product ratio.

6.2 Results and Discussions

6.2.1 High-yield Epitaxial Growth of 4H/*fcc* Au@Cu NRs

The epitaxial coating process is illustrated in Figure 6.1. The characteristic 4H/*fcc* heterophase of the Au core (Figure 6.1a) is perfectly copied by the 4H/*fcc* Cu shell (Figure 6.1b), on the surface of which the electrocatalytic CO₂RR takes place with various types of products (Figure 6.1c).

Figure 6.1 Schematic illustration of the synthesis of 4H/*fcc* crystal-phase-heterostructured Au@Cu NR and its application in electrocatalytic CO₂RR. (a) Synthesis of crystal-phase-

heterostructured 4H/*fcc* core-shell Au@Cu nanorods. (b) Electrochemical CO₂ reduction by 4H/*fcc* Au@Cu nanorods.

The crystal-phase-heterostructured 4H/*fcc* Au NRs are first synthesized with a nearly 100% yield (Figure 6.2 a,b). The detailed synthetic method is described in section 3.3.9.

Figure 6.2 SEM and TEM characterization of the crystal-phase-heterostructured 4H/*fcc* Au NRs. (a) Low-magnification SEM and (b) low-magnification TEM images of as-synthesized crystal-phase-heterostructured 4H/*fcc* Au NRs.

After that, the growth of copper coating is realized in the presence of Au NRs. With careful control of the growth kinetics, uniform Cu coating was realized in a high yield, as shown in Figure 6.3 a,b. Note that the Au@Cu NRs tend to aggregate into bundles on the SEM substrate (Figure 6.3a).

Figure 6.3 SEM and TEM characterization of the crystal-phase-heterostructured 4H/*fcc* Au@Cu NRs. (a) Low-magnification SEM and (b) low-magnification TEM images of as-synthesized crystal-phase-heterostructured 4H/*fcc* Au@Cu NRs.

The low-magnification TEM image of the crystal-phase-heterostructured 4H/*fcc* Au@Cu NRs (Figure 6.4a) shows the uniform coating of a Cu layer with an average thickness of ~ 6-9 nm. The slight crystal lattice difference between 4H/*fcc* Cu shell and 4H/*fcc* Au core result in the observation of Moiré pattern, which is more clearly seen in Figure 6.4c. The epitaxial growth can be observed from the continuous lattice fringes from the darker Au core to the lighter Cu shell. To gain a closer and cleared observation on the epitaxial growth, C_s-corrected DF-STEM image is taken at the Au-Cu interface (Figure 6.4d), with a corresponding FFT pattern showing the crystallographic information (Figure 6.4e). The two parallel sets of diffraction dots in Figure 6.4e suggested that Cu and Au, although bears a theoretical lattice mismatch of 12%, are of the same crystal phase. The epitaxy is more evidently shown by taking FFT patterns of selected areas in Figure 6.4d, where two sets of characteristic diffraction pattern of 4H and *fcc* phases are observed in Figure 6.4f1 (area in red square in d) and Figure 6.4f2 (area in green square in d), respectively. A EDS linear scan was conducted to detect the element distribution of the Au and Cu element (Figure 6.4g,h), showing a typical Au@Cu core-shell profile.

Figure 6.4 High-magnification TEM, Cs-corrected TEM, and EDS characterizations of crystal-phase-heterostructured 4H/*fcc* Au@Cu NRs. (a) Low-magnification, (b) high-magnification, and (c) high-resolution TEM images of crystal-phase-heterostructured 4H/*fcc* Au@Cu NRs. (d) Cs-corrected dark-field STEM image at the Au-Cu interface with (e) corresponding FFT pattern. (f1, f2) FFT patterns of selected regions in (d) in red and green squares, respectively. (g) DF-STEM image and corresponding EDS linear scan profile of element Au and Cu.

Moreover, the thickness of the epitaxially grown Cu shell can be controlled by simply adjusting the initial concentration of $\text{Cu}(\text{NO}_3)_2$ and $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$. When the concentration of $\text{Cu}(\text{NO}_3)_2$ is reduced from 1 mM to 0.5 mM and 0.2 mM (corresponding amount of $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ is reduced from 10 μL to 5 μL and 2 μL), the Cu shell thickness can be reduced from $\sim 6\text{--}9$ nm (Figure 6.5a-c) to $\sim 4\text{--}6$ nm (Figure 6.5d-f) and $\sim 1\text{--}4$ nm (Figure 6.5h-j), respectively. Ultrathin Cu coating with less than 1 nm of thickness (Figure 6.5k-m) can be

obtained when 0.2 mM of Cu(NO₃)₂ and 4 μL of N₂H₄·H₂O are used. All the aforementioned Cu shells are epitaxially grown with the 4H/*fcc* heterophase.

Figure 6.5 Thickness control of epitaxially grown Cu shell. (a) BF TEM and (b) DF STEM image of Au@Cu NR with shell thickness of ~6-10 nm. (c) EDS linear scan profile of elements Au and Cu in (b). (d) BF TEM and (e) DF STEM image of Au@Cu NR with shell thickness of ~4-6 nm; (f) EDS linear scan profile of element Au and Cu in (e). (h) BF TEM and (i) DF STEM image of Au@Cu NR with shell thickness of ~1-4 nm; (j) EDS linear scan profile of element Au and Cu in (i). (k) BF TEM and (l) DF STEM image of Au@Cu NR with shell thickness of < 1 nm; (m) EDS linear scan profile of element Au and Cu in (l).

However, free-standing by-product of Cu nanoclusters is observed when the Cu shell is less than 6 nm. Therefore the Au@Cu NRs with ~6-9 nm thick of Cu shell is chosen as our model nanocatalyst for the electrocatalytic CO₂RR characterizations.

The metallic states of Au in Au NRs and Au and Cu in Au@Cu NRs are confirmed using XPS (Figure 6.6). It is worth mentioning that satellite peaks corresponding to a mixed CuOx is detected along with the strong metallic Cu peaks, indicating the existence of a small portion of oxidized Cu.

Figure 6.6 XPS spectra of 4H/*fcc* Au NRs and 4H/*fcc* Au@Cu NRs, showing the core level peaks of (a) Au 4f of 4H/*fcc* Au NRs, (b) Au 4f of 4H/*fcc* Au@Cu NRs, and (c) Cu 2p of 4H/*fcc* Au@Cu NRs. The satellite peaks at 962.2 eV and 943.8 eV in (c) are attributed to Cu oxide.

The existence of Cu oxide is further confirmed by C_S-corrected BF-STEM image, in which a ~ 1 nm thick of Cu oxide layer is observed as the outmost shell. However it is not seen in most 4H/*fcc* Au@Cu NRs, which coincide with the weak XPS signals of Cu oxide in Figure 6.6c.

Figure 6.7 C_S-corrected STEM image of one Au@Cu nanorod with a thin layer of Cu oxide.

6.2.2 Electrocatalytic CO₂RR by 4H/*fcc* Au@Cu NRs

In CO₂RR, the loading density of Cu is found to be critical to achieve its optimal performance.¹⁹ Therefore, different loading density of 4H/*fcc* Au@Cu NRs are tested using the FE of C₂H₄, one of the most important CO₂RR product, as an indicator. As shown in Figure 6.8, at the loading density of around 109 μg , the FE (C₂H₄) approaches to a maximum value of ~ 30%.

Figure 6.8 Optimization of loading density for CO₂RR performance in terms of FE of C₂H₄.

At the optimal loading density, the FEs of different kinds of products are summarized in Figure 6.9a and Figure 6.10a. The corresponding specific current densities of the different products are calculated as shown in Figure 6.9b and Figure 6.10b. At the potential of – 1.10 V, FE (C₂H₄) reaches a maximum of 31.7%. At the potential of – 0.84 V, the total FE, counting FE (CO), FE (HCOOH), FE (CH₄), and FE (C₂H₄) reaches a maximum of 94.6%. Moreover, the specific current density of C₂H₄ exceeds C₁ products at the potential of – 1.10 V. These results suggest that at a lower potential, around –1.10 V, the 4H/*fcc* Cu@Au NRs showed most promising performance towards high selectivity of C₂H₄ along with a high C₂H₄/C₁ product ratio.

The Tafel plot shown in Figure 6.10c provided the information on the reaction kinetics. The slope of 162 mV·dec^{–1} represent the conversion process from CO₂ to CO₂^{*} radical. The stability of 4H/*fcc* Cu@Au NRs under CO₂RR is demonstrated in Figure 6.10d. After a

total testing time of more than 7 hours, the i-t curve remains flat and steady, indicating the excellent stability of the Cu@Au NRs during the CO₂RR test.

Figure 6.9 Electrocatalytic CO₂RR performance of 4H/*fcc* Au@Cu NRs. (a) Cumulative FEs of various CO₂RR products. (b) Partial current densities (*J*) of various CO₂RR products. (c) Chrono-amperometry results at the corresponding potentials in CO₂-saturated 0.1 M KHCO₃ solution.

To demonstrate the superior performance of 4H/*fcc* Cu, OAm-capped *fcc* Cu NPs with similar diameters of ~ 15-20 nm are prepared. The TEM image (Figure 6.10a) and XRD pattern (Figure 6.10b) confirm the size and crystal phase of the as-synthesized *fcc* Cu NPs.

Figure 6.10 Characterizations of *fcc* Cu nanoparticles. (a) TEM image and (b) X-ray diffraction pattern of oleylamine-capped *fcc* Cu nanoparticles.

The as-synthesized *fcc* Cu NPs are tested under the same conditions as that of 4H/*fcc* Au@Cu NRs. A performance comparison between the *fcc* Cu NP and the 4H/*fcc* Au@Cu NR is summarized in Figure 6.11. The overall current densities of 4H/*fcc* Au@Cu NRs and *fcc* Cu NPs in Figure 6.11a show different onset potentials between the two catalysts, indicating the much higher overall CO₂ reduction activity of 4H/*fcc* Au@Cu NRs. Particularly, 4H/*fcc* Au@Cu NRs demonstrate outstanding activity toward C₂H₄ production. As shown in Figure 6.11b, the C₂H₄ partial current densities of 4H/*fcc* Au@Cu NRs and *fcc* Cu NPs increases dramatically as the potential becomes more negative. The onset potential of -0.58V for 4H/*fcc* Au@Cu NRs is 0.21V higher than that of -0.79 V for *fcc* Cu NPs. At a potential lower than -1.13V, as shown in Figure 6.11c, the FE(C₂H₄) of 4H/*fcc* Au@Cu NRs exceeds that of *fcc* Cu NPs, reaching a maximum value of 48.5%. Moreover, the Tafel plot in Figure 6.11d reveals that 4H/*fcc* Au@Cu has a Tafel slope of 164 mV dec⁻¹, while *fcc* Cu shows a slope of 249 mV dec⁻¹. It suggested that the reaction kinetics of CO₂RR on 4H/*fcc* Au@Cu was intrinsically faster than that on *fcc* Cu, and their rate-limiting steps could be the one electron reduction of CO₂ to generate CO₂^{•-} intermediate.

Figure 6.11 Comparison of CO₂RR performance between 4H/*fcc* Au@Cu NRs and *fcc* Cu NPs. (a) Total current densities and (b) partial current densities (C₂H₄) of 4H/*fcc* Au@Cu NRs and *fcc* Cu NPs at different potentials. (c) Faradaic efficiencies of C₂H₄ at different potentials. (d) Tafel slopes of CO₂ to CO₂* radical conversion.

The post-test stability of 4H/*fcc* Au@Cu NRs is further proved by the SEM images of the as-fabricated electrode before (Figure 6.12a) and after (Figure 6.12b) the test, showing the well-maintained uniform coating of the 4H/*fcc* Au@Cu NRs on the carbon fiber throughout the test.

Figure 6.12 SEM images of 4H/*fcc* Au@Cu NRs loaded on carbon paper electrode taken (a) before and (b) after the electrocatalytic CO₂RR reaction.

To further confirm the stability of the 4H/*fcc* crystal phase of Cu, TEM and HRTEM images are taken on the 4H/*fcc* Au@Cu NRs after the CO₂RR test (Figure 6.13). As shown in Figure 6.13a, the characteristic Moiré pattern suggest the existence of Au@Cu core-shell structure. The HRTEM image in Figure 6.13b and the corresponding FFT pattern (Figure 6.13c) in the selected area in red square showed clearly the co-existence of 4H and *fcc* Cu shell, with the two parallel sets of diffraction points.

Figure 6.13 Post-test TEM characterizations of 4H/*fcc* Au@Cu NRs. (a) Low magnification TEM and (b) HRTEM images of 4H/*fcc* Au@Cu NRs after the CO₂RR test. (c) FFT pattern of the squared area in (b).

The much higher C₂H₄ selectivity of 4H/*fcc* Au@Cu NRs compared to *fcc* Cu NPs may be attributed to the novel crystal phase heterostructure of Cu, which facilitates the conversion of intermediate species to C₂H₄ and suppresses the pathway to CH₄. The high density of phase boundaries in the 4H/*fcc* Cu shell provides rich abrupt interfaces at the surface, which

may further boost the catalytic activity of the Cu shell.¹⁰ The synergistic effect between Au and Cu could have also contributed to the high CO₂RR activity and relatively good durability.^{4,8} The exact mechanism behind the enhanced selectivity and activity toward C₂H₄ production is, however, still not very clear.

6.3 Conclusions

To conclude, a facile method has been developed to obtain high-yield crystal-phase-heterostructured 4H/*fcc* Au@Cu core-shell NRs under ambient condition. The epitaxially grown 4H/*fcc* Cu shell exhibit excellent catalytic activity towards CO₂RR, with a much lower onset potential, much higher C₂H₄ selectivity compared to *fcc* Cu NPs and a relatively good stability. The study provides a novel direction in the design of Cu-based CO₂RR nanocatalyst, i.e., engineering the crystal phase of Cu for optimal catalytic activity, selectivity, and durability.^{4,8}

References

- (1) Seh, Z. W.; Kibsgaard, J.; Dickens, C. F.; Chorkendorff, I.; Norskov, J. K.; Jaramillo, T. F. Combining Theory and Experiment in Electrocatalysis: Insights into Materials Design. *Science* **2017**, 355.
- (2) Bushuyev, O. S.; De Luna, P.; Dinh, C. T.; Tao, L.; Saur, G.; van de Lagemaat, J.; Kelley, S. O.; Sargent, E. H. What Should We Make with Co₂ and How Can We Make It? *Joule* **2018**, 2, 825-832.
- (3) Raciti, D.; Wang, C. Recent Advances in Co₂ Reduction Electrocatalysis on Copper. *ACS Energy Lett.* **2018**, 3, 1545-1556.
- (4) Ross, M. B.; Dinh, C. T.; Li, Y.; Kim, D.; De Luna, P.; Sargent, E. H.; Yang, P. Tunable Cu Enrichment Enables Designer Syngas Electrosynthesis from Co₂. *J. Am. Chem. Soc.* **2017**, 139, 9359-9363.
- (5) Chen, C. S.; Handoko, A. D.; Wan, J. H.; Ma, L.; Ren, D.; Yeo, B. S. Stable and Selective Electrochemical Reduction of Carbon Dioxide to Ethylene on Copper Mesocrystals. *Cataly. Sci. Technol* **2015**, 5, 161-168.
- (6) Li, Y.; Cui, F.; Ross, M. B.; Kim, D.; Sun, Y.; Yang, P. Structure-Sensitive Co₂ Electroreduction to Hydrocarbons on Ultrathin 5-Fold Twinned Copper Nanowires. *Nano Lett.* **2017**, 17, 1312-1317.

- (7) Jeon, H. S.; Kunze, S.; Scholten, F.; Roldan Cuenya, B. Prism-Shaped Cu Nanocatalysts for Electrochemical Co₂ Reduction to Ethylene. *ACS Catal.* **2018**, *8*, 531-535.
- (8) Kim, D.; Resasco, J.; Yu, Y.; Asiri, A. M.; Yang, P. Synergistic Geometric and Electronic Effects for Electrochemical Reduction of Carbon Dioxide Using Gold-Copper Bimetallic Nanoparticles. *Nat. Commun.* **2014**, *5*, 4948.
- (9) Lee, S. Y.; Jung, H.; Kim, N. K.; Oh, H. S.; Min, B. K.; Hwang, Y. J. Mixed Copper States in Anodized Cu Electrocatalyst for Stable and Selective Ethylene Production from Co₂ Reduction. *J. Am. Chem. Soc.* **2018**, *140*, 8681-8689.
- (10) Dinh, C.-T.; Burdyny, T.; Kibria, M. G.; Seifitokaldani, A.; Gabardo, C. M.; García de Arquer, F. P.; Kiani, A.; Edwards, J. P.; De Luna, P.; Bushuyev, O. S. et al. Co₂ Electroreduction to Ethylene Via Hydroxide-Mediated Copper Catalysis at an Abrupt Interface. *Science* **2018**, *360*, 783-787.
- (11) Lee, S.; Park, G.; Lee, J. Importance of Ag–Cu Biphasic Boundaries for Selective Electrochemical Reduction of Co₂ to Ethanol. *ACS Catal.* **2017**, *7*, 8594-8604.
- (12) Rasul, S.; Anjum, D. H.; Jedidi, A.; Minenkov, Y.; Cavallo, L.; Takanabe, K. A Highly Selective Copper-Indium Bimetallic Electrocatalyst for the Electrochemical Reduction of Aqueous Co₂ to Co. *Angew. Chem. Int. Ed.* **2015**, *54*, 2146-2150.
- (13) Duan, Y. X.; Meng, F. L.; Liu, K. H.; Yi, S. S.; Li, S. J.; Yan, J. M.; Jiang, Q. Amorphizing of Cu Nanoparticles toward Highly Efficient and Robust Electrocatalyst for Co₂ Reduction to Liquid Fuels with High Faradaic Efficiencies. *Adv. Mater.* **2018**, *30*, e1706194.
- (14) Kusada, K.; Kobayashi, H.; Yamamoto, T.; Matsumura, S.; Sumi, N.; Sato, K.; Nagaoka, K.; Kubota, Y.; Kitagawa, H. Discovery of Face-Centered-Cubic Ruthenium Nanoparticles: Facile Size-Controlled Synthesis Using the Chemical Reduction Method. *J. Am. Chem. Soc.* **2013**, *135*, 5493-5496.
- (15) Fan, Z.; Zhang, H. Crystal Phase-Controlled Synthesis, Properties and Applications of Noble Metal Nanomaterials. *Chem. Soc. Rev.* **2016**, *45*, 63-82.
- (16) Fan, Z.; Luo, Z.; Huang, X.; Li, B.; Chen, Y.; Wang, J.; Hu, Y.; Zhang, H. Synthesis of 4h/Fcc Noble Multimetallic Nanoribbons for Electrocatalytic Hydrogen Evolution Reaction. *J. Am. Chem. Soc.* **2016**, *138*, 1414-1419.
- (17) Fan, Z.; Chen, Y.; Zhu, Y.; Wang, J.; Li, B.; Zong, Y.; Han, Y.; Zhang, H. Epitaxial Growth of Unusual 4h Hexagonal Ir, Rh, Os, Ru and Cu Nanostructures on 4h Au Nanoribbons. *Chem. Sci.* **2017**, *8*, 795-799.
- (18) Chen, Y.; Fan, Z.; Luo, Z.; Liu, X.; Lai, Z.; Li, B.; Zong, Y.; Gu, L.; Zhang, H. High-Yield Synthesis of Crystal-Phase-Heterostructured 4h/Fcc Au@Pd Core–Shell Nanorods for Electrocatalytic Ethanol Oxidation. *Adv. Mater.* **2017**, *29*, 1701331.
- (19) Kim, D.; Kley, C. S.; Li, Y.; Yang, P. Copper Nanoparticle Ensembles for Selective Electroreduction of Co₂ to C₂-C₃ Products. *Proc. Natl. Acad. Sci. U. S. A.* **2017**, *114*, 10560-10565.

Chapter 7*

Discussion and Future Work

The chapter gives a general discussion to conclude the thesis and discusses the originality of the research works introduced in this thesis. First, five types of metals in the unusual 4H phase, including four noble metals and one transition metal, have been obtained for the first time. The solution-based epitaxial growth of secondary metals on the 4H Au NRBs is believed to be a general method to obtain unusual crystal phases of metals in a hybrid form. Second, an exploration of the synthetic conditions for novel Au nanostructures was carried out, leading to the successful discovery of crystal-phase-heterostructured 4H/fcc Au NRs. The robust and high-yield synthesis allows a further study on the electrocatalytic performance of 4H/fcc Au@Pd core-shell NRs, which is obtained by applying the epitaxial growth strategy developed in the first work. In the third work, high-yield synthesis of 4H/fcc Au@Cu NRs is prepared, which is then detailed studied in the electrocatalytic CO₂RR. . Based on the current research status, some outstanding questions and exploration directions that can be focused on in the near future is also discussed.

7.1 General Discussion

7.1.1 Discussion on the Epitaxial Growth of 4H/*fcc* Au@M NRBs

By carefully controlling the kinetics of epitaxial growth, 4H phase of Ir, Rh, Os, Ru, and Cu is obtained for the first time. This general approach uses the pre-synthesized 4H Au NRB as a crystal-phase template and deposit the secondary metal shell by reducing the metal precursor with strong reducing agent under ambient condition. Although a partial 4H-to-*fcc* phase transition in the 4H Au NRBs is observed, the dominant phase of the bimetallic core-shell NRB, i.e. Au@Ir, Au@Rh, Au@Os, Au@Ru and Au@Cu NRBs, is still 4H. This suggests that as a robust method, it can be further extended to grow other novel nanostructures with new crystal phases. For example, instead of reducing one type of metal, several metal precursors can be reduced simultaneously, leading to probable formation of various multimetallic heterostructures. Moreover, this universal template strategy can also be extended to grow non-metal species such as semiconductor nanostructures, so that one can study the fascinating properties arisen from the metal-semiconductor junction. The importance of this work lies not only in the introduction of the new crystal phases of 5 types of metals, but also in its potential of obtaining other novel crystal structures. The strategy has been well applied in the following works to prepare novel nanocatalysts for clean energy applications.

7.1.2 Discussion on the High-yield Synthesis of 4H/*fcc* Au NRs and Epitaxial Growth of 4H/*fcc* Au@Pd NRs

In this work, a one-pot colloidal method for the high-yield synthesis of 4H/*fcc* crystal-phase-heterostructured Au NRs is developed for the first time. Compared to the previously reported similar Au-OAm systems, this method is robust, ready to scale-up, and environmental friendly. Interestingly, the similar structure of Au has been proposed in a report in 2015, predicting a possible 1D Au nanostructure in which 4H and *fcc* crystal phases grows alternatively and periodically.¹ Although in this work, 4H and *fcc* crystal phases appear randomly with non-regular length, it is still a big step toward the controlled

growth of crystal phase heterostructure. Moreover, via the epitaxial growth strategy developed in the first work, crystal-phase-heterostructured 4H/*fcc* Pd, a catalytically active noble metal, is successfully obtained. The bimetallic 4H/*fcc* Au@Pd core-shell NRs showed outstanding catalytic performance as compared to the commercial catalysts, i.e. Pd black and Pt/C, with much higher activity and better stability toward the EOR. Note that the commercial catalysts are both in the common *fcc* phase. This work provides a new template to engineer the crystal phase of noble metal nanostructures, which can be produced in large quantity and high yield. Since the purity of nanocatalysts is critical to further study their catalytic performances, the crystal-phase-heterostructured 4H/*fcc* Au NRs can serve as a universal template for the growth of other novel crystal-phase-heterostructured bi-/multi-metallic nanostructures or metal-semiconductor hybrids towards practical applications.

7.1.3 Discussion on the High-yield Epitaxial Growth of 4H/*fcc* Au@Cu NRs

Following the previous project, a facile method is further developed to obtain high-yield crystal-phase-heterostructured 4H/*fcc* Au@Cu core-shell NRs under ambient condition. In this work, *fcc* Cu NPs are synthesized with same surfactant and similar size compared to the 4H/*fcc* Au@Cu NRs. Since Au has no other CO₂RR product besides CO, this work allows a direct comparison of the catalytic performance between 4H/*fcc* Cu and *fcc* Cu. Surprisingly, the epitaxially grown 4H/*fcc* Cu shell exhibit excellent catalytic activity towards CO₂RR, with a much higher C₂/C₁ selectivity compared to *fcc* Cu NPs and a relatively good stability. This study provides a novel direction in the design of Cu-based CO₂RR nanocatalyst, i.e., via engineering the crystal phase of Cu for optimal catalytic activity, selectivity, and durability in CO₂RR.

7.2 Reconnaissance Work not Included in Main Chapters

As introduced in section 5.2.1, a thorough investigation of the synthetic conditions was carried out based on the Au-OAm system developed for the syntheses of 2H Au SSs and 4H Au NRs.²⁻⁴ The main chapters of this thesis focus on the development of various 1D

Au-based nanostructures, the experimental conditions of which are more close to those of 4H Au NRBs. Meanwhile, some preliminary results suggest that when the experimental conditions are tuned toward those of 2H Au SSs, 2D Au nanostructures can be obtained. In this section, the preliminary results will be introduced and discussed.

With the arising of various 2D semiconducting nanomaterials, 2D metal nanostructures is drawing increasing attention for their fascinating optical and catalytic properties.^{5,6} Inspired by the graphene-templated growth of ultrathin *hcp* Au SSs, an optimization of the synthetic conditions towards high-yield, free-standing *hcp* Au SSs was carried out.

7.3 Outstanding Questions and Future Works

In spite of the achievement introduced in this thesis, many opportunities and challenges lie in the way towards systematic and comprehensive study on the structure-property relationship of noble metal nanomaterials with novel crystal phases.

To start with, theoretical studies on the formation mechanism of the crystal-phase-heterostructured 4H/*fcc* Au NR is still lacking. Although time-dependent experiments were carried out, it is still in the stage of “observation first, explanation second” mode of study. To unravel the growth pathway of unusual crystal phase, simulations to compare the energy difference is needed. Meanwhile, to support the theoretical data, in-situ TEM observation of the growth behavior should be studied simultaneously. In fact, most research efforts have focused on the controlled synthesis of different 2D morphologies and the explanation on the formation mechanism.

Secondly, a systematic comparison between different crystal phases of noble metals is desired. To date, noble metal nanomaterials with same morphology, surfactant but different crystal phases still cannot be obtained. Therefore, a perfect model to study the phase-dependent properties is still lacking. In another word, although phase-controlled synthesis has been achieved to some extent, it is still difficult to accurately design the exact final

product as desired. The Au-OAm system is, although relatively simple, still hard to understand.

Thirdly, it would be very interesting to prepare heterostructures composed of Au with novel phases and semiconductor nanostructures. The excellent optical and electronic properties of Au nanostructures can trigger the generation of “hot electrons” at the Au-semiconductor interface. Note that Au nanostructures obtained from the Au-OAm system is a particularly suitable template for the secondary growth of semiconducting nanomaterials, since most syntheses for semiconducting nanomaterials relies on the OAm as well.⁷ Therefore, another important future direction is to further extend the phase-based property investigation to Au-semiconductor nanostructured hybrids, so that the optical and electronic applications of Au-semiconductor hybrids can be greatly enriched via the crystal phase engineering.

References

- (1) Zhang, H. Ultrathin Two-Dimensional Nanomaterials. *ACS Nano* **2015**, *9*, 9451-9469.
- (2) Fan, Z.; Bosman, M.; Huang, X.; Huang, D.; Yu, Y.; Ong, K. P.; Akimov, Y. A.; Wu, L.; Li, B.; Wu, J. et al. Stabilization of 4h Hexagonal Phase in Gold Nanoribbons. *Nat. Commun.* **2015**, *6*, 7684.
- (3) Huang, X.; Li, S.; Huang, Y.; Wu, S.; Zhou, X.; Li, S.; Gan, C. L.; Boey, F.; Mirkin, C. A.; Zhang, H. Synthesis of Hexagonal Close-Packed Gold Nanostructures. *Nat. Commun.* **2011**, *2*, 292.
- (4) Fan, Z.; Huang, X.; Chen, Y.; Huang, W.; Zhang, H. Facile Synthesis of Gold Nanomaterials with Unusual Crystal Structures. *Nat. Protoc.* **2017**, *12*, 2367.
- (5) Fan, Z.; Huang, X.; Tan, C.; Zhang, H. Thin Metal Nanostructures: Synthesis, Properties and Applications. *Chem. Sci.* **2015**, *6*, 95-111.
- (6) Chen, Y.; Fan, Z.; Zhang, Z.; Niu, W.; Li, C.; Yang, N.; Chen, B.; Zhang, H. Two-Dimensional Metal Nanomaterials: Synthesis, Properties, and Applications. *Chem. Rev.* **2018**, *118*, 6409-6455.
- (7) Fan, Z.; Zhang, X.; Yang, J.; Wu, X. J.; Liu, Z.; Huang, W.; Zhang, H. Synthesis of 4h/Fcc-Au@Metal Sulfide Core-Shell Nanoribbons. *J. Am. Chem. Soc.* **2015**, *137*, 10910-10913.

Publication List

- [1] **Y. Chen**, Z. Fan, Z. Zhang, W. Niu, C. Li, N. Yang, B. Chen, H. Zhang*, Two-Dimensional Metal Nanomaterials: Synthesis, Properties, and Applications. *Chemical Reviews*, **2018**, *118*, 6409-6455.
- [2] **Y. Chen**, Z. Fan, Z. Luo, X. Liu, Z. Lai, B. Li, Y. Zong, L. Gu, H. Zhang*, High-Yield Synthesis of Crystal-Phase-Heterostructured 4H/fcc Au@Pd Core-Shell Nanorods for Electrocatalytic Ethanol Oxidation. *Advanced Materials*, **2017**, *29*, 1701331.
- [3] **Y. Chen**, J. Wang, Z. Fan, X. Liu, Z. Lai, B. Li, B. Chen, Y. Zong, L. Gu, X. Wang, H. Zhang*, 4H and 4H/fcc Au@Cu Core-Shell Nanostructures for Electrocatalytic CO₂ Reduction. *submitted*
- [4] Z. Fan, **Y. Chen (co-first author)**, Y. Zhu, J. Wang, B. Li, Y. Zong, H. Zhang*, Epitaxial Growth of Unusual 4H hexagonal Ir, Rh, Os, Ru and Cu Nanostructures on 4H Au Nanoribbons. *Chemical Science*, **2017**, *8*, 795-799.
- [5] Z. Lai, **Y. Chen (co-first author)**, C. Tan, X. Zhang, H. Zhang*, Self-Assembly of Two-Dimensional Nanosheets into One-Dimensional Nanostructures. *Chem*, **2016**, *1*, 59-77.
- [6] B. Li, **Y. Chen (Co-first author)**, X. Ge, J. Chai, X. Zhang, T. Hor, G. Du, Z. Liu*, H. Zhang*, Mussel-inspired One-pot Synthesis of Transition Metal and Nitrogen Co-doped Carbon (M/N-C) as Efficient Oxygen Catalysts for Zn-air Batteries, *Nanoscale*, **2016**, *8*, 5067-5075.
- [7] Z. Fan, X. Huang, **Y. Chen**, W. Huang, H. Zhang*, Facile Synthesis of Gold Nanomaterials with Unusual Crystal Structures. *Nature Protocols*, **2017**, *12*, 2367-2378
- [8] Z. Fan, Z. Luo, **Y. Chen**, J. Wang, B. Li, Y. Zong, H. Zhang*, Synthesis of 4H/fcc-Au@ M (M= Ir, Os, IrOs) Core-Shell Nanoribbons for Electrocatalytic Oxygen Evolution Reaction, *Small*, **2016**, *12*, 3908-3913.
- [9] L. Zhang, S. Roy, **Y. Chen**, E. Chua, K. See, X. Hu*, M. Liu*, Mussel-Inspired Polydopamine Coated Hollow Carbon Microspheres, a Novel Versatile Filler for

- Fabrication of High Performance Syntactic Foams. *ACS Applied Materials and Interfaces*, **2014**, 6, 18644-18652.
- [10] Q. Li, W. Niu, X. Liu, **Y. Chen**, X. Wu, X. Wen, Z. Wang, H. Zhang*, Z. Quan*, Pressure-Induced Phase Engineering of Gold Nanostructures. *Journal of American Chemical Society*, **2018**, 140, 15783-15790.
- [11] Z. Fan, Z. Luo, X. Huang, B. Li, **Y. Chen**, J. Wang, Y. Hu, H. Zhang*, Synthesis of 4H/fcc Noble Multimetallic Nanoribbons for Electrocatalytic Hydrogen Evolution Reaction. *Journal of American Chemical Society*, **2016**, 138, 1414-1419.
- [12] N. Yang, H. Cheng, X. Liu, Q. Yun, **Y. Chen**, B. Li, B. Chen, Z. Zhang, X. Chen, Q. Lu, J. Huang, Y. Yang, L. Gu, H. Zhang*, Novel Amorphous/crystalline Hetero-phase Pd Nanosheets: One-pot Synthesis and Highly Selective Hydrogenation Reaction. *Advanced Materials*, **2018**, 30, 1803234.
- [13] B. Li, J. Quan, A. Loh, J. Chai, **Y. Chen**, C. Tan, X. M. Ge, T. Hor, Z. L. Liu,* H. Zhang,* Y. Zong*, A Robust Hybrid Zn-Battery with Ultralong Cycle Life. *Nano Letter*, **2017**, 17, 156-163.
- [14] N. Yang, Z. Zhang, B. Chen, Y. Huang, J. Chen, Z. Lai, **Y. Chen**, M. Sindoro, A. Wang, H. Cheng, Z. Fan, X. Liu, B. Li, Y. Zong, L. Gu, H. Zhang*, Synthesis of Ultrathin PdCu Alloy Nanosheets Used as Highly Efficient Electrocatalyst for Formic Acid Oxidation”, *Advanced Materials*, **2017**, 29, 1700769.
- [15] Z. Zhang, Y. Liu, B. Chen, Y. Gong, L. Gu, Z. Fan, N. Yang, Z. Lai, **Y. Chen**, J. Wang, Y. Huang, M. Sindoro, W. Niu, B. Li, Y. Zong, Y. Yang, X. Huang, F. Huo, W. Huang, H. Zhang*, Submonolayered Ru Deposited on Ultrathin Pd Nanosheets used for Enhanced Catalytic Applications. *Advanced Materials*, **2016**, 28, 10282-10286.
- [16] Z. Liu, X. Zhang, Y. Gong, Q. Lu, Z. Zhang, H. Cheng, Q. Ma, J. Chen, M. Zhao, B. Chen, **Y. Chen**, X. Wu, P. Yin, L. Gu, Y. Du, *Nano Research*, **2018**, <https://doi.org/10.1007/s12274-018-2212-8>.
- [17] Z. Lai, A. Chaturvedi, Y. Wang, T. Tran, X. Liu, C. Tan, Z. Luo, B. Chen, Y. Huang, G. Nam, Z. Zhang, **Y. Chen**, Z. Hu, B. Li, S. Xi, Q. Zhang, Y. Zong, L. Gu, C. Kloc, Y. Du,* H. Zhang*, Preparation of 1T'-Phase $\text{ReS}_{2-x}\text{Se}_{2(1-x)}$ ($x=0-1$) Nanodots for Highly Efficient Electrocatalytic Hydrogen Evolution Reaction. *Journal of American Chemical Society*, **2018**, 140, 8563-8568.

- [18] Q. Lu, A. Wang, Y. Gong, W. Hao, H. Cheng, J. Chen, B. Li, N. Yang, W. Niu, J. Wang, Y. Yu, X. Zhang, **Y. Chen**, Z. Fan, X. Wu, S. Li, L. Gu*, H. Zhang*, Crystal phase-based Epitaxial Growth of Hybrid Noble Metal Nanostructures on 4H/fcc Au Nanowires, *Nature Chemistry*, **2018**, *10*, 456-461.
- [19] X. Zhang, Z. Luo, P. Yu, Y. Cai, Y. Du, D. Wu, S. Gao, C. Tan, Z. Li, M. Ren, T. Osipowicz, S. Chen, Z. Jiang, J. Li, Y. Huang, J. Yang, **Y. Chen**, C. Ang, Y. Zhao, P. Wang, L. Song, X. J. Wu, Z. Liu, A. Borgna, H. Zhang*, Lithiation-induced Amorphization of Pd₃P₂S₈ for Highly Efficient Hydrogen Evolution. *Nature Catalysis*, **2018**, *1*, 460-468.
- [20] Z. Luo, C. Tan, Z. Lai, X. Zhang, J. Chen, **Y. Chen**, B. Chen, Y. Gong, Z. Zhang, X. Wu, B. Li, Y. Zong, L. Gu, H. Zhang*, A Simple Electrochemical Method for Conversion of Pt Wires to Pt Concave Icosahedra and Nanocubes on Carbon Paper for Electrocatalytic Hydrogen Evolution. *Science China Materials*, **2019**, *1*, 115-121.
- [21] B. Chen, H. Bi, Q. Ma, C. Tan, H. Cheng, **Y. Chen**, X. He, L. Sun, T. Lim, L. Huang, H. Zhang*, Preparation of Graphene-MoS₂ Hybrid Aerogels as Multifunctional Sorbents for Water Remediation *Science China Materials*, **2017**, *11*, 1102-1108.