Noble metal-based nanomaterials with amorphous phase : preparation and catalytic applications

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**NANYANG
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**NOBLE METAL-BASED NANOMATERIALS WITH
AMORPHOUS PHASE: PREPARATION AND
CATALYTIC APPLICATIONS**

CHENG HONGFEI

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

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CHENG HONGFEI

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

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Authorship Attribution Statement

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

Chapter 4 is published as Nailiang Yang, Hongfei Cheng, Xiaozhi Liu, Qinbai Yun, Ye Chen, Bing Li, Bo Chen, Zhicheng Zhang, Xiaoping Chen, Qipeng Lu, Jingtao Huang, Ying Huang, Yun Zong, Yanhui Yang, Lin Gu, Hua Zhang. Amorphous/crystalline hetero-phase Pd nanosheets: one-pot synthesis and highly selective hydrogenation reaction. *Advanced Materials* 30, 1803234 (2018). DOI: 10.1002/adma.201803234.

The contributions of the co-authors are as follows:

- Prof Hua Zhang proposed the initial research direction and edited the manuscript drafts.
- Dr Nailiang Yang and I prepared the manuscript drafts. The manuscript was revised by Dr Ye Chen, Dr Bo Chen, Dr Zhicheng Zhang, Dr Qipeng Lu and Mr Jingtao Huang.
- Dr Nailiang Yang and I designed all the experiments, conducted the experiments regarding material synthesis, transmission electron microscopy (TEM) characterization, and sample preparation for the other characterizations at School of Materials Science and Engineering, and test catalytic performance at School of Chemical Biochemical Engineering. Dr Nailiang Yang and I also analyzed all the data.
- Mr Xiaozhi Liu and Prof Lin Gu assisted in scanning TEM (STEM) characterizations.
- Mr Qinbai Yun performed all the X-ray diffraction (XRD) characterizations.
- Dr Bing Li and Dr Yun Zong assisted in X-ray photoelectron spectroscopy (XPS).
- Dr Bo Chen performed inductively coupled plasma-optical emission spectrometry (ICP-OES).
- Dr Ying Huang performed atomic force microscopy (AFM).
- Dr Xiaoping Chen and Prof Yanhui Yang assisted in the test of catalytic performance.

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- With the help from Dr Nailiang Yang, I designed all the experiments, conducted the experiments regarding material synthesis, TEM characterization, Fourier-transform infrared spectroscopy, and sample preparation for the other characterizations at School of Materials Science and Engineering, and test catalytic performance at School of Chemical Biochemical Engineering.
- Mr Xiaozhi Liu and Prof Lin Gu assisted in STEM characterizations.
- Mr Qinbai Yun performed all the XRD characterizations.
- Dr Min Hao Goh and Dr Xiaoying Qi assisted in XPS.
- Dr Bo Chen performed ICP-OES.
- Dr Xiaoping Chen and Prof Wen Liu assisted in the test of catalytic performance.

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Abstract

In amorphous phase, atoms are randomly arranged, which have lower average coordination number and more dangling bonds than those in crystalline phase, as a result, more active sites could be exposed for catalytic reactions. Up to date, different kinds of amorphous materials, such as metal oxides, transition metal chalcogenides and hydroxides, have been reported to exhibit superior catalytic performance compared to their crystalline counterparts. In catalytic reactions, noble metals have shown intrinsically high activity and excellent durability compared to the other kind of materials. However, it is challenging to prepare amorphous metal nanomaterials due to the strong interatomic metallic bonding.

In addition to amorphous phase, recently, amorphous/crystalline heterophase is arising as another research hotspot. Similar to the widely reported heterostructures with different materials, which could combine the advantages of individual components, overcome their drawbacks, and generate new properties/functions, the heterophase nanostructures with homogeneous compositions could combine the properties of different phases and some unique properties might arise from the phase interfaces. However, so far the reported metal nanomaterials with amorphous/crystalline heterophase are prepared by physical methods, which have many drawbacks compared with wet-chemical methods. Hence, it is desirable to develop wet-chemical methods for preparing heterophase metal nanomaterials.

Herein, this thesis focuses on the wet-chemical synthesis of amorphous and amorphous/crystalline heterophase noble metal-based nanomaterials. Furthermore, the phase-dependent physicochemical properties and catalytic applications of the as-prepared nanomaterials will be explored. Specifically, three research works will be discussed.

First, a one-pot wet-chemical method is developed for synthesizing a series of amorphous/crystalline heterophase Pd nanosheets. The crystallinity of the Pd nanosheets can be controlled by fine-tuning the experimental conditions. These nanosheets are used as heterogeneous catalysts to study the chemoselectivity in hydrogenation of 4-nitrostyrene. The amorphous phase-dominant Pd nanosheets show an excellent chemoselectivity, while

those crystalline phase-dominant Pd nanosheets exhibit a higher catalytic activity. This work might pave the way to preparing various heterophase nanostructures for promising applications.

Second, the aforementioned wet-chemical method is extended to the synthesis of amorphous/crystalline heterophase PdCu nanosheets and the aging process of the synthesized PdCu nanosheets is systematically studied, during which their crystallinity increases, accompanied with changes in some physicochemical properties. As a proof-of-concept application, their aging effect on catalytic hydrogenation of 4-nitrostyrene is investigated. As a result, the amorphous phase-dominant nanosheets initially show excellent chemoselectivity. After aging for 14 days, their catalytic activity is greater than that of crystalline phase-dominant nanosheets. This work demonstrates the intriguing properties of heterophase nanostructures, providing a new platform for future studies on the regulation of functionalities and applications of nanomaterials by phase engineering.

Third, a unique thiol molecule, namely bismuthiol I, is discovered, which can induce the transformation of Pd nanomaterials from face-centered cubic (*fcc*) phase into amorphous phase without destroying their integrity. This ligand-induced amorphization is realized by post-synthetic ligand exchange under ambient conditions and applicable to *fcc* Pd nanomaterials with different capping ligands. Importantly, the obtained amorphous Pd nanoparticles exhibit remarkably enhanced activity and excellent stability towards electrocatalytic hydrogen evolution in acidic solution. This work presents a facile and effective method for preparing amorphous Pd nanomaterials and demonstrates their promising electrocatalytic application.

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Abbreviations

AFM	Atomic Force Microscopy
EDS	Energy Dispersive X-ray Spectroscopy
FFT	Fast Fourier Transform
FTIR	Fourier-Transformed Infrared Spectroscopy
GC	Gas Chromatography
GC-MS	Gas Chromatography-Mass Spectroscopy
HER	Hydrogen Evolution Reaction
HRTEM	High-Resolution Transmission Electron Microscopy
NMR	Nuclear Magnetic Resonance Spectroscopy
SAED	Selected Area Electron Diffraction
SEM	Scanning Electron Microscopy
STEM	Scanning Transmission Electron Microscopy
TEM	Transmission Electron Microscopy
XAFS	X-ray Absorption Fine Structure
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction
<i>fcc</i>	face-centered cubic
<i>hcp</i>	hexagonal close-packed

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 Pd-based nanomaterials with amorphous phase, including amorphous nanostructures and amorphous/crystalline heterophase nanostructures. Based on this, three research works have been conducted, which are the synthesis of amorphous/crystalline heterophase Pd nanosheets for hydrogenation reaction, aging effects on amorphous/crystalline heterophase PdCu nanosheets, and ligand exchange-induced amorphization of Pd nanomaterials. In this chapter, the research background, hypothesis, objectives and scope of this thesis are first elaborated. Then, a brief description is given to each of the aforementioned research works, which are going to be discussed in detail in Chapter 4-6. Finally, the key findings and outcomes of this thesis are summarized.

1.1 Hypothesis

This thesis tests the hypothesis that noble metal-based nanomaterials with amorphous phase will display different physicochemical properties and thus different catalytic performance compared to their crystalline counterparts. The unique properties of amorphous nanomaterials may arise from the random atomic arrangement and/or the amorphous/crystalline interfaces.

Amorphous phase differs from crystalline phase in the atomic ordering. In crystalline phase, atoms are periodically packed in large range and the smallest repeating unit is called unit cell, whereas, in amorphous phase, atoms are randomly arranged and only very short range of ordering may exist. As a result, there are tremendous defects and dangling bonds in amorphous phase, which could be potentially highly active sites for chemical reactions.^[1] In addition, for crystalline alloys, different elements may be able to form homogeneous solid solutions in a certain composition range, and element segregation may occur; while the composition of amorphous alloys can vary in a very wide range, which permits continuous control over physicochemical properties.^[1]

The abovementioned properties render amorphous materials with promising catalytic applications. It has been widely reported that various amorphous nanomaterials, such as transition metal dichalcogenides,^[2] metal oxide,^[3] metal hydroxide^[4] and metal phosphate,^[5] outperform their crystalline counterparts in various electrocatalytic reactions. In addition of these aforementioned materials, noble metals and their alloys generally exhibit intrinsically high activity and excellent durability in a wide range of catalytic reactions. Therefore, constructing amorphous structures of noble metal-based materials is expected to be able to further enhance their catalytic performance.

Apart from amorphous phase, the amorphous/crystalline heterophase is also expected to be promising for catalytic applications, because the amorphous/crystalline interfaces may bring some unique properties, and the heterophase could combine the properties of amorphous phase and crystalline phase.

However, unlike other compounds, such as oxides, hydroxides and metal dichalcogenides, it is much more challenging to prepare noble metal nanomaterials with amorphous structure, due to the strong interatomic metallic bonds.^[6] Although the catalytic applications of amorphous metals and alloys have been studied several decades ago, which are also called metallic glasses, these amorphous metals and alloys were bulk materials prepared by rapid quenching of melts.^[1] This method is infeasible to prepare nanomaterials with controlled morphologies. As for the metals and alloys with amorphous/crystalline heterophase, so far they could only be prepared by physical methods, which require harsh conditions and expensive equipment.^[7-9] In contrast, wet-chemical methods have low cost and have been well developed for preparing sophisticated nanostructures of noble metals and their alloys. Therefore, in this thesis, the research works will adopt wet-chemical methods.

As known, noble metal-based nanomaterials have very promising applications in a variety of catalytic reactions.^[10, 11] It has been reported that their catalytic performance is dependent on crystal phases.^[12] In other words, catalytic performance is affected by atomic arrangement, hence, the noble metal nanomaterials with different crystallinities are expected to exhibit different catalytic performance.

1.2 Objectives and Scope

Based on the above hypothesis and research challenges, this thesis aims to develop effective wet-chemical methods for preparing amorphous and amorphous/crystalline heterophase noble metal-based nanomaterials, investigate their physicochemical properties, explore their catalytic applications and further provide reasonable explanations for synthesis-structure-property relationships. The research works introduced in this thesis are expected to provide guidance for future nanomaterial design, synthesis of noble metals with amorphous phase and their catalytic applications. More specifically, this thesis will focus on studying Pd and Pd-base alloy nanomaterials with amorphous phase. The catalytic applications include both selective hydrogenation catalysis and electrocatalysis. Based on the various property characterizations, mainly including transmission electron microscopy

(TEM), X-ray diffraction (XRD), Fourier-transformed infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS) and X-ray absorption fine structure (XAFS), rational analyses will be performed to provide possible explanations for the catalytic performance of target nanomaterials.

- An effective wet-chemical method will be explored to synthesize a series of amorphous/crystalline heterophase Pd nanosheets. The morphology and atomic structure of the nanosheets will be characterized by TEM. The crystallinity will be confirmed by XRD. Furthermore, the as-synthesized Pd nanosheets will be used for catalyzing the selective hydrogenation of 4-nitrostyrene to investigate the effect of heterophase on catalysis.
- The wet-chemical method will be extended to synthesize Pd-based alloy nanosheets with amorphous/crystalline heterophase. Their morphology, crystallinity, and composition will be characterized in detail. Moreover, the aging effect on the physicochemical properties and catalytic performance of the nanosheets will be systematically studied, in order to further understand the how the structure and properties are related.
- A universal and effective ligand exchange method will be developed to induce the amorphization of crystalline Pd nanomaterials. The phase transformation process as well as the electronic properties of the Pd nanomaterials will be studied. As a proof-of-concept application, the Pd nanomaterials after ligand exchange will be used for electrocatalytic hydrogen evolution reaction (HER). Furthermore, the relation between the catalytic performance, atomic structure and electronic properties will be interpreted.

1.3 Dissertation Overview

The thesis develops effective and facile wet-chemical methods for preparing amorphous and amorphous/crystalline heterophase noble metal-based nanomaterials, which is a

challenging research area and has tremendous room to be explored. Furthermore, this thesis demonstrates the promising catalytic applications of these novel nanomaterials and reveals the close relationships between atomic structure and physicochemical properties. This thesis paves the way to developing highly efficient catalysts by preparing noble metal-based nanomaterials with amorphous phase.

Chapter 1 describes the background and rationale for the research. The objectives, scope and overview of the thesis are provided.

Chapter 2 first reviews the research progress in the synthesis of amorphous and amorphous/crystalline heterophase metal nanomaterials with focus on the wet-chemical methods. Then, the superior catalytic performance of the aforementioned nanomaterials is demonstrated by discussing some typical examples.

Chapter 3 provides the detailed information on the chemicals and methods for the material preparation, characterizations, and performance measurement. To demonstrate the rational of the main techniques used for characterizing the physicochemical properties of materials in this thesis, their working principles and information interpretation are also elaborated.

Chapter 4 elaborates the wet-chemical synthesis and catalytic application of a series of amorphous/crystalline heterophase Pd nanosheets with controlled crystallinity. The crystallinity of the nanosheets can be tuned by simply tuning the reaction temperature. Notably, the as-synthesized nanosheets show heterophase-dependent selectivity and catalytic activity towards the selective hydrogenation of 4-nitrostyrene.

Chapter 5 presents the aging effects on the physicochemical properties of amorphous/crystalline heterophase PdCu nanosheets with different crystallinities. The crystallinity, surface ligands and binding energy of the PdCu nanosheets changed during aging process. Consequently, the amorphous-dominant nanosheets initially showed excellent selectivity towards the catalytic hydrogenation of 4-nitrostyrene. After 3-day aging, the amorphous-dominant nanosheets lost chemoselectivity but the catalytic activity

gradually increased and eventually surpassed the crystalline-dominant nanosheets.

Chapter 6 discusses the ligand exchange-induced amorphization of Pd nanomaterials. This method is applicable to Pd nanomaterials with different morphologies and different capping ligands. Importantly, the obtained amorphous Pd nanoparticles show dramatically enhanced electrocatalytic activity towards HER, which could be attributed to the amorphous structure as well as the electronic structure.

Chapter 7 draws the key conclusions from the results presented in this thesis. Reconnaissance studies that are closely related to the topic of this thesis and to be conducted in the near future are proposed.

1.4 Findings and Outcomes/Originality

This research has several novel outcomes as follows:

1. A facile wet-chemical method is newly developed for the synthesis of amorphous/crystalline heterophase Pd and PdCu nanosheets with controlled crystallinity. The crystallinity of the nanosheets can be manipulated by simply tuning the synthesis temperature, i.e., higher temperature leading to higher crystallinity. The obtained nanosheets have same thickness and almost identical morphology, thus they are ideal candidates for the study on crystallinity-dependent properties. This finding paves the way to the crystallinity-controlled wet-chemical synthesis of amorphous/crystalline heterophase noble metal nanomaterials.
2. The as-synthesized amorphous/crystalline heterophase Pd nanosheets exhibit heterophase-dependent catalytic performance towards the selective hydrogenation of 4-nitrostyrene. The amorphous phase-dominant Pd nanosheets exhibit an excellent chemoselectivity, while those crystalline phase-dominant Pd nanosheets show a higher catalytic activity. This finding reveals the strong dependence of catalytic performance on

heterophase structure and demonstrates the promising application of amorphous/crystalline heterophase nanomaterials.

3. For the first time, the aging effect on the physicochemical properties and catalytic performance of the amorphous/crystalline heterophase PdCu nanosheets is systematically studied. During the aging process, the nanosheet crystallinity increases, accompanied with changes in some physicochemical properties. As a result, the amorphous phase-dominant nanosheets initially show excellent chemoselectivity. After aging for 14 days, their catalytic activity even exceeds that of crystalline phase-dominant nanosheets. This finding demonstrates the intriguing properties of heterophase nanostructures, providing a new platform for future studies on the regulation of functionalities and applications of nanomaterials by phase engineering.

4. A unique thiol molecule, namely bithmuthiol I, is discovered, which can induce the amorphization of crystalline Pd nanomaterials by post synthetic ligand exchange at room temperature. This ligand exchange-induced amorphization is applicable to Pd nanomaterials with different morphologies and different capping ligands.

5. The amorphous Pd nanoparticles obtained by ligand exchange with bithmuthiol I show dramatically enhanced electrocatalytic activity towards HER, which results from the amorphous structure and modified electronic structure. This finding demonstrates an effective strategy for enhancing the performance of noble metal catalysts by amorphization.

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Chapter 2

Literature Review

This chapter reviews the current research status in terms of synthesizing amorphous and amorphous/crystalline heterophase metal nanomaterials. The commonly reported synthesis methods will be discussed, focusing on the wet-chemical synthesis. Then, the typical examples of the metal nanomaterials with amorphous phase for catalytic applications are provided, to demonstrate the importance of amorphous phase and amorphous/crystalline interface in catalysis. Finally, based on the literature review, the current research challenges are summarized and the problems to be solved in this thesis are presented.

2.1 Introduction

In crystalline phase, atoms are periodically arranged, whereas in amorphous phase, atoms are randomly arranged. Compared with crystalline phase, amorphous phase has a lot of atoms with low coordination number and abundant dangling bonds, therefore, amorphous materials are expected to have more active sites for catalytic reactions. In addition, amorphous alloys can have very wide range of compositions that may not be possible in crystalline phase, thus amorphous alloys allow continuous control over electronic properties.^[1] In amorphous alloys, different elements are chemically homogeneously distributed, while in their crystalline counterparts, element segregation are commonly observed.^[1] Actually, amorphous metals and alloys have been studied several decades ago, which are also called metallic glasses.^[1] In early days, amorphous metal alloys were bulk materials prepared by rapid quenching of melts.

With the development of nanomaterial synthesis and their excellent catalytic properties, in recent years, amorphous nanostructures for catalytic applications have drawn tremendous interest.^[2-4] Many research works have demonstrated that amorphous nanomaterials show better catalytic performance than their crystalline counterparts. As a typical example, amorphous molybdenum sulfide has been generally considered to exhibit better activity than its crystalline counterpart towards the electrocatalytic hydrogen evolution reaction (HER).^[4, 5] Similarly, it has also been reported that other amorphous materials, such as metal oxide,^[6, 7] metal hydroxide^[8] and metal phosphate,^[9] outperform their crystalline counterparts in various electrocatalytic reactions. Therefore, constructing amorphous nanostructures is an effective strategy to enhance the performance of catalysts.

Among the different kinds of materials for catalysis, transition metals, especially the VIII and IB elements, including Fe, Co, Ni, Cu and noble metals (Ru, Rh, Pd, Ag, Os, Ir, Pt, Au) (Figure 2.1), have intrinsically high activity for various catalytic reactions. However, due to the strong metallic bonding between atoms, these elements are thermodynamically stable in crystalline phase. Specifically, except for Fe, the thermodynamically stable phases of all the other metals are in close-packed patterns, i.e., either *hcp* or *fcc* phase (Figure 2.1).^[10]

Hence, it is challenging to obtain amorphous metal nanomaterials and their alloys. Consequently, up to now, the reported amorphous metal and alloy nanocatalysts are much less than the other kinds of aforementioned materials.

VIII			IB
26 Fe bcc	27 Co hcp	28 Ni fcc	29 Cu fcc
44 Ru hcp	45 Rh fcc	46 Pd fcc	47 Ag fcc
76 Os hcp	77 Ir fcc	78 Pt fcc	79 Au fcc

Figure 2.1 Partial periodic table showing the elements discussed in this section, in which the thermodynamically stable phases of the elements are indicated.

Apart from amorphous phase, very recently, amorphous/crystalline heterophase is emerging as an attractive research area, which exhibits some unique properties due to the presence of mixed phases and phase boundaries.

The following sections will focus on VIII and IB metals and their alloys (Figure 2.1). The common methods used to prepare amorphous metal nanomaterials and the typical examples of catalytic applications will be presented. Furthermore, the amorphous/crystalline heterophase metal nanomaterials and their unique physicochemical properties will be discussed.

2.2 Amorphous Metal Nanomaterials

Amorphous metal nanomaterials can be obtained by both wet-chemical synthesis and physical deposition. Wet-chemical synthesis, in which nanomaterials are synthesized in

solutions, has a lot of advantages over physical deposition, including low cost, effective control over the size, morphology and composition of nanomaterials. In addition, post-synthetic transfer or modification of the nanomaterials synthesized by wet-chemical methods can be easily manipulated, which is very important for catalytic applications. Therefore, the following discussions will focus on the wet-chemical methods for synthesizing amorphous metal nanomaterials. Table 2.1 summarizes the amorphous transition metal nanomaterials and their nanoalloys synthesized by wet-chemical methods, which will be discussed in detail based on the synthesis methods.

Table 2.1 Summary of wet-chemical synthesis of amorphous transition metal nanomaterials.

Methods	Materials	Size	References
Wet-chemical reduction	Pt-Ru/C	~1 nm	[11]
	Pd nanoparticles	<10 nm	[12-14]
	Au nanoparticles	1-2 nm	[15]
	Ni, NiCo alloy (2D handkerchief-like nanostructures)	-	[16]
	Au, Ag, Pt, Pd, Rh, Ir nanoparticles	a few nm	[17]
	Ni-Fe nanoparticles	4 nm	[18]
	Cu nanoparticles		[19]
	PdCu nanoclusters on graphene	1.7 nm	[20]
	Co nanoparticles	3.7±0.4 nm	[21]
	CuPt alloy nanotubes		[22]
	Fe nanoparticles	a few nm	[23]
	PtRuIr nanoparticles	2.2 nm	[24]
Microemulsion	Pd nanoparticles	2-5 nm	[25]
	Fe nanoparticles	3 nm	[26]
	Co nanoparticles	-	[27-30]

	NiCu, CoCu, CoNiCu, CoNi alloy nanoparticles	4-7 nm	[31]
Thermo-decomposition	Fe nanoparticles	A few nm	[32, 33]
	Fe@Fe ₃ O ₄ nanoparticles	4@2.5 nm	[34]
	FeCo nanoparticles	-	[35]
Sonochemical synthesis	Fe nanoparticles	a few to tens of nm (< 40 nm)	[36-43]
	FeNi alloy	a few nm	[44]
	Ni nanoparticles	~10 nm	[45]
	Ag nanoparticles	20 nm	[46]
	Fe, Co, FeNi nanoparticles	-	[47]
	Pt nanoparticles	a few nm	[48]
Photochemical synthesis	Pt film		[49]
Electrodeposition	AuNi alloy film, NiW alloy film	5 μ m	[50]
	AuNi alloy film	hundreds of nm to a few μ m	[51]
	NiFe nanotube arrays	diameter~300 nm, length~2 μ m	[52]
	PdCo nanotube arrays deposited on carbon fiber cloth	diameter~300 nm, length~3 μ m	[53]
	Co nanoparticles	100-150 nm	[54]

2.2.1 Wet-chemical reduction

In a typical and simplest wet-chemical synthesis, metal precursors are reduced by reductant in a solvent. Surfactants are usually added to prevent nanoparticle aggregation as well as control their size and shape. In this section, the wet-chemical reduction refers to the wet-chemical method in which precursors are reduced by reductant upon heating or at room

temperature, which means that no other energy sources, such as sonication, light, electricity, are supplied. Strong reducing agents, such as NaBH_4 ,^[13, 17, 23] are usually used to synthesize amorphous nanomaterials. The amorphous structure could also be obtained by rapid cooling.^[21] In addition to the reaction conditions which can be controlled artificially, the intrinsic properties of the metals could also affect the easiness to obtain amorphous structure. It has been reported that, for the nanoclusters of Au, Ag, Pt, Pd, Rh and Ir synthesized under same conditions, the 3M nanoclusters exhibit shorter range of ordering compared to their 2M counterparts.^[17] Due to the relativistic effects originating from the intrinsic electronic nature, the bonding between 3M atoms tends to be directional, meaning 3M metals tend to form crystalline structure.

Most of the amorphous nanomaterials prepared by wet-chemical reduction are in the form of nanoparticles (Table 2.1). To control the nanomaterial morphology, using a template to confine or direct the growth is an effective method. For example, using a collodion membrane as the template (Figure 2.2a), which has abundant nitro groups and passageways and thus can be used as a structure-introducing template, handkerchief nanostructures of amorphous Ni (Figure 2.2b) and NiCo alloy can be synthesized.^[16] As another example, using the pre-synthesized Cu nanowires as the sacrificial template, amorphous CuPt alloy nanotubes can be obtained by galvanic replacement reaction (Figure 2.2c-e).^[22] Na_2SO_3 is added to inhibit the disproportionation reaction of CuCl produced by the galvanic replacement reaction between H_2PtCl_6 and Cu. Interestingly, without adding Na_2SO_3 , crystalline CuPt nanotubes were obtained.

Figure 2.2 (a) Experimental set up in which the collodion membrane is used as template. (b) Amorphous Ni handkerchief nanostructures synthesized by the set up shown in (a).^[16] (c) SEM image of amorphous CuPt nanotubes. Inset: TEM image of a single CuPt nanotube. (d) XRD patterns. (e) Schematics showing the synthesis process of the amorphous CuPt nanotubes.^[22]

2.2.2 Microemulsion

Microemulsion is the mixture of oil, water and surfactant, which can be oil-in-water or water-in-oil. The surfactant has one hydrophilic head and one hydrophobic tail, thus it can form a monolayer at the oil/water interface to help the dispersion of water (or oil) droplet in oil (water). The water-in-oil type is also called reversed micelle, which is commonly used for nanomaterial synthesis. As shown in Figure 2.3a, two separated reversed microemulsions are first prepared. In one of the microemulsion, the water droplets contain metal salts, whereas in the other one, the water droplets contain reducing agent. Upon mixing these two microemulsions, collision and coalescence of these two types of water droplets will cause the reduction of metal salts, leading to the nucleation at the oil/water interface and subsequent growth towards the core of the droplet.^[55] Amorphous nanomaterials can also be synthesized by a single microemulsion, which means reductant

is directly added into the microemulsion containing metal salts.^[55] Pileni's group have successfully synthesized highly monodispersed amorphous Co nanoparticles in reversed micelles of cobalt(II) bis(2-ethylhexyl) sulfosuccinate ($\text{Co}(\text{AOT})_2$) (Figure 2.3b,c).^[30] The size distribution of the Co nanoparticles is highly dependent on the ratio (R) of reductant (sodium borohydride, NaBH_4) to $\text{Co}(\text{AOT})_2$ (Figure 2.3d-i).^[27] At lower ratio, the micelles function as nanoreactors where the nucleation and growth of Co nanoparticles take place, resulting in a large size distribution (Figure 2.3d,e). At higher ratio, the micelles are destroyed due to the excess reductant, resulting in a low size distribution (Figure 2.3f-i).

Figure 2.3 (a) Schematics showing the synthesis of nanomaterials by reversed microemulsion.^[55] (b) TEM image (inset: the corresponding SAED pattern and HRTEM image of Co nanoparticles synthesized by reversed microemulsion.^[30] (d-i) TEM images of Co nanoparticles synthesized by reversed microemulsions with different sodium borohydride concentrations. R = 0.5 (d), 1 (e), 2 (f), 4 (g), 6 (h), 8 (i), where R is defined as $[\text{NaBH}_4]/[\text{Co}(\text{OAT})_2]$. Insets: the corresponding low magnification TEM images.^[27]

2.2.3 Thermodecomposition

Thermodecomposition refers to the decomposition of metal precursors, which are usually carbonyl compounds. Metal carbonyls ($M(CO)_n$) are coordination complexes consisting of transition metals and carbon monoxide (CO) ligands, which can decompose upon heating, generating metal nanoparticles and meanwhile releasing CO gas. This method is often used to synthesize Fe and Co nanoparticles (Table 2.1). For example, the amorphous Fe nanoparticles can be synthesized by thermodecomposition of $Fe(CO)_5$ in oleylamine and kerosene.^[32] It was found that the surfactant, i.e., oleylamine, can significantly affect the uniformity as well as the crystallinity of the nanoparticles. With adding proper amount of surfactant, the nanoparticles are highly monodispersed with amorphous phase; while without adding oleylamine, the nanoparticles are aggregated with crystalline structure.

2.2.4 Sonochemical synthesis

In sonochemical synthesis, ultrasound is supplied for the chemical reaction system, which is usually in solution, thus sonochemical synthesis can be considered as a kind of wet-chemical synthesis. Ultrasound is a unique form of energy that is different from other energy sources (e.g., light, ionization, and heat) in terms of energy per molecule, interaction duration and pressure (Figure 2.4).

Figure 2.4 The interaction between different energy sources and matter.^[56]

The ultrasound frequency is roughly between 20 kHz and 1 GHz, and the speed of sound wave in solutions is around 1500 m/s. Therefore, the wavelength of the ultrasound is roughly from 10 to 10^{-4} cm, which is several magnitudes larger than the dimensions of molecules.^[57] Obviously, the interaction between the ultrasound and chemical species is not at molecular level. Actually, sonochemical reactions derive from the acoustic cavitation in solutions, i.e., the bubble formation, growth, and implosive collapse. Bubble collapse can generate intensive heating and high pressure with very short lifetime, forming the so called hot spots. In these gas hot spots, the temperature can exceed 5000 K, the pressure is ~ 1000 atm, and the heating and cooling rates are above 10^{10} K $\cdot$ s $^{-1}$.^[57] As a result, extreme conditions are created for chemical reactions at the gas-liquid interface while the bulk solution is at low temperature, which provide the chance for the formation of non-equilibrium nanostructures, i.e., amorphous phase.

For example, amorphous Ag nanoparticles were formed by sonicating AgNO₃ in water under Ar-H₂ atmosphere.^[46] The acoustic cavitation pyrolyzed water into H $\cdot$ and OH $\cdot$, thus Ag⁺ was reduced by H $\cdot$. The as-prepared Ag nanoparticles have large size distribution with severe aggregation (Figure 2.5a) and the amorphous structure can be confirmed by XRD pattern (Figure 2.5b). The uniformity and dispersity of the nanoparticles prepared by sonochemical synthesis can be improved by adding stabilizing reagents. For instance, amorphous Fe nanoparticles with size of 3-8 nm were prepared via sonicating the solution containing Fe(CO)₅, octanol and polyvinylpyrrolidone (PVP) (Figure 2.5c), in which PVP functions as stabilizing reagent.^[39] The size distribution of the Fe nanoparticles can be further reduced by using oleic acid as the stabilizer (Figure 2.5d).^[39]

Figure 2.5 (a) TEM image of the amorphous Ag nanoparticles. (b) XRD patterns of the as-synthesized amorphous Ag nanoparticles and the crystalline Ag nanoparticles by annealing at 340 °C.^[46] (c) Amorphous Fe nanoparticles stabilized by PVP and the SAED patterns before (c1) and after (c2) crystallization. (d) Amorphous Fe nanoparticles stabilized by oleic acid.^[39]

Apart from the direct synthesis of amorphous nanoparticles, sonochemistry can also modify the crystallinity of the preformed nanoparticles. For example, by sonicating the preformed crystalline Pt nanoparticles in water, amorphous Pt nanoparticles were formed; while sonicating the preformed crystalline Pt nanoparticles in PVP or ethylene glycol solutions, the obtained Pt nanoparticles only became less ordered.^[48]

2.2.5 Electrodeposition

Electrodeposition is not so widely reported as the sonochemical synthesis. In the early works, the amorphous metallic materials prepared by electrodeposition are mainly thin films with the thickness from hundreds of nanometers to several micrometers.^[50, 51] Recently, electrodepositions has been reported to prepare amorphous nanoparticles^[54] and nanotube arrays (NTAs)^[52, 53].

Particularly, NTAs are one kind of unique nanostructures prepared by electrodeposition. The typical fabrication process of NTAs is illustrated in Figure 2.6a.^[53] Basically, ZnO nanorods were first electrodeposited onto the carbon fiber cloth (CFC) support that functioned as current collector. Next, PdCo alloy was coated onto the surface of ZnO nanorods. Finally, ZnO was etched away, leaving the PdCo alloy nanotubes. The SEM images (Figure 2.6b,c) and the corresponding EDX elemental mappings (Figure 2.6d-f) confirmed the morphology and uniform element distribution. Moreover, the TEM image (Figure 2.6g) demonstrates the hollow structure of the PdCo nanotubes and the SAED (Figure 2.6h) pattern verifies the amorphous structure.

Figure 2.6 (a) Schematic illustration of the fabrication process of PdCo NTAs. (b) low- and (c) high-magnification SEM images of PdCo NTAs. (d) SEM image of a single PdCo NT and the corresponding (e) Co-L and (f) Pd-L elemental mappings. (g) TEM image of a single PdCo NT. (h) High-magnification TEM image and the corresponding SAED pattern (inset).^[53]

2.3 Amorphous/Crystalline Heterophase Metal Nanomaterials

Noble metal nanocrystals have shown promising applications in optics, catalysis and electronics owing to their unique physiochemical properties, which strongly depend on their shape, size, exposed facet, dimension and atomic arrangement.^[58, 59] In addition of these intensively studied parameters, recently, crystal-phase engineering has been one of research hotspots in the construction of metal nanomaterials with novel properties.^[10, 60-62] In order to prepare novel nanostructures with multi-functionalities and/or enhanced properties, our group has recently proposed a concept of crystal-phase heterostructures, as one kind of hetero-phase structures in monometallic nanomaterials, for the investigation of crystal-phase-based applications.^[63]

Different from crystalline phase, amorphous phase is a unique structure with random atomic arrangement, and thus exhibiting some intriguing properties.^[2] Therefore, amorphous/crystalline heterophase nanostructures, as another kind of novel heterophase structures, might also exhibit unique properties and promising applications compared to their amorphous and crystalline counterparts. In a recent report, the amorphous/nanocrystalline heterophase Mn-based nanomaterial, synthesized by magnetron sputtering method, possessed a high mechanical strength.^[64] Moreover, various kinds of amorphous/crystalline heterophase nanomaterials, such as hydroxides,^[65] metal oxides,^[66] and transition metal dichalcogenides,^[67, 68] have been reported to display excellent catalytic performance. However, up to now, there are very few examples reporting the synthesis of metal nanomaterials with amorphous/crystalline heterophase for catalytic applications. Figure 2.7a illustrates the preparation of amorphous/crystalline heterophase PtPb nanoplates by ion irradiation.^[69, 70] Briefly, intermetallic PtPb nanoplates were first synthesized (Figure 2.7b,c), then carbon ions (C^+) are produced from the sputtering ion source, accelerated in the electric field and finally passed through the pre-synthesized PtPb nanoplates, generating a lot of defects and amorphous regions in the nanoplates (Figure 2.7d).^[69] The defects in the nanoplates can be controlled through tuning the C^+ flux.

Although the aforementioned physical methods can control the atomic structures of metal nanomaterials, they have a lot of drawbacks, such as requiring complicated equipment, high cost, harsh conditions, and limited choices of materials. In comparison, wet-chemical synthetic route is an attractive alternative because of the relatively low cost, ease of implementation, high-yield production and good versatility. Therefore, it is desirable to rationally design and use wet-chemical methods to prepare the amorphous/crystalline heterophase nanomaterials. Until now, for noble metal nanomaterials, there is rarely report on the controllable synthesis of amorphous/crystalline hetero-phase nanostructures and the investigation on the hetero-phase-based applications.

Figure 2.7 (a) Schematics showing the experimental set up of preparing amorphous/crystalline heterophase PtPb nanoplates by ion irradiation. (b,c) Low-magnification TEM image and HRTEM images of the pre-synthesized crystalline PtPb nanoplates. Insets in (c): the FFT patterns of the red squares (c1, c2) and the entire nanoplate (c3). (d) HRTEM image of a typical PtPb nanoplate after ion irradiation. Inset: the FFT pattern of the region enclosed by orange curves.^[69]

2.4 Catalytic Applications

2.4.1 Heterogeneous catalysis

In the early 1990s, it was reported that amorphous Fe powder exhibited much higher catalytic activity than crystalline Fe powder in cyclohexane dehydrogenation and hydrogenolysis reaction (Figure 2.8a).^[36] The amorphous Fe powder, prepared by sonochemical synthesis, is in the form of large aggregates composed of 10 nm nanoparticles, while the crystalline Fe powder is composed of 5 μm particles. As a result, the amorphous powder possesses a much larger surface area. Therefore, size effect, in addition to phase effect, contributed largely to the high catalytic activity. In a more recent study, for the crystalline and amorphous Fe nanoparticles with similar morphology and size, the amorphous one exhibited much better catalytic activity in producing hydrogen via hydrolysis of aqueous ammonia borane (Figure 2.8b,c), implying that amorphous phase has higher intrinsic catalytic activity.^[23]

Figure 2.8 (a) Catalytic activity of amorphous (solid line) and crystalline (dash line) Fe powder for the cyclohexane dehydrogenation and hydrogenolysis reaction.^[36] (b) Catalytic activity of crystalline and amorphous Fe nanoparticles in the hydrogen generation by hydrolyzing aqueous ammonia borane.^[23]

2.4.2 Electrocatalysis

In addition to the traditional heterogeneous catalytic reactions, amorphous metal nanomaterials have also demonstrated very promising applications in electrocatalytic reactions. Moreover, with the development of computational science, some mechanisms for the enhanced catalytic activity of amorphous metal nanomaterials have been rationally proposed based on theoretical calculations. For example, in electrocatalytic methanol oxidation reaction, amorphous CuPt nanotubes have demonstrated higher current density, lower onset potential and superior stability as compared to the crystalline counterpart and commercial Pt/C.^[22] The CO stripping measurement showed that the amorphous CuPt nanotubes have the highest CO tolerance (Figure 2.9d). XPS was performed to understand the CO tolerance. The Pt 4f in amorphous CuPt nanotubes show the highest binding energy (Figure 2.9e), indicating that the Fermi level in amorphous alloy shifts upward. As a result, the amorphous alloy has more 5d vacancies (Figure 2.9f), thus reducing the back-donation of electrons from Pt 5d to 5 σ orbital of CO and weakening the Pt-CO bond strength.

Figure 2.9 (a) CV curves, (b) onset potentials and (c) stability measurements in N₂-saturated 0.5 M CH₃OH and 0.1 M HClO₄ solution. (d) Schematics illustrating the CO tolerance. (e) XPS spectra. (f) Schematics illustrating the mechanism of CO tolerance.^[22]

The above example clearly demonstrates that amorphous phase could have different electronic structure compared with the corresponding crystalline phase. Besides, the amorphous/crystalline interface could also positively contribute to the catalytic activity, which is the motivation for preparing amorphous/crystalline heterophase nanomaterials. Figure 2.10a illustrates the irradiation of C⁺ ions onto PtPb nanoplates, which results in different amorphization degree with different ion flux.^[69] Consequently, these nanoplates

show volcano-like trends in the catalytic activity for methanol oxidation reaction (MOR), ethanol oxidation reaction (EOR) and oxygen oxidation reaction (ORR). As the amorphous region in the nanoplates increases, these catalytic activities first increase and then slightly decrease, which could be due to the amount of interface volume. As the ion flux increases, the amorphous region as well as the amorphous/crystalline interface increase, while when the amorphous region further increases, the amorphous/crystalline interface decreases. The similar phenomenon has been also reported in other kinds of nanomaterials, such as transition metal dichalcogenides,^[71] and metal hydroxides^[65]. It has been proposed that amorphous phase has more catalytically active sites, whereas the crystalline phase has better electric conductivity, hence the crystallinity and defects should be optimized to achieve optimal electrocatalytic performance.^[71]

Figure 2.10 (a) Schematics showing the structure evolution of the PtPb nanoplates by controlling the C^+ ion fluxes. (b) Specific and (c) mass activities of commercial Pt/C, crystalline PtPb nanoplates and C^+ -irradiated PtPb nanoplates for electrocatalytic MOR, EOR and ORR.^[69]

2.5 Question to Answer Based on Literature

Based on the above literature review, significant progress has been achieved in the synthesis of noble metal-based nanomaterials with amorphous phase and some examples have demonstrated their promising catalytic performance arising from the amorphous phase and/or amorphous/crystalline interfaces. However, there are still some challenges remaining in this research field.

First, there is still lack of effective and facile wet-chemical methods to synthesize amorphous/crystalline heterophase noble metal nanomaterials. So far, many reported amorphous/crystalline heterophase nanomaterials prepared by wet-chemical methods are compounds, such as oxides, transition metal dichalcogenides, hydroxides, while for metal nanomaterials, it is thermodynamically unfavored to obtain amorphous phase due to the intrinsically strong metallic bonds, especially for noble metals. Up to now, very few examples of amorphous/crystalline heterophase metal nanomaterials have been reported and all of them are prepared by physical methods, such as ion sputtering. Compared with wet-chemical methods, physical methods have many drawbacks. They usually require complicated equipment and harsh condition (such as ultrahigh vacuum), which are very costly. Moreover, the reported physical methods are effective for creating defects and amorphous phase in nanomaterials, but they are unable to effectively control the other parameters, such as size, dimension, and morphology, which are also very important for affecting nanomaterial properties. In contrast, wet-chemical methods are cost-effective, facile and powerful in controlling the various parameters of the nanomaterials. In addition, the nanomaterials prepared by wet-chemical methods can be well dispersed in solutions, which could easily undergo post-synthetic treatment for specific applications and are advantageous for many catalytic reactions in solutions.

Second, as known, amorphous phase is thermodynamically unstable for metals, hence it tends to transform into crystalline phase. However, the stability of metal nanomaterials and the associated changes in physicochemical properties have not been systematically studied.

Third, although many amorphous metal nanomaterials have been reported, most of them are nanoparticles with irregular shapes and large dispersity. For crystalline nanomaterials, various shapes with defined exposed facets have been obtained because of anisotropic atomic arrangements and unique crystallographic symmetry. In comparison, the atomic isotropy of the amorphous structure makes it favor spherical shape, thus it is very challenging to obtain amorphous nanomaterials with other morphologies, such as nanosheets, by direct wet-chemical synthesis. Alternatively, post-synthetic ligand exchange could induce phase transformation and retain the nanomaterial morphology, but up to now, there is still lack of reports on an effective and universal ligand that can induce crystalline-to-amorphous phase transformation of noble metal nanomaterials.

2.6 PhD in Context of Literature

This thesis mainly focuses on the wet-chemical methods for preparing amorphous and amorphous/crystalline heterophase noble metal-based nanomaterials, and further explores their catalytic applications. The major contributions of this thesis to the research area are listed below:

First, a facile wet-chemical method is demonstrated for synthesizing a series of amorphous/crystalline heterophase Pd nanosheets. The crystallinity of the nanosheets can be controlled by simply tuning the reaction temperature. Notably, the as-synthesized nanosheets show heterophase-dependent selectivity and catalytic activity towards the selective hydrogenation of 4-nitrostyrene.

Second, the above wet-chemical method is extended to the synthesis of amorphous/crystalline heterophase PdCu nanosheets with controlled crystallinities and the aging effects on their physicochemical properties are systematically studied. The crystallinity, surface ligands and binding energy of the PdCu nanosheets changed during aging process. Consequently, the amorphous-dominant nanosheets initially showed excellent selectivity towards the catalytic hydrogenation of 4-nitrostyrene. After 3-day aging, the amorphous-dominant nanosheets lost chemoselectivity but the catalytic activity

gradually increased and eventually surpassed the crystalline-dominant nanosheets.

Third, ligand exchange-induced amorphization of Pd nanomaterials is demonstrated. This method is applicable to Pd nanomaterials with different morphologies and different capping ligands. Importantly, the obtained amorphous Pd nanoparticles show dramatically enhanced electrocatalytic activity towards HER, which could be due to the amorphous structure as well as the electronic structure.

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Chapter 3

Experimental Methodology

This chapter discusses the rationale for material selection, synthetic methods and proof-of-concept applications in each project. The detailed information on chemicals and experimental procedures for the one-pot wet-chemical synthesis of amorphous/crystalline heterophase Pd and PdCu nanosheets, as well as the ligand exchange-induced amorphization of Pd nanomaterials will be provided. Furthermore, the measurement of catalytic hydrogenation reaction and electrocatalytic hydrogen evolution reaction will be described. Finally, the basic working principles and data interpretation of the main characterization techniques used for these projects will be discussed, which include transmission electron microscopy, X-ray diffraction, X-ray photoelectron spectroscopy, Fourier-transform infrared spectroscopy, and X-ray absorption spectroscopy.

3.1 Rationale for Selection

Since amorphous phase is thermodynamically unstable in transition metals, it is easy to transform into crystalline phase, such as at elevated temperature,^[1] under e-beam irradiation^[2]. Therefore, the wet-chemical methods used for synthesizing noble metal nanomaterials with amorphous phase should be conducted under mild conditions, otherwise the initially formed amorphous phase would crystallize if the temperature is too high or reaction time is too long. In wet-chemical synthesis, reaction temperature can be easily and precisely controlled, which can significantly influence the nucleation and growth of nanomaterials. Therefore, controlling the temperature is highly promising to achieve the control of crystalline-to-amorphous ratio.

In addition of reaction conditions, atomic structure of nanomaterials is closely related to their size.^[3] For bulk metals, usually only one crystal phase can stably exist under ambient conditions, which is the so-called thermodynamically stable phase. However, when the material size is reduced to nanoscale, metastable phases could appear and stably exist. For example, the thermodynamically stable phase for bulk Ag is face-centered cubic (*fcc*) phase, whereas 4H phase could exist in Ag nanowires, and the 4H-to-*fcc* ratio is dependent on the nanowire diameter.^[4] A possible explanation for this is the balance between bulk energy and surface energy. When the size of a material is reduced to a certain nanometer scale, its surface energy might dominate the total energy of the system. Consequently, the crystal phase of nanomaterials could be different from the bulk counterparts to achieve a minimum total energy state. Moreover, nanomaterials are usually capped by surfactants, which can also help to stabilize the metastable phases.^[5] Therefore, to obtain noble metal nanomaterials with amorphous phase, it is rational to synthesize nanostructures with at least one dimension being small enough, normally several nanometers.

Previously, our group has successfully synthesized ultrathin *fcc* PdCu alloy nanosheets, which have a thickness of ~1 nm and are synthesized at 60 °C.^[6] Considering the ultrathin thickness and mild reaction condition are in accord with the above discussions, it is expected that by modifying the reaction conditions, such as choosing proper ligands, tuning

reaction temperature and time, amorphous/crystalline heterophase Pd-based nanosheets can be obtained. Therefore, the synthesis method of amorphous/crystalline heterophase Pd and PdCu nanosheets, which are described in Chapter 4 and Chapter 5, are developed by modifying the synthesis method of the previously reported crystalline PdCu nanosheets. Pd nanomaterials can efficiently catalyze hydrogenation reactions under ambient conditions, i.e., at atmospheric pressure and room temperature. Mild conditions can well preserve the heterophase of the nanosheets, therefore, catalytic hydrogenation reactions under ambient conditions are chosen as a proof-of-concept application to study the heterophase effect on catalytic performance. Furthermore, since amorphous phase is unstable, it tends to transform into crystalline phase even under ambient conditions, which may further induce changes in other physicochemical properties. Therefore, aging effect on the properties and catalytic performance of the heterophase nanosheets is further studied.

Besides controlling the wet-chemical synthesis conditions, ligand exchange has also been reported for phase control of metal nanomaterials.^[7-9] Our group have reported that thiols can induce the 4H-to-*fcc* phase transformation of Au nanoribbons by post-synthetic ligand exchange.^[9] Besides, it has been reported that thiol molecule can induce the transformation of Pd nanosheets from *fcc* phase to amorphous phase.^[8] However, due to the ultrathin thickness and the strong interaction between thiol molecules and Pd element, holes are formed in the Pd nanosheets after ligand exchange.^[8] These examples clearly demonstrate the strong bonding between thiols and noble metals, which can induce phase transformation. Therefore, in this thesis, one of the research works is to obtain amorphous Pd nanomaterials by ligand exchange with thiols, which can induce crystalline-to-amorphous phase transformation of various kinds of *fcc* Pd nanomaterials without destroying their integrity. Pd nanomaterials are also widely used for electrocatalytic reactions, such as hydrogen evolution reaction (HER), formic acid oxidation. In addition, as mentioned above, e-beam irradiation is possible to induce phase transformation of metal nanomaterials, thus supply of electrons, i.e., by applying voltage, could induce crystallization of amorphous nanomaterials. Hence, electrocatalytic HER is chosen as a proof-of-concept reaction, which cannot only study the crystallinity effect of Pd nanomaterials on electrocatalytic

performance but also investigate the stability of amorphous nanomaterials under electrical cycling.

3.2 Chemicals and Materials

Palladium(II) acetylacetonate ($\text{Pd}(\text{acac})_2$), copper(II) acetylacetonate ($\text{Cu}(\text{acac})_2$), molybdenum hexacarbonyl ($\text{Mo}(\text{CO})_6$), trioctylphosphine oxide (TOPO), octanoic acid, hexane and 4-aminostyrene, oleylamine (98%), morpholine borane (MB, 95%), poly(vinylpyrrolidinone) (PVP, MW=55000), potassium bromide (KBr, ACS reagent, $\geq 99.0\%$) potassium chloride (KCl, ACS reagent, $\geq 99.0\%$), sodium tetrachloropalladate(II) (Na_2PdCl_4 , 98%), L-ascorbic acid, Pd black (99.95% trace metals basis), platinum on carbon (Pt/C, 10 wt% loading, matrix activated carbon support) and other chemicals used in the experiments without special mention were purchased from Sigma-Aldrich. N, N-dimethylformamide (DMF) was purchased from Fisher Scientific. 4-nitrostyrene (stabilized by 4-tert-butylcatechol) was purchased from Tokyo Chemical Industry Co., Ltd. Bismuthiol I ($\geq 99.0\%$) was purchased from Fluka. Ethanol (absolute, 99.9%) and *n*-hexane were purchased from Merck (Nordic European Centre, Singapore). Nafion alcohol solution (5 wt%) was purchased from Alfa Aesar. The Milli-Q water was obtained from the Milli-Q System. All the chemicals were used as received without further purification.

3.3 Synthesis of Amorphous/Crystalline Heterophase Pd Nanosheets for Selective Hydrogenation Reaction

3.3.1 Synthesis of Pd nanosheets

In a typical synthesis of Pd nanosheets (Sample 1), 20 mg of $\text{Pd}(\text{acac})_2$ and 260 mg of TOPO were added into 16 mL of octanoic acid stored in a 50 mL round-bottom flask with magnetic stirring under N_2 bubbling for 30 min. Then 20 mg of $\text{Mo}(\text{CO})_6$ and 3 mL of DMF were added into the aforementioned mixture. After the flask was bubbled with N_2 under magnetic stirring for another 60 min, it was immersed into a water bath at 48 °C. The solution color evolved from yellow to dark blue within 30 min. After the reaction was

kept at 48 °C for 40 min, the final product, i.e., Pd nanosheets, was obtained by centrifugation at 6,000 rpm for 5 min. The as-obtained nanosheets were washed with hexane for three times, and then dispersed in hexane with a concentration of 0.3 mg/mL. Samples 2-5 with different crystallinities can be obtained by using the same synthetic method at different temperatures, i.e., 52, 60, 80, and 100 °C, respectively.

3.3.2 Catalytic hydrogenation of 4-nitrostyrene

In a typical experiment, 500 μ L of Pd catalyst in hexane (0.3 mg/mL) and 74.5 mg of 4-nitrostyrene were added into 2.5 mL of ethanol in a 5 mL flask. A H₂ balloon was introduced after the flask was purged with H₂ for 5 min. The reaction was performed at room temperature (25 °C). Liquid samples were analyzed by gas chromatography (GC) equipped with a flame ionization detector and an HP-CP8713 capillary column.

3.4 Aging Effect Study on Amorphous/Crystalline Heterophase PdCu Nanosheets

3.4.1 Synthesis method

In order to synthesize the amorphous phase-dominant PdCu (*a*-PdCu) heterophase nanosheets, 20 mg of Pd(acac)₂, 8 mg of Cu(acac)₂, 260 mg of TOPO, and 16 mL of octanoic acid were added into a 50 mL round-bottom flask under magnetic stirring and N₂ bubbling for 60 min. After 60 mg of Mo(CO)₆ were added into the aforementioned mixture, it was magnetically stirred for 60 min. Then 3 mL of DMF were added and the mixture was stirred for 40 min under N₂ atmosphere. After that, the flask was immersed into a water bath at 40 °C and kept at 40 °C for 20 min. After the flask was naturally cooled down to room temperature, hexane was added and the final product was obtained by centrifugation at 6,000 rpm for 5 min. The as-obtained nanosheets were washed twice with hexane, and then dispersed in hexane.

In order to synthesize crystalline phase-dominant PdCu (*c*-PdCu) nanosheets, 20 mg of Pd(acac)₂, 2 mg of Cu(acac)₂, 260 mg of TOPO, and 16 mL of octanoic acid were added

into a 50 mL round-bottom flask under magnetic stirring and N₂ bubbling for 60 min. After 20 mg of Mo(CO)₆ and 3 mL of DMF were added into the aforementioned mixture, it was magnetically stirred for 60 min. Then the flask was immersed into a water bath at 80 °C and kept at 80 °C for 30 min. After the flask was naturally cooled down to room temperature, hexane was added and the final product was obtained by centrifugation at 6,000 rpm for 5 min. The as-obtained nanosheets were washed with hexane twice, and then dispersed in hexane.

3.4.2 Aging process

The samples were stored in hexane at room temperature (25 °C). After aging for 1 day, 2 days, 3 days, 7 days and 14 days, a proper amount of sample was taken from the vial and used for characterizations.

In a typical measurement of catalytic performance during the aging process, 100 µL of PdCu catalyst in hexane (0.3 mg/mL in terms of Pd) and 37 mg of 4-nitrosyrene were added into 2.5 mL of ethanol in a 5 mL flask, and all the rest procedures are the same as those described in section 3.3.2.

3.5 Ligand Exchange-Induced Amorphization of Pd Nanomaterials for Highly Efficient Electrocatalytic Hydrogen Evolution Reaction

3.5.1 Synthesis of crystalline Pd nanomaterials

Synthesis of crystalline Pd nanoparticles capped by oleylamine (Pd NPs-OAm) The Pd NPs-OAm were synthesized by a previously reported method with slight modification.^[10] In the typical synthesis, 40 mg of Pd(acac)₂ were dissolved in 15 mL of OAm by magnetically stirring at 70 °C under N₂ flow. After 30 min, the solution was heated to 90 °C, denoted as Solution A. Meanwhile, 100 mg of MB were dissolved in 3 mL of OAm at room temperature, which was denoted as Solution B. Solution B was quickly injected into Solution A at 90 °C. The resultant solution immediately turned into

dark and was maintained at 90 °C for 30 min. After the solution was naturally cooled to room temperature, the Pd nanoparticles were precipitated from the reaction mixture by adding 15 mL of ethanol and centrifuging at 8,000 rpm. Then, the Pd nanoparticles were washed with toluene and acetone twice (by first dispersing these NPs in 5 mL of toluene and then adding 20 mL of acetone to precipitate them), and finally dispersed in toluene for further use.

Synthesis of crystalline Pd nanosheets capped by octanoic acid (Pd NSs-OA) The Pd NSs-OA were synthesized at 100 °C using the method described in section 3.3.1.

Synthesis of crystalline Pd nanocubes capped by poly(vinylpyrrolidone) (Pd-NCs-PVP) The Pd-NCs-PVP were synthesized by a previously reported method with slight modification.^[11] In the typical synthesis, 60 mg of L-ascorbic acid, 105 mg of PVP, 185 mg of KCl and 5 mg of KBr were dissolved in 8 mL water. The solution was placed in a 20 mL open vial and heated at 80 °C for 10 min under magnetic stirring. Then, 57 mg of Na₂PdCl₄ dissolved in 3 mL of water were added into the vial. After that, the vial was capped and heated at 80 °C for 3 h. Finally, the product was obtained by centrifugation and washed with ethanol for five times.

3.5.2 Ligand exchange process

1 mL of the as-synthesized Pd NPs-OAm, Pd NSs-OA and Pd-NCs-PVP with concentration ~0.1 mg/ml was mixed with 1 mL of methanol solution containing 10 mg of bismuthiol I. The mixed solution was sealed in a closed vial and placed in a water bath that was kept as 25 °C. After a certain time, the Pd nanomaterials were collected by centrifugation and washed with ethanol for three times.

The Pd NPs-OAm after ligand exchange with bismuthiol I at 25 °C for 1 and 24 h are denoted as Pd NPs-Bis-1h and Pd NPs-Bis-24h, whereas the Pd NPs-OAm after ligand exchange with bismuthiol I at 70 °C for 24 h are denoted as Pd NPs-Bis-24h(70).

3.5.3 Electrocatalytic hydrogen evolution reaction

HER measurements were conducted on the Autolab workstation (PGSTAT12) at room temperature. Glassy carbon electrode (GCE) was used as working electrode, which has a diameter of 3 mm and is coated with catalysts. The Ag/AgCl (3 M KCl) and graphite rod were used as reference electrode and counter electrode, respectively. The Ag/AgCl electrode was calibrated with respect to a reversible hydrogen electrode (RHE). Prior to the electrochemical test, GCE was successively polished with 300 nm and 50 nm Al₂O₃ slurry. After it was washed with Milli-Q water and ethanol to obtain a clean surface and dried in air, 5 μ L of Pd NPs-Bis catalyst solution with 1.57 mg mL⁻¹ Pd measured by ICP-OES were dropped onto its surface to achieve the Pd loading of 0.112 mg cm⁻². After being dried in air for 2 h, 2 μ L of Nafion ethanolic solution (0.1 wt%) were dropped onto the electrode surface. The electrode was dried in air for 2 h and then used as the working electrode for the electrochemical measurement. Using the same procedure, the Pd NPs-OAm, commercial Pt/C and Pd black working electrodes were prepared. The loading amount of noble metals for all catalysts on GCE was kept the same.

The HER test was performed in N₂-saturated 0.5 M H₂SO₄ aqueous solution. Linear sweep voltammetry (LSV) was conducted at a scan rate of 5 mV s⁻¹. The accelerated durability tests were carried out in N₂-saturated 0.5 M H₂SO₄ aqueous solution at room temperature, and the potential cycling sweeps from 0.04 V to -0.18 V (versus reversible hydrogen electrode (RHE)) at scan rate of 100 mV s⁻¹ for 10,000 cycles. After potential cycling, the LSV curve was recorded at a scan rate of 5 mV s⁻¹. In order to obtain the solution resistance (R_s), electrochemical impedance spectroscopy (EIS) was measured from 100 kHz to 0.1 Hz, and all data were corrected with R_s (Figure 3.1). The current density for the HER measurement was calculated by dividing the measured current by the geometric surface area of the electrode.

Figure 3.1 EIS curves of (a) Pt/C, (b) Pd black, (c) Pd NPs-Bis-1h, (d) Pd NPs-Bis-24h, (e) Pd NPs-OAm, and (f) Pd NPs-Bis-24h(70).

The number of active sites and the electrochemically active surface area (ECSA) of the catalysts are estimated by Cu underpotential deposition (UPD) method (Figure 3.2), which

is widely reported.^[12, 13] In this method, the number of active sites was calculated according to the Cu UPD stripping charge (Q_{Cu} , $\text{Cu}_{\text{upd}} \rightarrow \text{Cu}^{2+} + 2\text{e}^-$) with the following equation:

$$n = Q_{\text{Cu}}/(2Fm)$$

where F is the Faraday constant (96485 C mol^{-1}), and m is the metal mass loading ($1.2 \times 10^{-6} \text{ g}$).

The turnover frequency (TOF, $\text{H}_2 \text{ s}^{-1}$) can be calculated based on the following equation:

$$\text{TOF} = I/(2Fnm)$$

where I is the current (A) during the LSV measurement. The factor 2 is the number of electrons transferred, because forming one H_2 molecule requires two electrons.

Assuming a value of $420 \mu\text{C cm}^{-2}$ for a saturated Cu_{upd} monolayer formation on active metal sites,^[12, 13] the ECSA can be calibrated as follows:

$$\text{ECSA} = Q_{\text{Cu}}/(m \times 420 \mu\text{C cm}^{-2})$$

The number of active sites and ECSA in Pd NPs-OAm were calculated to be $3.22 \times 10^{-4} \text{ mol g}^{-1}$ and $14.8 \text{ m}^2 \text{ g}^{-1}$, respectively. The number of active sites and ECSA in Pd NPs-Bis-1h were calculated to be $6.44 \times 10^{-4} \text{ mol g}^{-1}$ and $29.6 \text{ m}^2 \text{ g}^{-1}$, respectively. The number of active sites and ECSA in Pd NPs-Bis-24h were calculated to be $7.95 \times 10^{-4} \text{ mol g}^{-1}$ and $36.5 \text{ m}^2 \text{ g}^{-1}$, respectively.

Figure 3.2 Calibration of the number of active sites and the ECSA by using the Cu UPD method. Cyclic voltammetry curves of (a) Pd NPs-OAm, (b) Pd NPs-Bis-1h, and (c) Pd NPs-Bis-24h, which were collected at a scan rate of 10 mV s^{-1} in N_2 -saturated $0.5 \text{ M H}_2\text{SO}_4$ in the presence and absence of 10 mM CuSO_4 .

3.6 Characterizations

3.6.1 Transmission electron microscopy

Transmission electron microscopy (TEM)^[14] is a very useful tool for obtaining the morphological, crystallographic, and compositional information of nanomaterials, where electrons are emitted by the electron gun on the top, accelerated by an electric field, deflected by a column of magnetic lenses, and finally transmit through an ultrathin specimen to form an image. Then an imaging device magnifies and focuses the image.

When a specimen is irradiated by an electron beam, various signals can be generated (Figure 3.3a). Those transmitted electrons include inelastically scattered (with energy loss), elastically scattered (without energy loss), and unscattered electrons. These electrons contain the major information in TEM for imaging and selected-area electron diffraction (SAED). In addition, by analyzing the energy loss of the transmitted electrons, chemical information can be obtained using electron energy-loss spectroscopy (EELS). Backscattered electrons, secondary electrons, and Auger electrons are shown in Figure 3.3b-d, respectively. The backscattered electrons are original primary incident electrons, which are scattered backward due to the interactions with the sample atomic nucleus (Figure 3.3b). If the incident electrons collide and eject inner shell electrons, as shown in Figure 3.3c, the electrons knocked off by incident electrons are secondary electrons, that is, they are not the primary incident electrons but they are from the specimen atoms. If the inner shell electrons are ejected, these atoms are in an ionized state, and subsequently the vacancy in the inner shell is filled by an outer-shell electron with a higher energy level, generating an energy surplus. Therefore, either X-rays are emitted, or Auger electrons (the third electrons) can also escape from the sample surface to use up this excess energy (Figure 3.3d). In TEM, the backscattered, secondary, and Auger electrons are normally not used although it is possible to use secondary electrons in scanning TEM (STEM).

Figure 3.3 (a) Signals generated when electron beam is incident onto the sample. (b-d) Schematic illustrations of the backscattered electron, secondary electron and Auger electron.^[14]

X-rays, including characteristic X-rays and Bremsstrahlung (continuum) X-rays, are formed by incident electrons with core electrons of specimen atoms. The X-rays are used for analyzing chemical information, which is called X-ray energy-dispersive spectroscopy (EDS).

TEM allows for various techniques to acquire different information of the specimen. In this report, the techniques used to analyze samples are imaging, SEAD and EDS, therefore, these three techniques will be elaborated as follows.

Imaging

The primary function of TEM is to directly observe the morphology, structure, size, and distribution of nanomaterials. In TEM images, sufficient contrast is needed to recognize a sample. There are different types of image contrast, including mass-thickness contrast,

diffraction contrast, and Z-contrast.

In the area with higher mass or higher thickness, more electrons will be scattered at larger angles. After deflection by the objective lens, the electrons at larger angles are excluded by the objective aperture, and thus fewer electrons from the high mass area contribute to the imaging, forming a darker imaging on the image plane.

Diffraction contrast is induced by diffraction phenomena from crystalline samples. For example, the sample contains grains A and B, and we suppose that the incident electrons are either diffracted or transmitted (unscattered). Grain A is at the Bragg diffraction position, so some of the incident electrons are diffracted and the rest of electrons are transmitted (unscattered). Grain B is not at the Bragg diffraction position, so all the incident electrons are transmitted (unscattered), which contribute to the imaging. This means that, in grain B, more electrons contribute to the imaging as compared to grain A, therefore grain B appears brighter than grain A. In amorphous samples, since no diffraction happens over the sample, the image contrast comes only from mass-thickness contrast.

In Z-contrast, Z represents the atomic number. Z-contrast is mainly used for STEM imaging. In the dark-field imaging of STEM, the scattered electrons are detected and used to form the images. For the element with higher atomic number, more electrons will be scattered, therefore it will appear brighter. Therefore, STEM imaging is also an important technique for composition analysis. In addition, for STEM, the thickness contrast has similar effect with the Z-contrast.

SAED

Electron diffraction is caused by the wave nature of the electrons. Since the wavelength of electrons is very short, which is comparable with crystal lattices, diffraction occurs when electrons pass through the sample. Electron diffraction gives information on the specimen structure, crystallinity and lattice parameters. In TEM, it is possible to select a small area for diffraction, so it is common to get a SAED pattern.

Similar to XRD, the formation of electron diffraction can be described by Bragg's law. As illustrated in Figure 3.4a, when the crystal is at the Bragg diffraction orientation, the geometry relationship follows the equation:

$$2\theta = r/L$$

where L is the camera length. According to Bragg's law,

$$2\sin\theta = \lambda/d$$

Since θ is very small, θ approximately equals to $\sin\theta$, and thus,

$$\frac{r}{L} = \frac{\lambda}{d}, \text{ or } rd = L\lambda$$

Here, the product $L\lambda$ is camera constant.

Figure 3.4 (a) Schematics illustrating the Bragg diffraction in TEM. (b-d) Representative diffraction patterns of single crystalline (b), polycrystalline (c) and amorphous (d) samples.^[14]

From the electron diffraction patterns, the crystal structure and lattice parameter can be determined. For single crystalline structures, diffraction spots can be clearly observed (Figure 3.4b). By observing the pattern of the spots and the distance between the spots and the central beam, the crystal structure as well as the lattice parameters of the sample can be determined. For polycrystalline structures, since each crystallite is oriented in different direction and each crystallite will have a set of diffraction spots, the superposition of diffraction spots results in a set of concentric circles (Figure 3.4c). For amorphous samples, atoms are randomly arranged, so diffraction will not occur. As a result, no diffraction spots or concentric rings can be observed (Figure 3.4d).

EDS

The electron in an inner shell may be excited by the incident electron beam, and then eject from the shell, thus an electron hole is created. Subsequently, an outer-shell electron, which has higher energy, fills the hole. During this process, energy will be released because the outer shell has higher energy compared with the inner shell, which may be released as an X-ray. The energy and number of the released X-rays can be detected by energy-dispersive spectrometer. For each element, the energy difference between two shell is characteristic, which equals to the energy of the released X-ray, thus, by measuring the X-ray energy, the elemental composition can be determined.

Figure 3.5 (a) Electronic structure of atoms illustrating the formation of characteristic X-rays between different energy levels; (b) Simplified diagram showing the characteristic X-ray lines in EDS.^[14]

Figure 3.5 illustrates the electronic structures, including the first (K), second (L), third (M), and fourth (N) shells. On the right of Figure 3.5a, it shows the principal quantum number (n), azimuthal quantum number (l), total angular momentum quantum number (j), and outer shell electron configurations. If an electron in the K shell is ejected, an electron on the L_3 or L_2 may fill it, producing K_{α_1} or K_{α_2} X-ray lines, respectively. However, if it is filled by M_3 or M_2 electrons, K_{β_1} or K_{β_2} lines are resulted. Similarly, other L and M lines are defined from other shells as illustrated.

3.6.2 X-ray diffraction

In X-ray crystallography,^[15] X-rays are incident onto a specimen and diffracted by the atoms in the specimen. For crystalline samples, the incident X-rays will be diffracted into specific directions, thus by detecting the angle and intensity of the diffracted X-rays, the crystal structure can be determined.

Figure 3.6 (a) Schematics illustrating the Bragg's law. (b) Typical XRD patterns of crystalline and amorphous structures.^[15]

In crystals, atoms are arranged in a regular form, and X-rays are a kind of electromagnetic waves. Through the interaction between the electrons of atoms and the incident X-rays, atoms can scatter X-ray waves. Because X-rays have a wavelength comparable with the crystal lattice spacings, diffraction occurs when X-rays pass through a crystal. The diffracted X-rays can have constructive interference and destructive interference. The constructive interference is produced when the following conditions are satisfied, which is called Bragg's Law (Figure 3.6a):

$$N\lambda = 2d\sin\theta$$

where n represents any integer, λ stands for the incident X-ray wavelength, d represents the spacing between diffracting planes, and θ denotes the incident angle. In modern nomenclature, it is unnecessary to retain n in the Bragg equation. To be convenient, both sides of the above equation are divided by n and d/n is defined as d_{hkl} , thus the Bragg's law becomes:

$$\lambda = 2d_{hkl}\sin\theta$$

In the original equation, the diffraction is considered as n order diffraction from the plane with smallest integers, such as (111). While in the modified equation, all diffractions are considered as the first order from each plane families, such as (111) and (222). In XRD, usually λ is known, θ can be measured, and thus the d spacing can be calculated.

For crystalline samples, the XRD pattern would show peaks, and the smaller the crystal size, the broader the peaks; while for amorphous samples, no peaks can be observed, instead, a broad hump would appear at 2θ around 30° (Figure 3.6b).

3.6.3 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) is a surface technique (usually within 10 nm from the surface) that can analyze the oxidation states of elements and quantitatively analyze the composition of the sample.^[16]

XPS utilizes the photoelectric effect, as shown in Figure 3.7. When X-ray photons are irradiated onto the sample, the core electrons of the element can be emitted from the sample. XPS measures the kinetic energy ($K.E.$) and number of the emitted electrons. The $K.E.$ is expressed by the following equation:

$$K.E. = h\nu - (B.E. + \phi)$$

where $h\nu$ is the X-ray photon energy that depends on the X-ray source, ϕ is the work function of the instrument, and $B.E.$ is the binding energy of the core electron, which is the characteristic of each core atomic orbital in each element. The $B.E.$ of a core electron represents the extent of the attraction by the nuclei, which depends on the number of protons in the nucleus, the distance between the core electrons and their nuclei, the density of electrons around the respective atom, ion, molecule, or solid, and the electron-electron interactions present.

Figure 3.7 (a) A schematic that illustrates the photoelectric effect. (b) A typical spectrum collected by XPS.^[16]

3.6.4 Fourier-transform infrared spectroscopy

Fourier-transform infrared spectroscopy (FTIR)^[17, 18] is widely used to analyze organic compounds by passing infrared radiation (usually $4000\text{--}400\text{ cm}^{-1}$) through a sample and determining the absorption of the incident radiation. The absorption of the incident infrared radiation arises from the vibrations of the atoms in molecules, thus an absorption peak will appear at the energy corresponding to the vibration frequency of a certain part in a molecule. Chemical bonds are undergoing a series of different vibrations. In this sense, molecules appear to behave as they were balls connected to springs, with the balls representing atoms and the springs representing chemical bonds. The fundamental bond vibrations include asymmetrical and symmetrical stretching vibrations, out-of-plane and in-plane bending modes (Figure 3.8). Each chemical bond has characteristic vibrational frequency, which is determined by the nature of the bond and its chemical environment.

Figure 3.8 Fundamental vibration modes of chemical bonds, where + and – denote movement above and behind the plane of the paper, respectively.^[18]

For molecules that show infrared absorptions, namely ‘infrared-active’ molecules, during the vibrations their electric dipole moment must change. For example, The dipole moment of a heteronuclear diatomic molecule changes during bond expansion and contraction, thus such kind of molecule is infrared active. In comparison, the dipole moment of a homonuclear diatomic molecule remains zero during bond vibrations, thus such kind of molecule is infrared-inactive.

3.6.5 X-ray absorption spectroscopy

X-ray absorption spectroscopy (XAS)^[19, 20] is widely used to determine the electronic structure and/or local geometric of materials. When X-rays with intensity of I_0 are incident onto a sample with thickness t , according to Beer’s law, the intensity I_t of the transmitted X-ray intensity is:

$$I_t(t) = I_0 e^{-\mu(E)t}$$

where $\mu(E)$ represents the X-ray absorption coefficient that depends on the target density (d), the photon energy (E) of the incident X-rays, the atomic number (Z) and atomic mass (m) of the element:

$$\mu(E) \sim dZ^4 / mE^3$$

XAS measures the absorption coefficient with varying incident photon energy (Figure 3.9a). When the photon energy of the incident X-ray equals to the binding energy of a core electron, the absorption coefficient will sharply increase, giving a rising edge in the spectrum. The edges are named by the shells where core electron is excited. For example, excitation of a 2s or 2p electron takes place at L-edge, and excitation of a 1s electron takes place at K-edge.

Figure 3.9 (a) A schematic showing the incident and transmitted X-ray beam.^[20] (b) Cu K-edge XAFS spectrum of a copper foil, which highlights the XANES and EXAFS regions.^[21]

X-ray absorption fine structure (XAFS) refers to the details of X-ray absorption by an atom at energies close to and above the core-level binding energies of that atom, which can be divided into two regions: X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine-structure spectroscopy (EXAFS) (Figure 3.9b).

XANES is also referred to as the near edge X-ray absorption fine structure (NEXAFS). It is the region very close to the absorption edge (typically within 30 eV of the absorption edge), which arises from the transitions of photoelectrons to unoccupied bound states and thus is greatly affected by coordination chemistry (e.g., tetrahedral, octahedral coordination) and formal oxidation state of the atom absorbing incident X-rays.^[20]

If the incident photon energies are greater than ~30 eV above the absorption edge, photoelectrons are promoted to a free or continuum state, thus EXAFS is not related to

chemical bonding but depends on the atomic structure surrounding the atom absorbing incident X-rays. EXAFS is used to determine the interatomic distances, coordination number, and structural and thermal disorder around a particular atomic species.^[20]

Figure 3.10 (a) Conversion to k-space. (b) Fourier transform to R-space.^[21]

To perform the Fourier transform,^[21] which is critical to XAFS data analysis, the EXAFS data in E-space, i.e., $\chi(E)$, must be first converted to $\chi(k)$ in the k-space (Figure 3.10a), where k is expressed as:

$$k = [2m(E-E_0)/h^2]^{1/2}$$

The oscillation waves decay with extended k , thus to compensate for the wave decay, $\chi(k)$ data are usually weighted with some power, which is denoted as k^n ($n = 1, 2, 3$). For analyzing the EXAFS data collected from heavy atoms, the k^3 -weight is most frequently used; whereas for lighter coordination atoms, the k - or k^2 -weight is more suitable, which can maximize their contributions in the low k region. Then, the $k^n\chi(k)$ function is converted to the R -space through Fourier transform (FT) (Figure 3.9b). By applying the FT technique to the EXAFS oscillations, which are the superposition of different sinusoidal functions from many shells, the contributions from different shells can be separated. Because of the phase-shift in the EXAFS equation, the peak position in the FT curve does not correspond to interatomic distance, instead, typically it is 0.3-0.5 $\text{\AA}$ shorter than the interatomic distance for the first shell atoms.

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Chapter 4*

Synthesis of Amorphous/Crystalline Heterophase Pd Nanosheets for Selective Hydrogenation Reaction

In this chapter, the results for the synthesis of the amorphous/crystalline heterophase Pd nanosheets by a one-pot wet-chemical method will be presented. The crystallinity of heterophase Pd nanosheets can be controlled by fine-tuning the experimental conditions. These nanosheets are used as the heterogeneous catalysts to study the chemoselectivity in hydrogenation of 4-nitrostyrene. It is found that the crystallinities of amorphous/crystalline heterophase Pd nanosheets play a critical role in the catalytic activity and chemoselectivity in the hydrogenation of 4-nitrostyrene. The amorphous phase-dominant Pd nanosheets exhibit an excellent chemoselectivity, while those crystalline phase-dominant Pd nanosheets show a higher catalytic activity.

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4.1 Introduction

Noble metal nanocrystals have shown various promising applications in optics, catalysis, electronics, and so on, owing to their unique physiochemical properties, which strongly depend on their size, shape, exposed facet, dimension, and atomic arrangement.^[1-4] In order to prepare novel nanostructures with multi-functionalities and/or enhanced properties, one of the effective strategies is to synthesize heterostructures with different materials, which could combine the advantages of individual components and/or overcome their drawbacks.^[5] Similar to the heterostructures composed of different materials, crystal-phase heterostructure, as one kind of heterophase structures in monometallic nanomaterials, was proposed for the investigation of crystal-phase-based applications.^[3] Importantly, the crystal-phase heterostructures can be used for the epitaxial growth of novel nanostructures for promising applications.^[6, 7]

Different from crystalline phase, amorphous phase is a unique structure with random atomic arrangement, and thus exhibiting some intriguing properties^[8]. Therefore, amorphous/crystalline heterophase nanostructures, as another kind of novel heterophase structures, might also exhibit unique properties and promising applications compared to their amorphous and crystalline counterparts. In a recent report, a Mn-alloy material consisting of nanocrystalline domains embedded in amorphous structure was prepared by magnetron sputtering method.^[9] This heterophase material possessed a high mechanical strength, which results from the quasi-dislocation-free nanocrystals and the fully relaxed amorphous shells. As another example, the amorphous/crystalline heterophase PtPb nanoplates,^[10, 11] prepared by ion irradiation, showed excellent performance in electrocatalytic reactions, which might be attributed to the amorphous/crystalline phase interfaces, rich defects and small amorphous domains. These works imply that amorphous/crystalline heterophase nanomaterials deserve more research attention for various promising applications.

However, the aforementioned amorphous/crystalline heterophase nanomaterials were prepared by physical methods, i.e., magnetron sputtering and ion irradiation, which suffer

from harsh conditions and requires special equipment. In comparison, wet-chemical synthetic route is an attractive alternative because of the relatively low cost, ease of implementation, high-yield production and versatility. Therefore, it is desirable to rationally design and use wet-chemical methods to prepare the amorphous/crystalline heterophase nanomaterials. However, nanomaterials synthesized by wet-chemical methods are usually in thermodynamically stable phases. As known, the thermodynamically stable phases for noble metals are either face-center cubic (*fcc*) or hexagonal close-packed (*hcp*) phase, thus it is very challenging to obtain amorphous noble metal nanomaterials due to the strong metallic interactions between atoms^[12]. Therefore, it is also very challenging to get a series of amorphous/crystalline heterophase nanomaterials with a controllable crystallinity. Until now, for noble metal nanomaterials, there is rarely report on the controllable synthesis of amorphous/crystalline heterophase nanostructures and the investigation on the heterophase-based applications.

Noble metals, such as Pd, have been widely used as the heterogeneous catalysts for hydrogenation reactions,^[13-16] which are very important in the industrial and fine chemical fields^[14, 17]. However, it is very challenging to achieve the highly selective hydrogenation of molecules containing both C=C double bonds and nitro groups, since both functional groups can be readily hydrogenated.^[14, 17] Hydrogenation of 4-nitrostyrene (NS), which is commonly used as the model reaction.^[16, 18, 19] to test the selectivity and activity of heterogeneous catalysts.

4.2 Results and Discussion

4.2.1 Synthesis and characterization of amorphous/crystalline heterophase Pd nanosheets

In a typical experiment, the heterophase Pd nanosheets with different crystallinities were prepared by heating the reaction solutions at various temperatures (48-100 °C) for 40 min (see section 3.3.1 for details). During the reaction, CO was released by the decomposition of Mo(CO)₆, which reduced the precursor Pd(acac)₂.^[20] The Pd nanosheets obtained at

48 °C are denoted as Sample 1 (Figure 4.1). Transmission electron microscopy (TEM) (Figure 4.1a) and dark-field scanning TEM (DF-STEM) (Figure 4.1b) images confirm that the nanosheets with high purity were obtained. The spherical aberration-corrected STEM-high-angle annular dark-field (C_s -corrected STEM-HAADF) image (Figure 4.1c) shows that a typical nanosheet is composed of crystalline and amorphous domains, in which the crystalline domains are marked by the dashed yellow curves for clarity. The crystalline and amorphous areas are further identified by the bright spots (Figure 4.1d) and diffuse ring (Figure 4.1e) in the corresponding selected-area fast Fourier transform (FFT) patterns, respectively. Moreover, the weak ring in the selected area electron diffraction (SAED) pattern (Figure 4.1f) further reveals their poor crystallinity. The average width of the folded edge in nanosheets was measured to be ~ 1.0 nm (Figure 4.1g), which corresponds to the thickness of nanosheets^[21] and thus proves their ultrathin structure.

Figure 4.1 Characterization of the heterophase Pd nanosheets in Sample 1. (a) TEM and (b) DF-STEM images showing the nanosheet morphology. (c) C_s -corrected STEM-HAADF image showing the heterophase structure, in which the crystalline domains are marked by the dashed yellow curves. (d,e) The corresponding FFT patterns of the selected regions marked by the red and green squares, respectively, in (c). (f) SAED pattern of Sample 1. (g) TEM image of a folded Pd nanosheet, showing the folded edge with measured width of ~ 1.0 nm.^[32]

This synthetic method is quite general. By simply tuning the synthetic temperature, a series of heterophase Pd nanosheets with different crystallinities, referred to as Samples 2-5, are obtained at 52, 60, 80 and 100 °C, respectively. All of the nanosheets (Figures 4.2a-d) possess a similar thickness of ~ 1.0 nm, measured from the folded edges in high-magnification TEM images (Figures 4.2e-h).

Figure 4.2 (a-d) TEM images of the heterophase Pd nanosheets (Samples 2-5). (e-h) TEM images of folded Pd nanosheets in Samples 2-5, showing the folded edge with the thickness of ~ 1.0 nm. (i-l) SAED patterns of Samples 2-5, respectively. ^[32]

The crystallinity of the nanosheets increases from Sample 1 to Sample 5, as evidenced by the increasingly intensive diffraction rings in the SAED patterns (Figure 4.1f, Figure 4.2i-1), and increasing crystalline areas (Figure 4.1c, Figure 4.3). By measuring the areas of the amorphous and crystalline domains in the C_S -corrected STEM-HAADF images, the percentages of the crystalline areas in Samples 1-5 are estimated to be ~11%, 19%, 65%, 83% and 96%, respectively.

Figure 4.3 Characterization of the heterophase Pd nanosheets with different crystallinities. (a-d) DF-STEM and (e-h) C_S -corrected STEM-HAADF images of the heterophase Pd nanosheets in Samples 2-5, respectively. The crystalline domains are marked by the dashed yellow curves in (e), while the amorphous domains are marked by the dashed light-blue curves in (f-h).^[32]

Moreover, the crystallinity of the heterophase Pd nanosheets was characterized by X-ray diffraction (XRD). As shown in Figure 4.4, there is no obvious diffraction peak for Sample 1, indicating that the dominant phase of Sample 1 is amorphous, consistent with the aforementioned results (Figure 4.1). The intensity of diffraction peaks attributed to the *fcc* Pd (PDF# 46-1043) increases from Sample 1 to Sample 5 (Figure 4.4), indicating the increased crystallinity.

Figure 4.4 XRD spectra of Samples 1-5. ^[32]

The thickness of the nanosheets was also characterized by atomic force microscopy (AFM), which proved these nanosheets from different samples have similar thickness around 3.0 nm (Figure 4.5). This is about 2 nm thicker than that measured by TEM, due to the octanoic acid molecules coating on the Pd nanosheets. ^[22]

Figure 4.5 (a-e) AFM images of Pd nanosheets in Samples 1-5, showing the thickness of ~3.0 nm.

^[32]

Furthermore, X-ray photoelectron spectroscopy (XPS) taken from Samples 1-5 was used to confirm their different electronic structures (Figure 4.6). The Pd(0) 3d_{3/2} and Pd(0) 3d_{5/2} peaks gradually shift to lower binding energy from Sample 1 to Sample 5. This observation, i.e., the amorphous nanosheet has a greater binding energy, is consistent with the previous report.^[23] Meanwhile, there is no signal from Pd(II), indicating the metallic state of the synthesized Pd nanosheets.

Figure 4.6 (a) XPS spectra of Pd 3d for Samples 1 to 5. (b) The magnification of the Pd(0) 3d_{3/2} peaks for Samples 1 to 5 after normalization. (c) The magnification of the Pd(0) 3d_{5/2} peaks for Samples 1 to 5 after normalization.^[32]

4.2.2 Catalytic hydrogenation of 4-nitrostyrene

Hydrogenation reactions are important to produce valuable synthetic intermediates in the synthesis of pharmaceuticals, polymers, herbicides, and other fine chemicals.^[14] In heterogeneous catalysis, it is challenging to achieve chemoselective hydrogenation of molecules that contain several reducible groups.^[17] As a proof-of-concept application, in order to study the correlation between the chemoselectivity/catalytic activity and the crystallinity of noble metal catalysts, the heterophase Pd nanosheets are used to catalyze the hydrogenation of 4-nitrostyrene (NS), which is commonly used as the model reaction.^[16, 18, 19] The products generated by the hydrogenation of NS are presented in Figure 4.7a. The selective hydrogenation of generates 4-nitroethylbenzene (EN) and 4-aminostyrene (AS), respectively, and the hydrogenation of both C=C bond and nitro group generates the fully hydrogenated product, i.e., 4-ethylbenzenamine (EA). The reaction

process was tracked by gas chromatography (GC), and the products were determined by GC-mass spectrometry (GC-MS) and nuclear magnetic resonance spectroscopy. The hydrogenation reaction was conducted at room temperature under H_2 atmosphere (see section 3.3.2 for details). Figure 4.7b-e show the time-dependent catalytic curves for the hydrogenation of NS by Samples 1-5, respectively, in which the conversion curve (blue) describes the percentage of NS converted to the products, whereas the selectivity curve (red, black or green) describes the molar ratio of the corresponding product (EN, EA, or AS) in the total products.

Based on the experimental results, it was found that Sample 1 possessed the high selectivity (>99%) toward the generation of EN throughout the reaction (Figure 4.7b), and a 100% conversion of NS was achieved after 240 min of hydrogenation (see Figures A1-3 in Appendix for the characterization of the catalytic products). The excellent selectivity toward EN (>99%) did not decrease even after hydrogenation for 30 h (Figure A4, Appendix), meaning that EN cannot be converted to the fully hydrogenated product (EA) by using Sample 1 as the catalyst. In comparison, in the hydrogenation reaction catalyzed by Sample 5 (Figure 4.7e), i.e., the Pd nanosheets with the highest crystallinity among Samples 1-5, EN was the main product at the initial stage. As the hydrogenation reaction time was elongated, EN was gradually converted to the fully hydrogenated product EA. After hydrogenation for 240 min, EA was the only product with a high purity over 99%.

Figure 4.7 Catalytic performance of the heterophase Pd nanosheets with different crystallinities. (a) Hydrogenation reaction of NS. (b-e) Time-dependent catalysis in the hydrogenation of NS by using Samples 1-5, respectively, as the catalysts. Reaction conditions: room temperature, H_2 balloon. ^[32]

Besides the chemoselectivity, the catalytic activity is also dependent on the crystallinity of the heterophase Pd nanosheets. Compared with Sample 1, Sample 2 also exhibits high chemoselectivity (>99%) of EN, but its catalytic activity is higher than Sample 1. It only takes 150 min to achieve the 100% conversion of NS (Figure 4.7c). To the best of our knowledge, Sample 2 is the best heterogeneous catalyst to hydrogenate the C=C double bond under mild conditions with high catalytic selectivity (>99%) and 100% conversion (Table 4.1). Comparing the time-dependent catalytic curves of Samples 3-5 (Figure 4.7c-e), all of the catalysts produce the fully hydrogenated product, i.e., EA. Among them, Sample 4 shows the highest catalytic activity, which completely converted NS to the fully hydrogenated product (EA) with a purity of >99% in 60 min (Figure 4.7d). Moreover, Samples 2 and 4 also exhibited good stability. The catalytic selectivity was retained after recycling for five times (Figure 4.8).

Table 4.1 Summary of the chemoselectivity in the hydrogenation of 4-nitrostyrene or 3-nitrostyrene.

Catalyst	P (Bar)	T (°C)	t (h)	Conversion (%)	Selectivity (%)			Ref.
					EN	AS	EA	
Pd/SiO ₂ ^a	H ₂ flow	70	1	100	63	0	26	[16]
Pd ₁₃ Ga ₅ ^a	H ₂ flow	70	1	22	>99	0	0	
Pd ₁₃ Pb ₉ ^a	H ₂ flow	70	1	10	5	93	2	
Pd ₃ Bi ^a	H ₂ flow	70	1	10	27	43	25	
PdZn ^a	H ₂ flow	70	1	7	>99	0	0	
Rh ^a	H ₂ flow	70	1	<1	>99	0	0	
Rh ₃ Pb ₂ ^a	H ₂ flow	70	1	15	>99	0	0	
Pt/TiO ₂ (thioglycerol) ^a	10	80	0.5	100	--	97	--	[18]
Pt/TiO ₂ (α -lipoic acid) ^a	10	80	0.5	100	0	100	0	
Co _{0.23} Ru _{0.77} ^a	1	25	12	100	1	99	0	[24]
Au/TiO ₂ ^b	9	130	6	98.5	0	95.9	3.9	[13]
Pd/C ^b	9	130	0.03	99.0	24.1	0	75.9	
Pt/C ^b	9	130	0.03	96.7	44.8	2.9	52.3	
Au-Pd/TiO ₂ ^b	9	130	0.03	99.5	57.0	0	43	
Pt/Al ₂ O ₃ ^b	10	50	1	100	76.4	23.6	0	[15]
Pt/FeO _x ^b	10	50	1	97.8	3.9	96	0.1	
Pt@Ionic Liquid ^b	1	R. T.	4	91	61	11	6	[17]
Pt-B@Ionic Liquid ^b	1	R. T.	2	90	83	3.1	3.4	
Au ₂₅ /ZnAl- HT-300 ^b	10	90	9	100	0	99	1	[25]
1.5 wt % Au- TiO ₂ ^b	10	135	9	100	2.1	20.7	52.7	
Sample 1 ^a (~11%) ^c	1	R. T.	4	100	>99	0	<0.1	This work
Sample 2 ^a (~19%) ^c	1	R. T.	2.5	100	>99	0	<0.1	
Sample 3 ^a (~65%) ^c	1	R. T.	6	100	0	0	>99	
Sample 4 ^a (~83%) ^c	1	R. T.	1	100	0	0	>99	
Sample 5 ^a (~95%) ^c	1	R. T.	4	100	0	0	>99	

Abbreviations:

EN: 4-nitroethylbenzene and 3-nitroethylbenzene. AS: 4-aminostyrene and 3-aminostyrene. EA: 4-ethylbenzenamine and 3-ethylbenzenamine. R. T.: Room temperature. a: Hydrogenation of 4-nitroethylbenzene. b: Hydrogenation of 3-nitroethylbenzene. c: Percentage of crystalline phase.

Figure 4.8 Recycling tests of Samples 2 and 4 in the hydrogenation of NS. Reaction conditions: room temperature, H₂ balloon, 150 min for Sample 2, 60 min for Sample 4.^[32]

The time-dependent catalytic curves of Samples 1-5 (Figure 4.7b-e) show that the amorphous phase-dominant samples (Samples 1 and 2) exhibit higher chemoselectivity towards the hydrogenation of C=C double bonds and lower catalytic activity, compared with the crystalline phase-dominant samples (Samples 3-5). The possible reasons can be explained as follows. Firstly, Sample 1 presents a higher binding energy than Sample 5 (Figure 4.6), indicating the electron density around Pd atoms in amorphous phase is lower than that in crystalline phase. It suggests the weaker Pd-Pd metallic bonds in amorphous phase, leading to a lower surface energy.^[26] Therefore, the amorphous Pd surface would preferentially adsorb and hydrogenate the groups with lower polarity, i.e., C=C bonds, but impede the hydrogenation of the functional groups with higher polarity, i.e., nitro groups, resulting in the excellent chemoselectivity in the amorphous phase-dominant samples (Samples 1 and 2). Secondly, the lower electron density around Pd atoms in the amorphous phase-dominant samples (Samples 1 and 2) could result in a stronger surface binding with H atoms, and thus reduce the hydrogenation activity.^[27] Thirdly, although the same ligand is used during our synthesis in order to eliminate the ligand effect in catalysis, the different

atomic arrangement in different phases indicates the different coordination environment at the ligand/metal interface,^[28, 29] which may affect the chemoselectivity and catalytic activity.^[30, 31] However, there is still lack of effective technique to directly characterize the detailed surface and interface structures of metal nanomaterials.^[31]

4.3 Conclusion

In summary, a one-pot wet-chemical method for synthesizing amorphous/crystalline heterophase Pd nanosheets has been developed. The crystallinity of these nanosheets can be easily tuned by simply changing the reaction temperature. These nanosheets are used as the heterogeneous catalysts to study their chemoselectivity in hydrogenation of 4-nitrostyrene. It is found that the crystallinities of amorphous/crystalline heterophase Pd nanosheets play a critical role in the chemoselectivity and catalytic activity in the 4-nitrostyrene hydrogenation. The amorphous phase-dominant Pd nanosheets show an excellent chemoselectivity, while those crystalline phase-dominant Pd nanosheets exhibit a higher catalytic activity. This work not only presents a novel synthetic method for heterophase nanomaterials, but also provides a new strategy in controlling the chemoselectivity and catalytic activity for fine chemical industries. It is believed that more unique properties and promising applications in catalysis, optics, electronics, magnetism, mechanics, photothermal therapy, etc. will be discovered based on the synthesis of novel heterophase nanomaterials.

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Chapter 5*

Aging Effect Study on Amorphous/Crystalline Heterophase PdCu Nanosheets

This chapter will discuss the experimental results of aging effects on amorphous/crystalline heterophase PdCu nanosheets. Based on the study presented in Chapter 4, the one-pot wet-chemical synthesis method is further extend to the synthesis of two types of amorphous/crystalline heterophase PdCu nanosheets, in which one is amorphous phase-dominant and the other one is crystalline phase-dominant. The aging process of the synthesized PdCu nanosheets is conducted at ambient conditions, during which their crystallinity increases, accompanied with changes in some physicochemical properties. As a proof-of-concept application, their aging effect on catalytic hydrogenation of 4-nitrostyrene is investigated. As a result, the amorphous phase-dominant nanosheets initially show excellent chemoselectivity. After aging for 14 days, their catalytic activity is higher than that of crystalline phase-dominant nanosheets.

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5.1 Introduction

In the previous chapter, i.e., Chapter 4, the wet-chemical synthesis of a series of amorphous/crystalline heterophase Pd nanosheets has been discussed, which showed heterophase-dependent catalytic selectivity and activity in the hydrogenation of 4-nitrostyrene. This work presents a novel synthetic method for heterophase catalysts, but it is for monometallic nanomaterials. It has been widely reported that bimetallic/multimetallic nanomaterials can exhibit enhanced catalytic performance compared with the monometallic components, arising from the synergistic effects between different elements.^[1] In view of this, to enrich the family of heterophase nanomaterials, synthesis method for heterophase Pd nanosheets is successfully extended to prepare PdCu nanosheets with controlled amorphous/crystalline heterophase structures.

This work presents a novel synthetic method for heterophase nanomaterials by kinetic control, i.e., by controlling the reaction temperature. Besides reaction kinetics, thermodynamics is another important factor in controlling the phase of nanomaterials, such as changing the thermodynamic stability of different phases by size control,^[2] phase transformation from metastable phase to stable phase by thermal annealing.^[3] As known, amorphous phase is a metastable phase in metals, which tends to transform into thermodynamically stable crystalline phase. Hence, the properties of amorphous/crystalline heterophase nanomaterials, surface ligands are further studied from thermodynamics point of view, i.e., investigating the aging effect under ambient conditions.

During the aging process, the crystallinity of the PdCu nanosheets gradually increased. As a result, the surface ligands, binding energy of Pd and catalytic performance of the nanosheets were changed, which were evidenced by Fourier-transformed infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS) and catalytic reaction measurements, respectively. The results are discussed in detail in the following sections.

5.2 Results and Discussion

5.2.1 Aging effect on the crystallinity

For the first time, the amorphous/crystalline heterophase PdCu nanosheets with high purity (Figure 5.1a,e) have been synthesized (see 3.4.1 for details). The amorphous phase-dominant PdCu nanosheets (denoted as *a*-PdCu, Figure 5.1b) were synthesized at reaction temperature of 40 °C. The spherical aberration-corrected scanning transmission electron microscopy-high angle annular dark-field (C_s -corrected STEM-HAADF) image (Figure 5.1c) shows that the most area of the obtained nanosheet is amorphous, which is further proved by the weak diffuse ring in the selected area-electron diffraction (SAED) pattern (Figure 1d) and the absence of peaks in the X-ray diffraction (XRD) pattern (Figure 5.2). When the reaction temperature changed to 80 °C, the crystalline phase-dominant PdCu nanosheets (denoted as *c*-PdCu, Figure 5.1f) were synthesized. The C_s -corrected STEM-HAADF image shows that the most area of the obtained nanosheet is crystalline (Figure 5.1g), and the average interplanar spacing of most crystalline areas is measured to be 2.3 Å, which can be assigned to the 1/3(422) spacing of *fcc* structure but is slightly smaller than that of Pd^[4], suggesting that the majority of the exposed facets is {111} plane^[4, 5] and Cu atoms are incorporated into Pd lattice. The good crystallinity is further proved by the clear diffraction rings in the SAED pattern (Figure 5.1h) and the strong peaks in the XRD pattern (Figure 5.2). Compared with the pure Pd (#00-046-1043), the XRD peaks of *c*-PdCu slightly shifted to higher angles, indicating the smaller crystal lattice due to the incorporation of Cu atoms. Both types of the PdCu nanosheets have an ultrathin thickness of ~1.2 nm, as measured by the folded edges in TEM images (Figure 5.3). This value is ~2 nm thinner than that measured by atomic force microscopy (AFM) (Figure 5.4), due to the presence of ligands on the surfaces of nanosheets.^[6, 7] In both *a*-PdCu and *c*-PdCu, the Pd and Cu atoms are uniformly distributed through the whole nanosheets (Figure 5.5a,b), and the Cu content is ~12 at% based on both energy-dispersive X-ray spectroscopy (EDS) (Figure 5.5c,d) and inductively coupled plasma-optical emission spectroscopy (ICP-OES).

Figure 5.1 (a) Low- and (b) high-magnification TEM images, (c) C_s -corrected STEM-HAADF image (the areas within yellow curves are crystalline domains), and (d) SAED pattern of the a -PdCu nanosheets. (e) Low- and (f) high-magnification TEM images, (g) C_s -corrected STEM-HAADF image, and (h) SAED pattern of the c -PdCu nanosheets. ^[22]

Figure 5.2 XRD patterns of the as-synthesized a -PdCu and c -PdCu nanosheets. ^[22]

Figure 5.3 TEM images of a folded as-synthesized (a) *a*-PdCu and (b) *b*-PdCu nanosheet, showing the folded edge with measured width of ~ 1.2 nm. ^[22]

Figure 5.4 AFM images of the as-synthesized (a) *a*-PdCu and (b) *b*-PdCu nanosheet, showing the folded edge with measured thickness of ~ 3.2 nm. ^[22]

Figure 5.5 STEM image and the corresponding EDS mappings of the as-synthesized (a) *a*-PdCu and (b) *c*-PdCu nanosheets. EDS elemental spectra of (c) *a*-PdCu and (d) *c*-PdCu nanosheets, in which their elemental compositions are shown.^[22]

After aging, i.e., being stored in hexane under ambient conditions, for 14 days, the morphology of both *a*-PdCu and *c*-PdCu remained unchanged (Figure 5.6a,c), and there is no observable element segregation or leakage during the aging process (Figure 5.7). However, more crystalline areas were observed in *a*-PdCu (Figure 5.6b), while no obvious change was observed in *c*-PdCu (Figure 5.6d). In the XRD pattern of *a*-PdCu (Figure 5.8), some weak peaks appeared, further indicating that the crystallinity of *a*-PdCu slightly increased. Noble metals normally have crystalline structures due to the strong metallic bonding,^[8] hence their amorphous phase is thermodynamically unstable, which tends to transform into crystalline phase.

Figure 5.6 (a) TEM image and the (b) C_s -corrected STEM-HAADF image (the areas within yellow curves are crystalline domains) of *a*-PdCu nanosheets after aging for 14 days. (a) TEM image and the (b) C_s -corrected STEM-HAADF image (the areas within yellow curves are crystalline domains) of *c*-PdCu nanosheets after aging for 14 days.^[22]

Figure 5.7 The STEM images and corresponding EDS mappings of (a) α -PdCu and (b) c -PdCu after aging for 14 days. The EDS elemental spectra of (c) α -PdCu and (d) c -PdCu after aging for 14 days. ^[22]

Figure 5.8 Comparison of the XRD patterns of the as-synthesized (0 day) α -PdCu and the α -PdCu after aging for 14 days. ^[22]

5.2.2 Aging effect on the surface ligands

During the aging process, FTIR was used to monitor the change of surface ligands on the heterophase PdCu nanosheets. The normalized FTIR spectra of *a*-PdCu and *c*-PdCu are shown in Figure 5.9. For the as-synthesized *a*-PdCu and *c*-PdCu nanosheets (Figure 5.9a), the peaks located within 2800-3000 cm^{-1} are attributed to the $-\text{CH}_2-$ stretching,^[9, 10] mainly arising from the alkyl chain of octanoic acid (Figure 5.10a). In the FTIR spectrum of $\text{Mo}(\text{CO})_6$ (Figure 5.10b), there is a strong and broad absorption band centered at ~ 1900 cm^{-1} , which is assigned to the CO coordination groups.^[11] Therefore, in the FTIR spectra of PdCu nanosheets, the broad band centered at ~ 1860 cm^{-1} is assigned to the absorption of CO groups due to the decomposition of $\text{Mo}(\text{CO})_6$, indicating the intermediate complexes containing CO groups are also present on the surface of final products. This is consistent with nanomaterials synthesized using CO gas as the reductant, in which CO is present on the products.^[4] For the as-synthesized samples (Figure 5.8a), *a*-PdCu showed a relatively stronger absorption peak of CO groups as compared to the *c*-PdCu, implying that the amorphous phase-dominant nanosheets adsorbed more CO groups.

Figure 5.9 (a) FTIR spectra of the as-synthesized *a*-PdCu and *c*-PdCu. FTIR spectra of (b) *a*-PdCu and (c) *c*-PdCu with different aging time. ^[22]

As the aging time increased, the relative intensity of CO absorption for both *a*-PdCu (Figure 5.9b) and *c*-PdCu (Figure 5.9c) gradually decreased with respect to the $-\text{CH}_2-$ absorption. However, after aging for 14 days, the CO absorption was still observed in the FTIR spectrum of the *a*-PdCu, while it disappeared in the FTIR spectrum of *c*-PdCu. As discussed above, although the crystalline domains in the *a*-PdCu increased after aging for

14 days, the crystallinity of *a*-PdCu is still lower than that of *c*-PdCu, resulting in the different ratios of the adsorbed CO to octanoic acid on their surface.

Figure 5.10 FTIR spectra of (a) octanoic acid and (b) $\text{Mo}(\text{CO})_6$.^[22]

5.2.3 Aging effect on the binding energy

The aging effects on the electronic properties of heterophase PdCu nanosheets were analyzed by XPS. The XPS results (Figure 5.11a) show that the Pd element in both *a*-PdCu and *c*-PdCu is predominantly in metallic state. Comparing the as-synthesized samples, the Pd element in *a*-PdCu shows higher binding energy compared to *c*-PdCu (Figure 5.11b). Eventually, after aging for 14 days, although the binding energy peaks of *a*-PdCu shifted to lower value, it is still higher than that of *c*-PdCu (Figure 5.11c). This result is consistent with previous works,^[6, 12] which could be due to the differences of crystallinities and surface ligands.

Figure 5.11 (a) Comparison of XPS spectra for the as-synthesized *a*-PdCu and *c*-PdCu (i.e., aging for 0 day), and the samples after aging for 14 days. The magnification of the normalized (b) Pd 3d_{3/2} and (c) Pd 3d_{5/2} peak. ^[22]

During the aging process, the changes of the binding energies are shown in Figure 5.12 in detail. As the aging time elongated, both the *a*-PdCu and *c*-PdCu samples show similar trend in the binding energy change of Pd. During aging, in the first three days, the binding energy peaks shifted to lower value (red shift), which is due to not only the increase in crystallinity but also the desorption of CO group, as the CO group is electron withdrawing and can result in higher binding energy of the underlying metal atoms. While from the third day onwards, the binding energy peaks shifted to the higher value (blue shift) (Figure 5.12), which could be due to the adsorption of oxygen.^[13] During the aging process, the surface atoms of PdCu nanosheets were gradually oxidized, as shown by the deconvoluted XPS spectra of *a*-PdCu samples, in which the relative intensity of Pd²⁺/Pd⁰ clearly increased after aging for 14 days (Figure 5.13). Surface oxidation can greatly increase the distance of nearest neighbor Pd-Pd bond and lead to a significant charge transfer from Pd to O,^[13] which could also cause the binding energy peaks of Pd shifting to higher energy level. In fact, all these processes, including the crystallinity increase, desorption of ligands, and surface oxidation took place concurrently during the aging process, but the dominant process may be different in the whole aging process, thus the binding energy peaks showed red shift followed by blue shift.

Figure 5.12 (a) XPS spectra of Pd 3d in *a*-PdCu samples with different aging time. (b,c) Magnification of normalized Pd 3d_{5/2} and Pd 3d_{3/2} peaks in (a), respectively. (d) XPS spectra of Pd 3d in *c*-PdCu samples with different aging time. (e,f) Magnification of normalized Pd 3d_{5/2} and Pd 3d_{3/2} peaks in (d), respectively.^[22]

Figure 5.13 XPS spectra of Pd 3d in *a*-PdCu: (a) the as-synthesized sample (i.e., aging for 0 day), and (b) the sample after 14-day aging.^[22]

5.2.4 Aging effect on the catalytic performance

As known, Pd and Pd-based alloys possess good catalytic performance in hydrogenation reactions,^[14-16] which are very important in the industrial and fine chemical fields^[17, 18]. Herein, as a proof-of-concept application and in order to get deeper insight on the previous

work reported in Chapter 4, the aging effect on the selective hydrogenation of 4-nitrostyrene (NS) was studied, which is commonly used as the model reaction^[19, 20], using the heterophase PdCu nanosheets as catalysts. The hydrogenation reaction of NS was conducted at room temperature in one atm H₂ atmosphere (see section 3.4.2 for details), and all the possible products are shown in Figure 5.14a. The 1-ethyl-4-nitrostyrene (EN) and 4-aminostyrene (AS) are the products for the hydrogenation of C=C and -NO₂, respectively, and 4-ethylbenzenamine (EA) is the fully hydrogenated products. To understand the catalytic activity with respect to the aging time of heterophase PdCu nanosheets, the amount of catalyst was kept low so that the activity differences during the hydrogenation reaction were significant. In addition, based on the kinetic curves of the catalytic hydrogenation, since the catalysts will lose their activity with extended reaction time (the conversion/selectivity curves tend to be flat after 120-min reaction), the conversion of substrate and the selectivity of products within 30-min reaction were used as the indicator of catalytic activity in the following discussion (Figure 5.16). The *a*-PdCu after aging for 1 day showed very high selectivity (>99.9%) towards EN, which was maintained even after 4-hour reaction (Figure 5.14b). This high selectivity towards EN was maintained after aging for 2 days (Figure 5.14c), meanwhile, the conversion rate of NS was increased, indicating that the catalytic activity was increased. After aging for 3 days and onwards, *a*-PdCu did not show selectivity towards EN, generating both EN and EA (Figure 5.14d-f), but the catalytic activity was still gradually increased with time, as evidenced by the increased generation rate of the fully hydrogenated product, i.e., EA (Figure 5.16a). In contrast, the *c*-PdCu nanosheets showed different behavior during the aging process, which did not show chemoselectivity towards EN through the whole aging process (Figure 5.15). As for the catalytic activity, based on the selectivity of the fully hydrogenated product, i.e., EA, the catalytic activity first slightly increased after aging from 1 day to 3 days, and then it slowly decreased (Figure 5.16b).

Figure 5.14 (a) Hydrogenation reaction of NS. (b-f) The kinetic curves showing the catalytic performance of *a*-PdCu after aging for 1 day, 2 days, 3 days, 7 days, and 14 days, respectively. ^[22]

Figure 5.15 (a-d) The kinetic curves showing the catalytic performance of *c*-PdCu after aging for 1 day, 3 days, 7 days, and 14 days, respectively. ^[22]

Figure 5.16 The catalytic results of 30-min hydrogenation reaction using (a) *a*-PdCu and (b) *c*-PdCu with different aging time as catalysts. ^[22]

In the as-synthesized heterophase *a*-PdCu and *c*-PdCu nanosheets, the different crystallinities and different surface ligands result in the different electronic structures of the surface metal atoms, which eventually lead to the different selectivity in the catalytic hydrogenation reaction. This could also account for the selectivity change of the *a*-PdCu sample after aging for 3 days. Importantly, during the aging process, the *a*-PdCu showed an increased catalytic activity and eventually surpassed the *c*-PdCu sample, which could result from their different amorphous/crystalline heterophase structures. In *a*-PdCu, although the crystallinity increased with prolonged aging time, the size of crystalline domains is much smaller than that in the *c*-PdCu sample, as evidenced by the HRTEM image (Figure 5.6b,d) and the weak peak in the XRD pattern (Figure 5.8). As a consequence, the amorphous/crystalline phase boundaries in the aged *a*-PdCu samples significantly increased compared with the as-synthesized *a*-PdCu, which could contribute to the enhanced catalytic activity.^[21]

5.3 Conclusion

In conclusion, we have prepared two kinds of amorphous/crystalline heterophase PdCu nanosheets by a facile one-pot wet-chemical method, of which one is amorphous phase-dominant (*a*-PdCu) and the other one is crystalline phase-dominant (*c*-PdCu). Systematic studies were conducted to investigate the aging effect on the structures, properties and catalytic performance of the heterophase PdCu nanosheets. It was found that in the first 2 days of the aging process, the *a*-PdCu showed very high chemoselectivity in the hydrogenation of 4-nitrostyrene, while the *c*-PdCu did not show chemoselectivity. After 3-day aging, the *a*-PdCu lost the chemoselectivity, but its catalytic activity gradually increased, while the catalytic activity of *c*-PdCu gradually decreased and eventually became lower than that of the *a*-PdCu after aging for 14 days. Based on the structural analysis, FTIR and XPS results, the differences in chemoselectivity and catalytic activity of heterophase PdCu nanosheets could be attributed to the different amorphous/crystalline heterophase structures, surface ligands and binding energies. This work demonstrates the intimate correlation between the heterophase structure and their physiochemical properties, which may inspire more discoveries in the preparation and mechanism studies of

amorphous/crystalline heterophase structures. Importantly, the amorphous phase-dominant sample exhibited promising catalytic performance during the aging process, indicating that the metastable phase deserves intensive research effort and more interesting phase-dependent functions are expected to be discovered. This work on heterophase structures provides a strategy for phase engineering of nanomaterials for various promising applications.

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Chapter 6

Ligand Exchange-induced Amorphization of Pd Nanomaterials for Highly Efficient Electrocatalytic Hydrogen Evolution Reaction

This chapter presents the results on the discovery of a unique thiol molecule, namely bismuthiol I, which can induce the transformation of Pd nanomaterials from face-centered cubic (fcc) phase into amorphous phase without destroying their integrity. This ligand-induced amorphization is realized by post-synthetic ligand exchange under room conditions and applicable to fcc Pd nanomaterials with different capping ligands. Importantly, the obtained amorphous Pd nanoparticles exhibit remarkably enhanced activity and excellent stability towards electrocatalytic hydrogen evolution in acidic solution. X-ray photoelectron and X-ray absorption fine structure analyses imply that modified electronic structure and increased bond length in amorphous structure could weaken the interaction between Pd and hydrogen, which may account for the improved catalytic activity.

6.1 Introduction

In the exploration of highly efficient electrocatalysts for clean energy generation, amorphous materials have demonstrated superior performance compared with the crystalline counterparts due to the abundant active sites in amorphous structure. As a typical example, amorphous molybdenum sulfide has been generally considered to exhibit better activity than its crystalline counterpart towards the electrocatalytic hydrogen evolution reaction (HER).^[1, 2] Similarly, it has also been reported that other amorphous materials, such as metal oxide,^[3, 4] metal hydroxide^[5] and metal phosphate,^[6] outperform their crystalline counterparts in various electrocatalytic reactions. Therefore, constructing amorphous structures is an effective strategy to enhance the performance of electrocatalysts.

Among the different kinds of materials for electrocatalysis, noble metals possess intrinsically high activity and excellent stability. However, due to the strong metallic bonds between noble metal atoms,^[7] up to now, it is still very challenging to prepare amorphous noble metal nanomaterials. Among the noble metals, Pd has more reserves and lower cost than Pt, thus it is a promising alternate to the prevalent Pt catalyst for various electrocatalytic reactions, such as formic acid oxidation, ethanol oxidation and HER.^[8] Based on the aforementioned superior performance of amorphous materials, developing amorphous structure for Pd nanomaterials is expected to be able to further enhance their catalytic activity, but there is still lack of a facile, effective and versatile method to prepare amorphous Pd nanomaterials for electrocatalytic applications.

Herein, the discovery of a unique thiol molecule, namely bismuthiol I (1,3,4-Thiadiazole-2,5-dithiol, $C_2H_2N_2S_3$) is reported, which can transform face-centered cubic (*fcc*) Pd nanomaterials into amorphous phase by post-synthetic ligand exchange under ambient conditions. Taking oleylamine-capped *fcc* Pd nanoparticles (~6 nm) as an example, time-dependent study shows that bismuthiol I can induce the amorphization of the outer atoms at the early stage, which causes lattice expansion of inner atoms and eventually transforms the whole nanoparticle into amorphous phase. This ligand exchange method is also applicable to other *fcc* Pd nanomaterials with different morphologies and different ligands,

including Pd nanosheets capped by octatonic acid, and Pd nanocubes capped by polyvinylpyrrolidone. Importantly, the resulted amorphous Pd nanoparticles show dramatically enhanced activity towards electrocatalytic HER compared with the original crystalline nanoparticles.

6.2 Results and Discussion

6.2.1 Ligand exchange-induced amorphization of Pd nanoparticles

The monodisperse crystalline Pd nanoparticles were first synthesized by a reported method with slight modification.^[9] The as-synthesized Pd nanoparticles (Figure 6.1a) are capped by oleylamine (Pd NPs-OAm) with an average size around 6 nm and possess good crystallinity, as evidenced by the selected area electron diffraction (SAED) pattern (inset in Figure 6.1a) and high-resolution transmission electron microscopy (HRTEM) image (Figure 6.1d). The corresponding X-ray diffraction (XRD) peaks (Figure 6.1c) can be indexed to *fcc* Pd (PDF #46-1043). Due to the strong interaction between Pd and thiol group, the oleylamine on the as-synthesized Pd nanoparticles can be easily replaced by thiol molecules. The ligand exchange process is conducted by simply mixing the Pd NPs-OAm with bismuthiol I solution at room temperature (see section 3.5.2 for details). After mixing for 1 hour, the crystallinity of the nanoparticles was greatly reduced (denoted as Pd NPs-Bis-1h), as confirmed by the reduced peak intensity in the XRD pattern (Figure 6.1c). HRTEM image shows that the crystalline structure of the nanoparticles transformed into a core-shell structure consisting of crystalline core and amorphous shell (Figure 6.1e). In crystalline phase, Pd atoms are arranged in close-packed pattern, while in amorphous phase, Pd atoms are randomly arranged in non-close-packed pattern. As a result, lattice expansion would occur in the crystalline core to accommodate the lattice discrepancy between the amorphous shell and crystalline core.^[10] The lattice expansion is indicated by the peak shift in the XRD patterns (Figure 6.1c). The peaks of Pd NPs-Bis-1h shift to smaller diffraction angles compared with those of Pd NPs-OAm, implying that lattice constants are increased during the ligand exchange process. As expected, by extending the ligand exchange time, the crystalline portion in the nanoparticles gradually becomes smaller, as indicated by the

gradually decreased intensity of the diffraction peaks in the XRD patterns (Figure 6.1c), eventually generating amorphous Pd nanoparticles capped by bismuthiol I (Pd NPs-Bis-24h) after ligand exchange for 24 h (Figure 6.1f).

Figure 6.1 (a) TEM image and the corresponding SAED pattern of Pd NPs-OAm. Inset in the upper right: molecular structure of oleylamine. (b) TEM image and the corresponding SAED pattern of Pd NPs-Bis-24h. Inset in the upper right: molecular structure of bismuthiol I. (c) XRD patterns of Pd NPs-OAm, and Pd NPs-Bis obtained after ligand exchange for 1, 8 and 24 h. The green and blue dash lines indicate the peak positions of Pd NPs-Bis-1h and Pd NPs-OAm, respectively. (d-f) HRTEM images of a single Pd NP-OAm (d), Pd NP-Bis-1h (e), and Pd NP-Bis-24h (f).

The chemical states of the elements in Pd nanoparticles are characterized by X-ray photoelectron spectroscopy (XPS). The XPS spectra of Pd 3d (Figure 6.2a) show that the Pd element in both Pd NPs-OAm and Pd NPs-Bis-24h is predominantly in metallic state, but the Pd 3d peaks of Pd NPs-Bis-24h slightly shift to higher energy, which could be due to the presence of thiol molecules^[11-13] and the amorphous structure^[14, 15]. The deconvoluted XPS spectra of Pd NPs-OAm (Figure 6.2b) show that a little amount of Pd is in oxidation state due to the surface oxidation, which is common in metallic

nanomaterials. However, in the deconvoluted spectra of Pd NPs-Bis-24h (Figure 6.2c), the intensities of the oxidation peaks are obviously stronger than those in Pd NPs-OAm, which could be due to the formation of palladium sulfide (PdS_x)^[16] on the nanoparticle surface. The chemical states of S in Pd NPs-Bis-24h are more complicated. As shown in Figure 6.2d, the main peak located at 163.8 eV is assigned to thiolate (SR^-).^[16] The second strongest peak located at 162.4 eV is assigned to sulfides, indicating the formation of PdS_x , which is consistent with the above analysis of Pd 3d spectrum (Figure 6.2c). The other two small peaks at 165.0 eV and 168.5 eV are related to physisorbed thiols and oxidized S-species, respectively.

Figure 6.2 (a) Comparison of XPS spectra of Pd 3d in Pd NPs-OAm and Pd NPs-Bis-24h. (b-d) XPS spectra of Pd 3d in Pd NPs-OAm (b), Pd 3d in Pd NPs-Bis-24h (c), and S 2p in Pd NPs-Bis-24h (d), respectively.

Moreover, X-ray absorption fine structure (XAFS) was measured to further understand the electronic structures and atomic structures of the Pd nanoparticles. X-ray absorption near-edge structure (XANES) spectra (Figure 6.3a) show that the Pd NPs-OAm, Pd NPs-Bis-1h and Pd NPs-Bis-24h display similar pattern with the Pd foil, indicating that the Pd element in all these nanoparticles is mostly in metallic state, which is consistent with the aforementioned XPS results. The Fourier-transformed extended X-ray absorption fine structure (EXAFS) spectra (Figure 6.3b) provide information on the atomic structure. The main peak located at $\sim 2.46 \text{ \AA}$ (without phase shift correction) in the EXAFS spectra of Pd foil represents the nearest coordination shells of Pd atoms, which means the nearest average Pd-Pd bond length. Compared with Pd foil, the Pd NPs-OAm show dramatic reduction in the peak intensity due to the size effect. As particle size decreases, the ratio of surface atoms to inner atoms increases, leading to a decrease in the average coordination number of Pd atoms and thus reducing the peak intensity of the nearest Pd-Pd coordination shell.^[17, 18] In comparison, the main peaks in the spectra of Pd NPs-Bis-1h and Pd NPs-Bis-24h shift to larger distance with respect to Pd NPs-OAm. For the Pd NPs-Bis-1h, the core of the nanoparticles is still in crystalline phase, thus this peak shift indicates that the Pd-Pd bond length in the core is longer than that in the Pd NPs-OAm, which agrees with the aforementioned peak shift in the corresponding XRD pattern. In addition of peak shift, the Pd NPs-Bis-1h and Pd NPs-Bis-24h also show reduced peak intensity compared with Pd NPs-OAm. Since the particle size was not reduced after ligand exchange (Figure 1a,b), this reduction in peak intensity is attributed to the increased atomic disordering^[17, 18]. As expected, the Pd NPs-Bis-24h show even lower peak intensity compared with Pd NPs-Bis-1h, because the atomic disordering increases when extending the ligand exchange duration. Furthermore, it is noted that in the EXAFS spectra of Pd NPs-Bis-24h, there is a weak peak centered at $\sim 1.8 \text{ \AA}$, which is assigned to the Pd-S bond,^[10] suggesting the formation of PdS_x and consistent with XPS analyses.

Figure 6.3 (a) XANES and (b) Fourier-transformed EXAFS spectra of Pd foil, Pd NPs-OAm, Pd NPs-Bis-1h and Pd NPs-Bis-24h.

6.2.2 Generality of the ligand exchange-induced amorphization

In addition to oleylamine-capped nanoparticles, bismuthiol I treatment can also transform other *fcc* Pd nanomaterials with different shapes and different capping ligands into amorphous phase, verifying the generality of this ligand-induced amorphization method. For example, the ultrathin Pd nanosheets with thickness around 1 nm (Figure 6.4a, a1), synthesized by our previously reported method,^[14] have very good crystallinity (Figure 6.4a2) with octanoic acid on the surface (denoted as Pd NSs-OA). After ligand exchange with bismuthiol I, the *fcc* structure of the Pd nanosheets transformed into amorphous structure (denoted as Pd NSs-Bis-24h) (Figure 6.4b, b1, b2) without destroying the morphology. Due to the ultrathin thickness of nanosheets and the strong interaction between Pd and thiol bond, usually nanosheets can be easily destroyed (Figure 6.5) or become porous after ligand exchange with thiol molecules^[13]. Thus, bismuthiol I is a unique thiol molecule that can be used to prepare amorphous nanomaterials while preserving the ultrathin nanostructures.

Figure 6.4 (a) Low-magnification TEM image with the corresponding SAED pattern (inset), (a1) high-magnification TEM image, and (a2) HRTEM image of Pd NSs-OA. Upper inset in (a): the molecular structure of octanoic acid. (b) Low-magnification TEM image with the corresponding SAED pattern (inset), (b1) high-magnification TEM image, and (b2) HRTEM image of Pd NSs-Bis-24h. Upper inset in (b): the molecular structure of bismuthiol I.

Figure 6.5 (a) TEM image and (b) SAED pattern of Pd NSs-OA after ligand exchange with 1-octadecanethiol. (c) TEM image and (d) SAED pattern of Pd NSs-OA after ligand exchange with 3-methylmercapto-5-mercapto-1,2,4-thiadiazole.

As another example, *fcc* Pd nanocubes with an average edge length around 10 nm (Figure 6.6a, a1, a2), synthesized by a previously reported method,^[19] are single crystalline (Figure 6.6a2), which is different from the polycrystalline nanoparticles and nanosheets. In addition, the Pd nanocubes are capped by poly(vinylpyrrolidone) (denoted as Pd NCs-PVP),

which is more bulky and has stronger interaction with Pd compared with oleylamine and octanoic acid. Nevertheless, bismuthiol I can easily transform the nanocubes into amorphous phase (denoted as Pd NCs-Bis-24h) (Figure 6.6b, b1, b2). XRD characterizations (Figure further confirm the significantly reduced crystallinity of Pd NSs-OA and Pd NCs-PVP after ligand exchange with bismuthiol I. It is noted that some core-shell structures with crystalline core and amorphous shell can still be observed in Pd NCs-Bis-24h (Figure 6.6b3), hence weaker diffraction peaks are still present in the corresponding XRD pattern (Figure 6.6c).

Figure 6.6 (a) TEM image, (a1) SAED pattern, and (a2) HRTEM image of Pd NCs-PVP. Inset in (a): the molecular structure of poly(vinylpyrrolidone). (b) TEM image, (b1) SAED pattern, and (b2, b3) HRTEM images of Pd NCs-Bis-24h. Inset in (b): the molecular structure of bismuthiol I. (c) XRD patterns of Pd NSs-OA, Pd NSs-Bis-24h, Pd NCs-PVP, and Pd NCs-Bis-24h.

6.2.3 Temperature effect on the ligand exchange-induced amorphization

When the ligand exchange temperature was increased from 25 °C to 70 °C, the obtained Pd nanoparticles are denoted as Pd NPs-Bis-24h(70) (Figure 6.7a), which also have amorphous structure, as evidenced by the HRTEM image, SAED pattern and XRD pattern. (Figure 6.7b-d). However, the XPS spectra (Figure 6.7e, f) show that binding energy of Pd and S significantly shifted to higher and lower values, respectively, suggesting that palladium sulfides (PdS_x) were formed. Therefore, at elevated temperature, amorphous PdS_x is formed.

Figure 6.7 Characterization of Pd NPs-OAm after ligand exchange with bismuthiol I at 70 °C for 24 h: (a) large-scale TEM image, (b) HRTEM image, (c) SAED pattern, and (d) XRD pattern. Comparison of (a) Pd 3d and (b) S 2p XPS spectra for Pd NPs-OAm after ligand with bismuthiol I at 25 °C and 70 °C for 24 h.

6.2.4 Electrocatalytic HER

As known, Pd-based nanomaterials are promising catalysts for various electrocatalytic reactions.^[8, 20] Herein, as a proof-of-concept application, the amorphous Pd NPs-Bis-24h and partially amorphous Pd NPs-Bis-1h are used for electrocatalytic HER. The HER measurements were conducted in 0.5 M H₂SO₄ aqueous solution (see section 3.5.3 for details). The electrocatalytic activities of Pd-NPs-OAm, Pd NPs-Bis-1h and Pd NPs-Bis-24h were evaluated by linear sweep voltammograms (LSV) and compared with commercial Pt/C and Pd black. As shown in Figure 6.8a, the amorphous Pd NPs-Bis-24h show much better electrocatalytic activity than the crystalline Pd NPs-OAm as well as partially amorphous Pd NPs-Bis-1h, which is even better than the commercial Pd black. Specifically, at the overpotential of 80 mV, the current density of amorphous Pd NPs-Bis-24h (39.9 mA cm⁻²) is 23.5, 10.9 and 3.3 times those of crystalline Pd NPs-OAm (1.7 mA cm⁻²), partially amorphous Pd NPs-Bis-1h (3.7 mA cm⁻²), and Pd black (12.1 mA cm⁻²), respectively. Furthermore, the amorphous Pd NPs-Bis-24h show a very low Tafel slope of 30.0 mV dec⁻¹, which is close to that of commercial Pt/C (29.1 mV dec⁻¹) (Figure 6.8b), indicating the fast kinetics of hydrogen evolution over Pd NPs-Bis-24h. For comparison, the HER performances of Pd NPs-Bis-24h and other reported Pd-based electrocatalysts are summarized in Table 6.1. It is found that, among the catalysts with the small Tafel slope of 29-31 mV dec⁻¹, our Pd NPs-Bis-24h show the lowest overpotential at 10 mA cm⁻², while among the catalysts exhibiting the comparable overpotentials at 10 mA cm⁻² (below 60 mV), our Pd NPs-Bis-24h display the smallest Tafel slope. This result clearly demonstrates the outstanding activity of amorphous Pd NPs-Bis-24h for HER in acidic solution. Furthermore, the turnover frequency (TOF) values of Pd NPs-OAm, Pd NPs-Bis-1h and Pd NPs-Bis-24h are calculated based on the estimated number of active sites (see section 3.5.3 for details). The TOF value of Pd NPs-Bis-24h is estimated to be 2.33 H₂ s⁻¹ at overpotential of 80 mV, which is much higher than those of Pd NPs-OAm (0.24 H₂ s⁻¹), Pd NPs-Bis-1h (0.27 H₂ s⁻¹) and some reported electrocatalysts, such as Ni-Mo,^[21] Ni₅P₄,^[22] α-Mo₂C and γ-Mo₂N^[23] (Figure 6.8c). Considering the surface atoms of Pd NPs-Bis-24h are sulfurized according to the aforementioned XPS and XAFS analyses, control experiments were conducted to figure out whether the high activity of Pd NPs-Bis-24h may

originate from PdS_x . Note that when the ligand exchange was conducted at 70 °C, the resulted Pd nanoparticles could be completely sulfurized and also show amorphous phase, which are denoted as Pd NPs-Bis-24h(70) (Figure 6.7). The electrocatalytic HER measurement shows that the Pd NPs-Bis-24h(70) exhibit the worst catalytic activity (Figure 6.8a), and the Tafel slope is as high as 65.4 mV dec^{-1} , which is more than twice that of Pd NPs-Bis-24h (Figure 6.8b). These results suggest the catalytically active sites in Pd NPs-Bis-24h originate from Pd instead of PdS_x .

Figure 6.8 (a) Polarization curves of Pd NPs-Bis-24h(70), Pd NPs-OAm, Pd NPs-Bis-1h, Pd black, Pd NPs-Bis-24h, and Pt/C in 0.5 M H_2SO_4 aqueous solution at a scan rate of 5.0 mV s^{-1} . (b) Tafel slopes obtained from the polarization curves in (a). (c) Comparison of the TOF values of Pd NPs-Bis-24h, Pd NPs-Bis-1h, Pd NPs-OAm, and some previously reported electrocatalysts. (d) Durability test of Pd NPs-Bis-24h. The polarization curves were recorded before and after 10,000 potential cycles between 0.04 V and -0.18 V (vs. RHE) in 0.5 M H_2SO_4 aqueous solution.

Table 6.1 Comparison of catalytic performance of our Pd NPs-Bis-24h and recently reported Pd-based nanomaterials for electrocatalytic HER in 0.5 M H₂SO₄.

Materials	Scan rate (mV/s)	Overpotential @ 10mA/cm ²	Tafel slope (mV/dec)	Catalyst loading (mg/cm ²)	Reference
Pd NPs-Bis-24h	5	59.6	30.0	0.112	This work
Pd _{3.02} Te nanowires on reduced graphene oxide nanosheets	5	48	63	0.285	[24]
PdCo@CN	-	80	31	0.285	[25]
Pd nanoparticle-graphitic carbon nitride	10	53	35	0.07	[26]
PdCu _{1.3} alloy nanoparticles	1	50	34	0.28	[27]
Au@AuPd nanocrystals	5	55	34	0.17	[28]
AuPd nanocrystals on reduced graphene oxide	-	55	40	0.09	[29]
Pd nanocrystals on reduced graphene oxide	-	69	60		
carbon nanofiber-PdNi nanoparticles	-	55	57	-	[30]
Ag@PdAg nanocubes	2	93	70	0.407	[31]
PdCu nanocrystals	5	80	51	0.13	[32]
PdCu@Pd nanocubes	-	68	35	0.14	[33]
Au@Pd _{1.0} nanoparticles	-	79	66	0.102	[34]
Pd nanocubes@Mo	-	97	45	0.255	[35]
C/N-co-doped Pd coated Ag nanowires	5	111	64	0.6	[36]
Co@Pd nanoparticles embedded in nitrogen-doped porous carbon	-	98	55.7	0.08	[37]
Pd-Si nanocomposites	5	153	70	0.283	[38]

Li-incorporated Pd ₃ P ₂ S ₈ nanodots	5	91	29	0.23	[39]
Pd/Bi/Cu hierarchical nanoarchitectures	5	79	61	0.023	[40]

In addition of activity, stability is also an important parameter to assess the performance of catalysts. After 10,000 potential cycling between 0.04 V and -0.18 V (versus reversible hydrogen electrode (RHE)), there is almost no shift in the polarization curves of Pd NPs-Bis-24h, indicating their good stability (Figure 6.8d). Importantly, after the stability test, TEM images show that the amorphous structure was retained (Figure 6.9). These results demonstrate that the Pd NPs-Bis-24h could serve as a promising HER electrocatalyst with excellent activity and durability in acidic solution.

Figure 6.9 (a) Large-scale and (b) High-resolution TEM images of Pd NPs-Bis-24h after the electrocatalytic stability test. Inset in (a): the corresponding SAED pattern.

Based on the above results, the superior electrocatalytic HER performance of Pd NPs-Bis-24h compared with Pd NPs-OAm would be attributed to the modified electronic structures due to the ligand effect and amorphous structure. First, the aforementioned Fourier-transformed EXAFS spectra (Figure 6.3) show that Pd NPs-Bis-24h have longer Pd-Pd bond length than Pd NPs-OAm, which could result in increased Fermi level and thus

weaker interaction towards reactants.^[41] Second, XPS spectra show the binding energy of core electrons. The Pd 3d binding energy of Pd NPs-Bis-24h shifts to higher binding energy compared with Pd NPs-OAm, which means the Fermi level of Pd NPs-Bis-24h shifts upward,^[42] consistent with the aforementioned Fourier-transformed EXAFS analysis. All these analyses suggest that the modified electronic structures of Pd NPs-Bis-24h result in weaker binding toward hydrogen. According to the Volcano plot of electrocatalytic HER, when the hydrogen adsorption energy (ΔG_{H^*}) tends to be zero, the HER activity would be the best.^[43, 44] The crystalline Pd has been demonstrated to display negative ΔG_{H^*} , which means the binding between Pd and hydrogen is too strong to catalyze hydrogen evolution efficiently. Thus, in principle reducing the binding of Pd towards hydrogen would increase its catalytic activity, which could account for the remarkably enhanced HER performance of the amorphous Pd NPs-Bis-24h as compared with the crystalline Pd NPs-OAm. Moreover, the amorphous Pd NPs-Bis-24h and crystalline@amorphous Pd NPs-Bis-1h have very similar electronic structure and almost identical Pd-Pd bond length based on their XANES and Fourier-transformed EXAFS spectra, but the HER performance of Pd NPs-Bis-24h is much better than that of the Pd NPs-Bis-1h, implying that the amorphous core of nanoparticles could also positively affect the electrocatalytic performance.^[45] Last but not least, after bismuthiol I binds with Pd nanoparticles, the chemical states of S atoms shift to higher binding energies, generating some Pd-based thiolates (Figure 6.10), which may also contribute to the active sites for HER. The majority of surface S atoms in Pd NPs-Bis-24h are located at 163.8 eV and 165.0 eV (Figure 6.10b), which have the same binding energy as the bridging S_2^{2-} and apical S^{2-} in amorphous MoS_x .^[46] These S atoms are reported to be active sites of amorphous MoS_x in electrocatalytic HER, as their hydrogen adsorption energy is near zero.^[46,47]

Figure 6.10 XPS spectra of S 2p in (a) bismuthiol I and (b) Pd NPs-Bis-24h.

6.3 Conclusion

In conclusion, the discovery of a thiol molecule, namely bismuthiol I, has been systematically discussed, which can induce the amorphization of various *fcc* Pd nanomaterials under ambient conditions without destroying their morphologies. Time-dependent experiment of crystalline Pd nanoparticles show that the particle surface first became amorphous, which induced lattice expansion of the inner atoms and eventually caused the complete amorphization of the nanoparticle. Importantly, the obtained amorphous Pd nanoparticles showed much enhanced activity and good durability towards the electrocatalytic HER. XPS and XAFS analyses suggest that modified electronic structure and increased bond length in amorphous structure could weaken the interaction between Pd and hydrogen, which may account for the improved catalytic activity. This work paves the way to achieving phase transformation from stable phases to metastable phases under mild conditions and demonstrates the promising application of amorphous noble metal nanomaterials.

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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 amorphous/crystalline Pd-based nanosheets and discovers a universal ligand which can induced amorphization of Pd nanomaterials. Importantly, this thesis has demonstrated the superior catalytic performance of amorphous phase-dominant nanostructures compared with crystalline phase-dominant counterparts. Furthermore, future works that can help to gain more insights and alleviate the challenges in this research field are also proposed. In future, the mechanism of the ligand exchange-induced amorphization will be investigated, and moreover, a new method for preparing amorphous noble metal-based nanomaterials based on galvanic replacement reaction will be developed.

7.1 General Discussion

7.1.1 Discussion on synthesis of amorphous/crystalline heterophase Pd nanosheets for selective hydrogenation reaction

For the first time, the amorphous/crystalline heterophase Pd nanosheets via a one-pot wet-chemical method have been successfully synthesized. Importantly, the crystallinity of heterophase Pd nanosheets can be fine-tuned by adjusting the experimental conditions. Particularly, the crystallinities of amorphous/crystalline heterophase Pd nanosheets play a critical role in the chemoselectivity and catalytic activity in the 4-nitrostyrene hydrogenation. Moreover, with proper control over the crystallinity of the Pd nanosheets, the catalyst with excellent chemoselectivity (>99.5%) and high catalytic activity has been successfully obtained.

The novelty and significance of this work are listed below:

(1) Amorphous/crystalline heterophase structure is a newly emerging member in the heterophase family. A recent paper revealed its excellent mechanical properties in the physical field.^[1] However, the reported material was prepared by physical method. It requires special equipment and the choice of materials is limited. In this work, a facile one-pot wet-chemical method is developed to synthesize Pd nanosheets under mild conditions, which is the first report on the preparation of amorphous/crystalline heterophase noble metal nanomaterials through wet-chemical method.

(2) As known, it is very challenging to obtain amorphous noble metal nanomaterials due to the strong metallic interactions between atoms.^[2] Therefore, it is also very challenging to get a series of amorphous/crystalline heterophase nanomaterials with a controllable crystallinity. In this work, besides pioneering the synthesis of amorphous/crystalline heterophase Pd nanosheets, the crystallinity of the amorphous/crystalline heterophase Pd nanosheets can be further controlled via a simple process, i.e., only controlling the reaction temperature.

(3) To the best of our knowledge, there is no report on the applications of amorphous/crystalline heterophase noble metal nanomaterials in chemical field. According to previous reports, it is difficult to achieve the highly selective hydrogenation of the molecules that contain both C=C double bonds and nitro groups, since both functional groups can be readily hydrogenated^[3, 4]. To test the chemoselectivity, the hydrogenation of 4-nitrostyrene is commonly used as the model reaction^[5, 6]. In this work, for the first time, it is demonstrated that the chemoselectivity and activity in the hydrogenation of 4-nitrostyrene are strongly dependent on the crystallinity of the amorphous/crystalline heterophase Pd nanosheets. The amorphous phase-dominant Pd nanosheets exhibit an excellent chemoselectivity (>99.5%) in the hydrogenation of C=C bonds, while those crystalline phase-dominant Pd nanosheets show a higher catalytic activity, obtaining the fully hydrogenated product with a high purity of >99.5%.

7.1.2 Discussion on aging effect study on amorphous/crystalline heterophase PdCu nanosheets

With further study on the previous work, for the first time, two novel types of amorphous/crystalline heterophase PdCu nanosheets are prepared, in which one is amorphous phase-dominant (*a*-PdCu), and the other one is crystalline phase-dominant (*c*-PdCu). Since amorphous phase is thermodynamically unstable in metals, which tends to transform into crystalline phase, the phase transformation behavior of the synthesized heterophase PdCu nanosheets and the heterophase-dependent properties have been systematically studied. As a proof-of-concept application, the heterophase PdCu nanosheets are used as catalysts for the hydrogenation of 4-nitrostyrene. As a result, the amorphous phase-dominant nanosheets initially show excellent chemoselectivity. After aging for 14 days, their catalytic activity exceeds the directly synthesized crystalline phase-dominant nanosheets. This work demonstrates the intriguing properties of heterophase nanostructures, providing a new platform for future studies on the regulation of functionalities and applications of nanomaterials by phase engineering.

The novelty and significance of our manuscript are listed below:

(1) It is very challenging for wet-chemical synthesis of ultrathin 2D noble metal-based nanoalloys with amorphous/crystalline heterophase. Because the thermodynamically stable phases for noble metals are close-packed structures, which have high crystallographic symmetry, the 2D structure is not thermodynamically favored for metal nanocrystal growth^[7]. In addition, in the amorphous phase, atoms are randomly arranged, thus the atomic isotropy makes it also very challenging to obtain the anisotropic 2D structures^[8]. Furthermore, to form alloys with controlled amorphous/crystalline heterophase, introducing additional elements would make it even more complicated. This work demonstrates a facile wet-chemical method for synthesizing nanomaterials with controlled 2D morphology, heterophase nanostructure, and composition.

(2) For the first time, this work presents a systematic study on the crystallinity, surface ligands and electronic properties of the heterophase PdCu nanosheets during the aging process. It was found that the *a*-PdCu nanosheets show increased crystallinity. Moreover, the ratio of CO groups to octanoic acid on the nanosheet surface is reduced during aging, but it is higher in the as-synthesized and aged *a*-PdCu samples as compared to the corresponding *c*-PdCu samples. Furthermore, based on XPS results, the binding energy of Pd in the heterophase nanosheets shows shift during aging, but the as-synthesized and aged *a*-PdCu samples have higher binding energy as compared to the corresponding *c*-PdCu samples. This work is expected to inspire more insight understanding of the formation mechanism of amorphous/crystalline heterophase and more fundamental study on the heterophase-dependent properties.

(3) The change in physiochemical properties will affect the functions, hence we further studied the aging effect on the catalytic performance of the heterophase PdCu nanosheets. It was found that the *a*-PdCu nanosheets initially showed excellent chemoselectivity in the hydrogenation of 4-nitrostyrene. Impressively, after aging for 14 days, they exhibited better catalytic activity as compared to the crystalline phase-dominant nanosheets. This indicates that the heterophase deserves intensive research effort and more interesting phase-

dependent functions are expected to be discovered.

7.1.3 Discussion on ligand exchange-induced amorphization of Pd nanomaterials for highly efficient electrocatalytic hydrogen evolution reaction

For the first time, a thiol molecule, namely bismuthiol I (1,3,4-thiadiazole-2,5-dithiol, $C_2H_2N_2S_3$) is discovered, which can transform *fcc* Pd nanomaterials into amorphous phase by post-synthetic ligand exchange at ambient conditions. This method is applicable to Pd nanomaterials with different morphologies and different capping ligands. Notably, the obtained amorphous Pd nanoparticles show dramatically enhanced activity towards electrocatalytic HER compared with the original crystalline Pd nanoparticles.

The novelty and significance of this work are listed below:

- (1) A unique thiol molecule, namely bismuthiol I, has been discovered, which can effectively induce the amorphization of *fcc* Pd nanoparticles by a facile post-synthetic ligand exchange method under ambient conditions. Time-dependent experiments imply that during the ligand exchange process, bismuthiol I first induced the disorder of the outer atoms, which led to the lattice expansion of the core atoms and eventually caused the entire nanoparticle transforming into amorphous phase. The obtained amorphous Pd nanoparticles are predominantly in metallic state.
- (2) This ligand exchange method can be easily used for other *fcc* Pd nanomaterials with different morphologies and different capping ligands, demonstrating its generality. Notably, unlike other commonly used thiols, such as 1-octadecanethiol, which can destroy the ultrathin Pd nanostructure like nanosheets, the bismuthiol I can well preserve the integrity of ultrathin Pd nanosheets.
- (3) Compared with the original crystalline Pd nanoparticles, the obtained amorphous Pd nanoparticles show dramatically enhanced activity towards electrocatalytic HER, which is even better than commercial Pd black. The Tafel slope of the amorphous Pd nanoparticles

is as low as 30 mV dec⁻¹, which is very close to that of commercial Pt/C. XPS and XAFS results suggest that the enhanced electrocatalytic activity could be attributed to the modified electronic structure and amorphous atomic structure. Importantly, both the catalytic activity and atomic structure of the amorphous Pd nanoparticles remained almost unchanged after 10,000 potential cycling, demonstrating the excellent stability.

7.2 Future Work

7.2.1 Ligand exchange-induced amorphization of Pd-based alloy nanomaterials

Chapter 6 has described the ligand exchange-induced amorphization of Pd nanomaterials, which is intriguing and shows promising electrocatalytic application, however, the mechanism of the amorphization is still unclear. It is speculated that it is due to not only the strong bonding between Pd and S, more importantly, but also the special molecular structure of the bismuthiol I. Control experiments have been done by using different types of sulfides and thiols for the ligand exchange process. Based on experimental results, theoretical calculations will be conducted to figure out the amorphization mechanism.

With the deep understanding on the ligand-induced amorphization of Pd nanomaterials, this method will be further extended to Pd-based alloys. It has been widely reported that alloying Pd with other metals can significantly improve the catalytic performance of Pd owing to the synergistic effect. Hence, it is desirable to prepare amorphous Pd-based alloys to develop highly efficient catalysts. Herein, the ligand exchange-induced amorphization that has been discussed in Chapter 6 will be further generalized to Pd-based alloys.

7.2.2 Synthesis of amorphous noble metal nanomaterials by galvanic replacement

Based on literature review presented in Chapter 2, monodispersed amorphous Co nanoparticles have been reported^[9]. Using the pre-synthesized Co nanoparticles as the seeds, galvanic replacement reactions can occur between the Co nanoparticles and noble

metal ions. If the noble metal nanoparticles can retain the structure of the seeds, then amorphous noble metal nanoparticles may be obtained.

Figure 7.1 Schematics illustrating the synthesis of amorphous noble metal nanomaterials.

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Appendix

Figure A.1 (a) GC of the substrate, i.e., NS. The retention time for NS is 12.3 min. (b) MS of the signal at 12.3 min. (c) NMR of NS.

Figure A.2 GC of the commercialized AS. The retention time for AS is 12.6 min.

Figure A.3 (a) GC of the product obtained by using Sample 1 as catalyst after the hydrogenation of NS for 4 h. (b) MS of the signal at 11.2 min, and (c) NMR of the product obtained by using Sample 1 as catalyst after the hydrogenation of NS for 4 h.

Figure A.4 GC of the product obtained by using Sample 1 as catalyst after the hydrogenation of NS for 30 h.

Publication List

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3. **Hongfei Cheng**[†], Nailiang Yang[†], Xiaozhi Liu, Qinbai Yun, Min Hao Goh, Bo Chen, Xiaoying Qi, Qipeng Lu, Xiaoping Chen, Wen Liu, Lin Gu, Hua Zhang*, “Aging amorphous/crystalline heterophase PdCu nanosheets for catalytic reactions”, *Natl. Sci. Rev.* 2019 (accepted). ([†]equal contribution)
4. Qinglang Ma[†], **Hongfei Cheng**[†], Yifu Yu, Ying Huang, Qipeng Lu, Shikui Han, Junze Chen, Rong Wang, Anthony G. Fane, Hua Zhang*, “Preparation of Superhydrophilic and Underwater Superoleophobic Nanofiber-Based Meshes from Waste Glass for Multifunctional Oil/Water Separation”, *Small* 2017, 13, 1700391. ([†]equal contribution)
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