Synthesis of noble metal nanomaterials with new crystal phases for electrocatalytic reaction

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**SYNTHESIS OF NOBLE METAL NANOMATERIALS WITH NEW CRYSTAL
PHASES FOR ELECTROCATALYTIC REACTION**

WANG JIE

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

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PHASES FOR ELECTROCATALYTIC REACTION**

WANG JIE

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

2019

Statement of Originality

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

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Authorship Attribution Statement

This thesis consists of content from papers which have been published in the following peer-reviewed journals, in which I was the first author.

Chapter 4 is published as.

- Prof. Zhang Hua proposed the idea, supervised the whole project and revised the manuscript drafts.
- I conducted the materials preparation, characterizations and analysis of all the experimental data. I prepared the manuscript, which was revised together with Prof. Zhang Hua.
- Dr. Gu Lin helped to measure the aberration-corrected STEM of all the samples, and help to analyze the data.
- Dr. Zhang Jian helped to conduct electrochemical test of all of the samples.
- All the authors gave suggestions to revise the manuscript together.

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- Dr. Gu Lin helped to measure the aberration-corrected STEM of all the samples, and help to analyze the data.
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- All the authors gave suggestions to revise the manuscript together.

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- I conducted the materials preparation, characterizations and analysis of all the experimental data. I prepared the manuscript, which was revised together with Prof. Zhang Hua.
- Dr. Gu Lin helped to measure the aberration-corrected STEM of all the samples, and help to analyze the data.
- Dr. Liu Guigao helped to conduct electrochemical test of all of the samples.
- All the authors gave suggestions to revise the manuscript together.

23-08-2019

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Abstract

To prepare noble metal nanomaterials with unconventional crystal phase is of extraordinary interest for the research of new features of noble metal nanomaterials towards a series of applications. Hence, the target of this thesis is to produce noble metal nanomaterials with unconventional crystal phase and then investigate their features in a range of catalytic applications.

Firstly, the crystal phase-controlled preparation of PtCu alloy nanostructures on hexagonal 4H phase Au nanoribbons (referred to as 4H-Au NRBs) has been accomplished by tuning the thickness of PtCu shell on the 4H-Au NRB core, forming 4H-Au@PtCu core-shell NRBs. When the shell is thin, 4H-PtCu is obtained because of the epitaxial relationship between PtCu shell and Au substrate; and when the shell is thick, face-centered cubic (*fcc*) phase PtCu (*fcc*-PtCu) is prepared as the epitaxial relationship between Au substrate and PtCu film is broken. Significantly, the phase-dependent electrocatalytic features of the as-synthesized PtCu alloy nanostructures in the ethanol oxidation reaction are explored. Note that, the 4H-Au@4H-PtCu NRBs possess a much higher specific activity of 50.2 mA/cm², which is 2.1 times that of 4H-Au@*fcc*-PtCu NRBs (24 mA/cm²) and 5.9 times that of Pt black (8.5 mA/cm²).

Secondly, by using hexagonal 2H phase Au nanosheets as the templates, high-yield preparation of mixed phase 2H/*fcc* Au@Ir core-shell nanosheets have been accomplished. Significantly, similar with the case using 4H Au nanoribbons as the templates, the crystal phase of Ir nanostructures is controlled by tuning the layer numbers of the Ir shell, *i.e.*, thin Ir shell epitaxially grown on Au core inherits 2H phase while thick Ir shell crystallize in *fcc* phase. However, different from the case using 4H Au nanoribbons as the templates, the Au core transforms to *fcc* phase simultaneously when Ir shell gets thicker as the epitaxial relationship between Au and Ir could be preserved regardless of shell thickness. Thus the resultant 2H/*fcc* ratio in the Au@Ir nanosheets could be controlled by tuning the layer numbers of shell atoms. Note that, the phase-dependent electrocatalytic features of the as-

synthesized Au@Ir nanosheets in the hydrazine electro-oxidation reaction (HzOR) are probed. Note that, the 2H/*fcc* Au@Ir nanosheets possess a remarkable mass activity of 507.5 mA/mg_{Au+Ir}, which is 1.96 times that of the *fcc* Au@Ir nanosheets (259 mA/mg_(Au+Ir)) and 3.36 times that of the Ir black (151 mA/mg_{Au+Ir}).

Thirdly, because of the difference between the cases using 2H Au nanosheets and 4H Au nanoribbons as the templates, respectively, 2H Au and 4H Au should play different role in the seed-mediated synthesis. Inspired by this, 2H Au nanosheets and 4H Au nanoribbons are employed as the seed to deposit a thin layer of PdFe alloy shell, generating 2H Au@PdFe nanosheets and 4H Au@PdFe nanoribbons, respectively. Impressively, the phase-dependent electrocatalytic features of the as-prepared 2H Au@PdFe nanosheets and 4H Au@PdFe nanoribbons in the methanol oxidation reaction (MOR) in alkaline media are studied. Note that, 2H Au@PdFe nanosheets possess the highest mass activity of 4.39 A/mg_{Pd}, which is 1.2, 2.8 and 12.5 times those of 4H Au@PdFe nanoribbons, Pt/C and Pd black, respectively.

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Abbreviations

NPs	Nanoparticles
NRs	Nanorods
NRBs	Nanoribbons
OAm	Oleylamine
FFT	Fast Fourier Transformation
EDS	Energy Dispersive X-ray Spectroscopy
HRTEM	High Resolution Transmission Electron Microscopy
SAED	Selected Area Electron Diffraction
SEM	Scanning Electron Microscopy
TEM	Transmission Electron Microscopy
XRD	X-ray Diffraction
HAADF	High-Angle Annual Dark-Field
CV	Cyclic voltammetry
ECSA	Electrochemical Active Surface Area
EOR	Ethanol Oxidation Reaction
HzOR	Hydrazine Oxidation Reaction
MOR	Methanol Oxidation Reaction
RHE	Reversible Hydrogen Electrode
SCE	saturated calomel electrode
<i>bcc</i>	Body-centered cubic
<i>fcc</i>	Face-centered Cubic
<i>fmt</i>	Face-centered Tetragonal
2H	Hexagonal Close-packed 2H
4H	Hexagonal Close-packed 4H
ICP-OES	Inductive Coupled Plasma-optical Emission Spectroscopy

Chapter 1

Introduction

To explore the impact of atomic structure on the performance of noble metal-based catalysts, this thesis focuses on developing effective wet-chemical synthesis methods and investigating the catalytic applications of noble metal nanomaterials with unconventional crystal phase, including 2H, and fcc. Thus, this chapter provides the first acquaintance to this thesis. First, the hypotheses and research background are presented. Second, the objectives and scope are illustrated in details. Following that, the dissertation introduction of every chapter is also briefly displayed. Finally, on account of the research results, the observations and results are concluded comprehensively.

1.1 Hypothesis/Problem Statement

Noble metal nanomaterials are quite promising candidates for electrocatalytic catalysts^[1]. Previous studies have found that uncommon phase endows noble metal nanomaterials with significantly increased electrocatalytic activity^[2]. However, whether or not the crystal phase takes the most important place is still unclear. Therefore, it is indispensable to accomplish crystal phase-controlled synthesis of noble metal nanomaterials possessing high purity.

In order to accomplish the crystal phase-controlled synthesis of noble-metal nanostructures, harsh experiment conditions, including high pressure, high temperature, or high-vacuum environment are always required.^[4] Compared to the harsh conditions, epitaxial growth is a valuable strategy for controlling the crystal phase of noble metal nanomaterials under mild conditions.^[5] For example, our group have prepared a wide range of metals (e. g. Ag, Pt, Pd, Ru, Rh, Ir and Cu) as well as alloys (PtAg, PdAg and PtPdAg) crystallized in 4H phase by employing 4H Au nanoribbons or 4H/*fcc* Au NWs as templates *via* the epitaxial growth.^[6] Interestingly, when the templates are replaced by 2H Au square sheets firstly reported by Huang et al.,^[4b] 2H-*to-fcc* phase change can be achieved by epitaxial deposition of Ag^[7], Pt or Pd^[8] on the 2H Au nanosheets. Hence, the epitaxial growth method is quite versatile to control the phase of not only the shell but also the templates. Hence, it is reasonable to employ epitaxial growth method to prepare noble metal nanomaterials possessing novel crystal phase to investigate their crystal phase-dependent electrocatalytic features.

1.2 Objectives and Scope

To realize the investigation of crystal phase-dependent features of noble metal nanomaterials, the following works are present in this thesis. Firstly, the crystal phase-controlled synthesis of PtCu alloy nanostructures on hexagonal 4H phase Au nanoribbons (4H-Au NRBs) has been achieved. 4H-PtCu and *fcc* phase PtCu (*fcc*-PtCu) alloy

nanostructures are successfully prepared by tuning the thickness of PtCu shell on the 4H-Au NRB core. Importantly, the phase-dependent electrocatalytic features of the as-synthesized PtCu alloy nanostructures in the ethanol oxidation reaction (EOR) in alkaline media are investigated. Secondly, crystal phase-controlled preparation of Ir nanostructures has been accomplished. By using 2H Au nanosheets as the templates, 2H/*fcc* Au@Ir nanosheets and *fcc* Au@Ir nanosheets can be both prepared by tuning the thickness of Ir shell. Interestingly, the epitaxial relationship between Au core and Ir shell can be preserved regardless of shell thickness while the ratio of 2H to *fcc* area in 2H/*fcc* Au@Ir nanosheets is relative to the shell thickness. Furthermore, the phase-dependent electrocatalytic features of the as-synthesized Au@Ir nanosheets in the hydrazine oxidation reaction (HzOR) are learned. Thirdly, by using 2H Au nanosheets and Au nanoribbons as the templates, respectively, 2H/*fcc* Au@PdFe nanosheets and 4H Au@PdFe nanoribbons is prepared by epitaxial deposition of Pd and Fe ions. Moreover, the crystal phase-dependent electrocatalytic features of the PdFe alloy nanostructures in the methanol oxidation reaction (MOR) are investigated.

1.3 Dissertation Overview

The thesis focuses on the investigation of crystal phase-dependent features of noble metal nanostructures in a series of electrocatalytic applications.

Chapter 1 presents a logic for the research scope and points out the relative objectives.

Chapter 2 highlights the latest investigation progress of the crystal phase-controlled preparation and the application of noble metal nanostructures with unfamiliar crystal phase.

Chapter 3 talks about the principles behind the synthesis and characterization techniques. An explanation of the selection of the specific method is required.

Chapter 4 presented a versatile strategy for the crystal phase-controlled preparation of 4H PtCu alloy grown on 4H Au nanoribbons epitaxially. When the shell grows thick enough, the crystal phase of PtCu alloy will be *fcc*. In addition, both of the as-prepared 4H-PtCu

and *fcc* PtCu alloy nanocrystals are utilized to recommend the crystal phase-dependent ethanol oxidation reaction.

Chapter 5 developed a versatile strategy for the crystal phase-controlled synthesis of 2H Ir nanostructures grown on 2H Au nanosheets epitaxially. When the shell grows thick enough, the crystal phase of Ir will be *fcc*. The epitaxial relationship between Au core and Ir shell will be preserved no matter how thick the shell is. Thus, when Ir shell is thick enough, the crystal phase of Au core will be transformed from 2H to *fcc* completely along with the phase transition of Ir. In addition, the 2H/*fcc* Au@Ir and *fcc* Au@Ir nanosheets are used to demonstrate the phase-dependent hydrazine oxidation reaction.

Chapter 6 aroused a versatile strategy for the crystal phase-controlled synthesis of PdFe alloy grown on 2H Au nanosheets and 4H Au nanoribbons epitaxially, respectively. Additionally, both the 2H/*fcc* Au@PdFe nanosheets and 4H Au@PdFe nanoribbons are employed to suggest crystal phase-dependent methanol oxidation reaction.

Chapter 7 summaries the novelty and significance of this thesis and suggests some reconnaissance work that can be done.

1.4 Originality

This investigation resulted in a series of fresh observations by:

1. Setting up a crystal phase-controlled method to prepare **noble metal nanomaterials** with high purity by using template-supported growth method, which supplies a good platform for exploring their crystal phase-dependent features
2. The crystal phase-dependent features of the PtCu alloy, Au@Ir core-shell and PdFe alloy nanostructures have been well-studied.

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Chapter 2

Literature Review

This chapter offers an inclusive literature review about the latest evolution on preparation and structure engineering of noble metal nanomaterials possessing unfamiliar crystal phase. A detailed summary will be presented based on the newest research progress of noble metal nanomaterials with unfamiliar phase, including the preparation and characterization techniques. Then, the utilization of these materials in various applications will also be summarized with the emphasis on catalysis, energy storage and conversion fields.

Noble metal nanomaterials have been intensely investigated because of their inherent features in several significant employment including SERS, catalysis, NIR photothermal therapy, catalysis, and clean energy and so forth.^[1] Up to now, remarkable development in controlling the size, shape, composition and architecture of various kinds of noble metal nanocrystals has been witnessed, which act as crucial factors to influence the physical and chemical features of noble metal.^[2,3] Not until recently did crystal structure/phase of noble metal come to scientists' attention, which can also greatly influence their functional physicochemical features.^[4]

For noble metals in bulk status, Au, Pt, Ir, Pd, Ag, and Rh are always constructed in the fcc phase while Ru normally crystallize into 2H structure; after their size is reduced to the nanometer scale, their crystal structure could be changed because the surface energy remarkably influence the total systemic energy now.^[5] Up to date, gold nanomaterials of 2H^[6a] and 4H phase,^[4a] silver crystallized in body-centered tetragonal (bct) phase,^[4c] fcc Ru nanoparticles (NPs)^[6b] and Rh nanostructures in 2H phase^[6c] have been obtained.

Frankly to say, the crystal structure directed-preparation of noble metal nanocrystals is left to be a huge challenge since it is always achieved by using extreme conditions including high pressure^[6b] and high temperature^[6d]. For example, Sun group are able to derive the fct FePt and FePtAu nanoparticles from their fcc counterparts through annealing fcc FePt and FePtAu nanoparticles at high temperature (600 °C) in 2013;^[7] in 2008, Guo et al demonstrated that high pressure (24.8 GPa) can induce phase distortion in cold-compressed palladium nanocubes exposing {100} crystal facets from *fcc* to *fct* along [001] crystal direction.^[8] Considering that high temperature and high pressure could lead to serious aggregation or degradation of noble metal nanomaterials which limit their further investigations to a large extent, it is worthwhile to note that ligand exchange and metal coating are advantageous methods for phase transformation. For instance, in 2015, Fan et al^[9] achieved a 2H-to-*fcc* phase transition of gold nanonanosheets under ambient conditions without high temperature and high pressure through surface ligand exchange as well as growth of a thin metal film on the gold surface; by using ligand exchange method did they also achieve 4H-to-*fcc* crystal phase transition under ambient conditions.^[4a] Note

that, modulating the crystal phase of noble metal nanocrystals is considered as a beneficial way to control the functional characteristics.^[2b,3b,6b,7a,10] Specifically, for instance, 4H Ag nanowire film presents notably higher SPR absorption in contrast to the Ag nanowire of the *fcc* phase;^[4a] *fcc*-FePt NPs exhibits enhanced activity and durability for ORR in 0.5 M H₂SO₄ than their common *fcc* counterpart -*fcc*-FePt NPs because of the stable intermetallic Fe, Pt arrangement in *fcc*-FePt NPs; *fcc* Ru surface possesses better re-activity for CO oxidation in contrast to that of 2H Ru, which is the conventional phase of Ru nanoparticles. As a result, without doubt, controlling the crystal phase of noble metal nanostructures is truly significant which should provide meaningful guidance on their applications but still remains underdeveloped to some extent.^[6c]

In this chapter, the latest investigation of crystal structure-directed preparation of noble metal nanocrystals should be reviewed by systematically introducing various synthetic strategies, and briefly discussing the advantageous application of the noble metal nanocrystals with unfamiliar crystal structure. Last but not least, plenty of perspectives about the relative challenges and opportunities would be provided.

2.1. Crystal phases of noble metal nanostructures

Most noble metal nanocrystals, including Au, Pt, Ir, Pd, Ag, and Rh except Ru and Os, always crystallize in *fcc* phase, which features ‘ABC’ stacking sequence when viewed through the $[111]_{fcc}$ direction; as for Ru and Os, which adopt 2H structure in the bulk, they tend to give ‘AB’ stacking sequence along the $[100]_{2H}$ direction. Recently, some noble metal nanomaterials have been found to be able to crystallize in diverse crystal phases if their size is reduced to nanometer scale owing to nanosize effect. Specifically to say, in spite of the high symmetry *fcc* phase commonly seen in various kinds of Au nanostructures, recent studies have demonstrated that ultrathin Au nanosheets can adopt a 2H crystal phase, presenting ‘AB’ stacking sequence along the $[001]_h$ zone axis, uncommonly observed in Au nanocrystals up to date;^[6a] with 4H hexagonal phase, has also been observed to exist in ultrathin Au NRs, which characterize a ‘ABCB’ stacking sequence along the $[001]_{4H}$ zone axis.^[4a] Besides gold nanostructures, silver nanoparticles has been found to adopt stable

non-*fcc* phase. In 2012, it is reported that a stable body-centered-tetragonal (bct) phase of high purity exists in Ag nanocrystals with five-fold twinning under ambient environments which is derived from the lattice distortion of *fcc* Ag because of the larger lattice strains in the core of the nanocrystals rather than in the side surface.^[4c] In 2002, Zhu group found that the Ag in the Ag-Si nanowire heterostructures which are derived from AAO template-directed electrochemical deposition of silver, is crystallized in 4H phase,^[11] and later, in 2006, they also observed 4H structure, coexisting with *fcc* phase, in Ag NWs obtained by electrochemical deposition of silver with alternating current and they could tune the concentration of a 4H phase via changing the diameter of Ag NWs.^[5] In 4H-Ag nanowires, the close-packed {0001} planes features a hexagonal atomic arrangement, which is analogical to the {111} planes of *fcc*-Ag nanowires, except that the bond length of Ag-Ag in *fcc* Ag is longer than that of 4H-Ag and the inter-planer distance of *fcc* Ag is smaller than that of 4H-Ag. Specifically to say, there are 6 nearest-neighbor Ag atoms in the identical basal plane in 4H Ag; the distance of the nearest atoms is $r_1 = 2.8862 \text{ \AA}$ while in the *fcc*-Ag, every atom is surrounded by 12 nearest-neighbor atoms whose distance is $r_0 = 2.8894 \text{ \AA}$.

Furthermore, 2H phase of Ag has also been observed in 2011 by Ayyub group who performed porous anodic alumina-assisted electrochemical deposition of silver nanostructures within constant potential of 2 mV, the lattice parameters of which is calculated to be $a = 2.83 \text{ \AA}$, $c = 6.38 \text{ \AA}$.^[6d] The main difference between *fcc*, 4H and 2H phase of silver is the stacking sequences viewed through the close-packed directions: *fcc*-Ag presents ‘ABCABC’ stacking sequence along $[111]_f$ direction, 4H-Ag features ‘ABCBAABCBA’ stacking sequence along $[001]_{4H}$ direction and 2H-Ag characterizes ‘ABAB’ stacking sequence along $[001]_{2H}$ direction (shown in **Figure 2.1**). Based on theoretical calculations for gold and silver, from the view of point of structure stability, *fcc* is better than 4H which is more stable than 2H ($fcc > 4H > 2H$).^[10] Worth noting that although bulk Rh commonly adopts *fcc* phase, in 2014, Li group indicated that Rh nanosheets, consisting of only one single atomic layer, crystallized in 2H phase. Their ultrathin nature can be confirmed by the high sensitivity towards electron beam irradiation in HRTEM characterization and the absence of diffraction peaks in X-ray diffraction pattern.^[6c]

Normally, Ru in the bulk state can only crystallize in 2H phase, but Ru in a nanoparticulate phase can adopt both fcc and 2H crystallization, according to Kitagawa group who can change the crystal phase of Ru nanoparticle by selecting different Ru precursor along with reducing agent: Ru(acac)₃ and triethylene glycol contribute to *fcc* Ru, presenting {111} *fcc* planes, a typical single five-fold-symmetry twinned nanocrystal featuring a decahedral structure; RuCl₃·nH₂O and ethylene glycol lead to 2H Ru, showing ‘ABAB’ stacking sequence along [100] direction.^[6b]

Figure 2.1. (A) Scheme of the preparation procedure of alternating 2H/*fcc* Au-Ag core-shell (CS) nanosheets. (B) TEM figure, (C) SAED, and (D, E) HRTEM figures of 2H/*fcc* Au@Ag core-shell (CS) nanosheets along the [110]_h/[101]_f direction. (F, H) HAADF-STEM figures and (G, I) the relative FFT patterns of the cross-section along the

$[1\bar{1}0]_h/[1\bar{2}1]_f$ and $[001]_h/[1\bar{1}1]_f$ direction. Reprinted with permission from ref 5b. Copyright 2016 American Chemical Society.

Furthermore, besides single-metallic nanocrystals, bimetallic nanocrystals, such as PtM (M=Fe, Co, Cu) can also adopt several kinds of novel phases different from than in the bulk state.^[3b,e] For example, in 2000, Sun et al. firstly announced that fcc FePt nanoparticles can be transferred to *fcc* FePt after heat treatment, that is, from a chemically disordered structure consisting of Fe and Pt atoms distributed in the *fcc* lattice randomly to a chemically ordered one with intermetallically-stacked Fe and Pt atoms (**Figure 2.1c**).^[7a] Besides *fcc* phase of PtFe bimetallic nanoparticles which can be obtained from fcc one after high-temperature annealing, simple cubic (sc) phase of bimetallic nanocrystals could also be derived from the *fcc* one by heat treatment.^[12] For instance, Liu et al. indicated that CoPt₃ nanowires adopting chemically ordered sc phase could be derived from CoPt₃ nanowires crystallized in chemically disordered fcc phase by high-temperature annealing, which result in a total phase change through a interdiffusion procedure.^[12a] Using the similar method, Abrun~a et al. produced ordered intermetallic sc Cu₃Pt nanoparticles at a very high temperature (1000 °C) for annealing treatment.^[12c] Furthermore, palladium and gold-based bimetallic nanomaterials in which the atoms involved occupy the sc lattice, including FePd₃, FeAu₃ and Fe₃Au nanoparticles, have also been observed.^[12b,d]

2.2. Crystal phase-controlled methods of noble metal nanocrystals

To date, there are two kinds of strategies consisting of direct synthesis and crystal structure transformation for the crystal structure-directed production strategies of precious metal nanocrystals. Briefly to say, the templated synthesis,^[6a,13] polyol method,^[4c,6b] solvothermal synthesis^[6c] and colloidal method,^[4a,14] could be classified into direct synthetic methods; while the methods related to the crystal structure transformation, consisting of high temperature,^[2b,7a,15] high pressure,^[8,16] ligand exchange^[4a,9b] and metal coating,^[4a,9] should be classified into crystal phase transformation methods. The following part includes the above synthetic techniques for the crystal structure modulation of precious metal nanocrystals.

2.2.1 Colloidal strategy

The colloidal strategy is an effective strategy to produce semiconductors and noble metal nanomaterials, including PtM (M=Bi, Pb) and Au.^[4a,14,17] For instance, in 2008, Yang et al.^[14] obtained PbPt nanorods adopting 2H crystal structure by using the colloidal synthesis method, named as standard Schlenk line technique under argon atmosphere, that is, mixing platinum acetylacetonate, lead acetylacetonate and tert-butylamineborane at first and then adding hexadecanethiol, adamantanecarboxylic and hexadecylamine in diphenylether to the mixture, after which the reaction would be performed at 180-200 °C under an argon atmosphere, which can lead to simultaneous reduction of Pt and Pb ions. Worth noting, not only lofty temperature but also elongated reaction time are key factors for the generation of PbPt nanorods with 2H crystal structure. According to Hou et al.,^[17] this method, the Schlenk line technique, is also useful for the production of BiPt nanoplates with 2H crystal structure. Specifically to say, adding oleylamine and NH₄Br to the mixture of platinum (II) acetylacetonate and bismuth(III) neodecanoate and increasing the reaction temperature to 200 °C, Pt and Bi ions could be simultaneously reduced, which would form BiPt nanoplates with 2H phase as well as a thickness of around 6 nm.

It is worth noting that Fan et al highlight the preparation of 4H Au NRBs of high yield by employing colloidal method for the first time.^[4a] Briefly to say, using oleylamine mixed in the solution of hexane and 1,2-dichloropropane, gold precursor (HAuCl₄ (3 mM)) is reduced. The mixed solvent was heated at 58 °C in a glass vial sealed tightly. After 16 hours, 4H Au nanoribbons can be formed and collected by centrifugation, as indicated in **Figure 2.2**, which feature 0.5-6.0 mm long, 15.0-61.0 nm wide, and 2.0-6.0 nm thick. As for the lattice parameters, it is estimated that for 4H Au NRBs, *a* is 2.866 Å while *c* is 9.662 Å.^[4a] Moreover, time-dependent experiments were performed to probe the generation mechanism of the 4H Au nanoribbons: after the first 4 hours, ultrathin Au NWs consisting of 2H structures as well as several stacking faults randomly distributed can be produced; during the following 4 hours, these ultrathin Au nanowires would grow further and form ribbon-like nanostructures (2.8-5.8 nm), in which hexagonal 4H domains could be found

but small still; after another 4 hours, the ribbon-like nanostructures could grow into wider ones which feature width of 8.0-20.0 nm, and more importantly, the hexagonal 4H domains can be observed all over the ribbons. Furthermore, considering that only fcc Au nanoparticles could be obtained without the addition of 1,2-dichloropropane in control experiment, it is reasonable to believe that 1,2-dichloropropane is influential to the reaction kinetics of the anisotropic growth of 4H Au nanoribbons.^[18]

Figure 2.2. (a) TEM figure of large-scale 4H Au NRBs and (b) a representative 4H Au nanoribbon, (c) SAED pattern of the related 4H Au NRB present in (b), observed along the $[110]_{4H}$ direction. (d and e) Aberration-corrected HRTEM figures of a distinctive 4H Au NRB. (f and g) Scheme of a crystal unit cell and atomic models indicating the top and side views of a distinctive 4H Au NRB, shown in the top and bottom panel, respectively. Reprinted with permission from ref. 5c. Copyright 2015, Nature Publishing Group

2.2.2. Template preparation method

Template preparation method is a facile, powerful strategy for growing noble metal nanocrystals adopting unusual phases, which enables the growth process to be isolated from the complex nucleation process.^[4a] As a result, a range of noble metal nanomaterials adopting unfamiliar crystal phase is prepared by utilizing this template synthetic strategy, whose crystal structure might not be the same as that in their bulk state owing to the size, morphology, and so forth.

2.2.2.1 Graphene oxide-supported synthesis

Graphene oxide (GO) sheets, consisting of a large amount of oxygen functional groups, including -COOH and -OH, are truly effective and advantageous templates to direct the deposition of noble metal nanostructures. Note that GO sheets are found to be efficient in directing the crystal structure-controlled synthesis of gold nanostructures. Specifically, in 2011, Huang et al produced ultrathin 2H AuSSs (approximately 2.4 nm, referring to around 16 gold atomic layers) by using GO as a template (**Figure 2.5**), that is, mixing GO sheets, HAuCl₄ and oleylamine with hexane and ethanol at first and then, heating the mixture at 55 °C for 16 h in a tightly-sealed glass vial, after which by centrifugation can the 2H AuSSs grown on the GO sheets be collected.^[13] It is calculated that the lattice distances of 2H AuSSs: $a = 2.96 \text{ \AA}$ and $c = 4.84 \text{ \AA}$.^[6a] From control experiment, it is reasonable to conclude that GO, acting as template, is necessary for the growth of AuSSs, because the yield, quality and uniformity of AuSSs would be obviously diminished without the addition of GO sheets. According to time-dependent experiments, Au nanodots were firstly generated on the GO sheets, which slowly fused with each other to form square-like Au dendritic nanostructures with plenty of crystal defects. Following that, it was from the center of dendritic nanostructures that the square sheet architectures began to emerge, which could gradually developed into well-defined AuSSs by consuming the remaining dendrites. Interestingly, when the reaction proceeds further, AuSSs became thicker, and simultaneously, *fcc* domains started to emerge in the gold square sheets, resulting in the generation of 2H/*fcc* alternating nanocrystals.^[6a] Without doubt, by depositing more Au on the 2H Au square

sheets can their thickness be enhanced.^[19] Specifically to say, the as-obtained AuSSs of 2H phase were added in the growth solution containing HAuCl_4 (3 mM), hexane, oleylamine and ethanol after post-treatment, all of which would be heated at 58 °C for another 10 h and contribute to the formation of thicker Au plates featuring 2H/*fcc* mixed crystal phase in the center (5 nm in thickness in the center) and *fcc* phase in the edge (7.3 nm in thickness in the edge) (**Figure 2.3**).

Figure 2.3. (a and b) Scheme of the preparation procedure and transmission electron microscopy figure of 2H Au nanosheets on the surface of graphene oxide sheets. Inset in (b): crystallographic models of a characteristic 2H Au nanosheet collected along the $[110]_h$ direction. HRTEM figure (c) and the relative SAED pattern of a distinctive 2H Au nanosheet collected along the axis of $[110]_h$ (d) and $[320]_h$ (e), respectively. Reprinted with permission from ref. 6a. Copyright 2011, Nature Publishing Group.

Besides the two-dimensional Au nanostructures mentioned above, GO-templated synthesis strategy can also be employed in producing one dimensional Au nanowires with ultrasmall thickness and specific crystal phase. For example, in 2011, Zhang group synthesized the

Au nanowires by mixing GO sheets, HAuCl_4 , oleylamine and hexane and heating them at 55 °C for 36 h, which resulted in the generation of alternating 2H/fcc Au nanowires.^[13] Note that, if the heating time is decreased to 10 h, tadpole-shaped Au nanowires, displaying 2H/fcc mixed structure in the tail area and pure fcc phase in the head region, can be yielded.

2.2.2.2. Anodized aluminum oxide-supported electrochemical deposition

The Anodized aluminum oxide -supported electrochemical deposition technique is efficient in synthesizing silver nanocrystals of different phase, which should be constructed by the anodization process of aluminum foil in advance to tune their pore diameter (from 10 to 100 nm). Following that, keeping a consistent voltage in AgNO_3 aqueous solution, Ag nanowires can be yielded by electrochemical deposition in the porous AAO templates, after which the porous AAO templates should be removed by immersing in sodium hydroxide solution under ambient conditions, inducing the production of free-standing Ag nanowires adopting a specific crystal phase. In 2002, Ag nanocrystals with 4H phase was found to exist in Ag-Si nanowire heterostructures, which were prepared by utilizing AAO-assisted electrochemical deposition method.^[11] Note that, by changing the diameter of Ag nanowires can the ratio of 4H parts be controlled.^[5] In a wide range of Ag nanowires possessing diverse diameters ranging from 8 to 75 nm, which were derived from changing the pore size of the porous anodized aluminum oxide templates, the ones with a diameter of 30 nm have the highest amount of 4H Ag (**Figure 2.4**). This is because 4H Ag nanowires characterize a more fascinating surface configuration than the fcc counterparts which features lower volume internal energy simultaneously. In fact, the kinetics of electrochemical deposition is critical for the production of Ag nanocrystals with different kinds of crystal structures. Specifically, Ayyub et al. synthesized Ag nanostructures adopting different crystal phase by mixing AgNO_3 and H_3BO_4 which can act as electrolyte at pH=2.5 and selecting diverse constant voltage which can influence the growth kinetics of Ag nanocrystals. In their experiment, 2H, 4H and fcc Ag can be produced at constant electrochemical voltages of 0.002 V, 0.2 V and 3 V, respectively.

Figure 2.4. HRTEM figure (a) of a distinctive 4H Ag nanowire. Insets in a: the bottom-left one displays the SAED pattern of the 4H silver nanowire present in (a); the top-right one displays the selected figure labeled in (a), overlaid with the jade-green dots, demonstrating the atom arrangement of 4H Ag nanowire along the $[-2113]$ zone axis. (b) The simulated cross-section of a distinctive 4H silver nanowire: red arrow indicates the surface of Ag nanowires dominated by $\{10\bar{1}1\}$ and $\{0001\}$ planes, and the black arrow spots the surface energy plot. Reprinted with permission from ref. 5a. Copyright 2006, American Chemical Society

2.2.2.3. Noble metal nanomaterials-templated synthesis of noble metal nanocrystals with novel crystal phase

Utilizing a specific kind of noble metal possessing novel crystal phase as a template is effective in directing the growth of another kind of noble metal nanocrystals with unfamiliar crystal structure. For example, according to Fan et al., using oleylamine to reduce AgNO_3 on the 2H Au nanosheets acting as a template at 38°C for 20 h, uncommon 2H Ag nanocrystals can be derived from the epitaxial growth of Ag shell, which could be obviously noticed in the HAADF-STEM figures and the relative FFT patterns, in which the lattice fringes consistently stretched from inside to outside.^[9b] As indicated in the TEM figure and the relative SAED pattern, fcc AuSSs were also observed to coexist with the 2H parts after the overgrowth of Ag, illustrating the incomplete 2H-to-*fcc* phase transformation

caused through the deposition of Ag assisted by oleylamine; without the addition of oleylamine, the overgrowth of Ag can result in a total 2H-to-*fcc* phase change.

Furthermore, Fan et al. also prepared 4H Ag nanostructure by employing 4H Au nanoribbons which played the role of a template by depositing Ag on the 4H Au nanoribbons epitaxially.^[4a] It is worthwhile noting that the epitaxial growth strategy is so effective that a wide range of other nanomaterials such as Pd, Pt, (**Figure 2.5 O-U**) nanostructures with 4H crystal phase could also be derived from the epitaxial deposition of Pd, Rh, Pt, Os, Ir, and Ru atoms on 4H Au NRBs surface in spite of the relatively large lattice mismatches between Au and these sorts of noble metal, which are reduced by NaBH_4 .^[9b, 20]

Figure 2.5. Detailed information of 4H/fcc Au@Ag core-shell NBs (A-G), 4H/fcc Au@Pd core-shell NBs (H-N) and 4H/fcc Au@Pt core-shell NBs (O-U); TEM figures (A, B, H, I, O, P), SAED pattern (C, J, Q), HRTEM figure (D, K, R), HAADF-STEM figure (E, L, S), as well as the relative STEM-EDS mappings (F, G, M, N, T, U). Reprinted with permission from ref. 5c. Copyright 2015, Nature Publishing Group.

Additionally, 4H Au nanoribbons can also induce the deposition of noble metal alloy nanomaterials adopting 4H phase by combining epitaxial growth and galvanic

replacement.^[21] Specifically, 4H Au@Ag core-shell nanoribbons are prepared at first by depositing Ag on 4H Au nanoribbons surface in an epitaxial way, which would be utilized as a template to support the growth of 4H PdAg alloy through the galvanic replacement reaction ($2\text{Ag} + \text{Pd}^{2+} \rightarrow 2\text{Ag}^+ + \text{Pd}$) at ambient conditions, after which 4H PdAg alloy nanostructure would inherit the phase of 4H Au nanoribbons, as indicated clearly in the HRTEM figures. Notably, this combination method is so effective that 4H PtAg alloy nanostructures and even trimetallic 4H PtPdAg alloy nanostructure can be produced in this way that epitaxially depositing Ag on the 4H Au nanoribbon template and using platinum nitride and the solution containing both palladium nitride and platinum nitride, respectively, for conducting the galvanic replacement with the Ag shell.

Besides the noble metal nanocrystals with unfamiliar crystal phase, the noble metal nanostructures adopting general crystal phase can also be utilized as a template to prepare another kind of noble metal nanostructure with unfamiliar crystal phase by using the epitaxial growth strategy. For instance, in 2015, Lee et al. succeeded in preparing *fcc* Ru nanostructures by epitaxially depositing Ru on the surface of *fcc* Pt, which adopted 2H phase in the bulk. It is intriguing that the shapes of Pt nanostructures can extensively influence the shapes of Ru nanostructures, that is, growing Ru on Pt nanocubes octahedral boxes while growing Ru on Zn-doped Pt concave nanocubes resulted in the generation of *fcc* Ru octopods. In a typical experiment for synthesizing Ru octahedral box, for example, they added platinum acetylacetonate into a mixture of 1,2-hexadecanediol and octadecylamine, and further heated them at 200 °C for 0.5 h in the presence of 1 atm CO only after evacuation at 80 °C for 10 min; following that, when the reaction cooled down, Ru(acac)₃ should be injected in the above mixture, all of which should be surrounded by 1 atm CO and heated at 260 °C for 2 h, and then Pt@Ru could be formed.^[22]

Moreover, in 2015, Gu et al. gained *fcc* Ru by depositing Ru atoms on the surface of *fcc* Pt in an epitaxial way through a hydrothermal reaction, inducing the production of *fcc* Pt@Ru core-shell tetrahedral surrounded by {111} facets of *fcc* Ru inheriting the phase of the core-*fcc* Pt, which made it possible to realize the control of not only shape but also phase in one one-step method.^[23]

Worth noting that bimetallic nanocrystals with *fcc* phase can also direct the deposition of Ru nanostructures with thermodynamically unstable phase. For example, in 2016, Yao et al. introduced an seed-mediated growth technique to prepare *fcc* Ru nanostructure by employing *fcc* Pd-Cu alloy nanocrystals as the seed whose lattice can be modulated by tuning the composition ratio of palladium and copper, which is critically influential to the growth mode of Ru, that is, PdCu₃ and PdCu_{2.5} with a negligible lattice mismatch in comparison with *fcc* Ru, tend to induce the epitaxial deposition of ruthium shell; while Pd, PdCu₂ and Cu deviated from *fcc* Ru, prefer to lead to nonepitaxial growth of Ru and result in the formation of 2H ruthium shell. Following that, by galvanic replacement between Cu of PdCu nanoparticles and RuCl₃, the yolk-shell structure of *fcc* PdCu@Ru nanoparticles could be generated.^[24]

Nonetheless, Xia group demonstrated a different conclusion regarding to the above one, that is, by using seed-mediated method can *fcc* Ru nanostructures such as Ru nanoframe and cubic nanocages be gained by replicating the phase of the seed-*fcc* Pd truncated octahedral or *fcc* Pd nanocubes, respectively,^[25] meaning that besides lattice mismatch, a series of other experimental parameters including solvent, pressure and surfactants and so forth, could largely influence the growth mode of noble metal nanostructures.

2.2.3. Polyol method

As is known to all, polyol method is an favorable strategy for the shape-modulated synthesis of a range of noble metal nanostructures.^[3a] Currently, the polyol method is found to be applicable toward the crystal structure modulation of noble metal nanocrystals as well.^[4c,6b] Briefly, PVP acting as stabilizing agents and polyols such as EG and TEG acting as solvents and reducing agents are always involved in this method; by mixing the precursor of noble metal and PVP with the polyol solvent, the mixture would go through heat treatment by refluxing, leading to the generation of noble metal nanocrystals. For instance, in 2012, by taking advantage of the polyol method, Sun et al. successfully prepared Ag nanowires possessing a five-fold twinning structure and adopting a *bct* phase

by refluxing a mixture consisting of silver nitrate, PVP, ethylene glycol, sodium chloride and ferric acetylacetonate at 160 °C for 1.5 h. In fact, the five-fold twinning structure can yield notable lattice strain which caused the tetragonal structure distortion accountable for the formation of a bct phase.^[4c] Besides Ag, Ru nanoparticles of different phase can be obtained by using the polyol method requiring heating the addition of the metal precursor, the solvent and the reductant and PVP as the capping agent by refluxing, according to Kitagawa et al. who gained pure fcc Ru nanoparticles by choosing Ru(acac)₃ and TEG and pure 2H Ru nanoparticles by selecting RuCl₃*nH₂O (metal precursor) and EG (solvent).^[6b]

2.2.4. Solvothermal synthesis

The solvothermal synthesis can also be employed in crystal phase-modulated preparation of noble metal nanomaterials with unfamiliar phase which should be performed at high temperature in a tightly sealed autoclave. For example, Li et al. succeeded in synthesizing ultrathin 2H Rh nanosheets by heating the solution containing rhodium acetylacetonate, benzyl alcohol, formaldehyde and PVP which should be packed into a Teflon-lined stainless steel autoclave and then warmed up to 180 °C for 8 h.^[26] PVP takes important part in the synthesis of Rh nanosheets, without which serious aggregation of Rh nanosheets would happen. Additionally, formaldehyde is also critically advantageous since it is able to yield CO molecules at high temperature, which attributed to the generation and maintenance of the ultrathin rhodium nanosheets.

2.2.5. High temperature

Generally speaking, high temperature is greatly favorable for the crystal structure-control preparation of bimetallic nanocrystals containing one kind of 3d-transition metals and one sort of noble metals.^[3b,7a,15] Normally, *fcc* bimetallic nanomaterials should be synthesized firstly which would go through heat treatment at elevated temperature, during which process the diffusion of the specific 3d-transition metal and noble metal atoms in the crystal cells would be facilitated, leading to the production of new crystal phase.^[15] For example, in 2000, Sun et al. obtained *fcc* FePt NPs by heating *fcc* FePt NPs at 600 °C in a nitrogen-

filled environment, which were prepared at first by reducing platinum acetylacetonate with diol and decomposing $\text{Fe}(\text{CO})_5$ with the mixture of reducing agent (oleylamine and oleic acid). The Fe and Pt atoms of the as-prepared *fcc* FePt NPs would be randomly distributed, which would be intermetallically stacked (**Figure 2.6**), referred as chemically ordered *fct* phase, after annealing treatment at high temperature (600 °C) .

Besides FePt NPs with *fct* crystal structure, employing the thermal annealing strategy, the CoPt and FePtAu NPs featuring *fct* crystal phase have been synthesized likewise.^[7b,15] In addition to the *fct* phase mention above, thermal annealing treatment of bimetallic nanocrystals would as well result in the generation of the *sc* structure.^[12] For instance, Chen et al. derived *sc* Pt_3Co nanowires from the thermal annealing treatment of the *fcc* Pt_3Co counterpart, which were produced at first by electrochemical deposition of H_2PtCl_6 and CoSO_4 on the anodized aluminum oxide template at a direct current, at 700 °C for 5 h in the presence of 5% H_2/N_2 , during which process this *fcc* to *sc* phase transition would occur thoroughly through a “cluster-in-cluster” transformation state. When all of these processes were completed, the anodized aluminum oxide template could be removed by NaOH aqueous solution and then the free standing *sc* Pt_3Co nanowires could be obtained.^[12a]

Additionally, PtCu_3 nanoparticles of *sc* phase could be synthesized by using this thermal annealing method while a higher temperature up to 1000 °C is needed. Also, bimetallic nanomaterials adopting *sc* phase including FePd_3 , FeAu_3 and Fe_3Au nanoparticles could be prepared similarly.

Figure 2.6. (a) XRD patterns of the assembly of FePt nanoparticle (4 nm) (I) and a range of assemblies of FePt nanoparticle (II–V) which were treated by annealing at 450 centigrade (II), 500 centigrade (III), 550 centigrade (IV) and 600 centigrade (V) when protected by N₂ gas for 30 min. (b, c) Scheme illustrating the crystal unit cells of *fcc* (b) and *fct* (c) FePt nanoparticles, respectively. (d) HAADF-STEM figure of a CoPt₃ nanoparticle crystallized in chemically ordered simple cubic phase. Yellow arrows demonstrate the platinum-abundant surface and the inset in (d) indicates the crystal cell collected along the [001] direction. (e) Multislice simulated HAADF-STEM figure of the perfect nanoparticle present in (d). (f) Perfect atom arrangement of the simple cubic CoPt₃ nanoparticle with a Pt-abundant surface. Reprinted with permission from ref. 5d. Copyright 2016, Royal Society of Chemistry

2.2.6. High pressure

High pressure is also a widely-utilized technique for the crystal phase-modulated synthesis of noble metal nanostructures.^[8,16,27] Normally, noble metal nanocrystals characterizing the *fcc* crystal phase should be produced in advance which should be loaded into a diamond anvil cell for the high pressure treatment contributing to the formation of non-*fcc* nanostructures. As a typical example, Guo et al. succeeded in synthesizing *fct* Pd nanostructures by utilizing high pressure to compress the *fcc* Pd nanocubes for inducing the *fcc*-to-*fct* phase transition (**Figure 2.7**). Briefly, exerting a high pressure (24.8 GPa) towards *fcc* Pd nanocubes (edge length=9 nm), which would be reduced from NaPdCl₄ aqueous solution mixed with KBr, *fct* Pd nanostructure featuring $a = 3.827 \text{ \AA}$, $c = 3.705 \text{ \AA}$,

seldom seen in the previous reports, can be produced (**Figure 2.7**). By comparison, if the loading pressure is just 20.1 GPa, the *fcc*-to-*fcc* phase transition of the compressed Pd nanoplates cannot be accomplished, suggesting that in addition to the loaded pressure, the deviation of the initial crystallinity between the single crystal nanocubes and nanoplates consisting of a number of stacking faults is also responsible for the phase transformation.^[8]

Additionally, Sun et al. reported a high pressure-induced multiple-step crystal structure transformation of alternating 2H/*fcc* Ag nanoplates synthesized at room temperature without the addition of any organic surfactants by a galvanic reaction between Ag^+ and the GaAs wafer with high concentration of silicon, in which the 2H parts existing as stacking faults would go through 2H-to-*fcc* phase transition at first under the pressure of 1.03 GPa at first. Following that, when the exerted pressure was up to 12 GPa, all the *fcc* Ag should be changed to *fcc* crystal phase. Thus, the multiple phase transition should be attributed to the clean surface of Ag nanoplates, in addition to the internal crystal stress.^[16]

Furthermore, the size of the noble metal nanocrystals is another influential parameter during the phase transformation induced by high pressure. Specifically, in 2008, Guo et al. probed the behavior of 50-100 nm Ag nanocrystals and 2-3.5 μm microcrystals at room temperature under high pressure of 30 GPa, both of which featured a *fcc*-to-*fcc* crystal phase change along the 3-fold rotational axis. However, the silver nanocrystals (50-100 nm) showed a more significant structure distortion in contrast to the Ag microcrystals with a size of 2-3.5 μm . Plus that Alivisatos group observed that ultrasmall silver nanoparticles (5-10 nm) presented a cubic-to-rhombohedral phase transition when compressed by a high pressure (10 GPa), which is not only reversible but also linearly pressure-dependent, further indicating the importance of the size in phase change of noble metal nanocrystals.^[27]

Figure 2.7. (a) The crystal phase and simulated X-ray diffraction patterns of *fcc* and *fct* phases. (b) TEM figure of the as-synthesized *fcc* palladium nanocubes. (c) X-ray diffraction patterns of the as-prepared palladium nanocubes treated by increasing pressure ranged from 0.3 to 24.8 GPa. Reprinted with permission from ref. 8. Copyright 2008, American Chemical Society.

2.3. Crystal structure-determined applications of noble metal nanocrystals

2.3.1. Oxygen reduction reaction (ORR)

Noble metal nanocrystals, are frequently employed as the ORR catalysts which is supposed to be a highly potential suitable successor to the common internal combustion engine because of its unique features.^[2,3b,3c,12c] Among the noble metal nanocrystals acting as the ORR catalysts, Pt-based alloys have aroused worldwide attention because: 1. platinum is

considered as the most effective monometallic catalyst in ORR; 2. Pt-transition metal alloys can not only cut down the amount of Pt which is very expensive but also enhance the catalytic activities due to the tailored electronic features of Pt. Up to date, the sizes, shapes and compositions of Pt-based alloys have been investigated thoroughly for maximizing their ORR catalytic activity. Not until recently has the influence of crystal structure on the ORR activities of platinum-contained alloy nanocrystals been noticed.

For example, in 2010, the ORR performance of FePt nanoparticles adopting *fcc* phase was 1.8 times better than that of FePt nanoparticles with *fcc* phase, because the d-electron interaction between iron and platinum atoms of the *fcc* FePt nanoparticles is much stronger than that of *fcc* FePt nanoparticles.^[2b] Furthermore, through growing a thin *fcc* Pt shell on *fcc* FePt nanoparticles can the ORR activity be significantly enhanced since the lattice stress caused by the mismatch between *fcc* FePt backbone and *fcc* Pt film could lead to a compressed Pt-Pt bond which should impair the interaction of oxygenated species and Pt atoms. The improved ORR activity and durability of the *fcc*-FePt NPs should originate from their well-ordered intermetallic structure of the *fcc*-FePt compared with *fcc*-FePt. This is because the intermetallic structure in the *fcc*-FePt offers some ideal catalytic facets with Pt atoms on the surface and endows much better preserved Fe and Pt composition in the acid solution. Furthermore, previous modeling studies suggested that, the *fcc* structure make Fe and Pt strongly interactive via their spin-orbit coupling.

Moreover, controlling the ratio of *fcc* phase in FePt nanoparticles, their ORR performance could be obviously strengthened under acidic conditions.^[2a] According to Sun group, the fully ordered *fcc* FePt nanoparticles without *fcc* parts featured the best ORR activity when compared with the Pt, *fcc* FePt and *fcc* FePt; the mass and specific activity of the fully ordered FePt nanoparticles are 690 mA/mg and 3.16 mA/cm², which were 5 and 11 times as large as those of Pt. Note that the catalytic durability of the *fcc* FePt nanoparticles (fully ordered) is prominent: it was after 20000 potential cycles that negligible loss of ORR performance could be observed and the phase, morphology and composition of *fcc* FePt nanoparticles could be conserved perfectly (**Figure 2.8**).

In addition to Fe, PtCo alloy nanostructures have also attracted great interest, which can also crystallize in chemically ordered phase-sc phase that is active for ORR catalytic reaction. As demonstrated by Wang et al.,^[12c] as for the ORR performance, the mass activity of sc Pt₃Co was 3.3 times of that of their *fcc* counterparts for ORR test and 8.7 times as large as that of the Pt/C. Plus that, the sc Pt₃Co nanoparticles exhibited remarkable stability that after 5000 potential cycles, a minor loss of up to 10 mV in their half wave potential was monitored; in contrast, for the *fcc* Pt₃Co nanoparticles, the relative degradation was larger than 30 mV, indicating the better ORR catalytic activity induced by chemically ordered phase.

In fact, for reducing the huge expense of Pt, the evolution of ORR catalysts with novel phase but lower cost should be highlighted, such as Pd-based alloy nanostructures. For example, Pd₃Fe nanoparticles, whose chemically ordered sc phase was quite active for ORR test under alkaline conditions, were worth underscoring. In the characterization of Goodenough et al., the sc Pd₃Fe nanoparticles showed more notable behavior in ORR performance than that of their *fcc* counterparts. Specifically, when compared with the *fcc* Pd₃Fe nanoparticles and the Pd/C, the sc Pd₃Fe nanoparticles exhibited the best mass activity, that is 97.4 mA/mg, 1.5 times the activity of the *fcc* Pd₃Fe nanoparticles, 2.1 times higher than that of the Pd/C, and even 1.3 times higher than that of the Pt/C, demonstrating the excellent ORR performance of chemically ordered sc Pd₃Fe nanoparticles which should be contributed to their unique electron configuration and Pd-Pd bond interaction.^[12b] In *fcc* Pd₃Fe NPs, as some Fe atoms are near neighbors, Fe atoms will be highly possible to leach out if one of the near-neighbor Fe atoms are leached out; while In sc Pd₃Fe NPs, the Fe atoms are surrounded by 12 nearest-neighbor Pd atoms, blocking the Fe-leaching channels. Thus, sc Pd₃Fe NPs show better ORR activity and stability towards *fcc* Pd₃Fe NPs.

Figure 2.8. (a) The oxygen reduction reaction polarization plots of Pt, *fcc* FePt nanoparticle, fully and partially ordered *fcc* FePt nanoparticles in 0.1 M HClO₄. The specific (b) and mass activity (c) of Pt, *fcc* FePt nanoparticle, fully and partially ordered *fcc* FePt nanoparticles at 0.9 V. (d) The oxygen reduction reaction polarization plots of *fcc* FePt nanoparticles (fully ordered one) before and after voltage scans from 0.6 V to 1.0 V. (e) HAADF-STEM of a *fcc* FePt nanoparticles (fully ordered one) after long-term stability test. Inset: atom arrangement of the chemically ordered *fcc* structure. (f) HAADF line scan profile of the spotted area in (e) along the direction indicated by the arrow. Reprinted with permission from ref. 2b. Copyright 2015, American Chemical Society.

2.3.2 Electrochemical oxidation reactions of formic acid and alcohol

The catalytic oxidation of a wide range of fuels, including alcohols, hydrogen and formic acid, is a notable anodic reaction, for which the noble metal nanostructures, particularly the platinum-contained alloy nanomaterials, have been regularly utilized but suffering from their limited stability at cruel electrochemical environments and devitalization caused by the intermediate reaction products including CO molecules during the oxidation process of alcohol and formic acid.

For example, according to Sun et al., by controlling the crystal phase besides the composition of Pt-based alloy nanomaterials, the catalytic performance, as well as the stability, towards the electrochemical oxidation reaction of alcohol and formic acid could

be maximized. Sun et al. employed FePtAu nanoparticles with the *fcc* phase (chemically disordered) and the *fct* phase (chemically ordered), respectively, for FAOR, and he found that the *fct* ones showed better performance under acidic conditions which exhibited 2809.9 mA/mg mass activity, highest among most of the reported FAOR electrocatalysts (Table 2.1), that could be preserved after current density-time test for 13 h. This significant performance should be contributed to the unique electronic structure caused by both the Au dopant and the chemically ordered *fct* phase, without which, the CO poisoning as well as acid dissolution would be easier to deactivate the catalysts such as the *fcc* FePtAu nanoparticles, *fct* FePt and the Pt.^[7b] Similar behavior of FePtAu nanoparticles has been observed in the MOR, *fct* FePtAu featuring both chemically ordered phase and Au doping, presented the best CO-tolerance activity for MOR.

Table 2.1. The catalytic activities of some recently reported representative electrocatalysts with different crystal phases towards FAOR. All the specific and mass activities represent the forward peak current densities of different catalysts.

Catalysts	Crystal phase	Electrolyte	Mass activity (A mg ⁻¹)	Specific activity (mA cm ⁻²)	Ref.
PtFeAu	<i>fct</i>	0.5 M H ₂ SO ₄ + 0.5 M HCOOH	2.81	15	[7b]
PtRuFe	<i>fcc</i>	0.1 M HClO ₄ + 0.5 M HCOOH	N.A.	2.15	[11b]
PtAgCu@PtCu	<i>fcc</i>	0.5 M H ₂ SO ₄ + 0.5 M HCOOH	N.A.	1.52	[11c]
PtAu/graphene	<i>fcc</i>	0.5 M H ₂ SO ₄ + 0.5 M HCOOH	2.31	N.A.	[11d]
Pt-around-Au nanocomposites	<i>fcc</i>	0.5 M H ₂ SO ₄ + 0.5 M HCOOH	1.38	N.A.	[11e]

Pt ₈₀ Cu ₂₀ nanocubes	fcc	0.1 M HClO ₄ + 2.0 M HCOOH	N.A.	2.15	[11f]
Pt ₃ Pb@Pt	fcc	0.1 M H ₂ SO ₄ + 0.5 M HCOOH	1.476	N.A.	[11g]
Pd ₅₀ Co ₅₀ nanoparticles	fcc	0.1 M HClO ₄ + 2.0 M HCOOH	0.774	N.A.	[11h]

Note that, Chapter 4 focuses on electrocatalytic ethanol oxidation reaction because of the advantages of EOR. Direct alcohol fuel cells based on liquid fuels are attracting worldwide interests as power sources for portable electronic devices and fuel-cell vehicles because of the superior energy density of liquid fuels to gaseous fuels.^[12e] Among a variety of liquid fuels, ethanol is extraordinarily favorable because ethanol is not as toxic as methanol, which could be prepared in great amount from agricultural products. Furthermore, ethanol is the dominant renewable biofuel.^[12f] Electrochemical ethanol oxidation reaction makes ethanol transfer to acetic acid under applied potential. As an important type of half reaction in alkaline direct alcohol fuel cells, EOR has a series of merits in contrast with other fuel cells, including the facile fuel storage and transportation, and the relatively high mass energy density. Pt-based nanocatalysts, are among the best EOR catalysts because of their outstanding performance and stability.^[12g]

2.3.3 Carbon monoxide oxidation

The CO oxidation is an increasingly critical reaction due to its wide applications in the real world including purifying reformat hydrogen through the control of CO oxidation and removing CO from the exhausted automobile gases.^[28]

In contrast to a wide range of noble metal nanocrystals, Ru nanomaterials are more and more attractive because of their excellent performance in the CO oxidation.^[6b,28] Up to now, the influence of the size of ruthenium nanostructures towards the CO oxidation has been thoroughly investigated, but not until recently has that of the crystal phase of Ru nanostructures been noticed, which can greatly influence their catalytic activity towards the CO oxidation.^[6b] Briefly, for 2H Ru nanoparticles, which is the common phase for Ru

nanocrystals, their catalytic performance towards the CO oxidation would be increased if the size was decreased; while for *fcc* Ru nanoparticles, their catalytic activity should be weakened when the size turned to be smaller. Moreover, 2H Ru nanoparticles featured better catalytic activity than the *fcc* counterpart when their size was smaller than 3 nm, but when their size became larger than 3 nm, it was the *fcc* Ru nanoparticles that showed more active catalytic performance.

Within *hcp* Ru, the CO oxidation begins with the oxidation of Ru (001) and results in the formation of a few RuO₂ (110) layers. Then the CO oxidation occurs on RuO₂ (110). As *fcc* Ru NPs are generally enclosed by (111) planes because of their lowest surface energy, the *fcc* Ru exhibits much better activity in comparison to the *hcp* Ru. Additionally, the defects including twin boundaries, five-fold symmetry axes, or distortion of the lattice parameter to fill space can also result in the higher catalytic activity of the *fcc* Ru NPs. However, the size dependences are different. This phenomenon could originate from the diverse in the electronic states and surfaces in the *fcc* and *hcp* structures, which might result in the generation process of oxide layers, the adsorption behavior of CO, or the activation energy.

2.4 Conclusion and perspectives

In summary, various kinds of strategies for the crystal phase-modulated preparation of noble metal nanomaterials have been introduced. Significantly, the physicochemical features (i.e. magnetic, electrical and optical properties) and the catalytic activities (i.e. ORR, EOR, MOR and CO oxidation) of noble metal nanomaterials are highly influenced by their crystal phase. Thus, the modulation of crystal phase has turned to be a novel encouraging and effective method to improve the functionalities of noble metal nanomaterials.

However, some challenges still exist. For example, the crystal phase-modulating of Pd and Pt nanomaterials is still of difficulty, which possess *fcc* structure in almost all the publication. Considering that Pd and Pt nanomaterials adopt unique and favorable catalytic features, it is greatly important to rationally modulate the crystal structure of Pd and Pt nanomaterials. Meanwhile, although the surface modification methods have realized adjustable control of the crystal phases of ultrathin noble metal nanomaterials, the

mechanism still needs more investigation, which could endow the synthesis of a series of novel nanomaterials. Furthermore, the synthesis yield of noble metal nanomaterials adopting unconventional crystal phases is temporally meagre, which is substantial to their promising applications.

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Chapter 3

Experimental Methodology

The reason for selecting the specific strategies and materials is inspected. The chemical items and experimental methods have been presented. The detailed information on chemicals and experimental procedures for the one-pot wet-chemical synthesis of noble metal nanomaterials possessing novel crystal phase have been provided. Also, the basic working principles and data interpretation of the main characterization techniques used for these projects have been discussed, which include scanning electron microscopy, transmission electron microscopy, X-ray diffraction, X-ray photoelectron. Following that, the measurement of electrocatalytic reactions and the methods of characterizing the experimental outcomes have been provided.

3.1 Rationale for selection

Firstly, PtCu, Ir and PdFe were chosen to be the target materials and template-supported growth method was utilized to conduct the crystal phase-modulated synthesis. Specifically, Pt-group based alloy are ideal candidates for electrocatalytic reactions and epitaxial growth strategy is meaningful to produce noble metal nanocrystals featuring unfamiliar crystal phase. Through using noble metal nanocrystals possessing unfamiliar crystal phase as templates, a series of 4H metals including monometallic nanostructures and alloys have been successfully prepared *via* the epitaxial growth.^[1e, 8b-f] Recently, 2H PtNi proved to possess superior electrocatalytic performance to the fcc counterpart. As a result, to develop the crystal phase-controlled synthesis is quite important in order to study on phase-dependent intrinsic property of noble metal nanomaterials.

3.2 Chemicals and Synthesis

3.2.1 Chemicals

Gold chloride hydrate ($\text{HAuCl}_4 \cdot x\text{H}_2\text{O}$, ~50% Au basis), iridium chloride (IrCl_3 , ACS reagent, 99.0%), palladium (II) acetylacetonate (99%), iron acetylacetonate (97%), n-hexane ($\text{CH}_3(\text{CH}_2)_4\text{CH}_3$, technical-grade) are all purchased from Sigma-Aldrich (Saint Louis, Missouri, USA). Platinum (II) acetylacetonate (97%), copper acetylacetonate (97%), oleylamine (OAM, 98%), chloroform (99.5%), and cetyltrimethylammonium bromide (CTAB, 99%) are purchased from Aladdin. Formic acid was analytical grade. Methanol (AR-grade, 99.99%) is bought from Fisher Scientific. Squalene and 1,2-dichloropropane (DCP) are bought from TEE HAI CHEM PTE LTD (TCI). Sodium hydroxide and ethanol (99.9%, absolute) are bought from Merck. Ethanol (absolute, 99.9%) is bought from Merck (Nordic European Centre, Singapore). Pt black is purchased from Shanghai Hesun Electric Co., Ltd. (Shanghai, China).

3.2.2 Preparation of 4H-Au NRBs.

The 4H Au NRBs could be produced based on the earlier published method with some modifications.^[1] Specifically, 500 mg of HAuCl₄ were added into a mixture containing 304.8 mL of hexane, 26.4 mL of OAM and 30 mL of 1,2-dichloropropane. Then, the mixed solution was warmed up to 58 °C for 16 h in a tightly-sealed glass vial. The 4H-Au nanoribbons were collected by centrifugation (5,000 r.p.m. / 1 min), washed 3 times with hexane and finally re-dispersed into 16 mL of OAM.

3.2.3 Preparation of 4H-Au@4H-PtCu Core-Shell NRBs.

In a typical experiment, 3.9 mg of Pt(acac)₂ and 2.6 mg of Cu(acac)₂ were both added to a glass vial containing 1 mL of OAM and 3.6 mg of CTAB. Subsequently, the mixture would be ultra-sonicated for 30 min and then 500 µL of the 4H-Au NRBs in OAM (11.36 mg/mL_{Au}) were added. After 30 min of ultra-sonication, the mixed solution was warmed up to 200 °C for 8 h in an oil bath with magnetic stirring. Following that, the as-obtained product was washed for at least 3 times with hexane by centrifugation (2,000 r.p.m. / 5 min) and finally re-dispersed into 1 mL of hexane.

3.2.4 Preparation of 4H-Au@fcc PtCu Core-Shell NRBs.

In a typical experiment, 3.9 mg of Pt(acac)₂ and 2.6 mg of Cu(acac)₂ were mixed with 1 mL of OAM and 36 mg of CTAB. The mixture was ultra-sonicated for 30 min and then 500 µL of the 4H-Au NRBs in OAM (11.36 mg/mL_{Au}) were added. After 30 min of ultra-sonication, the mixed solution was warmed up to 200 °C for 8 h in an oil bath with magnetic stirring. Following that, the as-obtained product was washed 3 times with hexane by centrifugation (2,000 r.p.m. / 5 min) and re-dispersed into 1 mL of hexane.

3.2.5 Preparation of 2H Au nanosheets

The 2H Au nanosheets were produced on the basis of the previously reported method with some modifications.^[2] Specifically, HAuCl₄ (12.4 mg), squalene (3 ml) and oleylamine

(660 μ l) were mixed with hexane (7.62 ml) and 1,2-dichloropropane (180 μ l). Following that, the mixed solution was warmed up in an oven at 58.6 $^{\circ}$ C for 16 h. Finally, the as-prepared product was washed with chloroform using centrifugation (5,000 r.p.m., 3 min) for 3 times and then re-dispersed into hexane (1 ml).

3.2.6 Preparation of Au@Ir nanosheets

The Au@Ir nanosheets were produced *via* the epitaxial deposition of Ir on 2H Au nanosheets by using squalene and oleylamine to reduce the iridium precursor. Specifically, 1 mL squalene, 1 mL oleylamine and 1 mg IrCl_3 were added into 0.5 mL of the 2H Au nanosheets solution (dispersed in hexane). The mixed solution was magnetically stirred under 1000 r/s for 30 min. Following that, the resulting homogeneous mixture was warmed up to 200 $^{\circ}$ C for 6 h. The final goods was washed three times with chloroform before further characterization and obtained by centrifugation (5,000 r.p.m., 3 min). To obtain thicker Au@Ir nanosheets with corrugated surface and more *fcc* area, the addition amount of Ir precursor (IrCl_3) should be increased accordingly. When enough Ir precursor is added (i.e. 13.36 mM), the overall Au@Ir dendritic nanosheets would be crystallized in *fcc* phase.

3.2.7 Fabrication of the cross-section samples of Au@Ir nanosheets.

The cross section of Au@Ir nanosheets are prepared in an FEI Nova NanoLab 600i system (containing both focused ion beam and SEM). Specifically, Au@Ir nanosheets are dropped on a Si substrate and dehydrated in air at first. Then the substrate loaded with Au@Ir nanosheets is put into the SEM chamber, and a specific Au@Ir nanosheet is rotated to make one of its two diagonals. A thin W shell is then settled on this area by electron beam-induced settling. Subsequently, two alignment marks are milled to recognize this area, followed by another settlement of a W shell with focused ion beam (FIB). Lastly, by using an in situ manipulator, the relative region is transferred to a TEM half-grid after final thinning of the sample with FIB.

3.2.8 Preparation of Au@PdFe nanosheets

The Au@PdFe nanosheets were produced by the epitaxial deposition of Pd and Fe atoms on 2H Au nanosheets by using the reducing agent of squalene and oleylamine. Specifically, 1 mL squalene, 1 mL oleylamine, 1 mg palladium acetylacetonate and 10 mg iron acetylacetonate were mixed with 0.5 mL of the 2H Au nanosheets solution (dispersed in hexane). The mixed solution was magnetically stirred under 1000 r/s for 30 min. Following that, the final mixture was warmed up to 210 °C for 18 h. The final goods was washed with chloroform by centrifugation (5,000 r.p.m., 3 min) for three times before further characterization.

3.2.9 Preparation of 4H Au@PdFe core-Shell nanoribbons.

Typically, 4 mg of palladium acetylacetonate and 1 mg of iron acetylacetonate would be added into a glass vial containing 1 mL of OAM. Subsequently, the mixture was sonicated for 30 min and then 500 μ L of the 4H Au NRs in OAM were added. After 30 min of ultra-sonication, the mixture was warmed up to 210 °C for 18 h in an oil bath with magnetic stirring. Following that, the as-obtained product was washed at least 3 times with chloroform by centrifugation (2,000 r.p.m. / 5 min) and finally re-dispersed into 1 mL of hexane.

3.3 Characterizations

Several techniques have been chosen to confirm the composition, crystal phase, morphology and other physical and chemical features of the noble metal nanomaterials with unfamiliar crystal phase, as follows.

3.3.1 Scanning electron microscopy (SEM)

SEM possesses much better resolution than optical microscopy over two orders because of electron beam instead of the light source, and this is because the resolution is greatly

influenced by the radiation wavelength while the wavelength of the electron beam is a lot shorter than that of the light source and thus provides better resolution. Various sorts of signals, including secondary electrons, back-scattered electrons and X-rays, can be produced by the collision between electrons and samples.

The SEM sample of crystal-phase-heterostructured 4H-Au@4H-PtCu and 4H-Au@*fcc*-PtCu NRBs was prepared by dropping 20 μL of 4H-Au@4H-PtCu or 4H-Au@*fcc*-PtCu NRBs solution (hexane) on a $0.5\text{ cm} \times 0.5\text{ cm}$ silicon substrate. The SEM sample of crystal-phase-heterostructured 2H/*fcc* Au@Ir nanosheets, *fcc* Au@Ir nanosheets, 2H Au@PdFe nanosheets and 4H-Au@4H-PdFe NRBs was prepared by dropping 10 μL of 2H/*fcc* Au@Ir nanosheets, *fcc* Au@Ir nanosheets, 2H Au@PdFe nanosheets and 4H-Au@4H-PdFe NRBs solution (ethanol) on a $0.5\text{ cm} \times 0.5\text{ cm}$ silicon substrate. All SEM samples were naturally dried under ambient condition.

3.3.2 Transmission electron microscopy (TEM)

Up to now, TEM is quite useful to study nanomaterials in grain boundaries, interlayer distance, crystallinity, lattice, and elemental compositions. Being irradiated, the electrons will interact with the sample since the electron beam passes on via the samples and the TEM figures are generated by collecting these electrons. Thus, the samples should satisfy two requirements. First of all, the samples should be thin enough to let the electron beam transmit. Secondly, the samples must be stable not only in high vacuum condition but also under the electron beam irradiation. TEM is indispensable in all of the work listed in this thesis because the atomic resolution is necessary for noble metal material research.

TEM samples 4H-Au@4H-PtCu, 4H-Au@*fcc*-PtCu NRBs, 2H/*fcc* Au@Ir nanosheets, *fcc* Au@Ir nanosheets, 2H Au@PdFe nanosheets and 4H-Au@4H-PdFe NRBs were prepared by dropping 5.0 μL of the corresponding sample solutions onto a carbon-coated copper grid (200 mesh). 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-Au@4H-PtCu, 4H-Au@*fcc*-PtCu NRBs, 2H/*fcc* Au@Ir nanosheets, and *fcc* Au@Ir nanosheets, were acquired from the high-resolution aberration-corrected TEM (JEOL JEM-ARM200F) operated at 200 kV.

3.3.3 X-ray photoelectron spectroscopy (XPS)

XPS is quite versatile in investigating the chemical composition, electronic states and chemical states of the surface of atoms of molecules. Being irradiated by high energetic electrons, photoelectron are generated from the sample surfaces. This process is called photoemission process, which follows an equation below: $h\nu$ (photon energy) = EB (electron binding energy) + EK (the kinetic energy of photoelectron). By using XPS, the elemental composition can be identified at any solid materials' surfaces, the energy distributions of photoelectrons could be obtained, and the thickness profile could be studied from 10 nm to several μm .

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).

3.3.4 X-Ray Diffraction (XRD)

XRD is quite valuable for the characterization of crystallographic features of the crystalline materials. Shimadzu XRD-6000 was employed to measure the thin film XRD pattern of the 4H-Au@4H-PtCu nanoribbons, 4H-Au@4H-PtCu nanoribbons, 2H/*fcc* Au@Ir nanosheets, *fcc* Au@Ir nanosheets, 4H-Au@4H-PdFe nanoribbons and, 2H/*fcc* Au@PdFe nanosheets. Specifically, all of the XRD patterns were measured in the range of 30° to 80°. The relative crystals were ground into micro-sized powders before depositing on silicon substrate for the measurement.

3.4 Applications: Fabrication and Performance Measurement of EOR, HzOR and MOR

CHI 760e (CHI 760e, Shanghai Chen hua Co., China) electrochemical workstation is utilized for studying all of the electrochemical features of 4H-Au@4H-PtCu NRBs, and 4H-Au@*fcc*-PtCu NRBs, 2H/*fcc* Au@Ir nanosheets, and *fcc* Au@Ir nanosheets, 2H Au@PdFe nanosheets and 4H-Au@4H-PdFe NRBs. A Pt wire is used as the counter electrode and a SCE is used as the reference electrode. All potentials are calculated to the E (RHE) from E (SCE) ($E(\text{RHE}) = E(\text{SCE}) + 0.05916 \times \text{pH} + 0.254 \text{ V}$). For preparing the working electrode, the catalyst ink would be pre-deposited on 0.25 cm^2 carbon paper (Toray TGP-H-060, purchased from Fuel Cell Store) with the Pt mass loading of $1.4 \mu\text{g}/\text{cm}^2$ for 4H-Au@4H-PtCu NRBs, and 4H-Au@*fcc*-PtCu NRBs, and the Pd mass loading of $5.36 \mu\text{g}/\text{cm}^2$ for 2H Au@PdFe nanosheets and 4H-Au@4H-PdFe NRBs.

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Chapter 4

Crystal-phase-dependent electrocatalytic features of PtCu alloy nanostructures in ethanol oxidation reaction

Crystal phase of nanomaterials greatly affecting their physicochemical features has attracted increasing research interest. Herein, we report the crystal phase-controlled synthesis of PtCu alloy nanostructures on hexagonal 4H phase Au nanoribbons, referred to as 4H-Au NRBs, to form 4H-Au@PtCu core-shell NRBs. By tuning the thickness of PtCu shell on the 4H-Au NRB core, 4H-PtCu and fcc phase PtCu (fcc-PtCu) alloy nanostructures are successfully prepared. Significantly, the phase-dependent electrocatalytic features of the as-synthesized PtCu alloy nanostructures in the ethanol oxidation reaction (EOR) are investigated. Impressively, the 4H-Au@4H-PtCu NRBs possess a much higher specific activity of 50.2 mA/cm², which is 2.1 times that of 4H-Au@fcc-PtCu NRBs (24 mA/cm²) and 5.9 times the activity of Pt black (8.5 mA/cm²).

4.1 Introduction

Crystal phase-controlled synthesis of nanomaterials is desired as their crystal phases can dramatically affect both of their physical and chemical features together with their various applications such as magnetism^[1a], electronics^[1b,c] and catalysis^[1d,e]. Among the prepared multi-metallic nanomaterials, Pt-based alloy nanomaterials are considered as one of the most promising nanocatalysts used in a wide range of reactions.^[2-5] Importantly, the atomic arrangement in Pt-based alloy is quite critical in tuning its catalytic performance. For instance, the structurally ordered PtFe nanoparticle is much better in activity and durability than the disordered counterpart for ORR in acid media.^[7] However, most of the Pt-based alloy nanomaterials crystallize in the thermodynamically stable phase, *i.e.*, the *fcc* phase. Recently, Pt-based alloy nanomaterials with non-thermodynamically stable phase or metastable phase have attracted more and more attention owing to their significant catalytic performance.^[1f,6,8] For example, PtNi alloy nanomaterials with 2H crystal phase have been successfully prepared.^[6] Compared with the *fcc*-PtNi nanomaterials, the obtained 2H-PtNi nanomaterials possess much higher electrocatalytic performance in HER.^[6] Therefore, it is critically important to prepare Pt-based alloy nanomaterials with unfamiliar crystal phases, and investigate the role of novel crystal phase in catalytic applications.

Recently, we reported a novel crystal phase, *i.e.* the hexagonal 4H phase, of Au nanoribbons (NRBs), referred to as 4H-Au NRBs, *via* a facile colloidal synthesis.^[8a] By using them as templates, a series of 4H metals including monometallic nanostructures and alloys have been successfully prepared *via* the epitaxial growth.^[1e, 8b-f] These studies offer a strategy to prepare PtM nanostructures with uncommon 4H crystal phase, enabling the further investigation on the phase-dependent electrocatalytic features of PtM alloy nanostructures.

Herein, for the first time, PtCu alloy nanostructures with 4H hexagonal crystal phase, referred to as 4H-PtCu are successfully prepared by the epitaxial deposition of PtCu alloy on the pre-synthesized 4H-Au NRBs to form 4H-Au@4H-PtCu core-shell nanostructures.

Interestingly, by increasing the shell thickness, the *fcc*-PtCu alloy shell is formed and the 4H-Au@*fcc*-PtCu core-shell nanostructures are obtained. Impressively, the 4H-Au@4H-PtCu NRBs and 4H-Au@*fcc*-PtCu NRBs can be used as ideal models to study the crystal phase-dependent catalytic performance of Au@PtCu nanostructures. Furthermore, 4H-Au@4H-PtCu and 4H-Au@*fcc*-PtCu NRBs are utilized for the ethanol oxidation reaction (EOR). The 4H-Au@4H-PtCu NRBs exhibit the specific activity of 50.2 mA/cm², 5.9 times and 2.1 times those of Pt black (8.5 mA/cm²) and 4H-Au@*fcc*-PtCu NRBs (24 mA/cm²), respectively, and is also superior to those of previously reported Pt-based EOR nanocatalysts.

4.2 Results and Discussions

Figure 4.1. (a) Low- and (b) high-magnification TEM figures of the 4H-Au NRBs. (c) HRTEM figure and (d) the relative FFT pattern of a distinctive 4H-Au NRB collected along the direction of $[110]_{4H}$.

The 4H-Au NRBs would be first produced by our earlier developed strategy,^[8a] which are characterized by TEM (**Figure 4.1 a and b**), the HRTEM (**Figure 4.1c**), and the relative SAED pattern (**Figure 4.1d**). The as-obtained 4H-Au NRBs are then utilized as the core (**Scheme 4.1a**) to deposit PtCu alloy nanostructures with different crystal phases. Typically, a homogeneous mixture of the as-prepared 4H-Au NRBs, Pt(acac)₂, Cu(acac)₂, and cetyl trimethyl ammonium bromide (CTAB) dispersed in oleylamine (OAM) was warmed up to 200 °C for 8 h under magnetic stirring. At a CTAB concentration of 10 mM, 4H-PtCu is prepared (b in **Scheme 4.1**), while at a CTAB concentration of 100 mM, *fcc*-PtCu is obtained (c in **Scheme 4.1**).

Scheme 4.1. Scheme of the preparation procedure of 4H-Au@PtCu core-shell NRBs by using 4H-Au NRB as template. Schemes of (a) 4H-Au NRB, (b) 4H-Au@4H-PtCu NRB, and (c) 4H-Au@*fcc*-PtCu NRB.

Figure 4.2. (a) Low-magnification TEM figure of 4H-Au@4H-PtCu NRBs. (b) TEM figure and (c) the relative SAED pattern of a typical 4H-Au@4H-PtCu NRB. Inset in b: enlarged TEM figure of the dashed area in b (scale bar, 10 nm). (d) HAADF-STEM figure, and (e-g) the relative STEM-Eds maps of a representative 4H-Au@4H-PtCu NRB. (h) Aberration-corrected high-resolution HAADF-STEM figure of a typical 4H-Au@4H-PtCu NRB. (h1, h2) High-resolution HAADF figures of the relative dashed areas in (h). (i1, i2) The relative FFT patterns of h1 and h2, respectively, as marked in h.

As indicated in **Figure 4.2 a and b**, after coating both Pt and Cu atoms on 4H-Au NRBs using 10 mM CTAB, the thickness of PtCu was measured to be 2.4 ± 0.5 nm (**Figure 4.3**). Two sets of diffraction spots without other randomly distributed diffraction spots were observed in the SAED pattern (**Figure 4.2 c**), affirming the epitaxial deposition of the PtCu shell on the 4H-Au NRB with a typical $[110]_{4H}$ -zone axis. As observed in the aberration-corrected HAADF-STEM figure of a distinctive 4H-Au@4H-PtCu NRB (**Figure 4.2H**), the lattice fringes continuously stretch from the gold backbone to the PtCu film, proving that PtCu shell is epitaxially coated on 4H-Au NRBs. In addition, the relative FFT patterns (**Figure 4.2-i1 and i2**) and aberration-corrected HAADF-STEM figures (**Figure 4.2-h1 and h2**) taken from the selected areas in Figure 1h (marked by blue and yellow squares, respectively) demonstrated that both core and shell areas feature the 4H crystal phase. A distinctive HAADF-STEM figure (**Figure 4.2d**) and the relative STEM-EDS mappings (**Figure 4.2 e-g**) of the 4H-Au@4H-PtCu NRBs showed consistent deposition of the PtCu shell on 4H-Au template, further recommended by the STEM-EDS line scan profile (**Figure 4.4**). The atomic ratio of Au/Pt/Cu was calculated to be 83.99/7.04/8.96 (**Figure 4.5**), indicating a Pt/Cu ratio of 0.78.

Figure 4.3. (a) TEM figure and (b) thickness distributions of the PtCu shells of 4H-Au@4H-PtCu NRBs.

Figure 4.4. (a) HAADF-STEM figure and (b) the relative STEM-EDS line scan profile along the dotted line in (a) of a typical 4H-Au@4H-PtCu NRB.

Figure 4.5. A distinctive STEM-EDS spectrum of the 4H-Au@4H-PtCu NRBs. The atomic ratio of Au/Pt/Cu is 83.99/7.04/8.96.

Figure 4.6. (a) Low-magnification TEM figure of 4H-Au@*fcc*-PtCu NRBs. (b) TEM figure and (c) the relative SAED pattern of a representative 4H-Au@*fcc*-PtCu NRB. Inset in b: enlarged TEM figure of the dashed square in b (scale bar, 10 nm). (d) HAADF-STEM and (e-g) the relative STEM-Eds mapping of a representative 4H-Au@*fcc*-PtCu NRB. (h) Aberration-corrected high-resolution HAADF-STEM figure of a distinctive 4H-Au@*fcc*-

PtCu NRB. (h1, h2) High-resolution HAADF figures from the relative dashed areas in (h). (i1, i2) The relative FFT patterns of h1 and h2, respectively, as marked in h.

When 100 mM CTAB was used instead of 10 mM, the crystal phase of PtCu shell grown on the 4H-Au NRBs became *fcc* (**Figure 4.6**). Specifically, the deposition of Pt and Cu atoms was dominated by a non-epitaxial way and the thickness of PtCu shell is approximately 5.7 ± 0.6 nm (**Figure 4.7**). The randomly distributed spots in the SAED pattern suggested that PtCu shell were grown on 4H-Au surface non-epitaxially, and crystallized in *fcc* crystal phase, while the SAED pattern also exhibited a representative $[110]_{4H}$ -zone diffraction pattern, indicating that 4H phase of Au NRBs could be preserved (**Figure 4.6c**). **Figure 4.6h** showed a distinctive aberration-corrected HAADF-STEM figure of the 4H-Au@*fcc*-PtCu NRB, in which the different atomic arrangement of the core and shell areas could be clearly noticed. The relative FFT patterns in **Figure 4.6-i1 and i2**, referring to the selected areas in the core and shell labeled by blue and yellow squares, respectively, suggested that the Au core adopted the 4H phase (**Figure 4.6-h1 and i1**), while the PtCu shell featured the *fcc* phase (**Figure 4.6-h2 and i2**). The representative HAADF-STEM figures and STEM-EDS mappings of a 4H-Au@*fcc*-PtCu NRB in **Figure 4.6 d-g** confirmed the uniform coating of PtCu film on 4H-Au core, consistent with the relative EDX line scanning profile (**Figure 4.8**). The atomic ratio of Au/Pt/Cu was calculated to be 66.64/14.40/18.96 (**Figure 4.9**), indicating that the atomic ratio of Pt/Cu (0.76) in the 4H-Au@*fcc*-PtCu NRBs was similar to that (0.78) of the 4H-Au@4H-PtCu NRBs (**Figure 4.5**). The concentrations of Au, Pt and Cu in 4H-Au@4H-PtCu and 4H-Au@*fcc*-PtCu NRBs were further confirmed by ICP-MS (**Table 4.1**), and the atomic ratios of Pt/Cu were 0.76 in 4H-Au@4H-PtCu and 0.81 in 4H-Au @ *fcc*-PtCu, similar to those measured by EDS.

Figure 4.7. (a) TEM figure and (b) thickness distribution of the PtCu shells of 4H-Au@*fcc*-PtCu NRBs.

Figure 4.8. (a) HAADF-STEM figure and (b) the relative STEM-EDS line scan along the dotted line of a distinctive 4H-Au@*fcc*-PtCu NRB.

Figure 4.9. A typical STEM-EDS spectrum of the 4H-Au@*fcc*-PtCu NRBs. The atomic ratio of Au/Pt/Cu is 66.64/14.40/18.96.

In addition, the XPS spectrum confirmed that the valence states of Pt and Cu on the surface of 4H-Au@4H-PtCu and 4H-Au@*fcc*-PtCu NRBs were predominately metallic Pt and Cu (**Figure 4.10**).^[11a]

Figure 4.10. XPS spectra of 4H-Au@4H-PtCu NRBs, showing the core level peaks of (a) Au 4f, (b) Pt 4f, and (c) Cu 2p. XPS spectra of 4H-Au@*fcc*-PtCu NRBs, showing the core level peaks of (d) Au 4f, (e) Pt 4f, and (f) Cu 2p.

Figure 4.11. (a) XRD patterns of 4H-Au NRBs. (b) Enlarge area indicated in the dashed rectangle in (a).

As indicated in **Figure 4.11**, the crystal structure of 4H-Au NRBs is affirmed by XRD, which displays a typical 4H feature, namely 5 characteristic peaks located at 36.2°, 37.4°, 37.9°, 40.9° and 65°, corresponding to (100)_{4H}, (101)_{4H}, (004)_{4H}, (102)_{4H} and (110)_{4H}, respectively.^[8a] Also, the *fcc* Au still exists, originated from the presence of Au nanoparticles (i.e. the by-products acquired during the synthesis of 4H Au NRBs), as the peaks of 38.2°, 44.3°, 65°, and 77.5°, corresponding to (111)_f, (200)_f, (220)_f, and (311)_f, respectively, can be clearly observed.^[12b]

Figure 4.12. (a) Low-magnification TEM image of 4H-Au@4H-PtCo NRBs. (b) High-resolution TEM image of a representative 4H-Au@4H-PtCo NRB. (b1, b2) Enlarged high-resolution TEM images of the corresponding blue (b1) and yellow (b2) dashed areas in b. (b3, b4) The corresponding FFT patterns of b1 and b2, respectively, as marked in b. (c) HAADF-STEM image, and the corresponding STEM-EDS element maps of a representative 4H-Au@4H-PtCo NRB.

Figure 4.13. (a) HAADF-STEM image and (b) the corresponding STEM-EDS line scanning profile of a representative 4H-Au@4H-PtCo NRB along the white line in a.

Figure 4.14. A representative STEM-EDS spectrum of the 4H-Au@4H-PtCo NRBs. The atomic ratio of Au/Pt/Co is 90.9/5.9/3.2.

Figure 4.15. (a) Low-magnification TEM image of 4H-Au@*fcc*-PtCo NRBs. (b) High-resolution TEM image of a representative 4H-Au@*fcc*-PtCo NRB. (b1, b2) Enlarged high-resolution TEM images from the corresponding blue (b1) and yellow (b2) dashed areas in b. (b3, b4) The corresponding FFT patterns of b1 and b2, respectively, as marked in b. (c) HAADF-STEM and the corresponding STEM-EDS element mapping of a representative 4H-Au@*fcc*-PtCo NRB.

Figure 4.16. (a) HAADF-STEM image and (b) the corresponding STEM-EDS line scanning profile of a representative 4H-Au@*fcc*-PtCo NRB along the white line in a.

Figure 4.17. A representative STEM-EDS spectrum of the 4H-Au@*fcc*-PtCo NRBs. The atomic ratio of Au/Pt/Co is 71.7/19.4/8.9.

As indicated in **Figure 4.12a**, after depositing Pt and Co atoms on the surface of 4H-Au NRBs using 10 mM CTAB, the surface of 4H-Au@4H-PtCo NRBs is smooth. As observed in the high resolution TEM (HRTEM) image of a typical 4H-Au@4H-PtCo NRB (**Figure**

4.12b), the inter-planar distance of 0.24 nm (in the central area) and 0.22 nm (in the edge area) should be attributed to the lattice spacing of (004)_{4H} planes of Au and PtCo, respectively. Furthermore, the lattice fringes continuously extend from the Au backbone to the PtCo shell, confirming the epitaxial relationship between PtCo shell and 4H-Au NRB. In addition, the corresponding fast Fourier transform (FFT) patterns (**Figure 4.12-b3** and **b4**) and HRTEM images (**Figure 4.12-b1** and **b2**) taken from the selected areas in **Figure 4.12b** (marked by blue and yellow squares, respectively) demonstrate that both core and shell areas featured the 4H crystal phase. A typical HAADF-STEM image and the corresponding STEM-EDS element mappings (**Figure 4.12c**) of the 4H-Au@4H-PtCo NRB show uniform coating of the PtCo shell on the surface of 4H-Au core, which can be further confirmed by the STEM-EDS line scan profile (**Figure 4.13**). The atomic ratio of Au/Pt/Co is measured to be 90.9/5.9/3.2 (**Figure 4.14**), indicating a Pt/Co ratio of 1.8.

When 100 mM CTAB is used instead of 10 mM, the crystal phase of PtCo shell grown on the 4H-Au NRBs becomes *fcc* (**Figure 4.15**). As indicated in **Figure 4.15a**, the surface of 4H-Au@*fcc*-PtCo NRBs is relatively rough. As shown in **Figure 4.15b**, the inter-planar distance of 0.24 nm (in the central area) and 0.22 nm (in the edge area) should be attributed to the lattice spacing of (004)_{4H} planes of Au and (111)_f planes of PtCo, respectively. Also, **Figure 4.15b** shows a typical HRTEM image of the 4H-Au@*fcc*-PtCo NRB, in which the different atomic arrangement of the core and shell areas could be clearly noticed. The corresponding FFT patterns in **Figure 4.15-b3** and **b4**, referring to the selected areas in the core and shell labeled by blue and yellow squares, respectively, suggest that the Au core adopts the 4H phase (**Figure 4.15-b1** and **b3**), while the PtCo shell features the *fcc* phase (**Figure 4.15-b2** and **b4**). Specifically, the deposition of Pt and Co atoms is dominated by a non-epitaxial way. The representative HAADF-STEM images and STEM-EDS element mappings of a 4H-Au@*fcc*-PtCu NRB in Figure S13c confirm the uniform coating of PtCo shell on the surface of the 4H-Au NRBs, consistent with the corresponding EDX line scanning profile (Figure 4.16). The atomic ratio of Au/Pt/Co is measured to be 71.7/19.4/8.9 (Figure 4.17), indicating that the atomic ratio of Pt/Co (2.2) in the 4H-Au@*fcc*-PtCo NRBs is similar to the atomic ratio of Pt/Co (1.8) in the 4H-Au@4H-PtCo NRBs (**Figure 4.14**).

Figure 4.18. (a) CV curves of 4H-Au@4H-PtCu NRs, 4H-Au@fcc-PtCu NRs, and Pt black in 0.5 M H₂SO₄. (b) The ECSA-normalized CV curves of 4H-Au@4H-PtCu NRs, 4H-Au@fcc-PtCu NRs, and Pt black in mixed solution containing ethanol (1 M) and KOH (1 M) filled with N₂ (Scan rate of 50 mV/s). (c) Histograms of specific and mass activities of 4H-Au@4H-PtCu NRs, 4H-Au@fcc-PtCu NRs, and Pt black toward EOR

measured in N₂-saturated mixed solution containing ethanol (1 M) and KOH (1 M) at scan rate of 50 mV/s. (d) Chronoamperometric results of ethanol oxidation at 0.7 V (vs. RHE) using 4H-Au@4H-PtCu NRBs, 4H-Au@*fcc*-PtCu NRBs and Pt black in mixed solution containing ethanol (1 M) and KOH (1 M). (e, f) Reaction pathways for the oxidation of ethanol on (e) *fcc* PtCu(111) and (f) 4H PtCu(110) surface. Insets are the corresponding structures of reaction intermediates, where the blue, bronze, gray, red, and white balls represent Pt, Cu, C, O, and H atoms, respectively.

Furthermore, the as-prepared 4H-Au@4H-PtCu and 4H-Au@*fcc*-PtCu NRBs were used for electrocatalytic EOR measurements in alkaline electrolyte (**Figure 4.18**). **Figure 4.18a** showed the cyclic voltammograms (CVs) lines tested in 1 M KOH. Specific activities were used to characterize the catalytic performances of these catalysts by calculating the current density (j_s) normalized the ECSAs. The electrochemically active surface area (ECSA) of Pt-based electrodes was determined by the underpotential hydrogen adsorption/desorption method.^[12c] As each surface platinum atom has the capacity to adsorb close to one hydrogen atom, the charge associated with hydrogen adsorption and desorption (eq 1) indicates the number of surface platinum atoms.

The value of 210 $\mu\text{C cm}^{-2}$ is an average value for the charge associated with monolayer formation of hydrogen atoms on a polycrystalline platinum surface. Hence, the ECSA can be calculated as follows:

$$\text{ECSA} = Q_{\text{Hupd}} / (m \times 210 \mu\text{C cm}^{-2}) \quad (2)$$

Figure 4.18b showed the CVs of 4H-Au@4H-PtCu, 4H-Au@*fcc*-PtCu and the Pt black catalyst obtained in the mixture containing 1 M ethanol and 1 M KOH solution. Specifically, 4H-Au@4H-PtCu NRB exhibited the highest forward peak value (50.2 mA/cm²), which was 2.1 and 5.9 times than that of 4H-Au@*fcc*-PtCu NRB and the Pt black catalysts, respectively (**Figure 4.18 c**). In terms of mass activities (**Figure 4.18c**), the peak current densities of 4H-Au@4H-PtCu NRB (4.22 A/mg) were 1.9, and 4.7 times the activity of 4H-Au@*fcc*-PtCu NRB and the Pt black catalysts, respectively. Moreover, the catalytic activities of 4H-Au@4H-PtCu NRB towards EOR also showed significant

increase in contrast to a wide range of reported Pt group metal-based catalysts (**Table 4.2**). The catalytic stabilities of the above-mentioned electrocatalysts were assessed by the chronoamperometric measurement at 0.7 V (vs. RHE) measured in the mixture containing 1 M ethanol and 1 M KOH solution (**Figure 4.18d**). Specifically, the polarization current of 4H-Au@4H-PtCu, 4H-Au@*fcc*-PtCu, and Pt black exhibited a fast decrease in the beginning due to the formation of intermediate issues. However, the current decay on 4H-Au@4H-PtCu NRBs electrode was significantly slower than that on 4H-Au@*fcc*-PtCu NRBs and the Pt black electrode. Furthermore, after chronoamperometric measurement, the remaining current density value of 4H-Au@4H-PtCu NRBs (41.7 mA/cm^2) was 3.8, and 9.1 times than that of 4H-Au@*fcc*-PtCu NRB (11.1 mA/cm^2) and Pt black catalysts (4.6 mA/cm^2), respectively (**Figure 4.19**). Worth noting that not only the morphology but also the crystal phase of 4H-Au@4H-PtCu NRBs and 4H-Au@*fcc*-PtCu NRBs can be well maintained after chronoamperometric measurement (**Figure 4.20** and **Figure 4.21**). These results showed that the as-prepared 4H-Au@4H-PtCu and 4H-Au@*fcc*-PtCu NRBs possessed advantageous catalytic performance for the EOR.

Figure 4.19. CV curves of 4H-Au@4H-PtCu NRBs, 4H-Au@*fcc*-PtCu and Pt black before (solid line) and after (dotted line) the chronoamperometric measurement. Scan rate is 50 mV/s.

To understand the excellent activity of 4H PtCu in EOR, density functional theory (DFT) calculations were carried out, in which the dominant exposed facets, *fcc* PtCu (111) and

4H PtCu (110), respectively, were selected as models (**Figure 4.18e** and **f**). For EOR on *fcc* PtCu (111) surface, the first step is the cleavage of α -C-H bond to form $^*\text{CH}_3\text{CHOH}$ (**Figure 4.18e**). The corresponding energy barrier (E_a) is calculated to be 1.05 eV. In the following two steps, the produced $^*\text{CH}_3\text{CHOH}$ continually dehydrogenates to form $^*\text{CH}_3\text{CO}$ by conquering a E_a of 0.42 eV. The formed $^*\text{CH}_3\text{CO}$ can further react with surface $^*\text{OH}$ to generate CH_3COOH , while the calculated E_a is 0.95 eV. During the whole process, the first step (cleavage of α -C-H bond), with the highest E_a , is the rate determining step. The EOR process on 4H PtCu (110) are via the same mechanism (**Figure 4.18f**). Moreover, the E_a for the dehydrogenation of $^*\text{CH}_3\text{CHO}$ and oxidation of $^*\text{CH}_3\text{CO}$ (0.42 and 0.93 eV) are found to be similar to those on *fcc* PtCu (111) surface (0.42 and 0.95 eV). Interestingly, the cleavage of α -C-H bond on 4H PtCu (110) surface just need to overcome an energy barrier of 0.22 eV, making the rate determining step of EOR on 4H PtCu (110) to be the oxidation of $^*\text{CH}_3\text{CO}$ with a E_a of 0.93 eV. Therefore, 4H PtCu (110) can present higher specific and mass activities for EOR than *fcc* PtCu (111) owing to the lower E_a of the rate determining step (0.93 eV vs 1.05 eV).

Thus, it is rational to conclude that 4H-PtCu alloy nanostructures are more favorable for electrochemical catalytic reactions than the *fcc* counterparts. The superior EOR performance of the 4H-Au@4H-PtCu alloy catalysts can be contributed to their unique crystal phase, compositions as well as the architecture. First of all, the incorporation of Cu can control the electronic structure of Pt, and then enhance the catalytic performance and enhance the tolerance against CO poisoning during EOR.^[12] Secondly, the competent affinity of the PtCu alloy shells deposited on the 4H-Au NRs endow the catalysts with fantastic electrical conductivity and chemical stability, thus facilitating speedy electron transfer during the electrochemical catalytic reactions with coherent architecture.^[11] Furthermore, most importantly, as compared to 4H-Au@*fcc*-PtCu NRs, the beneficial catalytic performance of 4H-Au@4H-PtCu NRs should be ascribed to the unique 4H phase PtCu shell.^[6,12]

Figure 4.20. (a) Low-magnification SEM image of 4H-Au@4H-PtCu NRBs deposited on carbon paper and (b) high-magnification SEM images of 4H-Au@4H-PtCu NRBs after the EOR stability test. (c) TEM image and (d) the relative SAED pattern acquired of a distinctive 4H-Au@4H-PtCu NRB after EOR stability test. (e) A distinctive HRTEM image of a 4H-Au@4H-PtCu NRB after the EOR stability test.

Figure 4.21. (a) Low-magnification SEM image of 4H-Au@*fcc*-PtCu NRBs deposited on carbon paper and (b) high-magnification SEM images of 4H-Au@*fcc*-PtCu NRBs after the EOR stability test. (c) TEM image and (d) the relative SAED pattern acquired of a distinctive 4H-Au@*fcc*-PtCu NRB after EOR stability test. (e) A distinctive HRTEM image of a 4H-Au@*fcc*-PtCu NRB after the EOR stability test.

Table 4.1. ICP results of 4H-Au@4H-PtCu and 4H-Au@*fcc*-PtCu.

	4H-Au@4H-PtCu			4H-Au@ <i>fcc</i> -PtCu		
Element	Au	Pt	Cu	Au	Pt	Cu
Concentration (ppm)	276.2	22.9	9.8	146.8	29.2	11.8
Pt/Cu atomic ratio	0.76			0.81		

Table 4.2. The catalytic activities of some recently reported representative Pt-based and Pd-based electrocatalysts towards EOR under alkaline conditions. All the specific and mass activities represent the forward peak current densities of different catalysts.

Catalysts	Electrolyte	Mass activity (A mg ⁻¹)	Specific activity (mA cm ⁻²)	Ref.
3D hierarchical PtCu	0.5 M KOH + 2 M Ethanol	0.4	3.2	[13]
Sub 5 nm Pt ₆₈ Cu ₃₂	0.5 M KOH + 0.5 M Ethanol	2.33	19.3	[14]
PtCu nanowires	1 M KOH + 1 M Ethanol	2.1	51	[15]
Pt ₅₄ Rh ₄ Cu ₄₂ cubic nanobox	1 M KOH + 1 M Ethanol	4.09	14.9	[16]
Au@Pt concave nanocube	1 M NaOH + 1 M Ethanol	0.92	18	[17]
PtRhNi octahedran	0.1 M KOH + 0.5 M Ethanol	3.39	13.6	[18]
Pd/Ni(OH) ₂ /rGO	1 M KOH + 1 M Ethanol	1.42	4.1	[19]
PdAg nanodendrites	1 M KOH + 1 M Ethanol	2.6	3.7	[20]
PdCu nanowires	1 M KOH + 1 M Ethanol	3.47	9.2	[21]
4H-Au@fcc-PtCu	1 M KOH + 1 M Ethanol	2.26	24	This work

4H-Au@4H-PtCu	1 M KOH + 1 M Ethanol	4.22	50.2	This work
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4.3 Conclusions

In summary, PtCu alloy nanostructures with 4H crystal phase have been produced for the first time via the epitaxial deposition on the template of 4H-Au NRs. The crystal phase of PtCu shell can be changed by controlling the concentrations of CTAB added in this system to obtain *fcc*-PtCu alloy nanostructures. The as-obtained 4H-PtCu and *fcc*-PtCu alloys served as ideal models to study the phase-dependent features. As a proof-of-concept, both 4H-PtCu and *fcc*-PtCu alloys proved to be excellent electrocatalyst for EOR. Impressively, 4H-PtCu alloy exhibited a specific activity of 50.2 mA/cm², much better than that of the *fcc*-PtCu counterparts (specific activity of 24 mA/cm²) and even superior to most of the reported Pt group metal based EOR electrocatalysts. These findings reveal the significance of crystal phase modulation in the phase-controlled synthesis of unfamiliar multi-metallic nanocrystals. We believe that the strategy presented here may offer new opportunities for the preparation of novel nanostructures with modulated crystal phases to tailor their electrical, optical, magnetic and catalytic features for potential applications.

Meanwhile, it is worth mentioning that the shell thickness in the synthesis of core-shell nanostructures with uncommon thermodynamic unstable crystal phase is quite important. Firstly, changing the thickness of shell in the as-obtained 4H/*fcc* Au@PtM nanocatalysts can change the crystal phase of shell with neglectable change of the initial crystal phase of core. as it will be difficult to distinguish the catalytic performances from the unusual 4H phase and the usual *fcc* phase. Furthermore, the performance comparison between the shell with thermodynamically unstable (4H) and stable (*fcc*) crystal phase indicated that thermodynamically unstable crystal phase could also bring about better catalytical activities. Therefore, the next project also aims to investigate the effect of shell thickness on the crystal phase transformation in the core-shell nanostructures with other kind of thermodynamically unstable crystal phase and further study the influence of the corresponding crystal phase transformation towardselectrocatalytic applications.

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Chapter 5

Thickness-modulated 2H-to-fcc phase transition in Au@Ir core-shell nanosheets

Crystal phase of nanostructure largely influencing their physicochemical features has aroused more and more attention. Herein, high-yield preparation of mixed phase hexagonal close-packed 2H/fcc Au@Ir core-shell nanosheets have been accomplished by using 2H Au nanosheets as the templates. Significantly, the crystal phase of the Au@Ir core-shell nanosheets would be modulated through tuning the thickness of the Ir shell, i.e., thin Ir shell epitaxially grown on Au core inherits 2H phase while thick Ir shell crystallize in fcc phase. Interestingly, the Au core transforms to fcc phase simultaneously when Ir shell gets thicker as the epitaxial relationship between Au and Ir could be preserved regardless of shell thickness and thus the resultant 2H/fcc ratio in the Au@Ir nanosheets could be modulated. Note that, the phase-dependent electrocatalytic features of the as-synthesized Au@Ir nanosheets in the hydrazine electro-oxidation reaction (HzOR) are studied. Impressively, the 2H/fcc Au@Ir nanosheets possess a remarkable mass activity of 507.5 mA/mg_{Au+Ir}, which is 1.96 times that of the fcc Au@Ir nanosheets (259 mA/mg_{Au+Ir}) and 3.36 times that of the Ir black (151 mA/mg_{Au+Ir}).

5.1 Introduction

Noble metal nanomaterials have aroused exceptional concern in the world on account of their fascinating activity in photothermal therapy,^[1] plasmonics,^[2] surface enhanced Raman spectroscopy (SERS),^[2,3] catalysis^[1,4] and so on. The performance of noble metal nanomaterials closely relates to their composition, size and shape.^[1, 2a, 4] Up to date, several reports showed that the features and performances of noble metal nanomaterials could be extraordinarily influenced by their crystal phase.^[5-8] For example, the *fcc-to-fct* phase transition of FePt nanoparticles not only enhanced performance but also improved stability in the oxygen reduction reaction.^[6] In another case, 2H PtNi alloy nano-multipods exhibited promoted HER activity in contrast to their *fcc* counterparts.^[7] Therefore, the investigation on the crystal phase-modulated features of noble metal nanostructures is of critical importance.

Furthermore, the crystal-phase-modulated preparation of noble-metal nanostructures always requires harsh experiment conditions, including high temperature, high pressure, or high-vacuum environment are always required.^[9] Compared to the harsh conditions, epitaxial growth is a valuable method for the phase modulation under mild conditions.^[11] For example, our group have prepared a wide range of metals (e. g. Ag, Pt, Pd, Ru, Rh, Ir and Cu) as well as alloys (PtAg, PdAg and PtPdAg) crystallized in 4H phase by employing 4H Au nanoribbons or 4H/*fcc* Au nanowires as the core *via* the epitaxial growth.^[12b-e] Interestingly, when the templates are replaced by 2H Au square sheets firstly reported by Huang et al.,^[9b] 2H-to-*fcc* phase change could be achieved by epitaxial deposition of Ag^[14], Pt or Pd^[15] on the 2H Au nanosheets. Hence, the epitaxial growth method is quite versatile to control the phase of not only the shell but also the templates.

Herein, for the first time, 2H Ir nanostructures can be derived from 2H/*fcc* Au@Ir nanosheets through the epitaxial coating of few iridium atom layers on the 2H Au nanosheets. Moreover, Ir shells will crystallize into *fcc* phase when the shells grow thick enough, and the shell thickness, that is, the numbers of Ir atoms deposited, would be

facilely changed though the addition volume of the Ir precursor. Interestingly, the epitaxial relationship between the iridium film and the gold template could be preserved no matter how thick the film is, and thus the atomic arrangement of the Au core will change (from 2H to *fcc*) simultaneously when the atomic arrangement of Ir shell changes as the shell grows thicker. The ratio of 2H/*fcc* in Au@Ir nanosheets could be continuously modulated. Furthermore, the as-prepared 2H/*fcc* Au@Ir and *fcc* Au@Ir nanosheets are employed for the hydrazine oxidation reaction (HzOR). 2H/*fcc* Au@Ir nanosheets exhibit a significant mass activity (507.5 mA/mg (Au+Ir)), which are 1.96 times the activity of *fcc* Au@Ir nanosheets catalysts and 3.36 times the activity of Ir black electro-catalyst.

5.2 Results and Discussion

Figure 5.1. (a) Low-magnification TEM figure of 2H Au nanosheets. (b) XRD patterns of 2H Au nanosheets. (c) Bright-field TEM figure of a representative 2H Au nanosheets. (d) SAED pattern of a typical 2H Au nanosheet along the $[110]_h$ direction.

Scheme 5.1. Scheme of the preparation of 2H/*fcc* Au@Ir nanosheets and *fcc* Au@Ir nanosheets from 2H Au nanosheets (a). The phase transition of 2H Au nanosheets can be controlled by (b) adding less Ir precursor (1.67 mM) in the growth solution to obtain 2H/*fcc* Au@Ir nanosheets or (c) adding more Ir precursor (13.4 mM) in the growth solution to obtain *fcc* Au@Ir nanosheets.

The 2H Au nanosheets were prepared according to our previously reported strategy with some modifications.^[9b] TEM figures shows that the as-obtained 2H Au nanosheets have parallelogram shape with the edge length ranging from 100 to 600 nm (**Figure 5.1a**). **Figure 5.1b** exhibits the XRD spectrum of the 2H Au nanosheets, in which the diffraction peaks at 37° (Au (002)_h), 41° (Au (101)_h), and 65° (overlapping of Au (022)_f and Au (110)_h) indicate the existence of 2H Au lattice, while the peaks at 38° (Au (111)_f), 44.6° (Au (002)_f) and 77.8° (Au (113)_f) are originated from *fcc* Au lattice of Au nanoparticles formed as byproducts of the reaction for preparing the 2H Au nanosheets (the several dark dots in **Figure 5.1a**). **Figure 5.1c** demonstrates a representative TEM figure of a single 2H Au nanosheet and its relative SAED pattern (**Figure 5.1d**) verifies the formation of 2H structure as the diffraction dots can be ascribed to (1-10), (1-11) and (002) planes of 2H Au when it is projected along the [110]_h direction.^[9b] The as-prepared 2H Au nanosheets (**Scheme 5.1a**) are then used to mediate the deposition of Ir shell. Typically, a homogeneous mixture of 2H Au nanosheets, IrCl₃, oleylamine and squalene were warmed

up to 200 °C for 12 h under magnetic stirring. The crystal phase of the Au@Ir nanosheets should be easily modulated by controlling the addition quantity of the IrCl_3 precursor (Scheme 5.1c).

Figure 5.2. (a) SEM, (b) HAADF-STEM, and (c) TEM figures of 2H/*fcc* Au@Ir nanosheets. (d) High-magnification TEM figure and (e) the relative SAED pattern of a

representative 2H/*fcc* Au@Ir nanosheet along the $[110]_h/[101]_f$ orientation. (f) HAADF-STEM figure and (g-i) the relative STEM-EDS spectrum of a representative 2H/*fcc* Au@Ir nanosheet. (j) Aberration-corrected HAADF-STEM figure of a representative 2H/*fcc* Au@Ir nanosheet. (j1) and (j2) are enlarged figures from the selected areas in (j). (k1) and (k2) are the relative selected-area FFT patterns of j1 and j2.

The typical SEM (**Figure 5.2a**), HAADF-STEM (**Figure 5.2b**) and TEM (**Figure 5.2c**) show that the Au@Ir core-shell nanosheets prepared by adding 1.67 mM Ir precursor generally maintain the shape of Au nanosheets. The representative TEM figure of single Au@Ir nanosheet (**Figure 5.2d**) and its relative SAED pattern (**Figure 5.2e**) confirm that the core-shell nanosheets possess 2H-dominant crystal structure. Specifically, the SAED pattern (**Figure 5.2e**) can be as attributed to the $[110]_h$ zone pattern, indicating the existence of the 2H phase. For further studying the crystal phase of the Au@Ir nanosheets, plan-view aberration-corrected HAADF-STEM figures (**Figure 5.2j**) are collected. The edge area (**Figure 5.2-j1**) of the Au@Ir nanosheet features a typical stacking mode of ‘ABCABC’ projected along the $[101]_f$ direction while the central area (**Figure 5.2-j2**) exhibits atom stacking mode of ‘ABAB’ projected along the $[110]_h$ direction with random twins and stacking faults (SF). The *fcc* structure in the edge area and the 2H-dominant structure in the central area can be further proved by the relative FFT pattern taken in the edge (**Figure 5.2-k1**) and central (**Figure 5.2-k2**) area. The HAADF-STEM figure (Figure 1f) and STEM-EDS figures (**Figure 5.2g-i**) and STEM-EDS line scan of the single Au@Ir nanosheet (**Figure 5.3**) confirm the conformal and complete covering of the Ir shell on the Au nanosheets.

Figure 5.3. (a) HAADF-STEM figure and (b) the relative STEM-EDS line scan of a typical

2H/*fcc* Au@Ir nanosheet.

Figure 5.4 A typical STEM-EDS spectrum of 2H/*fcc* Au@Ir nanosheets. The average atomic ratio of Au/Ir is 96.22/3.78.

The STEM-EDX spectrum (**Figure 5.4**) shows that the average atomic ratio of Au/Ir in the Au@Ir nanosheets is around 96.22/3.78. In order to further learn the epitaxial relationship between gold backbone and iridium film, FIB is employed to carve the Au@Ir nanosheets along one of its diagonals to observe its cross-section (**Figure 5.5a**). The EDS line scanning profile of the cross-sectional view of the Au@Ir nanosheet (**Figure 5.5b**) can demonstrate the conformal and complete covering of the Ir shell on the Au surface. The aberration-corrected HAADF-STEM figures from the cross-sectional view of an Au@Ir nanosheet taken in the center (**Figure 5.5c**) and edge (**Figure 5.5d**) area show the continuous lattice fringes extending from gold substrate to iridium film, revealing the coherent epitaxial relationship between core and shell. The enlarged aberration-corrected HAADF-STEM figure observed in the central area (**Figure 5.5-c1**) features $[001]_h$ zone lattice pattern and the relative FFT pattern (**Figure 5.5-c2**) further confirms the $[001]_h$ zone axis. In contrast, the enlarged aberration-corrected HAADF-STEM figure observed in the edge area (**Figure 5.5-d1**) exhibits $[-111]_f$ zone lattice pattern and the relative FFT pattern (**Figure 5.5-d2**) also affirm the $[-111]_f$ zone axis.

Figure 5.5. (a) Low-magnification HAADF-STEM figure exhibiting the cross-sectional view of an 2H/*fcc* Au@Ir nanosheet. (b) The STEM-EDS line scan observed along the line indicated in (a). (c, d) Aberration-corrected HAADF-STEM figures show the center (c) and side (d) parts of the cross-sectional view of 2H/*fcc* Au@Ir nanosheet in a. (c1) an enlarged HAADF figure of the marked region in (c) and the relative FFT diffraction patterns (c2). (d1) an enlarged HAADF figure of the marked parts in (d) and the relative FFT diffraction patterns (d2).

Figure 5.6. XPS spectra of 2H/*fcc* Au@Ir nanosheets. (a) Au 4f, (b) Ir 4f.

The XPS spectrum confirms the chemical states of Au(0) and Ir(0) in the as-prepared 2H/*fcc* Au@Ir nanosheets (**Figure 5.6**). It is well known that bulk Ir is crystallized in *fcc* phase, ^[18] and this is the first time for the success in the preparation of Ir nanostructure with an unfamiliar 2H crystal phase.

Figure 5.7a-c shows the SEM (**Figure 5.7a**), HAADF-STEM (**Figure 5.7b**) and TEM figures (**Figure 5.7c**) of the as-obtained Au@Ir core-shell nanosheets with 13.36 mM Ir precursor added feature rough dendritic surface. **Figure 5.7d** shows a typical TEM of such dendritic Au@Ir nanosheet and the relative SAED pattern (**Figure 5.7e**) indicates that the crystal phase of the Au@Ir dendritic nanosheets is *fcc* phase with the (101)_f direction, which is uncommon as nearly all the published two-dimensional *fcc* noble metal nanostructures exhibit unique (111)_f orientation. ^[13a, 13g, 18b] Additionally, the presence of two sets of spots as well as the absence of randomly distributed spots demonstrates that Ir is epitaxially deposited on the Au nanosheets. Moreover, the diffraction spots, marked with a subscript “T”, are originated from the twin structure in the Au@Ir dendritic nanosheets. The presence of twins or stacking faults can be further confirmed by the aberration-corrected HAADF-STEM figures in both the center and edge area (**Figure 5.7j and k**), in which the same atomic arrangement that should be attributed to *fcc* phase stretches from the Au substrate to the Ir film coherently, which could also be verified by the FFT pattern (inset figures in **Figure 5.7j and k**). The lattice distance (0.22 nm) in the edge area should be referred to *fcc* Ir {111} planes while the lattice distance (0.23 nm) in the central area should be attributed to the *fcc* Au {111} planes. Moreover, stacking faults and twin structure can be obviously noticed in the aberration-corrected HAADF-STEM figures, matching the SAED result. As shown in the HAADF-STEM (**Figure 5.7f**) as well as the relative STEM-EDS mapping figure (**Figure 5.7g-i**) of a representative Au@Ir dendritic nanosheet, not only Au but also Ir atoms are homogeneously distributed in the nanosheet, indicating the conformal and complete coating of Ir layers on Au surface, also confirmed by the STEM-EDS line scan of the Au@Ir dendritic nanosheet (**Figure 5.8**). According to STEM-EDS spectrum (**Figure 5.9**), the average atomic ratio of Au/Ir in the Au@Ir dendritic nanosheets is 59.17/40.83.

Figure 5.7. (a) SEM, (b) HAADF-STEM, and (c) TEM figures of *fcc* Au@Ir nanosheets. (d) HRTEM figure and (e) the relative SAED pattern of a distinctive *fcc* Au@Ir nanosheets along the $[101]_f$ direction. (f) HAADF-STEM figure and (g-i) the relative STEM-EDS mappings of a representative *fcc* Au@Ir nanosheet. (j, k) Aberration-corrected HAADF-STEM figure of a distinctive *fcc* Au@Ir nanosheet collected from the central (j) and the edge area (k). Insets in (j, k): the relative FFT patterns for HAADF-STEM figures shown

in (j) and (k).

Figure 5.8. (a) HAADF-STEM figure and (b) the relative STEM-EDS line scan of a typical *fcc* Au@Ir dendritic nanosheet.

Figure 5.9. A typical STEM-EDS spectrum of *fcc* Au@Ir dendritic nanosheets. The average atomic ratio of Au/ Ir is 59.17/40.83.

For further confirming the crystal phase of the Au@Ir dendritic nanosheets, a typical Au@Ir dendritic nanosheet is cut by focused ion beam along its long diagonal to observe the cross-section plane (**Figure 5.10**). The cross section shows dendritic core-shell structure with the dendrite length of 3.25 ± 0.65 nm (**Figure 5.10a**). STEM-EDS mapping of the cross-sectional view (**Figure 5.10-a1-a4**) further suggests the Au core-dendritic Ir shell architecture. Lattice fringes coherently extending from the center (Au) to the edge (Ir) area is obvious in the center (**Figure 5.10-b, b1 and b2**) and edge (**Figure 5.10-c, c1 and c2**) areas, demonstrating that Ir dendritic shell was epitaxially coated on Au core and the whole structure features the $[001]_f$ zone lattice pattern (**Figure 5.10-b3, b4, c3 and c4**).

Figure 5.10. (a) Low-magnification HAADF-STEM figure exhibiting the cross-sectional view of a typical *fcc* Au@Ir dendritic nanosheet. (a1-a4) High-magnification HAADF-STEM figure of the cross-sectional view of the *fcc* Au@Ir dendritic nanosheet (a1) and the STEM-EDS mappings of Au (a2) and Ir (a3) and the corresponding overlapped figure (a4) of the highlighted area marked in (a). (b) Aberration-corrected HAADF-STEM figures showing the central part of the cross-sectional view of the *fcc* Au@Ir dendritic nanosheet

in a. (b1) and (b2) are aberration-corrected HAADF-STEM figures from the selected area indicated in (b). (b3) and (b4) are the relative FFT diffraction patterns for the aberration-corrected HAADF-STEM figures shown in (b1) and (b2), respectively. (c1) and (c2) are aberration-corrected HAADF-STEM figures from the highlighted area indicated in (c). (c3) and (c4) are the relative FFT diffraction patterns for the aberration-corrected HAADF-STEM figures shown in (c1) and (c2), respectively.

Figure 5.11. XPS spectra of *fcc* Au@Ir dendritic nanosheets. (a) Au 4f, (b) Ir 4f.

XPS data of the *fcc* Au@Ir dendritic nanosheets confirms the chemical states of Au(0) and Ir(0) (**Figure 5.11**). Thus, the 2H-to-*fcc* phase transition of the intrinsic (110)_{*h*}-directed 2H Au nanosheets to the *fcc* Au@Ir dendritic nanosheets with uncommon (101)_{*f*} orientation, could be safely corroborated.

Figure 5.12. HAADF-STEM figures of Au@Ir nanosheets synthesized by the standard procedure with different amount of Ir precursor: (a) 1.67 mM, (b) 3.34 mM, (c) 6.68 mM, and (d) 13.36 mM. The overall reaction volume was kept the same. Inset shows the atomic ratio of Au/Ir. (e-h) XRD patterns of Au@Ir nanosheets prepared using different concentrations of Ir precursor: (e) 1.67 mM, (f) 3.34 mM, (g) 6.68 mM, and (h) 13.36 mM.

In our study, the thickness of the Ir shells of Au@Ir nanosheets could be easily modulated through tuning the amount of Ir precursor with consistent amount of 2H Au nanosheets and the total volume of solution fixed. We have used XRD to learn the crystal phase of Au@Ir nanosheets possessing diverse numbers of Ir layers and learned that the thicker the shell, the more the *fcc* area. When the amount of Ir precursor is 1.67 mM (**Figure 5.12a**), the surface of the Au@Ir nanosheets is smooth and the atomic ratio of Au/Ir is 93.45/6.5 (inset in **Figure 5.12a**). Meanwhile, the diffraction peaks including Au (002)_h (ca. 37°), Au

(101)_h (ca. 41°), and Au (110)_h (ca. 65°) are all characteristic peaks of the 2H lattice (indicated by blue or green lines), while *fcc* parts also exist as the peaks of 38° (Au (111)_f), 44.6° (Au (002)_f) and 77.8° (Au (113)_f) (covered by yellow lines) can be clearly observed (**Figure 5.12e**). Interestingly, the ratio of 2H to *fcc* parts is smaller and smaller when the Ir shells grow thicker. Specifically, when the amount of Ir precursor is enhanced to 3.34 mM (**Figure 5.12b**), the surface of the Au@Ir nanosheets turns to be rough and the atomic ratio of Au/Ir is lowered to 88.01/11.99 (inset in **Figure 5.12b**), indicative of the thicker shell. In addition, the intensity ratio of the peaks at 37°, 41°, and 65° (characteristic peaks of 2H Au lattice) towards the peaks of 38° and 44.6° (characteristic peaks of *fcc* Au lattice) is significantly decreased (**Figure 5.12f**), suggesting that the declined 2H area in Au@Ir nanosheets. As the amount of Ir precursor is further escalated to 6.68 mM, the surface of the as-prepared Au@Ir nanosheets becomes more corrugated (**Figure 5.12c**) and the Au/Ir ratio is further reduced to 73.79/26.21 (inset in **Figure 5.12c**). The relative peak intensity ratio of 2H Au lattice (37°, 41°, and 65°) to the peaks of *fcc* Au lattice (38° and 44.6°) is decreased to a greater degree (**Figure 5.12g**), demonstrating the even lower ratio of 2H parts in Au@Ir nanosheets. Notably, when the amount of Ir precursor is continuously boosted to 13.36 mM (**Figure 5.12d**), the Au/Ir ratio is decreased to 58.52/41.48 and the surface of the Au@Ir nanosheet is enclosed by a high density of branched arms. Under this condition, the peaks at 41° (Ir (111)_f) and 69.6° (Ir (022)_f) are increased due to the thicker Ir shell and the peak of 37° (Au (002)_h) almost disappears (**Figure 5.12h**), in addition to the further reduced peak intensity ratio of 65° (overlapping of Au (110)_h and Au (022)_f) to 38° (Au (111)_f), revealing that the crystal structure of Au@Ir nanosheets has been almost completely changed to *fcc*.

The continuous decline of the ratio of 2H phase in Au@Ir nanosheets with the increasing amount of Ir precursor should be assigned to the diverse growth modes.^[12a] With low amount of Ir precursor added, the deposition speed and the diffusion speed of Ir atoms would be comparable, and the growth of Ir adatoms should follow the layer-by-layer growth mode. With the addition volume of Ir precursor increased gradually, the growth mode of Ir atoms is progressively dominated by the deposition rate, following the layer-plus-island growth mode and further island growth mode. Particularly, when more Ir

precursor is added, the deposition rate would be greatly increased, and Ir could be nucleated when the deposition rate is high enough. Then, the subsequently reduced Ir atoms would grow on the Ir nuclei and form tiny Ir nanocrystals, which adopt an *fcc* crystal phase as *fcc* is the thermo-dynamically stable phase of Ir nanocrystals. Following that, the driving force of minimizing the total surface energy would bring about the agglomeration of the tiny *fcc* Ir nanocrystals or adherence to the Ir islands deposited on the Au nanosheets. As a result, the crystal phase of Ir is dominated by *fcc*.

Furthermore, the effect of deposition of Ir atoms on the Au core should be emphasized. As shown in **Scheme 5.1**, the phase transformation of the initial 2H Au nanosheets, should occur immediately after Ir atoms grown on the Au nanosheets by altering the stacking mode of the closed-packed planes, which would facilitate the generation of twins and stacking faults or the mixture of 2H and *fcc* parts as well as the shape change.^[10a] Note that, regardless of shell thickness, the epitaxial relationship between Au substrate and Ir film can be preserved. We speculate that the 2H-to-*fcc* phase transition in Au core caused by the epitaxial deposition of Ir shell should be originated from the interaction of epitaxial strain, and surface energy as well as phase instability. Firstly, the epitaxial stress originated from the lattice mismatch between gold substrate and iridium film, should be crucial to the crystal phase of both the Au backbone and the Ir shell.^[16] For example, Dubertret group demonstrated that the 7% lattice mismatch between the backbone (cadmium sulfide) and the film (zinc sulfide) in spherical CdS@ZnS (shell thickness: 7.5 monolayers) core-shell nanoparticles can create a radial strain of around 4 GPa towards CdS backbone.^[17] As the lattice mismatch between Au core ($\{001\}_h$ plane, $d=0.24$ nm^[9b]) and the Ir shell ($\{111\}_f$ plane, $d=0.22$ nm^[18]) is 6.3%, the effect of the lattice strain on the Au core should be impressive. Secondly, not only experimental results but also theoretical calculations suggested the crystal structure of inorganic nanocrystals should be notably influenced by the surface energy. Although the energy difference between different crystal phases (i.e. 2H, *fcc*) is really small in a wide range of transition and noble metals,^[9b, 19] the deposition of Ir would decrease the surface area to volume ratio by enhancing their thickness, contributing to the decline of the stability of the initial 2H nanostructure as well as the 2H-to-*fcc* phase transformation.

Figure 5.13. (a) HzOR performance of 2H/*fcc* Au@Ir nanosheets, *fcc* Au@Ir nanosheets, and the Ir black. All of them are loaded on carbon paper. (b) Comparison of the mass activity of 2H/*fcc* Au@Ir nanosheets, *fcc* Au@Ir nanosheets, and the Ir black at -0.9 V vs. SCE. The mass activity are currents normalized to the mass loading of the samples. (c) HzOR stability test of 2H/*fcc* Au@Ir nanosheets, *fcc* Au@Ir nanosheets, and the Ir black at -0.9 V vs. SCE.

2H/*fcc* Au@Ir nanosheets and *fcc* Au@Ir dendritic nanosheets are employed as electrocatalysts for hydrazine electro-oxidation (HzOR). HzOR can degrade hydrazine, always considered as aqueous contaminants, into clean nitrogen (N₂) and water (H₂O) (HzOR: N₂H₄ + 4OH⁻ → N₂ + 4H₂O + 4e⁻).^[24] As a critical anodic material for fuel cell, hydrazine can be electrochemically oxidized at quite low potential,^[21] and thus hydrazine electro-oxidation can lower the overall voltage of electrolysis^[22] with much lower power demand, which can obviously decrease not only the cost but also the overpotential of the whole electrolysis cell.^[23] **Figure 5.13** shows the HzOR performance of 2H/*fcc* Au@Ir

nanosheets, *fcc* Au@Ir nanosheets, and Ir black. The novel phase (2H) in 2H/*fcc* Au@Ir nanosheets endowed Au@Ir nanosheets with superior performance to the *fcc* counterparts in HzOR. Specifically, **Figure 5.13a**, shows that the onset potential (E_{on}) of 2H/*fcc* Au@Ir nanosheets is about 50 mV lower than that of *fcc* Au@Ir nanosheets, which is even lower than that of Ir black, indicating a quite better intrinsic activity. Furthermore, **Figure 5.13a and b** also exhibit quantitative comparison of the HzOR performance of 2H/*fcc* Au@Ir nanosheets, *fcc* Au@Ir nanosheets, and Ir black, in which the current densities are normalized to the ECSA of the carbon paper and the mass volume of Au and Ir of the 2H/*fcc* Au@Ir nanosheets and *fcc* Au@Ir nanosheets catalysts. At the same potential of -0.9 V (vs SCE), the electrode loaded with 2H/*fcc* Au@Ir nanosheets afford a significant specific activity (21.7 mA/cm^2) and mass activity ($507.5 \text{ mA/mg}_{(Au+Ir)}$), which are 2.11 times and 1.96 times better than that of the electrode loaded with *fcc* Au@Ir nanosheets catalyst; furthermore, the mass activity of the electrode loaded with *fcc* Au@Ir nanosheets catalyst is still much better (3.51 times for specific activity; 1.71 times for mass activity) in contrast to the electrode loaded with Ir black.

Figure 5.14. (a) Low-magnification SEM image of 2H/*fcc* Au@Ir nanosheets deposited on carbon paper and (b) high-magnification SEM images of 2H/*fcc* Au@Ir nanosheets after the HzOR stability test. (c) Bright-field TEM image and (d) the relative SAED pattern acquired along the $[110]_h/[101]_f$ direction of a distinctive 2H/*fcc* Au@Ir nanosheet after

H₂OR stability test. (e) HRTEM image of a distinctive 2H/*fcc* Au@Ir nanosheet after H₂OR stability test.

Figure 5.15. (a) Low-magnification SEM image of *fcc* Au@Ir nanosheets deposited on carbon paper and (b) high-magnification SEM image of *fcc* Au@Ir dendritic nanosheets after the H₂OR stability test. (c) Bright-field TEM image and (d) the relative SAED pattern acquired along the $[101]_f$ zone axes of a distinctive *fcc* Au@Ir dendritic nanosheet after H₂OR stability test. (e) HRTEM image of a distinctive *fcc* Au@Ir dendritic nanosheet after H₂OR stability test.

Moreover, according to the stability test shown in **Figure 5.13c**, both the 2H/*fcc* Au@Ir nanosheets and the *fcc* Au@Ir nanosheets displayed more than 80% of its initial current density after the harsh stability test (3600 s) in highly concentrated N₂H₄ solution (0.5 M). The SEM and TEM figures exhibit that the shape and surface roughness of 2H/*fcc* Au@Ir nanosheets (**Figure 5.14**) and *fcc* Au@Ir dendritic nanosheets (**Figure 5.15**) are greatly maintained after the stability test. Moreover, the 2H structure of 2H/*fcc* Au@Ir nanosheets and the *fcc* structure of *fcc* Au@Ir dendritic nanosheets are also well maintained after the stability test, as proven by the SAED pattern in **Figure 5.14d** and **Figure 5.15d** and HRTEM figure in **Figure 5.14e** and **Figure 5.15e**. The aforementioned analysis indicate that both the shape and crystal structure of 2H/*fcc* Au@Ir nanosheets and *fcc* Au@Ir

dendritic nanosheets are quite stable toward the electrocatalytic HzOR, revealing their beneficial long-term stability.

5.3 Conclusion

In summary, for the first time, we succeed in preparing 2H Ir nanostructures and achieving continuously tunable 2H-to-*fcc* phase transition of Au nanosheets via epitaxial deposition of Ir shell by tuning shell thickness. The more the Ir precursor added, the thicker the Au@Ir nanosheets, and the less the ratio of 2H domains. The Au@Ir nanosheets can be totally changed into *fcc* crystal phase as the shell is thick enough. Significantly, the as-prepared 2H/*fcc* Au@Ir nanosheets exhibited remarkably better performance than the *fcc* counterparts in HzOR, and even more better than the Ir black, demonstrating the beneficial activity enhancement endowed by the 2H crystal phase. It is reasonable to deem that the strategy present in our work, the rational phase-controlled synthesis of bimetallic nanostructures, will provide new insight in preparing novel nanomaterials possessing advantageous performance in various kinds of promising application.

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Chapter 6

Crystal-phase-dependent electrocatalytic features of PdFe alloy nanostructures in methanol oxidation reaction

The kinetics of autocatalytic surface reduction is sensitive to the atomic structures on seed surface. Herein, hexagonal 2H Au nanosheets and 4H Au nanoribbons are employed as the seed to support the epitaxial growth of PdFe alloy shell, generating 2H/fcc Au@PdFe nanosheets and 4H Au@PdFe nanoribbons, respectively. Significantly, the phase-dependent electrocatalytic features of the as-synthesized PdFe alloy nanostructures in the methanol oxidation reaction (MOR) are learnt. Impressively, 2H Au@PdFe nanosheets possess the highest mass activity of 4.39 A/mg_{Pd}, which is 1.2, 2.8 and 12.5 times those of 4H Au@PdFe nanoribbons, Pt/C and Pd black, respectively, which are also better than most of the published MOR electrocatalysts.

6.1 Introduction

Noble metal nanomaterials have aroused exceptional interests because of their beneficial features in photothermal therapy,^[1] plasmonics,^[2] surface enhanced Raman spectroscopy (SERS),^[2,3] catalysis^[1, 4] and so forth. The composition, shape and size of noble metal nanomaterials have been extensively investigated in order to maximize their performance in a wide range of application.^[1, 2a, 4] Besides the composition, size and shape, the crystal phase have been found as a critical issue that can extraordinarily affect the features and performances of noble metal nanomaterials.^[5-8] For example, 2H PtNi alloy nanomultipods exhibited promoted HER activity in contrast to their *fcc* counterparts.^[7] Thus, the crystal phase-dependent features of noble metal nanostructures deserves much more research attention.

To tune the crystal phase of noble-metal nanomaterials, severe experimental parameters, for example, high temperature,^[9a] high pressure,^[9b] or high-vacuum conditions are always indispensable.^[9c] Compared to the harsh conditions, epitaxial growth is much more facile because it can be achieved under ambient conditions in the solution-phase synthesis.^[10a] Typical synthetic procedures begin with preformed noble metal nanocrystals and followed by successive epitaxial deposition^[11] of secondary noble metal atoms. Although various kinds of seeds possessing different shapes^[10-15] have been used to prepare multimetallic architectures, all of the seeds are in their thermodynamically stable phase, *fcc* phase. Recently, interesting phenomenon has been observed by using the seeds with thermodynamically unstable phase. For example, our group have found that by using 2H Au nanosheets as the core, the epitaxial deposition of Au, Ag, Pd, and Pt atoms on the seed can induce 2H-to-*fcc* phase transformation. Also, by using 4H Au nanoribbons or 4H/*fcc* Au nanowires as the seed, a wide range of metals (e. g. Ag, Pt, Pd, Ru, Rh, Ir and Cu) as well as alloys (PtAg, PdAg and PtPdAg) crystallized in 4H phase have been prepared^[1c,8] *via* the seed-modulated growth. Hence, the seed-modulated growth involving the seed with uncommon crystal phase is quite versatile to tune the crystal phase of noble metal nanostructures and deserves much more attention.

Herein, by utilizing the preformed seeds with different crystal phase (2H Au nanosheets and 4H Au nanoribbons), 2H/*fcc* and 4H PdFe alloy nanostructures by the surface deposition of Pd and Fe atoms on the relative templates. Furthermore, the phase-dependent electrocatalytic features of the PdFe alloy nanostructures in the methanol oxidation reaction are learned. Impressively, 2H Au@PdFe nanosheets possess the highest mass activity of 4.39 A/mg_{Pd}, which is 1.2, 2.8 and 12.5 times the activity of 4H Au@PdFe nanoribbons, Pt/C and Pd black, respectively, which are also much better than most of the published MOR electrocatalysts.

6.2 Results and discussion

Figure 6.1. (a) Low-magnification TEM figure of 2H Au nanosheets. (b) Bright-field TEM figure of a representative 2H Au nanosheets. (c) SAED pattern of a typical 2H Au nanosheet along the $[110]_h$ direction.

First of all, the 2H Au nanosheets were produced based on our earlier published method with some modifications.^[9b] The as-prepared 2H Au nanosheets are exhibited in **Figure 6.1a and b**, most of which feature parallelogram shape. **Figure 6.1c** exhibites the relative SAED pattern of the representative 2H Au nanosheet. The diffracton dots can be ascribed to (1-10), (1-11) and (002) planes of 2H Au when it is projected along the $[110]_h$ zone axis.^[9b]

Figure 6.2. (a) SEM figure of 2H Au@2H PdFe NSs. (b) XRD pattern of 2H Au@2H PdFe NSs. (c, d) TEM figure and (e) the relative SAED pattern of a distinctive 2H Au@2H PdFe NS. (f) HAADF-STEM figure, and (g-i) the relative STEM-EDS maps of a distinctive 2H Au@2H PdFe NS. (j, k) Aberration-corrected high-resolution HAADF-STEM figure of a distinctive 2H Au@2H PdFe NS. (j1, k1) high-resolution HAADF figures of the highlighted parts indicated in (j) and (k). (j2, k2) the relative selected-area FFT patterns of j1 and k1.

The as-obtained 2H Au nanosheets are then utilized as the template to support the epitaxial deposition of PdFe alloy, causing the generation of 2H Au@PdFe core-shell nanosheets. Briefly, a homogeneous mixture of 2H Au nanosheets, 1.64 mM Pd(acac)₂, 14.2 mM Fe(acac)₃, oleylamine and squalene are heated at 210 °C for 18 h under magnetic stirring and Au@PdFe nanosheets is prepared. The as-prepared Au@PdFe core-shell nanosheets should be observed in the typical SEM figure (**Figure 6.2a**), and TEM figures (**Figure 6.2c and d**), which inherit the parallelogram shape from Au nanosheets. XRD pattern of the Au@PdFe core-shell nanosheets (**Figure 6.2b**) shows three characteristic peaks of the 2H lattice including 37° (Au (002)_h), 41° (Au (101)_h), and 65° (Au (110)_h). Meanwhile, the other peaks of 38° (Au (111)_f), 44.6° (Au (002)_f) and 77.8° (Au (113)_f) indicate the presence of *fcc* parts. The SAED pattern (**Figure 6.2e**) of a typical Au@PdFe nanosheet shown in **Figure 6.1d** can be referred to the [110]_h zone pattern as well as diffraction streaks along

the $[001]_h$ orientation, suggesting that the Au@PdFe nanosheets feature 2H-dominant crystal structure with random twins and stacking faults along the $[001]_h/[111]_f$ orientation. HRTEM figures collected at the center (**Figure 6.2j**) and the edge (**Figure 6.2k**) areas of a representative Au@PdFe nanosheet show that the center part features atom stacking mode of ‘ABAB’ along the $[110]_h$ direction with random twins and stacking faults (SF) (**Figure 6.2-j1**) while the edge part features a distinctive stacking mode of ‘ABCABC’ along the $[101]_f$ orientation (**Figure 6.2-k1**), which can be further proven by the relative FFT pattern of the chosen area in the central (**Figure 6.2-j2**) and edge (**Figure 6.2-k2**) area. The HAADF-STEM figure (**Figure 6.2f**) and the relative STEM-EDS mapping figures (**Figure 6.2g-i**) as well as the STEM-EDS line scan of the single Au@PdFe nanosheet (**Figure 6.3**) can demonstrate the conformal and complete deposition of the Pd and Fe atoms on Au nanosheets.

Figure 6.3. (a) HAADF-STEM figure and (b) the relative STEM-EDS line scan of a typical 2H Au@PdFe NRB.

Figure 6.4. A typical STEM-EDS spectrum of the 4H Au@4H PdFe NRBs. The atomic ratio of Au/Pd/Fe is 88.99/7.34/3.67.

The STEM-EDX spectrum (**Figure 6.4**) shows that the average atomic ratio of Au/Pd/Fe in the Au@PdFe nanosheets is 85.20/9.53/5.27, implying a Pd/Fe ratio of 1.95. Taken together, it is noteworthy that this is the first time for the success in the preparation of PdFe nanostructure with an uncommon 2H hexagonal crystal phase.

Figure 6.5. Low (a) and high (b) magnification TEM figures of the 4H Au NRBs. (c) HRTEM figure and (d) the relative FFT pattern of a distinctive 4H Au NRB obtained along the $[110]_{4H}$ orientation.

Secondly, the 4H Au nanoribbons were synthesized based on our earlier reported strategy^[8a], as exhibited in the TEM figures (**Figure 6.5 a and b**), the HRTEM figure (**Figure 6.5c**), and the relative SAED pattern (**Figure 6.5d**).

Figure 6.6. (a, c) Low magnification TEM figure of 4H Au@4H PdFe NRs. (d) TEM figure and (e) the relative SAED pattern of a distinctive 4H Au@4H PdFe NRB. (b) XRD pattern of 4H Au@4H PdFe NRs. (f) HAADF-STEM figure, and (g-i) the relative STEM-Eds maps of a distinctive 4H Au@4H PdFe NRB. (j, k) Aberration-corrected high-resolution HAADF-STEM figure of a typical 4H Au@4H PdFe NRB. (j1, k1) high-resolution HAADF figures from the highlighted parts indicated in (j) and (k). (j2, k2) the relative selected-area FFT patterns of j1 and k1.

Subsequently, the 4H Au NRs played the role of the core to direct the deposition of PdFe alloy nanostructures. Typically, a homogeneous mixture of the as-prepared 4H Au NRs, 6.56 mM Pd(acac)₂, 1.42 mM Fe(acac)₃ dispersed in oleylamine (OAM) and squalene warmed up at 210 °C for 18 h with magnetic stirring. **Figure 6.6a and c** display the TEM figures of the as-obtained Au@PdFe nanoribbons. The XRD pattern (**Figure 6.6b**) of 4H Au@PdFe nanoribbons shows 4 peaks of 36.2°, 37.4°, 40.9°, and 65°, indexed to the (100)_{4H}, (101)_{4H}, (102)_{4H} and (110)_{4H} planes of 4H lattice^[8a]; also, the peaks of 38.2°, 44.3° and 65°, which should be assigned to the (111)_f, (200)_f, and (220)_f planes of *fcc* lattice indicate the existence of *fcc* area in Au@PdFe nanoribbons.^[9a] The SAED pattern (**Figure 6.6e**) of the single 4H Au@PdFe nanoribbon (shown in **Figure 6.6d**) possesses a typical [110]_{4H}-zone diffraction pattern as well as a number of diffraction fringes along the [001]_{4H} orientation, recommending the presence twins or stacking faults in the [001]_{4H} orientation.

The aberration-corrected HAADF-STEM figures of a representative Au@4H PdFe NRB (**Figure 6.6j and k**) show that the lattice streaking consistently stretch from the Au substrate to the PdFe film, revealing the epitaxial relationship between them. Additionally, the relative FFT patterns (**Figure 6.6-j2 and k2**) of the enlarged area (**Figure 6.6-j1 and k1**) selected from **Figure 6.6j and k** (marked by green and yellow squares, respectively) indicate that both core and shell areas characterize a unique 4H crystal phase. HAADF-STEM figure (**Figure 6.6f**) and the relative STEM-Eds mappings (**Figure 6.6 g-i**) of a representative Au@PdFe nanoribbon display uniform deposition of Pd and Fe atoms on Au core, further affirmed by the STEM-EDS line scan figure (**Figure 6.7**).

Figure 6.7. (a) HAADF-STEM figure and (b) the relative STEM-EDS line scan of a typical 4H Au@4H PdFe NRB.

Figure 6.8. A typical STEM-EDS spectrum of the 2H Au@2H PdFe NRBs. The atomic ratio of Au/Pd/Fe is 85.20/9.53/5.27.

The atomic ratio of Pd/Fe on 2H-Au and 4H-Au should be easily modulated by tuning the

addition volume of Pd and Fe precursor. According to the STEM-EDX spectrum (**Figure 6.7**), the atomic ratio of Au/Pd/Fe in Au@PdFe nanoribbons is 88.99/7.34/3.67, indicative of a Pd/Fe ratio of 2.07, similar to that in Au@PdFe nanosheets. Combined together, it is worth highlighting that this is the first time for the successful synthesis of PdFe nanostructure with an uncommon 4H hexagonal crystal phase.

Figure 6.9. The CV curves (a), the ECSA-normalized CV curves (b), histograms of specific and mass activities (c) of 2H Au@2H PdFe NSs (red line), 4H Au@4H PdFe NRBs (blue line), Pd black (grey line) and Pt/C (green line) in a mixed solution filled with N₂ containing both 1 M methanol and 1 M KOH solution (scan rate: 50 mV/s). d) Chronoamperometric results of methanol oxidation at 0.7 V (vs. RHE) of the catalysts in a mixed solution consisting of 1 M methanol and 1 M KOH.

The electrocatalytic activity of 2H Au@PdFe nanosheets and 4H Au@PdFe nanoribbons are investigated by the MOR at room temperature and the Pt/C (20 wt.%) and Pd black are used as the reference catalysts. Before measuring the activity, the cyclic voltammetry (CV) curves were first recorded over these catalysts in 1.0 M KOH filled with N₂. As shown in

Figure 6.9a, the cathodic peaks from 0.5 to 0.9 V (vs. RHE) belong to the electroreduction of PdO to Pd. According to the strategy reported previously, the ECSA of catalysts could be thus calculated from the integrated charge in relation to the cathodic wave (Q (mC)) by the equation $ECSA = Q/(0.405 \times m_{Pd})$, where Q is the integrated charge associated with the cathodic wave for the electroreduction of monolayer PdO to Pd, 0.405 mC/cm^2 is the charge density for the formation of a fully covered PdO monolayer and m_{Pd} is the mass volume of Pd loaded (g). Herein, we obtain the ECSA values of 2H Au@PdFe nanosheets, 4H Au@PdFe nanoribbons and Pd black of 20.5, 15.6 and $27.3 \text{ m}^2/\text{g}$, respectively.^[16b] Additionally, the ECSA of Pt/C is also estimated to be $23.9 \text{ m}^2/\text{g}$ by the hydrogen stripping method^[16c] (**Figure 6.9a**). **Figure 6.9b** exhibits the CV curves of different catalysts tested in 1.0 M KOH aqueous solution consisting of 1.0 M methanol at 50 mV/s and the current is normalized by the mass loading of Pd or Pt. Evidently, both 2H Au@PdFe nanosheets and 4H Au@PdFe nanoribbons exhibit a lot better activities in contrast to those of the Pt/C and Pd black catalysts. Furthermore, it can be seen that the best catalyst among them is 2H Au@PdFe nanosheets. For particular comparison, the mass-specific peak currents in the forward scan of these catalysts are given in **Figure 6.9c**. It is clear that 2H Au@PdFe nanosheets show the best mass activity of 4.39 A/mg_{Pd} , which is 1.2, 2.8 and 12.5 times those of 4H Au@PdFe nanoribbons, Pt/C and Pd black, respectively, and also among the best in reported electrocatalysts (**Table 6.2**). Additionally, their specific current densities (J_s) are also calculated by normalized to their ECSA (**Figure 6.9a and b**). The peak activity of 2H Au@PdFe nanosheets reaches 21.5 mA/cm^2 , around 3.3 times that of Pt/C (6.5 mA/cm^2) and 16.5 times that of Pd black (1.3 mA/cm^2). Similarly, 4H Au@PdFe nanoribbons feature a rather high peak activity of 23.6 mA/cm^2 , being 2.6 and 17.2 times the activity of Pt/C and Pd black. Their durability is further investigated through the chronoamperometry measurement at 0.85 V (vs. RHE) for 6000 s. **Figure 6.9d** shows that both 2H Au@PdFe nanosheets and 4H Au@PdFe nanoribbons display much slower current decay over time in contrast to Pt/C and Pd black, indicating their much higher electrocatalytic stability.

Figure 6.10. (a) Low-magnification SEM image of 2H Au@PdFe nanosheets deposited on carbon paper and (b) high-magnification SEM image of 2H Au@PdFe nanosheets after the MOR stability test. (c) Bright-field TEM image and (d) the relative SAED pattern taken along the $[110]_h$ orientation of a distinctive 2H Au@PdFe nanosheet after MOR stability test. (e) HRTEM image of a distinctive 2H Au@PdFe nanosheet after MOR stability test.

Figure 6.11. (a) Low- and (b) high-magnification SEM image of 4H Au@PdFe nanoribbons after the MOR stability test. (c) Bright-field TEM image and (d) the relative SAED pattern acquired along the $[110]_h$ orientation of a distinctive 4H Au@PdFe nanoribbon after MOR stability test. (e) HRTEM image of a representative 4H Au@PdFe nanoribbon after MOR stability test.

The SEM and TEM figures exhibit that the shape of 2H/*fcc* Au@PdFe nanosheets (**Figure 6.10**) and 4H Au@PdFe nanoribbons (**Figure 6.11**) are greatly maintained after the stability test. Moreover, the 2H lattice of 2H/*fcc* Au@PdFe nanosheets and the 4H lattice of 4H Au@PdFe nanoribbons are also well maintained after the stability test, as confirmed by the SAED pattern in **Figure 6.10d** and **Figure 6.11d** and HRTEM figure in **Figure 6.10e** and **Figure 6.11e**, revealing their beneficial long-term stability.

6.3 Conclusion

Using the preformed seeds of 2H Au nanosheets and 4H Au nanoribbons as a typical example, we have achieved phase-controlled synthesis of PdFe alloy nanostructures possessing 2H/*fcc* or 4H crystal phase. Moreover, the phase-dependent electrocatalytic features of the as-synthesized PdFe alloy nanostructures in the methanol oxidation reaction (MOR) are studied. Notably, 2H Au@PdFe nanosheets possess the highest mass activity of 4.39 A/mg_{Pd}, which is 1.2, 2.8 and 12.5 times the activity of 4H Au@PdFe nanoribbons, Pt/C and Pd black, respectively, which are also superior to the majority of most of the earlier published MOR electrocatalysts. These findings reveal the significance of crystal phase modulation in the novel multi-metallic nanocrystals.

Table 6.1. ICP results of 2H-Au@PdFe nanosheets and 4H-Au@PdFe nanoribbons.

Template	2H-Au			4H-Au		
Element	Au	Pd	Fe	Au	Pd	Fe
Concentration (ppm)	199.9	25.1	6.9	205.1	34.8	8.9
Pd/Fe atomic ratio	1.95			2.07		

Table 6.2. The catalytic activities of some recently reported representative Pd-based and Pt-based electrocatalysts towards MOR under alkaline conditions. All the specific and mass activities represent the forward peak current densities of different catalysts.

Catalysts	Electrolyte	Mass activity (A mg ⁻¹)	Specific activity (mA cm ⁻²)	Ref.
v-PdCuCo	1 M KOH + 1 M Methanol	0.17	N. A.	[17]
Au/Ag/Pt NPs	1 M KOH + 1 M Methanol	1	1.35	[18]
PdAg /Ti _{0.5} Cr _{0.5} N	0.1 M KOH + 1 M Methanol	1.84	N. A.	[19]
Dentritic PdPtCu	1 M KOH + 1 M Methanol	4.296	8.45	[20]
Pd ₄₅ Pt ₅₅ nanowires	0.5 M NaOH + 1 M Methanol	1.97	N. A.	[21]
Pd ₁ Cu ₅ nanocages	1 M KOH + 1 M Methanol	1.09	2.03	[22]
Pd ₄ Cu ₁ nanosheet	1 M KOH + 1 M Methanol	4.875	N. A.	[23]
Pt/Ni(OH) ₂ /rGO NPs	1 M KOH + 1 M Methanol	1.07	N. A.	[24]
4H-Au@4H PdFe	1 M KOH + 1 M Methanol	3.69	23.6	This work
2H-Au@2H- PdFe	1 M KOH + 1 M Methanol	4.39	21.5	This work

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Chapter 7

Discussion and Future Work

This chapter concludes the whole thesis by summarizing the major significances and novelties of the aforementioned research works. Briefly, this thesis presents a facile one-pot wet-chemical method for synthesizing noble metal nanomaterials with modulated crystal phases. Importantly, this thesis has demonstrated the superior catalytic performance of noble metal nanomaterials possessing unfamiliar crystal phase to the noble metal nanomaterials with thermodynamically stable phase. Furthermore, future works that can help to gain more insights and alleviate the challenges in this research field are also proposed.

7.1 General Discussion

Herein, the focus is the crystal phase-modulated synthesis of a number of sorts of noble metal nanostructures including PtCu, Ir and PdFe. Furthermore, crystal phase-dependent electrocatalytic features of these noble metal nanostructures are investigated, including electrocatalytic EOR, HzOR and MOR.

7.1.1 Discussion on the crystal phase-dependent EOR features of PtCu alloy nanostructures

By carefully controlling the thickness of PtCu shell grown on 4H Au NRBs, 4H and fcc phase of PtCu alloy can be obtained by just tuning the adding amount of the surfactant (CTAB). 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 OAm, simultaneously. With less surfactant (10 mM CTAB), PtCu alloy shell is thin and crystallized in 4H phase; with more surfactant (100 mM CTAB), PtCu alloy shell is thick and crystallized in fcc phase. Furthermore, this thickness-controlled crystal phase method can also be found during the growth of PtCo alloy on 4H Au surface. This suggests that as a robust method, it can be further extended to control the crystal phase of other novel nanostructures. Furthermore, the as-obtained 4H-Au@PtCu NRBs with different crystal phases can serve as ideal models to study the phase-dependent properties since they have almost the same size, composition and morphology. Significantly, the 4H-Au@4H-PtCu NRBs show much better EOR activity as compared to the 4H-Au@*fcc*-PtCu NRBs towards the electrocatalytic EOR in alkaline media. The importance of this work lies not only in the introduction of the new crystal phases of PtCu and PtCu alloy nanostructures, but also in its potential of comparing the crystal phase-dependent catalytic performance. The crystal phase-dependent catalytic performance has been well studied in the following works.

7.1.2 Discussion on the crystal phase-dependent HzOR features of Au@Ir nanosheets

In this work, the thickness-dependent crystal phase change is observed during the growth of Ir nanostructures on 2H Au surface. Compared to the previously reported similar metal deposition-induced 2H-to-*fcc* phase transformation, in this work, the extent of 2H-to-*fcc* phase transformation can be controlled.^[1] The thickness-controlled 2H-to-*fcc* phase transformation is a big step towards the growth and applications of crystal phase heterostructure. Moreover, via the epitaxial growth strategy developed in the first work, crystal-phase-heterostructured 2H/*fcc* Ir, a catalytically active noble metal, is successfully obtained in the similar OAm system despite the usage of the different surfactant. The bimetallic 2H/*fcc* Au@Au@Ir core-shell NRs showed great catalytic performance as compared to the commercial catalysts, i.e. Ir black, with much higher activity and better stability towards the HzOR. 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 as compared with the previous synthesis method of 2H Au nanosheets.^[1] Since the purity of nanocatalysts is critical to further study their catalytic performances, the crystal-phase-heterostructured 2H/*fcc* Au nanosheets can serve as a universal template for the growth of other novel crystal-phase-heterostructured bi-/multi-metallic nanostructures towards practical applications.

7.1.3 Discussion on the crystal phase-dependent MOR features of PdFe alloy nanostructures

Following the previous projects, a facile method of template synthesis of noble metal nanostructures with unusual crystal phase is developed using 4H Au nanoribbons and 2H Au nanosheets as the template, and systematic investigation on the crystal phase-dependent catalytic applications is further performed. In this work, 2H and 4H PdFe nanostructures are synthesized with same surfactant by controlling the PdFe shell thickness epitaxially grown on the 2H Au nanosheets and 4H Au nanoribbons as the templates, respectively, both of which allow a direct comparison of the electrocatalytic MOR performance between

2H and 4H PdFe. Surprisingly, in terms of specific activity, the epitaxially grown 2H PdFe nanostructures exhibit better electrocatalytic MOR activity than the 4H PdFe nanostructures. Thus, 2H-based nanostructures should be paid more effort to develop for MOR.

7.2 Future Work

7.2.1 Investigation of the mechanism of the crystal phase transformation of 2H and 4H Au-templated bi- or trimetallic nanostructures

Chapter 4 and 5 has demonstrated the importance of shell thickness towards the phase transformation of 2H and 4H Au-templated bi- or trimetallic nanostructures and performed systematic investigation on the catalytic activity of the metal nanostructures with different crystal phase. However, the mechanism of the phase transformation is still unclear. It is speculated that it is due to lattice strain induced by the shell. Control experiments have been done by depositing different layers of shell atoms on 2H and 4H Au-templates, respectively. Based on experimental results, theoretical calculations will be conducted to figure out the lattice strain in diverse thicknesses.

7.2.2 Lattice mismatch-modulated phase transformation in 2H Au nanosheets-templated growth of multimetallic nanostructures

With the deep understanding on the lattice strain-induced phase transformation in 2H and 4H Au-templated bi- or trimetallic nanostructures, modulating the lattice mismatch between the core and shell can also bring about the corresponding phase transformation in the core and shell. Furthermore, previous studies have shown that lattice mismatch is quite important for controlling the crystal phase of Ru on Pd-Cu alloy.^[2] Through controlling atomic ratio of Pd to Cu, the atomic arrangement of the PdCu alloy core can be controlled and the unfamiliar *fcc* Ru overlayer can be derived by epitaxial deposition. Thus, the selective synthesis of *fcc* or 2H Ru crystal phases has been achieved^[1]. Therefore, lattice

mismatch could be used to modulate the transition of 2H-to-*fcc* crystal phase by depositing different amount of Pd and Cu precursor on the surface of 2H Au nanosheets.

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