Synthesis of noble metal-based nanocomposites for enhanced catalytic performance

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

SINGAPORE

**SYNTHESIS OF NOBLE METAL-BASED
NANOCOMPOSITES FOR ENHANCED CATALYTIC
PERFORMANCE**

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

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2017

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Abstract

Noble metals have been applied as heterogeneous catalysts for a long time. In recent decades, it was found that noble metal nanostructures exhibit superior catalytic performance than their bulk counterpart owing to the high surface-to-volume ratio. However, it is challenging for single-component nanomaterials to achieve multiple goals such as catalytic activity, selectivity and stability. Noble metal nanocomposites thus have drawn growing attention spontaneously.

This study aims to fabricate noble metal-based nanocomposites possessing enhanced catalytic performance. Experimental methods used include wet chemical reduction, solvothermal synthesis, and post synthetic modification. The as-synthesized materials were characterized by scanning electron microscope (SEM), transmission electron microscope (TEM), X-ray diffraction (XRD) and many other techniques. Ultraviolet-visible Spectroscopy (UV-Vis) and gas chromatography (GC) were used to monitor the catalytic reactions.

First of all, a facile and robust method was provided to prepare ultrathin bimetallic core-shell nanosheets (NSs), where the ultrathin 2D metallic NSs are incompletely covered by another atomically layered metal. Submonolayered Ru decorated-ultrathin Pd NSs was synthesized using this seed-mediated growth method for the first time, which is referred to as Pd@Ru NSs. The underpotential deposition process is responsible for the formation of Pd@Ru NSs. Impressively, the as-synthesized noble bimetallic Pd@Ru NSs exhibit superior catalytic performance toward the reduction of 4-nitrophenol and the semihydrogenation of 1-octyne as compared to the pure ultrathin Pd NSs and Ru NSs.

The second work elaborated the synthesis of 2D noble metal/porphyrinic metal-organic framework (MOF) composite *via* a seed-mediated growth method. Owing to the synergistic effect between the photothermal effect of Pd and the light-harvesting ability of the porphyrinic MOF Cu-TCPP, the composite exhibits superior catalytic performance than pure Pd NSs in the photo-oxidation of benzyl alcohol under high light irradiation intensity. Furthermore, the catalytic activity of the composite can be altered upon different light irradiation intensities.

In the last work, it was demonstrated that the pore size of NPs/MOF composite can be modified with alkyl chains of different lengths. The obtained products showed enhanced size-selective catalytic performance in the hydrogenation of olefins (triphenylethylene, trans-stilbene, cyclooctene), which revealed the flexibility of MOFs as supporting materials for heterogeneous catalysis.

Based on these accomplished works, a conclusion can be drawn that noble metal based nanocomposites provide better options for some chemical reactions in the following aspects. Firstly, coupling noble metal with another component may induce a synergistic effect, which can promote the catalytic activity. Secondly, combining noble metal with some functional materials, such as MOFs, can introduce some additional properties, which may be beneficial to the catalytic activity as well as selectivity. Last but not least, supporting materials can promote the dispersion and stability of noble metal nanostructures.

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Figure A.1 Scheme of the hexagonal nanosheet.

Abbreviations

2D	Two-dimensional
3D	Three-dimensional
BDC	Terephthalic acid
BET	Brunauer–Emmett–Teller
BF	Bright Field
BSE	Backscattered electrons
CTAB	Cetyl trimethylammonium bromide
CTAC	Cetyl trimethylammonium chloride
DF	Dark Field
DMF	Dimethylformamide
EDS	Energy Dispersive X-ray Spectroscopy
EA	Ethyl acetate
EG	Ethylene glycol
FFT	Fourier transform
FID	Flame ionization detector
FTIR	Fourier Transform Infrared Spectroscopy
GC	Gas Chromatography
HAADF-STEM	High-angle Annular Dark-field Scanning Transmission Electron Microscopy
HRTEM	High Resolution Transmission Electron Microscopy
IPA	Isopropyl alcohol
MIL	Materials Institute Lavoisier
MOF	Metal-organic Framework
MS	Mass spectrometer
NC	Nanocrystal
NDC	Naphthalenedicarboxylate
NH ₂ -BDC	2-amino-1,4-benzenedicarboxylic Acid
NMR	Nuclear Magnetic Resonance

NP	Nanoparticle
NS	Nanosheet
NW	Nanowire
OPD	Optical path difference
PSM	Post-synthetic modification
PVP	Polyvinylpyrrolidone
PXRD	Powder X-ray Diffraction
SAED	Selected Area Electron Diffraction
SEI	Secondary Electron Imaging
SEM	Scanning Electron Microscopy
SPR	Surface plasmon resonance
STEM	Scanning Transmission Electron Microscopy
TCPP	Tetrakis(4-carboxyphenyl)porphyrin
TEM	Transmission Electron Microscopy
UiO	University of Oslo
UV-vis	Ultraviolet-visible Spectroscopy
XRD	X-ray Diffraction
ZIF	Zeolitic Imidazolate Framework

Chapter 1

Introduction

This chapter is an overview of this whole PhD study. It starts with the hypothesis that noble metal-based nanocomposites may exhibit superior catalytic performance than pure metal nanostructures owing to synergistic effect and introduced functionality. Thus this PhD study aims to fabricate several noble metal-based nanocomposites possessing enhanced catalytic performance, including bimetallic ultrathin core-shell nanosheets, 2D noble metal/metal-organic framework (MOF) nanosheets and 3D noble metal/MOF core-shell composites. Dissertation overview part briefly concludes each chapter of this thesis. This research can lead to novel outcomes such as developing synthetic routes of the obtained noble metal composites, and correlating the enhanced catalytic performance with the synergistic effect between two components or the introduced functionality from the support materials.

1.1 Hypothesis

Noble metal nanostructures have been popularly studied as versatile catalysts for various chemical reactions owing to their distinctive properties from their bulk counterparts.^[1-4] However, it is challenging for single-component nanostructures to achieve multiple goals such as catalytic activity, selectivity and stability. It is believed that noble metal based nanocomposites provide better options for some chemical reactions in the following aspects:

- Coupling noble metal with another metal may induce strain effect, which can promote the catalytic activity.
- Combing noble metal with functional materials, such as light-harvesting metal-organic frameworks (MOFs), can introduce additional properties, which is beneficial to the catalytic activity.
- Supporting noble metal with microporous materials like MOFs can introduce size selectivity in catalysis. The selectivity can be further enhanced if the pore size is modified.

1.2 Objectives and Scope

This study aims to fabricate noble metal-based nanocomposites possessing enhanced catalytic performance, including catalytic activity, selectivity and stability. Although this field has been studied intensively as introduced in the Literature Review part, I can take advantage of my group's rich experience in synthesizing noble metal nanostructures and MOF crystals for distinctive design. The following works have been done to achieve this objective:

- Bimetallic ultrathin core-shell nanosheets were synthesized where the core was not completely covered. The composite NSs showed superior catalytic activity than the individual component. The synergistic effect between two metals was investigated.
- 2D noble metal/MOF composite was fabricated. Porphyrinic MOF NSs not only served as supporting material, but also introduced photo-electronic properties into the material. Thus the composite exhibited good performance in the photocatalysis reaction.
- Owing to the flexibility of MOFs, pore size of noble metal NPs/MOF core-shell composite was varied through post-synthetic modification. The catalytic selectivity of the composite was enhanced due to physical constraint.

1.3 Dissertation Overview

The thesis consists of seven chapters in total, addressing the application of noble metal based nanocomposites in chemical catalysis.

Chapter 1 provides a rationale for the research and outlines the goals and scope. It also briefly concludes each chapter of the thesis, as well as the outcomes obtained.

Chapter 2 summarizes background of this thesis. It mainly reviews literatures on noble metal composites for catalysis. Noble metal nanocomposites consist of bimetallic composites, metal-oxide composites, metal and non-oxide composites and metal/MOF composites. It will present current findings and deficiencies of these studies. And thus it helps to explain the motivation of this thesis.

Chapter 3 introduces experimental and characterization techniques applied in the study. Normal methods used for synthesis include wet chemical reduction synthesis of noble metal nanostructures and solvothermal synthesis of MOFs. Besides, MOFs underwent post synthetic modification for altered pore size. The as-synthesized materials were characterized by scanning electron microscope, transmission electron microscope, X-ray diffraction and many other techniques, which will be elaborated in detail respectively. The rationale for selection of methods will be given at the beginning of this chapter as well.

Chapter 4 provides a facile and robust method to prepare ultrathin bimetallic core-shell nanosheets (NSs), where the ultrathin 2D metallic NSs are incompletely covered by another atomically layered metal. Submonolayered Ru decorated-ultrathin Pd NSs was synthesized using this seed-mediated growth method for the first time, which is referred to as Pd@Ru NSs. The underpotential deposition process is responsible for the formation of Pd@Ru NSs. Impressively, the as-synthesized noble bimetallic Pd@Ru NSs exhibit superior catalytic performance toward the reduction of 4-nitrophenol and the semihydrogenation of 1-octyne as compared to the pure ultrathin Pd NSs and Ru NSs.

Chapter 5 elaborates the synthesis of 2D noble metal/porphyrinic MOF composite *via* a seed-mediated growth method. Owing to the synergistic effect between the photothermal effect of Pd and the light-harvesting ability of the porphyrinic MOF Cu-TCPP, the composite exhibits superior catalytic performance than pure Pd NSs in the photo-oxidation of benzyl alcohol under high light irradiation intensity. Furthermore, the catalytic activity of the composite can be altered upon different light irradiation intensities.

Chapter 6 studies modifying pore size of NPs/MOF composite with alkyl chains of different lengths. The obtained products showed enhanced size-

selective catalytic performance in the hydrogenation of olefins (triphenylethylene, trans-stilbene, cyclooctene), which revealed the flexibility of MOFs as supporting materials for heterogeneous catalysis.

Chapter 7 draws together the threads of this thesis. The whole work will be summarized and the extent to which the hypothesis is met will be addressed. Some possible future work will be proposed for further study.

1.4 Findings and Outcomes/Originality

This research led to several novel outcomes by:

1. Establishing a synthetic route of ultrathin bimetallic core-shell NSs where the core is incompletely covered by the shell.
2. Correlating the enhanced catalytic activity of bimetallic core-shell NSs with the synergistic effect between two metals.
3. Fabricating 2D noble metal/ porphyrinic MOF composite.
4. Utilizing photo-electronic properties of porphyrinic MOF in 2D noble metal/MOF composite for photo-catalytic reaction.
5. Modifying pore size of MOF through post-synthetic modification.
6. Altering the catalytic selectivity of noble metal/MOF composite with varying pore size.

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Chapter 2

Literature Review

In this chapter, background of this thesis is summarized. It mainly reviews literatures on noble metal-based nanocomposites for catalysis applications. Noble metal nanocomposites consist of bimetallic composites, metal-oxide composites, metal and non-oxide composites and noble metal/metal-organic framework (MOF) composites. MOFs are further divided into 3D MOFs and 2D MOFs. Besides the current findings present in this literature review, some questions are still left to answer. For example, one may wonder whether it is possible to expose both metals of a bimetallic core-shell structure during the catalysis, so that the synergistic effect between the two metals can be studied. Moreover, as functional supporting materials, can MOFs bring additional properties to the composites? These questions raised inspire the design and completion of this study.

2.1 Overview on Noble Metal Nanocomposites for Catalysis

With decades of research, noble metal nanoparticles (NPs) (Au, Pd, Pt, etc.) are considered to exhibit novel catalytic performance from their bulk counterparts due to a high surface-to-volume ratio.^[1-6] However, it is challenging for single-component NPs to achieve multiple goals such as catalytic activity, selectivity and stability. Noble metal nanocomposites have drawn growing attention spontaneously. This review will only focus on two-component nanocomposites. And they are divided into bimetallic composites, metal-oxide composites and metal and non-oxide composites.

2.1.1 Bimetallic composites

According to different mixing patterns, bimetallic composites can be further categorized into three types: core-shell nanostructures, heterostructures and alloyed nanostructures^[7]. (Figure 2.1) Synergistic effect arising between two metal components can often contribute to enhanced catalytic performance in terms of electron transfer, structural strain, interfacial collaboration and so on.^[7-9]

Figure 2.1 Schematic diagram of three major types of bimetallic composite nanomaterials: a) core-shell nanostructures; b) heterostructures; and (c) alloyed nanostructures. (Reprinted with permission from ref. 7)

Core-shell nanostructures. Seed-mediated growth method is generally used in synthesis of core-shell nanostructures to obtain various sizes, compositions and morphologies. For instance, Xia and coworkers^[10] developed a facile route to fabricate bimetallic nanodendrites composed of a dense array of Pt branches on a Pd core. Figure 2.2 indicates the epitaxial

growth of Pt on Pd seed. The exposed facets were mostly $\{111\}$, which showed outstanding catalytic activity in oxygen reduction reaction compared to Pt/C and Pt black catalysts. Khashab *et al.*^[11] reported synthesis of hollow Au@Pt NPs, and found that crystallinity of Pt shells was improved in presence of Au cores. Thus the core-shell NPs showed better catalytic activities for ethanol oxidation reactions than metallic Pt. More recently, Tsung's group^[12] managed to obtain Pd-Rh nanoboxes by triggering and controlling metal migration in Pd@Rh NPs. By evaluating the electrocatalytic performance, they drew a conclusion that the surface composition and lattice strain both crucially influenced the catalytic behaviors. According to the referred studies, shell thickness and coverage play an important role in their catalytic performances.^[13] Thick shells can possibly hinder the diffusion of reactants, and also reduce alloy effect of core and shell metals.

Figure 2.2 A) HRTEM image of a single Pd-Pt nanodendrite. B) Enlarged HRTEM image of the Pd core of the Pd-Pt nanodendrite shown in (A). C-F) Enlarged HRTEM images of the Pt branches 1, 2, 4, and 6 marked in (A), respectively. The lattice fringes from the Pd core to the Pt branches are proven to be continuous, indicating the epitaxial growth of Pt on Pd seed. (Reprinted with permission from ref. 10)

Besides typical 3D structures, bimetallic core-shell nanocomposite can be fabricated into 2D nanosheets, as shown in Figure 2.3. Ding and coworkers^[14] obtained such structure through a defect-mediated thin film growth method. The composite exhibited superior catalytic activity in the oxygen reduction reaction compared to Pt/C. In this configuration, the extended Pt surface atoms and the underlying Pd substrate simultaneously contribute to the enhanced activity by weakening the adsorption strength of oxygen species, while the ultrathin Pt overlayer guarantees the overall Pt utilization.

Figure 2.3 Schematic representation of the Pd@Pt bimetallic core-shell nanosheet. (Reprinted with permission from ref. 14)

Heterostructures. Compared with core-shell nanostructures, both metals and their interfaces are exposed in bimetallic heterojunctions. Using seed-mediated growth method, Xia's group^[15] obtained Pd–Ag hybrid dimers by slowing down injection rate of Ag precursor. The same group^[16] also synthesized Pd–Au dimers *via* controlled overgrowth of Pd on Au seeds. With this method, heterostructures with different sizes, compositions and morphologies can be achieved. Nam and coworkers^[17] proposed a salt-tuned synthetic route to form Au–Ag head–body nanosnowman structures. Low salt concentration favored fast nucleation and growth of Ag on DNA-modified Au NPs, thus enabled the formation of anisotropic nanostructures.

Alloyed nanostructures. Bimetallic alloys are NPs with two distinct types of metal atoms distributing homogeneously. Zhang's group^[18] found that presence of Cu^{2+} ions enabled the Au–Pd alloying process. The resultant alloy nanocrystals (NCs) were in hexoctahedral shape bounded by {431}

high-index facets, and thus showed good performance in formic acid electro-oxidation. The synthesis of alloyed nanostructures can also be achieved by selecting proper surfactants. For example, Han's group^[19] obtained rhombic dodecahedral Au–Pd NCs enclosed exclusively by 12 {110} through coreduction of Au and Pd precursors with reductant ascorbic acid and surfactant cetyltrimethylammonium chloride (CTAC). These {110} facets promoted SERS and electrocatalytic activities of NCs. Li's group^[20] synthesized one dimensional Au–Ag alloy nanowires (NWs) (Figure 2.4) using octadecylamine as solvent, reductant as well as surfactant. They believed that the noble-metal-induced reduction, the oriented attachment and the wire–wire fusion coexist as the growth mechanism of the bimetallic NWs.

Figure 2.4 a) TEM image of the NWs. b) HAADF-STEM image and elemental mapping of NWs, showing the presence and distribution of gold and silver elements. c) HRTEM image of NWs; inset in (c) is the corresponding fast Fourier transform (FFT) image, indicating the ultrathin nanowires are single crystals. (Reprinted with permission from ref. 20)

2.1.2 Metal-oxide composites

Oxides are generally used as support to provide a monodisperse nature for metal NPs. Several studies from Zhang's group^[21,22] revealed that single metal atoms anchored on iron oxide nanocrystallites possessed maximized atom efficiency, and showed excellent catalytic activity and stability in CO

oxidation. Some oxides can even serve to impart functionality to composites and thus promote catalytic performances.

Semiconductor oxides. TiO_2 is an important semiconductor often selected as support material. Noble metal- TiO_2 composites exhibited enhanced catalytic performances in various reactions. For example, Gao and Yin^[23] synthesized Au/TiO_2 photocatalysts without capping ligands by ligand-exchange method. So that the as-prepared composites had a close Au/TiO_2 Schottky contact, which resulted in a superior activity in both dye decomposition and water-reduction hydrogen production. Li *et al.*^[24] reported that the catalytic activity of Au/TiO_2 for CO oxidation reaction was very sensitive to the gold particle size. Catalysts with the longest perimeter interface showed highest activity, indicating the importance of Au-TiO_2 contact boundary in the reaction.

ZnO is another popular semiconductor intensively studied. Ravishankar and coworkers^[25] reported Au-ZnO hybrids experienced good catalytic activity for CO oxidation due to the formation of anionic and cationic Au sites, which was caused by the presence of Au-Zn and Au-O bonds on the interface. Matranga's group^[26] studied the plasmonic heating effect of Au supported on ZnO using laser irradiation. During catalytic conversion from CO_2 and H_2 reactants to CH_4 and CO products, they found CH_4 : CO product ratio could be tuned by adjusting laser intensity, as shown in Figure 2.5.

Figure 2.5 a) CO production rate and (b) CH₄ production rate plotted against the laser intensity using Au–ZnO as catalysts. (Reprinted with permission from ref. 26)

Porous oxides. Porous SiO₂ contains numerous mesopores, thus provides an ideal environment for confinement of noble metal NPs. For instance, Pt-SiO₂ has been considered as very efficient catalyst in various hydrogenation reactions for decades.^[27,28] The presence of supporter SiO₂ enabled catalysts to withstand extreme conditions such as high temperature and pressure.

2.1.3 Metal and non-oxide composites

Carbon. Carbon and its polymorphs (carbon nanotubes, graphene, etc.) drew lots of attention with respect to their tunable electronic structures. As supports for NPs, carbon nanotubes possess high surface area, unique physical properties, high electrical conductivity, inherent size and hollow geometry.^[29] On the other hand, graphene provides a 2D model of catalyst support.^[30] It also exhibits outstanding chemical, physical and mechanical properties. Noble-metal/graphene composites were intensively studied in recent years. Although carbon nanotubes and graphene are promising supports in catalysis, large-scale production remains to be a challenge for such materials.

Metal chalcogenides. Chalcogenide materials are usually semiconductors,

which can contribute to photocatalytic reactions. Banin *et al.*^[31] synthesized Pt-CdSe hybrids, and managed to control morphology by tuning pH conditions of the growth solution. Compared with nanorods, Pt-CdSe nanonets showed superior photocatalytic activity. The nanonet morphology enabled denser Pt surface coverage, and thus resulted in more efficient charge separation, which could produce more catalytic sites for the redox reactions. Rogach and coworkers^[32] discussed the effect of Pt cluster size on photocatalytic activity of Pt-CdS nanorods in hydrogen evolution reaction. They found subnanometer sized Pt clusters exhibited remarkable performance, even though they are less in amount compared to large Pt clusters. Zhang's group^[33] demonstrated the epitaxial growth of Pd, Pt and Ag nanostructures on MoS₂ nanosheet. As shown in Figure 2.6, Pt NPs exhibited major orientations of (111) and (101). The Pt-MoS₂ hybrids showed superior electrocatalytic performance in the hydrogen evolution reaction compared with Pt/C with the same Pt amount, which could be attributed to the defined orientations at the interface.

Figure 2.6 a) TEM image of Pt-MoS₂ hybrid nanosheet (scale bar, 100 nm). b) Enlarged TEM image of Pt NPs on MoS₂ nanosheet. The size of the Pt NPs is measured to be 1–3 nm (scale bar, 5 nm). c) SAED pattern of the Pt–MoS₂ hybrid nanosheet. The electron beam is perpendicular to the basal plane of the MoS₂ nanosheet. d–f) HRTEM images of Pt NPs on MoS₂ nanosheet. The lattice fringes for Pt and MoS₂ are measured respectively (scale bar, 2 nm). Inset in (f): photograph of the Pt–MoS₂ solution. (Reprinted with permission from ref. 33)

2.1.4 Noble metal/MOF composites

Metal organic frameworks (MOFs) are hybrid organic-inorganic supermolecular materials whose extended networks are formed by nodes of metal ions or clusters of metal ions coordinated to bi- and multinodal rigid organic linkers.^[34,35] (Figure 2.7) The directionality of coordination bonds defines pore structure in the lattice, and bond strength determines the stability of the network.^[36] As a result, the structure of MOFs can be designed and predicted somehow. MOFs can be achieved through numerous combinations of metal clusters and organic linkers. With light weight, high specific surface area and flexibility, MOFs are considered as good candidates in applications of gas storage,^[37] photocatalysis^[38] as well as chemical catalysis.^[34]

Figure 2.7 Metal–organic frameworks. (Reprinted with permission from ref. 35)

Due to the unique crystalline porous structure containing transition metals and organic ligands, MOFs have several possible active sites for catalysis,^[36] including metal nodes with unsaturated coordination sites,

functional groups on linkers, encapsulated species and even defects in frameworks. Compared to exposed metal coordination sites and reactive functional groups, encapsulating catalytically active species into MOFs is a more general approach to introducing catalytic ability. The encapsulated species could be metal NPs,^[39-41] metal oxide NPs^[42] or even functional molecules.^[43] In the area of heterogeneous catalysis, noble metal NPs/MOF nanocomposites have drawn most attention due to their excellent catalytic performance.

MOFs can serve as good support materials for metal NPs. It can not only prevent aggregation of NPs, but also provide a catalytic environment around NPs different from surrounding matrix phase due to the porous nature, particularly for NPs which are completely embedded. Catalytic activity and selectivity are highly determined by pore environment of MOFs. Due to the flexibility of MOFs, functional groups can be easily introduced into the composites.

2.1.4.1 3D MOFs

IRMOFs. Some prototypical MOF architectures were intensively studied by worldwide scientists in the recent decades. For instance, Yaghi's group synthesized one of the most popular MOFs, MOF-5,^[44] and its 16 isorecticular series (IRMOFs).^[45] This prototype is built up when octahedral Zn-O-C clusters and benzene links reticulate a primitive cubic structure. Benzene ligands can be functionalized with the organic groups -Br, -NH₂, -OC₃H₇, -OC₅H₁₁, -C₂H₄, and -C₄H₄. Pore size can be tunable from 3.8 to 29 Å by using the long molecular struts biphenyl, tetrahydropyrene, pyrene, and terphenyl. IRMOF-16 could reach porosity up to 91.1% of the unit cell volume in the absence of guest molecules.

ZIFs. Zeolites, which are aluminosilicate structures, are one of the most

important crystalline microporous support materials in industry. Chen and coworkers^[46] reported synthesis of thermally robust MOFs with zeolitic topologies, that are then called zeolitic imidazolate frameworks (ZIFs). ZIFs have tetrahedral metal ions (e.g., Zn, Co) bridged by imidazolate linkers (Im). The M-Im-M angle is quite close to the Si-O-Si angle (145 °) in zeolites. Thus enormous numbers of ZIFs are fabricated in the following years.^[47-49] (Figure 2.8) The outstanding chemical and thermal stability enabled ZIFs in various applications such as gas capture, catalysis and so on.

Figure 2.8 Several types of representative crystal structures of ZIFs (the three capital letters under each example, such as ANA, DFT, GIS, etc., stand for the zeolite structure code). (Reprinted with permission from ref. 49)

MILs. Férey *et al.*^[50,51] started the research on MIL-n type of MOFs (MIL = Materials Institute Lavoisier). They consist of trimetric metal clusters

(e.g., Fe, Cr, V, Ru, Mn, Co) jointed by dicarboxylate ligands. Popular MIL MOFs like MIL-53^[52,53] and MIL-88^[54] are highly flexible. Their shapes and pore sizes change upon host-guest interactions. MIL-101^[55] is crystalline mesoporous structure for Cr-terephthalate. With large cell volume, cage diameter (30~34Å) and Langmuir surface area ($\sim 5900 \pm 300 \text{ m}^2/\text{g}$), it presented extraordinary ability in gas storage^[56] and catalysis^[57].

UiOs. In 2008, Lillerud and coworkers^[58] synthesized a new Zr-based MOF UiO-66 (UiO = University of Oslo). Based on cubic framework of cationic $\text{Zr}_6\text{O}_4(\text{OH})_4$ nodes (formed in situ *via* hydrolysis of ZrCl_4) and terephthalic acid (BDC) linkers, UiO MOFs show significant chemical and thermal stability. The following studies^[59,60] demonstrated synthesis of $-\text{NH}_2$, $-\text{Br}$, $-\text{NO}_2$, and naphthalene-substituted UiO-66 analogues. (Figure 2.9)

Figure 2.9 Synthesis of substituted UiO-66 analogues. (Reprinted with permission from ref. 59)

Noble metal/3D MOF composites. A general route to disperse NPs inside MOF structures is *via* precursor infiltration into MOF cavities followed by decomposition, in which the precursor reduces to NPs. Using this method, quite a few NPs (e.g. Ru, Au, Pd, Pt) have been impregnated into MOFs (e.g. MOF-5, MOF-177, MIL-101(Cr), ZIF-8, ZIF-90).^[61] For example, Ru@MOF-5 ^[40] was obtained through hydrogenolysis of the precursor $[\text{Ru}(\text{cod})(\text{cot})]$ (cod = 1,5-cyclooctadiene, cot = 1,3,5-cyclooctatriene). The embedded Ru NPs were in a typical size range of

1.5 – 1.7 nm. Ru@MOF-5 could be used as catalyst for hydrogenation of benzene. Under relatively mild conditions (3 bar H₂, 75 °C), the reaction could be finished within 20 hours. Kaskel's group^[62] synthesized Pd/MIL-101(Cr) with Pd size around 1.5 nm, and found it exhibited superior catalytic activity in hydrogenation of olefins compared to Pd/C. Au@MOF structures also attract lots of attention. Xu and coworkers^[63] presented the first example of using Au@ZIF-8 as the catalyst for CO oxidation. Highest activity was achieved when they increased Au loading to 5 wt%. ZIF-8 could effectively protect Au NPs from aggregation during catalysis, thus increased recyclability of catalyst.

Besides the common impregnation route, Huo *et al.*^[64] developed a strategy utilizing pre-synthesized metal NPs as nucleation sites for MOF growth, which enabled precise size, composition as well as spatial distribution control of NPs in MOFs. This strategy was then extended to NPs including Pt, Au^[64] and Pd,^[65] incorporated into MOFs such as ZIF-8,^[64] UiO-66 and MIL-53.^[65] The same group^[65] reported that the as-prepared Pt/UiO-66 composites showed excellent shape-selectivity in olefin hydrogenation owing to complete confinement of MOF channels around NPs.

Figure 2.10 Scheme of the controlled encapsulation of nanoparticles in ZIF-8 crystals. (Reprinted with permission from ref. 64)

2.1.4.2 2D MOFs

The exfoliation of graphene from graphite leads to growing interest in 2D materials. With ultrathin thickness and large lateral size, such materials can be suited in various surface-active applications.^[66] MOF nanosheets were among the hottest topics because the 2D nature allows exposure of many active sites on the surface, which enables intensive interaction between active sites and substrate molecules. 2D MOFs may have promising performance in areas such as separation, sensing and catalysis.

Top-down synthesis. Top-down often refers to exfoliation of layered bulk MOFs. Such kind of MOFs is built up by strong in-plane coordination bonds and weak interlayer interactions (e.g. van der Waals Forces, hydrogen bonding). The first example of top-down synthesis of 2D MOFs was reported very recently by Zamora and coworkers^[67]. They synthesized bulk coordination polymer $[\text{Cu}_2\text{Br}(\text{IN})_2]_n$ (IN = isonicotinato) which contained strong in-plane Cu-O and Cu-N bonds. On the other hand, layers were interconnected by weak π - π stacking between the isonicotinato aromatic rings. Hence, the interlayer interaction was broken by subsequent probe sonication. The resultant nanosheets had a quite uniform thickness of $5 \pm 0.15 \text{ \AA}$, which was consistent with theoretical thickness of the single atomic layer of $[\text{Cu}_2\text{Br}(\text{IN})_2]_n$. Even though the authors didn't come up with any applications of this material, this work inspired the following research on 2D MOFs. Slightly later in 2011, Xu's group^[68] made progress in exfoliation of MOF-2 (ZnBDC, BDC = 1,4-benzenedicarboxylate) *via* simple ultrasonic treatment in acetone. The delaminated nanosheets had thickness ranging from 1.5 to 6.0 nm. They also found delamination only happened in acetone other than any other solvents, possibly because acetone could effectively prevent reforming of hydrogen bonding between layers. This work indicates that the solvent plays an important role in MOF delamination. Yang *et al.*^[69] obtained 2D $\text{Zn}_2(\text{bim})_4$ (bim = benzimidazole)

nanosheets through a new technique combining wet ball-milling and sonication, and they chose methanol and n-propanol mixture as solvent for exfoliation and stabilization. The 1nm-thick nanosheets were then utilized as building blocks for molecular sieving membranes, which proved to showing outstanding hydrogen gas permeance as well as H₂/CO₂ selectivity.

Bottom-up synthesis. Bottom-up method is direct synthesis of MOF nanosheets, and it is important to develop a strategy to control MOF growth only along lateral directions. Gascon *et al.*^[70] utilized interfacial synthesis to get a series of freestanding 2D MOF nanosheets. Taking the fabrication of CuBDC as example, they prepared the reaction medium with three solvent layers (different DMF/acetonitrile ratios) aligned vertically. The top layer was rich in acetonitrile, and contains Cu(NO₃)₂. The bottom layer had more DMF, and dissolved BDC ligands. In between there was another layer containing equal amount of DMF and acetonitrile, in which the growth of CuBDC nanosheets actually took place after slow diffusion of Cu²⁺ and BDC ligands. The nanosheet thickness was controlled within range of 5 to 25 nm, because the formed MOFs would precipitate to the bottom layer, and lost contact with Cu²⁺. This method proved to be universal in synthesis of ZnBDC, CoBDC, Cu(1,4-NDC), and Cu(2,6-NDC) (NDC = naphthalenedicarboxylate). Similar interfacial synthesis strategies were applied in several other reports.^[71,72] However, the limitations of such strategies are clear. Restacking and aggregation of nanosheets become an issue.

Zhang's group^[73] developed a facile surfactant-assisted approach to obtain MOF nanosheets with thickness less than 10 nm. For example, traditional synthesis method could only produce Zn-TCPP bulk crystals with layers stacking together. With the addition of surfactant such as poly(vinylpyrrolidone) (PVP), nanosheet structure was achieved. Through

attaching on MOF surface, PVP served to restrict the growth along vertical direction as well as stabilize the nanosheets. Various 2D MOF were fabricated using this method such as Cu-TCPP, Co-TCPP, Cd-TCPP. (Figure 2.11) Some small molecules can act like surfactant during synthesis. Do's group^[74] used pyridine in the fabrication of Cu-MOF nanosheets, while Lin *et al.*^[75] used formic acid in the preparation of Hf-MOF nanosheets. These surfactant-assisted strategies can efficiently stabilize MOF nanosheets, and prevent further aggregation and restacking.

Figure 2.11 a) Simple schematic illustration of the traditional synthesis and surfactant-assisted synthesis of Zn-TCPP MOF. The MOF layers are shown in blue and purple respectively, in order to make the layered structures clear. b–e) STEM images of Zn-TCPP nanosheets (b), Cu-TCPP nanosheets (c), Cd-TCPP nanosheets (d), and Co-TCPP nanosheets (e). (Reprinted with permission from ref. 73)

Noble metal/2D MOF composites. Since the research on 2D MOFs started only several years ago, there are only a few papers discussing NPs/2D MOF composites as catalysts. For instance, Zeng and coworkers^[76] synthesized

Cu-based MOF nanosheets *via* surfactant-assisted method. Then noble metal NPs (e.g., Au, Ag, Pt, Pd, Au_{0.4}Pt_{0.6}, Au_{0.4}Pd_{0.6}, and Au_{0.3}Pt_{0.3}Pd_{0.4}) were immobilized on nanosheet surfaces. Their catalytic activities for CO₂ hydrogenation and 4-nitrophenol reduction were investigated and compared. It turned out trimetallic and bimetallic NPs exhibited higher activity than monometallic ones. Another case was reported by Wang's group^[77]. They developed a synthesis strategy of 2D hierarchical-pore MOFs (H-MOFs) which contained both micropores and mesopores. Pd NPs were anchored on H-MOF-5. Owing to the unique structure and gas adsorption capacity of H-MOF-5, the composite showed excellent catalytic activity in reduction of nitroarene.

2.3 Questions to Answer Based on Literature

As mentioned above, various noble metal-based nanocomposites have been intensively studied and applied in catalysis. However, there are still some questions left to answer.

Firstly, lots of bimetallic core-shell nanostructures were fabricated, in which the core was completely covered by the shell. One may wonder whether it is possible to expose both metals during the catalysis. And is there any synergistic effect between the two components? Furthermore, it is valuable to develop a synthetic route for 2D ultrathin nanosheets because the 2D structures contain more surface catalytic sites than 3D structures.

Secondly, MOFs are introduced in detail due to their versatility and flexibility. One may wonder if the integration of noble metal and MOF can introduce functionality into the nanocomposites. For example, can light-harvesting MOFs promote the photo-catalytic performance of noble metals? Is 2D MOF sheet a reliable supporting material for noble metal NSs?

Last but not least, 3D MOFs have porous structure which can be conveniently engineered through chemical modification. For a 3D noble metal/MOF composite, is it possible to alter its catalytic performance through post synthetic modification? For instance, if the pore size of MOF is decreased, will the size selectivity be enhanced for chemical catalysis?

2.4 PhD in Context of Literature

This thesis mainly focuses on the synthesis of noble metal-based nanocomposites for their enhanced catalytic performance. Three projects in total are involved. Ultrathin bimetallic NSs, 2D noble metal/MOF NSs and 3D noble metal NPs/MOF composites are fabricated respectively. Their catalytic performances are examined in reactions including reduction of 4-nitrophenol, hydrogenation of olefins as well as photo-oxidation of benzyl alcohol.

Firstly, a facile and robust method was provided to prepare ultrathin bimetallic core-shell nanosheets (NSs), where the ultrathin 2D metallic NSs are incompletely covered by another atomically layered metal. Submonolayered Ru decorated-ultrathin Pd NSs was synthesized using this seed-mediated growth method for the first time, which is referred to as Pd@Ru NSs. The underpotential deposition process is responsible for the formation of Pd@Ru NSs. Impressively, the as-synthesized noble bimetallic Pd@Ru NSs exhibit superior catalytic performance toward the reduction of 4-nitrophenol and the semihydrogenation of 1-octyne as compared to the pure ultrathin Pd NSs and Ru NSs.

Secondly, 2D noble metal/porphyrinic MOF composite was synthesized *via* a seed-mediated growth method. Owing to the synergistic effect between the photothermal effect of Pd and the light-harvesting ability of the porphyrinic MOF Cu-TCPP, the composite exhibits superior catalytic

performance than pure Pd NSs in the photo-oxidation of benzyl alcohol under high light irradiation intensity. Furthermore, the catalytic activity of the composite can be altered upon different light irradiation intensities.

Lastly, the pore size of NPs/MOF composite was modified with alkyl chains of different lengths. The obtained products showed enhanced size-selective catalytic performance in the hydrogenation of olefins (triphenylethylene, trans-stilbene, cyclooctene), which revealed the flexibility of MOFs as supporting materials for heterogeneous catalysis.

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Chapter 3

Experimental Methodology

Experimental and characterization techniques applied will be introduced in this chapter. Conventional methods used for synthesis include wet chemical reduction synthesis of noble metal nanostructures and solvothermal synthesis of MOFs. Besides, MOFs underwent post synthetic modification for altered pore size. The as-synthesized materials were characterized by scanning electron microscope, transmission electron microscope, X-ray diffraction and many other techniques, which will be elaborated in detail respectively. The rationale for selection of methods will be given at the beginning of this chapter as well.

3.1 Rationale for Selection

This thesis involves synthesis and characterization of noble metal-based nanocomposites, such as bimetallic and metal/MOF nanomaterials. They have sizes ranging from several nanometers to hundreds of nanometers.

- For the synthesis of metal NPs and NSs, probably the most popular method was used – **wet chemical reduction synthesis**. Metal precursors are reduced in liquid solutions by reducing agents (e.g. ascorbic acid) in the presence of stabilizing agents (e.g. PVP, CTAB). This method allows precise control over size, shape and composition of monometallic and bimetallic nanostructures.
- **Solvothermal synthesis** was widely applied in the preparation of MOFs in this study. It is carried out in a closed vessel containing organic solvent at elevated temperature (can be higher than boiling point of the solvent). Normally, such synthesis process involves high pressures within the vessel. High temperature and pressure both promote dissolution of reaction ingredients into the solvent, and also enable the synthesis process.
- The organic linkers of MOFs can be conveniently modified through covalent bonds or dative bonds. Hence, **post synthetic modification (PSM)** was used to alter the pore size of MOFs for enhanced catalytic selectivity.

Various characterization techniques were used to study different properties of nanomaterials.

- **Scanning electron microscope (SEM)** is a powerful tool to reveal surface topography. So it was used to observe size and shape of

composite samples. SEM-EDX gave information about surface composition.

- Compared with SEM, **transmission electron microscope (TEM)** produces electron beam with higher energy, so it is capable of showing internal structures of samples. It was a necessary equipment to observe core-shell structures synthesized in this study. Besides, some special imaging modes of TEM, such as HRTEM and HAADF-STEM, can show the atomic structures directly. So lattice spacing as well as crystal defects can be seen.
- **X-ray diffraction (XRD)** helps to identify phases of crystalline materials. Because the samples were mainly crystalline composites, XRD was used to distinguish each component by comparing sample XRD patterns with reference patterns reported previously.
- **X-ray photoelectron spectroscopy (XPS)** provides information about electronic states of element that exists within a material. In the research of composites, XPS was used to analyze surface chemistry of sample composites and individual components.
- Absorption spectroscopy of materials in ultraviolet-visible spectral region is referred to as **ultraviolet-visible spectroscopy (UV-Vis)**. It was applied to study light absorption properties of the sample materials. Chemical compounds have their characteristic absorption peaks respectively. Thus it was also used to determine the kinetics or rate constant of a chemical reaction, such as reduction of p-nitrophenol, by monitoring the change in absorbance at certain peaks.
- **Fourier transform infrared spectroscopy (FTIR)** is another type

of absorption spectroscopy which measures in infrared region. Absorptions in such region correspond to different vibrational modes of molecules. Based on this knowledge, FTIR was used to prove presence of certain bonds within the samples.

- **Surface area and porosity analysis** gives information about surface area and pore size of samples, which are quite important in study of porous materials such as MOFs. Modified MOFs would show different surface area and porosity, thus influenced their performance in chemical catalysis.
- **Gas chromatography (GC)** separates and analyzes compounds which can be vaporized below 300°C without decomposition. In this study, several types of chemical catalysis were conducted, such as oxidation of benzyl alcohol and hydrogenation of olefins. After the catalysis, reaction mixtures were analyzed by GC to obtain reaction conversion and selectivity.
- For compounds which cannot be vaporized below 300°C or easily decompose upon heating, **nuclear magnetic resonance (NMR) spectroscopy** provides another option for analysis by exploiting the magnetic properties of certain atomic nuclei (^1H and ^{13}C). In this study, ^1H -NMR spectroscopy was applied to analyze reaction conversions in hydrogenation of triphenylethylene and trans-stilbene.

3.2 Synthesis

3.2.1 Wet chemical reduction method

Noble metal nanostructures can be obtained through numbers of synthetic

strategies. For example, “top-down” approaches refer to breakdown of bulk materials into nanoparticles. On the other hand, “bottom-up” approaches start with chemical reduction of metal precursors to atoms, followed by controlled growth of atoms into NPs or NSs. Usually, physical approaches are accompanied with limitations such as low yield, uncontrolled size and so on.^[1] Thus chemical synthesis methods, especially wet chemical reduction method, become quite attractive worldwide.

Stabilizing agents are commonly used in wet chemical reduction synthesis for the size and shape control of nanostructures. When they adsorb on a NP surface, a repulsive force is generated between NPs through electrostatic stabilization (e.g. citrate ions) or steric stabilization (e.g. PVP). The nanostructures obtained are then protected from aggregation. Furthermore, sometimes the adsorption of surfactants can be utilized to tune the surface energy of nanocrystals. Hence the growth habit of different facets is altered. For instance, Xia’s group^[2,3] found that the use of sodium citrate as capping agent could result in formation of Ag octahedrons enclosed by {111} facets, while PVP promoted the formation of Ag nanocubes enclosed by {100} facets.

The growth mechanism of NPs in wet chemical reduction synthesis was intensively studied by a lot of scientists.^[4] The preparation of Au NPs by the reduction of tetrachloroauric acid (HAuCl_4) with sodium borohydride (NaBH_4) was among the most popular systems. Kraehnert and coworkers^[5] proposed a 4-step growth process of Au NPs. (Figure 3.1) Step one is the nucleation of Au small clusters *via* a fast reduction of a small amount of gold precursor. Then clusters aggregate with each other, and grow into larger size in step two. Step three involves a diffusional growth, in which NPs grow into a relatively uniform size. In the last step, NPs continue growing rapidly and finally the rest precursor is used up. After years of research, several other models of growth mechanism were proposed even

with detailed calculations. However, they will not be discussed in this thesis due to lack of relevance.

Figure 3.1 Schematic illustration of the deduced process of gold nanoparticle formation. (Reprinted with permission from ref. 5)

3.2.2 Solvothermal synthesis

Within decades of research, numbers of synthesis methods were developed to achieve MOFs with controlled size and morphology.^[6] (Figure 3.2) Conventional solvothermal synthesis remains to be the most popular method because it is quite simple, scalable and versatile for many types of MOFs.

Figure 3.2 Overview of synthesis methods, possible reaction temperatures, and final reaction products in MOF synthesis. (Reprinted with permission from ref. 6)

Considering the structure of MOFs, there are at least two ingredients present in the solvent: metal salt and organic linker. Elevated temperature is often required to enhance the solubility of reaction species, so that MOFs can be formed uniformly inside the system when the precursor concentrations exceed the critical nucleation concentrations. The design of temperature program plays an important role in the synthesis process. For example, the microscale morphology of MOF-177 could be tuned from filaments to needles, rods or even cubes by simply changing heating temperature, time and cooling rate.^[7]

Solvent is another important factor in the solvothermal process because it influences the coordination between metal and linker and provides medium for the MOF growth. For instance, when the synthesis involves carboxylate ligands, solvents like DMF should be chosen for deprotonation of carboxylate. Considering such solvents can be transformed into amines at high temperature, the basicity of reaction medium is adjusted. The deprotonated carboxylate ligands can then coordinate with metal ions. Sometimes solvent also serves as guest molecules trapped inside the pores of MOFs and helps to support the structures. Flexible MOFs, such as MIL-88,^[8] show different cell parameters in various solvent systems.

Learning the factors influencing solvothermal process helps a lot in optimizing synthesis parameters of MOFs. Hence, it becomes possible to achieve MOFs with desired size and morphology by tuning the reaction conditions.

3.2.3 Post synthetic modification (PSM)

Functional groups can be introduced into MOFs through PSM to achieve altered physical or chemical features, which is an outstanding advantage of MOFs over other microporous inorganic solids such as zeolites. According

to the type of bond formed, there are two most common categories: covalent PSM and dative PSM.^[9]

Covalent PSM. As its name implies, covalent PSM refers to using a reagent to modify a component of the MOF, which is normally the organic linker, through a covalent bond. The target organic linkers usually contain pendant groups that is called “tags” allowing modification,^[9] like alcohol,^[10] amine,^[11] aldehyde^[12] and so on. PSM of amine-tagged MOFs are most extensively studied compared to others, possibly because NH₂-BDC is a quite versatile linker used in a wide range of MOFs. For instance, Yaghi’s group^[13] functionalized a amine-tagged MOF, IRMOF-3, with sulfonate and ethylenediamine groups through ring-opening reaction of 1,3-propanesultone and 2-methylaziridine respectively. The modified MOFs still maintained high crystallinity and porosity, which proved that this was an efficient route to binding various functional groups with MOFs. PSM of aldehyde-tagged linker was reported by Yaghi’s group as well.^[14] ZIF-90 contains an aldehyde tag in the 2-position of the imidazole unit, which served as target for PSM. ZIF-91 was achieved when aldehyde was reduced to alcohol. On the other hand, when aldehyde reacted with ethanolamine to form an imine bond, the resultant MOF was ZIF-92. However, ZIF-92 was nearly nonporous due to the presence of introduced large ethanolamine group.

Dative PSM. Dative PSM refers to formation of dative (i.e., metal-ligand) bond during modification. Hence, it could be an organic ligand coordinating with metal cluster of MOF, or a metal source bonding with linker of MOF^[9]. As early as 1999, Chui and coworkers^[15] found axial water molecule coordinated with Cu(II) in HKUST-1 structure could be removed by heating, then the exposed coordination site allowed the introduction of pyridine group. Similar strategy was applied by a number of studies in the following years. MOF can also serve as a platform for the anchoring of

organometallics in a dense and isolated way through dative PSM on organic linker. For instance, Canivet and coworkers^[16] grafted nickel-based organometallic catalyst onto ligand (NH₂-BDC) of (Fe)MIL-101-NH₂ using one-pot post-functionalization. The resultant MOF showed high catalytic activity and selectivity in ethylene dimerization producing 1-butene. Hence, this can be seen as a new way to developing MOF-based catalysts.

3.3 Characterization

3.3.1 Scanning electron microscope (SEM)

SEM is one of the most widely used electron microscopes. It generates high-energy electron beam to interact with sample atoms, and then collects signals containing information about sample's surface topography and composition. Combining the collected signals with position of electron beam scanning, an image can be produced with resolution even better than 10 nm. Most of SEMs are operated in high vacuum or low vacuum. For some specialized instruments, samples can be observed in variable pressures or at elevated temperatures.

An electron beam, that has energy in range of 0.2~40 keV, is emitted from an electron gun. A tungsten filament is usually used as the electron gun because it is not only very cheap, but also stable at very high temperature and low vapor pressure, which allows it to be electrically heated for electron emission. The emitted electron beam then goes through one or two condenser lenses, so spot size can be adjusted from 0.4 nm to 5 nm in diameter. Deflection coils and final lens serve to deflect the beam and control its position in the x and y axes, which enables the beam to scan over the sample surface.

High energy carried by electron beam is dissipated during electron-sample

interaction in forms of secondary electrons, backscattered electrons, characteristic X-rays and so on. Secondary electrons are emitted from sample surface due to electron beam bombardment, so they carry information about sample morphology and topography. Image based on such signal is called secondary electron image (SEI). SEI is also the most common mode used in SEM. On the other hand, some incident electrons are backscattered by the nuclei of sample atoms, which are so called backscattered electrons. Heavy atoms are capable of scattering more electrons, so image based on backscattered electrons (BSE) has contrasts between varied compositions. Different phases in multiphase samples can be roughly distinguished. After secondary electrons are struck out by electron beam, there are vacant energy levels left in sample atoms. Electrons in outer-shell tend to fall into inner-shell, and emit the energy difference in form of X-rays. Each element has its unique characteristic X-rays, thus this signal can be collected for element mapping or spot chemical analysis. This analytical technology is called energy-dispersive X-ray spectroscopy (EDX).

Sample preparation for SEM is quite simple. Minimal preparation is required for conductive samples as long as they can fit into the SEM chamber. However, for the electrically insulating samples such as MOFs, a coating step is necessary to prevent charge build-up, which can affect image quality seriously. Coating materials are usually Au or Pt due to their high conductivity. However, there are some drawbacks of such sputter coating process. Firstly, the surface of the sample is covered by the sputter-coated material instead of the original one. Hence, the atomic number-contrast cannot be evaluated. Moreover, it may lead to altered surface topography or false elemental information about the sample.

In summary, SEM was a very important tool for observing morphology of my samples. SEM-EDX was also frequently used to get information about

element composition.

3.3.2 Transmission electron microscope (TEM)

TEM is another commonly used electron microscope in research. Different from SEM, it collects information carried by transmitted electrons. So it can reveal internal structures of samples. Besides, TEM produces images with very high resolution owing to the small de Broglie wavelength of electrons. It is capable of capturing details as small as atoms, which is helpful for us to observe lattice spacing, grain boundaries and so on.

Similar with SEM, electron gun can be made of a tungsten filament in either hair-pin style or spike shape for thermionic electron emission. Lanthanum hexaboride (LaB_6) source is another option which uses a single crystal for field electron emission. A voltage bias (typically $\sim 100\text{--}300\text{ kV}$) is applied to emit an electron cloud within the surrounding cathode cap (also called Wehnelt cylinder). An anode located below serves to attract and accelerate electrons through a small hole to form a high energy electron beam. The spot size and position of beam are then controlled by a series of lenses and apertures. There are normally three types of lenses present within TEM column: the condenser lenses, the objective lenses and the projector lenses. After the beam is formed under the aid of condenser lenses, the objective lenses are used to focus the beam onto the sample. The projector lenses can expand the beam on the imaging device such as the phosphor screen. Some additional stigmators within column are used to correct asymmetrical beam distortions.

A good vacuum environment is necessary for TEM to increase the mean free path of the electron gas interaction and prevent the formation of electrical arc under high voltage bias. Typical TEM should be evacuated to low pressure on the order of 10^{-4} Pa . A high-voltage TEM even requires

ultra-high vacuums on the range of 10^{-7} to 10^{-9} Pa. Severe problems can happen if the vacuum system is damaged. For example, the deposition of gas onto the specimen can possibly be witnessed. Besides, electrical discharge may cause damage to the cathode cap.

Sample preparation for TEM is more complicated than that for SEM. TEM specimens should have thickness less than 100 nm for electron penetration. Powdered substances, viruses and other materials with dimensions small enough can be directly deposited onto copper grid for observation. Thick samples need to be thinned using mechanical milling, chemical etching, ion etching or other processes.

TEM has several image modes to fulfill various requirements. Bright field (BF) is the most commonly used one, in which contrast is formed due to electron weakening of the direct beam during the electron-specimen interaction. Thicker regions or heavier atoms tend to absorb more electrons, thus they will appear dark on the image. Contrarily, thinner regions or regions with lighter atoms will appear bright. For dark field (DF) images, only one or more diffracted beams can pass objective aperture and interact with the specimen. Such images can give information like planar defects, stacking faults or particle size. When the objective aperture is large enough to allow the direct beam as well as many diffracted beams to pass, high resolution TEM (HRTEM) images are obtained by the interference between the direct beam and the diffracted beams. This image mode enables direct observation of the atomic structure.

If the imaging plane is replaced by the back focal plane on the imaging apparatus, a diffraction pattern is formed, which is called selected area electron diffraction pattern (SAED). A single crystal will produce a pattern of dots, while a polycrystalline or amorphous material has a ring pattern. The diffraction pattern can provide important crystallographic information

about the space group symmetries in the crystal and the crystal's orientation to the beam path.

A scanning transmission electron microscope (STEM) is a TEM equipped with additional scanning coils, detectors and necessary circuitry. High-angle annular dark-field imaging (HAADF) is an imaging technique of STEM. Unlike TEM, the optics determining dark and bright field in STEM is placed after the interaction of the electron beam with the specimen, so the contrast mechanisms vary a lot. For HAADF, an annular dark field detector collects electrons from an annulus around the beam. An image can be formed only by incoherently scattered electrons with very high angle, so it is very sensitive to variations in the atomic number of atoms in the specimen.

Thanks to versatile imaging techniques of TEM, the internal structure of the synthesized core-shell composites could be observed. And it was also used to observe lattice spacing and atomic structure of the metallic samples.

3.3.3 X-ray diffraction (XRD)

XRD is a rapid and nondestructive technique used for characterization of crystalline materials. It is capable of revealing information about crystal structure, preferred orientation and so on. The XRD peak positions are determined by specific angles where constructive interference of diffracted X-ray beam from each set of lattice planes in the sample occurs. The peak intensities are determined by atomic orientation within the lattice. Hence, each material has its characteristic XRD pattern. Online database of XRD patterns can be used for phase identification of unknown crystalline samples.

XRD pattern is based on constructive interference of X-rays diffracted from

the sample. When the incident rays interact with sample lattice planes, constructive interference can be produced in a few specific directions, as described in Bragg's Law:

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

Here n stands for any integer, λ is the wavelength of the beam, d is the lattice plane spacing, and θ is the X-ray incident angle. With fixed X-ray wavelength, the diffraction angle is strongly dependent on the lattice spacing of the sample. For polycrystalline samples or powdered samples, XRD peaks for all possible diffraction directions are obtained owing to the random orientation. It is convenient to convert these peaks into d-spacings for phase identification.

For a typical XRD, there are three basic components: X-ray tube, sample holder and detector. In an X-ray tube, a filament is firstly heated to generate electrons. These electrons are accelerated by a voltage, and then strike a target material to produce characteristic X-rays. These X-rays consist of different wavelengths. So they need to be filtered by foils or crystal monochrometers. Eventually, monochromatic X-rays are emitted from the X-ray tube. The most commonly used target material is Cu, and the generated monochromatic X-rays are Cu K_α radiation with a wavelength of 1.5418Å. Passing through several aperture slits, the X-rays are directed onto the sample holder for interaction. The intensity of the reflected X-rays is recorded by the detector. The sample and detector can rotate simultaneously in a typical $\theta/2\theta$ mode. The sample rotates at an angle of θ , while the detector rotates at an angle of 2θ to collect the diffracted X-rays. At specific angles satisfying Bragg's Law, constructive interference happens. The increase in X-ray intensity is captured by the detector, and plotted as a peak on the monitor.

For the nanocomposites synthesized in this study, XRD was a useful tool to identify each component phase.

3.3.4 X-ray photoelectron spectroscopy (XPS)

XPS is a spectroscopic technique used for analyzing surface chemistry of materials. It can quantitatively measure the elemental composition, as well as empirical formula, chemical state of the elements present on the sample surface. XPS emits an X-ray beam to irradiate the sample, and then measures the kinetic energy and number of electrons that escape from the material surface. This analysis can reach an average depth around 5 nm. High vacuum or ultra-high vacuum conditions are required for operation of the system.

A typical XPS system consists of an X-ray source, an ultra-high vacuum chamber with pumps, an electron energy analyzer as well as a sample stage. The emission of X-rays is owing to accelerated electrons bombarding target materials, similar to XRD. But the most widely used target materials for XPS are Mg and Al. Then the beam of non-monochromatic X-rays is filtered to achieve a monochromatic beam. The resulting Mg K_{α} radiation has photon energy of 1253.6 eV for Mg source, while Al K_{α} radiation has photon energy of 1486.6 eV for Al source. Hence, after the interaction between X-rays and the sample, the emitted photoelectrons must have their kinetic energy within this range. The electron energy analyzer is in charge of measuring the kinetic energy and number of the emitted photoelectrons.

During the interaction between the monochromatic X-rays and the sample, photon energy is absorbed by sample atoms, resulting in ionization and emission of inner-shell electrons. And the kinetic energy of an emitted photoelectron can be measured by the electron energy analyzer. The difference between the photon energy and the kinetic energy equals to the binding energy of the electron, which is an important term representing the difference in energy between the ionized and neutral atoms. The final obtained XPS spectrum is a plot of the counts of electrons detected versus

the calculated binding energy of these electrons. Each element has its characteristic binding energy peaks because they correspond to its unique electron configuration within the atom, e.g. $1s$, $2s$, $2p$, $3s$, etc. So elements present on the surface of the sample can be directly identified. The count number of the electrons represents the amount of element present within the sampling volume. XPS spectrum can thus be used to calculate atomic percentage values except for hydrogen atoms.

XPS provides information about chemical state of material surface either in as-prepared state, or after physical or chemical treatments. The chemical state can be affected by the surrounding atoms, the bonding hybridization to the neighboring atoms and the oxidation state of the element. In short, chemical state is the local bonding environment of the element. For example, C $1s$ electron has a theoretical binding energy of 285.0 eV. In the actual bonding environment, subtle shifts can often be observed due to presence or absence of its different formal oxidation states. This phenomenon is called chemical shifts, and it provides further information for chemical state analysis.

In this thesis, XPS spectra were used to analyze chemical states and chemical shifts of the bimetallic nanocomposites, so that the change in electronic property of the sample elements could be evaluated.

3.3.5 Ultraviolet–visible spectroscopy (UV-Vis)

UV-Vis is a type of absorption spectroscopy or reflectance spectroscopy working in the region of ultraviolet-visible spectrum, where electronic transitions of atoms and molecules occur. The absorption or reflectance of light within this region determines the perceived color of compounds.

Photons in ultraviolet-visible range carry enough energy to promote a

molecular electron to a higher energy orbital (e.g. non-bonding to π^* anti-bonding or π bonding to π^* anti-bonding). When the emitted light beam passes through the sample, the sample molecules will absorb photons with energy that exactly matches the possible electronic transition within the molecules. Thus a decrease in light intensity is observed at a specific wavelength where the absorption happens.

Absorption coefficient is an important factor determining how far into a material light of a particular wavelength can penetrate before it is absorbed. Materials with high absorption coefficients absorb large amount of photons to get electrons excited into conduction band. The absorption coefficient depends on the material as well as the wavelength of light which is being absorbed. Typically, a sharp change in the absorption coefficient is witnessed for semiconductor materials. When photons carry less energy than the band gap, they cannot be absorbed. As the photon energy increases, more electrons can interact with the photon and result in the photon absorption.

A typical instrument used for measuring UV-Vis is called UV-Vis spectrophotometer. Light sources emit electromagnetic waves with wavelength ranging from 200 nm to 800 nm. A tungsten filament or light emitting diodes are frequently used as visible light source. A deuterium arc lamp or xenon arc lamp is good source of UV light. The diffraction grating is used to convert the UV and visible light into monochromatic light beam with single wavelength. Then the monochromatic beam is equally split into two beams through a beam splitter. One beam passes through a cuvette containing sample solution, while the other passes through a reference cuvette containing only the transparent solvent. The detector will measure the intensities of the transmitted light beams respectively. The intensity for the sample cuvette is denoted as I , while the intensity for the reference cuvette is recorded as I_0 . If I is equal to I_0 , there is no light absorption.

However, if I is less than I_0 , the difference in intensity can be presented as transmittance ($T = I/I_0$) or absorbance ($A = \log I_0/I$). It is convenient to choose any scanning wavelength range within UV-Vis spectrum. Eventually, a plot of transmittance or absorbance versus wavelength can be obtained.

Since NPs/MOF composites were used as catalysts in the photocatalytic reactions, UV-Vis helped a lot in figuring out the photo response of the material.

3.3.6 Fourier transform infrared spectroscopy (FTIR)

FTIR is a technique measuring the absorption spectrum of a sample (solid, liquid or gas) within very wide infrared range. The output signal collected by a detector is converted into spectrum through a Fourier transform. The instrument used for acquiring such spectra is called a FTIR spectrometer. Each chemical molecule produces its unique spectral pattern, which serves as a fingerprint of the molecule.

In infrared spectral region, molecules absorb radiation frequencies that match their vibrational frequencies, which are also called resonant frequencies. A molecule can have many vibrational modes, such as symmetric and antisymmetric stretching, scissoring, rocking wagging, twisting and so on. Only when a change in its dipole moment is achieved, the vibrational mode is IR active, thus an IR absorption band arises on the resulting spectrum.

In a typical FTIR spectrometer, a silicon carbide light source is usually heated to 1200K to generate infrared light beam. Then the emitted light is directed to an interferometer, which is the most important component of the spectrometer. A beam splitter located inside interferometer guides 50% of

the light towards a fixed mirror, while the other 50% travels to a moving mirror. Then two light beams are reflected back to the beam splitter from two mirrors respectively. Some fraction of the original light passes through the sample compartment, and captured by a detector. By varying the position of the moving mirror, the optical path difference (OPD) between the two arms to the interferometer can be changed accordingly. The plot of signal output versus the OPD is called an interferogram. The intensity reaches a maximum at 0 OPD, because constructive interference occurs at all wavelengths. In the presence of a sample, its IR absorption bands will modulate the background of interferogram. Eventually, the recorded interferogram is converted to an interpretable spectrum through Fourier transform.

As introduced above, FTIR is a convenient technique for identification of the unknown. After PSM of MOFs, it was used to suggest the presence of some specific functional groups, so that the success of the modification could be proved.

3.3.7 Surface area and porosity analysis

Surface area and porosity are important characteristics of porous solid materials. Even with the same dimensions, their surface area and porosity differ a lot, thus influencing their applications in gas storage, sensing, catalysis, etc. The surface area and porosity of materials can be measured *via* a gas adsorption analysis. The sample material is exposed to gases like nitrogen at various pressures, and the gas uptake quantity is tracked and evaluated. Analysis of these data gives information about surface area and porosity of the solid material.

According to gas adsorption theory, adsorption of gas molecules onto solid surface undergoes four stages with increasing pressure. At very low

pressure, gas molecules begin to adsorb at some isolated sites on the surface. (Stage 1) As pressure increases, the molecules gradually form a monolayer covering the solid surface. (Stage 2) Further increase of gas pressure leads to multi-layer coverage. These gas molecules even fill some small pores in the sample. (Stage 3) If the pressure keeps increasing, eventually a complete coverage is achieved, and all the pores are filled. (Stage 4)

The Brunauer, Emmett and Teller (BET) technique is used to calculate the surface area of a sample, which is an important factor determining how it interacts with other materials. Before the measurement, the sample needs to go through an activation process under heat and vacuum to remove any adsorbed species (e.g. solvent molecules, gas). As nitrogen gas is usually employed as the probe molecule for the measurement, the sample is exposed at liquid nitrogen conditions (77 K). The quantity of nitrogen gas adsorbed at each pressure will be calculated and plotted into an adsorption isotherm. From the isotherm, the quantity of molecules required to form a monolayer over the external surface of the solid is determined, thus the surface area can be calculated based on knowing area occupied by each adsorbed gas molecule. The cross-sectional area for nitrogen molecule is commonly taken as $16.2 \text{ \AA}^2 / \text{molecule}$. After a monolayer of adsorption is achieved, the gas molecules start to fill in the small pores with increasing pressure. And saturation is reached when all the pores are completely filled. The pressure will then be reduced gradually for a desorption process. Evaluation of the adsorption and desorption isotherms as well as the hysteresis between them provides information about the pore size distribution.

Surface area and porosity analysis is very important for porous materials like MOFs, because such technique can reveal the porous structure, which cannot be observed through any other techniques. When a NPs/MOF

composite is applied in a chemical catalysis, its pore size limits the size of reactants that can get inside the structure and contact with NPs.

3.3.8 Gas chromatography (GC)

GC is a powerful technique used for analysis and separation of chemical compounds. It is employed in testing the purity of sample, qualitative and quantitative analysis for different components of a mixture, etc. When coupled with a mass spectrometer (MS), the instrument can directly identify an unknown substance.

An unreactive carrier gas, usually helium or nitrogen, serves as the mobile phase for the chromatograph. On the other hand, the stationary phase is a microscopic layer of liquid or polymer coated on the internal walls of a column. When a sample is injected through the sample injector, it is quickly vaporized under heat, and directed through the column by the carrier gas. The components of the sample interact with the stationary phase within the column, and thus leave the column at a different time, which is called the retention time. Each eluted compound is detected by a detector, and plotted as a peak in the chromatogram. The flame ionization detector (FID) is a common detector used in GC. The components coming out from the column mixed with hydrogen and air is ignited in the flame. Then the pyrolysis of the compounds produces ions and electrons that conduct electricity. Owing to the presence of an electrical potential and a collector electrode, the resulting current can be measured.

For the operation of GC, the method can be conveniently tailored according to different samples to achieve better measurement. Conditions that can be varied include inlet temperature, detector temperature, column temperature program, carrier gas flow rates, etc.

The graph obtained from GC is called chromatogram, and it is a plot of compound signals against the retention time. The location of a peak can be used for qualitative analysis by comparing it with a standard reference, and the method for measurement must be kept the same. The area under a peak is proportional to the amount of the compound. So GC is also capable of quantitative analysis by calculating the peak areas through integration. For comparison between different compounds, calibration is required by using an external or internal standard as reference.

For my study, a mixture of reactants and products was obtained after each catalysis reaction. GC was a suitable technique for separation and identification of individual compound. Hence, it was used to evaluate most of the catalysis reactions, and figure out the catalytic activity and selectivity of the catalyst.

3.3.9 Nuclear magnetic resonance (NMR) spectroscopy

NMR spectroscopy is a non-destructive technique that can be used to determine the structure dynamics, reaction state, and chemical environment of molecules. It is designed based on NMR phenomenon. During the measurement, the resonance frequency of an atom is changed by its surrounding intramolecular magnetic field. Thus the structural information of the molecule is revealed.

Considering a nucleus as a mini bar magnet, NMR is a property strongly related to the nuclear spin (I), which can be integer, fraction or even zero. NMR active nucleus should have $I = \frac{1}{2}$. Isotopes such as ^1H , ^{13}C , ^{19}F and ^{31}P fulfill the requirement. Thus organic compounds containing such elements can be analyzed by NMR. When a nucleus with $I = \frac{1}{2}$ is placed in an external magnetic field (B_0), it can either be in lower energy state when it is aligned with the field, or it can be in higher energy state when it is

aligned against the field. Then a broad range of radio waves are applied. Nuclei in lower energy state can absorb the wave frequencies that match the energy difference ($\Delta E = \mu B_0 / I$, where μ is the magnetic moment of the nucleus in the field) and jump to the higher energy state. In the subsequent relaxation process, these nuclei will emit radio waves and relax back to their original state.

In a real molecule, the magnetic effect of nearby nuclei and electrons also contributes to the effective magnetic field working on a nucleus. Hence, a shift in absorption frequency relative to an isolated atom can be observed. In a NMR spectrum, resonance frequency of tetramethylsilane (TMS) is defined as zero. Absorption peaks for any other compounds are plotted against their chemical shift (δ) from the zero point. Normal range of δ for ^1H NMR is around 12 ppm.

When the effective magnetic field is affected by nearby nuclei and electrons, the nearby nuclei themselves are excited by radio waves. For the case of ^1H NMR, any particular ^1H atom has approximately 50% of the time in the lower energy state, and other 50% of the time in the higher energy state. When a ^1H has one neighboring nucleus, the resulting absorption signal will split into a doublet. Half is shifted downfield, while the other half is shifted upfield. More complexed system will produce triplet, quartet, etc. This phenomenon is called coupling.

As illustrated above, external magnetic field is produced by a magnet. The broad range of radio waves is emitted from a radiofrequency generator. Resulting signals are then amplified and detected. Similar to GC, ^1H NMR can be used for quantitative analysis because the area under each peak is proportional to the number of hydrogens that have identical resonance frequency. Software can directly convert the area into the vertical distance of the integration line, which is quite convenient for us to calculate the

ratios.

NMR spectra are sensitive, unique and predictable for different organic compounds. In my catalysis reactions, some chemicals couldn't be vaporized before decomposition, so they were not suitable for GC characterization. In such case, NMR is a powerful tool for evaluating the catalytic performance.

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Chapter 4

Submonolayered Ru Deposited on Ultrathin Pd Nanosheets Used for Enhanced Catalytic Applications

A facile and robust method to prepare ultrathin bimetallic core-shell nanosheets (NSs) will be introduced, where the ultrathin 2D metallic NSs are incompletely covered by another atomically layered metal. Submonolayered Ru decorated-ultrathin Pd NSs was synthesized using this seed-mediated growth method for the first time, which is referred to as Pd@Ru NSs. The underpotential deposition process is responsible for the formation of Pd@Ru NSs. Impressively, the as-synthesized noble bimetallic Pd@Ru NSs exhibit superior catalytic performance toward the reduction of 4-nitrophenol and the semihydrogenation of 1-octyne as compared to the pure ultrathin Pd NSs and Ru NSs.

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4.1 Introduction

The research on ultrathin 2D nanomaterials has become intensive in recent decade due to their distinctive properties associated with the dimensional confinement in 2D morphology, which are quite different from their bulk counterparts.^[1-5] As an important member of the 2D family, ultrathin noble metal nanosheets (NSs) often experience enhanced catalytic performance owing to their high surface area-to-volume ratio and exposure of high-density unsaturated atoms on the surface.^[6-10]

Structural modulation of noble metal nanostructures at the atomic scale can greatly alter their catalytic properties.^[7,8,11,12] For example, deposition of single or few layers of metal atoms on the surface of another single-crystal metal substrate can result in lattice strain, which may promote the surface reactivity greatly.^[13,14] Based on this idea, variety of bimetallic core-shell nanostructures with atomically thin shell were synthesized for their enhanced catalytic activities.^[15-18] However, if the core metal is completely covered by the shell, its catalytic sites are also blocked. Sometimes incomplete coverage is favored, because different metal atoms can be exposed during the catalysis.^[19-21] Considering the outstanding properties of ultrathin 2D NSs with atomically thin shell, it is highly desirable to develop a facile, versatile, and robust method to fabricate bimetallic core-shell NSs, in which core and shell atoms are both exposed.

Herein, a simple seed-mediated growth method was successfully developed to obtain the ultrathin Pd NSs deposited by submonolayered Ru, which is referred to as Pd@Ru NSs. The Pd@Ru NSs show superior catalytic activities in the reduction 4-nitrophenol and the semi-hydrogenation of 1-octyne compared to the pure ultrathin Pd NSs and Ru NSs.

4.2 Experimental section

4.2.1 General information

Chemicals were all purchased from Sigma-Aldrich (ACS grade) and used as received unless otherwise noted. Ethanol (absolute, 99.9%), acetone (99.9%) and n-decane (99%) were purchased from Merck (Nordic European Centre, Singapore). The Milli-Q water obtained from the Milli-Q System was used in all experiments. Samples used for transmission electron microscopy (TEM) measurements were prepared by dropping the ethanolic dispersion of nanosheets on holey carbon-coated copper grids and then dried under ambient conditions. The low-magnification TEM measurement was performed on a JEOL JEM-2100F operated at 200 kV. The high-angle annular dark-field scanning transmission electron microscope (HAADF-STEM) and energy-dispersive X-ray spectroscopy (EDS) elemental mapping were recorded on a high resolution aberration corrected transmission electron microscope (JEOL JEM-ARM200F) operated at 200 kV. Samples for X-ray photoelectron spectroscopy (XPS) were prepared by dropping the ethanolic dispersion of nanosheets on a piranha-cleaned Si and then dried under ambient conditions. The XPS data were collected with a Theta Probe electron spectrometer (ESCA-Lab-200i-XL, Thermo Scientific). The energy calibration was made against the C1s peak during analysis. Inductively coupled plasma optical emission spectrometry (ICP-OES) was performed on a Dual-view Optima 5300 DV ICP-OES system. The reactants and products in the semi-hydrogenation of 1-octyne were analyzed with a gas chromatograph (Agilent, 6890N) equipped with a HP-5 column (Agilent) and a flame ionization detector (FID). The UV-Vis spectra of the catalytic reaction solution in the reduction of 4-nitrophenol were recorded using Shimadzu UV-2700 UV-Vis spectrophotometer.

4.2.2 Pd nanosheets

The ultrathin Pd NSs were synthesized using a modified method following a previous report.^[22] Firstly, PVP (MW=29000, 30 mg), CA (170 mg), CTAB (60 mg), and Pd(acac)₂ (16 mg) were dissolved in DMF (10 mL) and magnetically stirred for 1 h for homogeneous mixture. The resulting orange-red solution was transferred into a 50 mL flask, and flushed with N₂ gas for 20 min. After W(CO)₆ (100 mg) was added into the solution, the flask was sealed under N₂ atmosphere and heated at 80 °C in oil bath for an hour. Eventually, the product was precipitated by acetone (30 mL), and further separated by centrifugation at 6000 rpm for 5 min. The mixture of ethanol (5 mL) and acetone (40 mL) was used to wash the product. A high speed centrifugation at 12000 rpm for 10 min was required for separation. The obtained Pd NSs were re-dispersed in EG (10 mL).

4.2.3 Pd@Ru nanosheets

PVP (MW=29000, 50 mg) and AA (50 mg) were dissolved in EG (5 mL), and mixed with the suspension of the pre-synthesized Pd NSs in EG (0.55 mg/mL, 5 mL). Then the mixture was magnetically stirred and heated to 160 °C in oil bath. The solution of Ru(acac)₃ in EG (0.8 mg/mL, 5 mL) was injected into the mixture using a syringe at the rate of 5 mL/h under magnetic stirring. After the mixture was kept at 160 °C for 1 h, it was naturally cooled down to ambient temperature. Finally, the product was precipitated by acetone (40 mL), separated *via* centrifugation at 12000 rpm for 10 min, and further washed three times with a mixture of ethanol (5 mL) and acetone (40 mL).

4.2.4 Reduction of 4-nitrophenol by NaBH₄

In a typical experiment, after the freshly prepared NaBH₄ solution (25 μ L, 2 M) in ice-cold water was added into the aqueous solution of 4-nitrophenol (4.95 mL, 0.15 mM), the colorless solution became yellow. Then, the aqueous suspension of Pd@Ru NSs (1.7 μ L, Pd: 7.6 mM, Ru: 1.0 mM) or Pd NSs (2.2 μ L, Pd: 6.8 mM) was quickly injected into the aforementioned solution and mixed with a pipette. The mixture was kept undisturbed during the catalytic reaction. The reaction was monitored by UV-Vis spectrometer, which was used to record the absorption intensity of the reactant and product in the aliquot samples taken out from the reaction solution at regular time intervals between 0 to 14 min (reaction time).

4.2.5 Semi-hydrogenation of 1-octyne

This catalytic reaction was carried out at room temperature and under static hydrogen atmosphere (1 bar). In a typical experiment, the ethanol (6 mL), ethanolic suspension of Pd@Ru NSs (11.6 μ L, Pd: 7.6 mM, Ru: 1.0 mM) or Pd NSs (14.7 μ L, Pd: 6.8 mM), 1-octyne (73.5 μ L, 0.5 mmol), and n-decane (10 μ L, 0.05 mmol) were successively added into a glass reactor. Here, n-decane was used as internal standard. The residual air in the reactor was expelled by flushing hydrogen for several minutes before the glass reactor was sealed. The pressure in the reactor was maintained at normal atmospheric pressure. Then the mixture was stirred at 600 rpm using a magnetic bar during the catalytic reaction. Small portion of the solution was taken out at different time intervals and analyzed with a gas chromatography.

4.3 Results and Discussion

4.3.1 Characterization

Ultrathin Pd NSs were firstly synthesized and observed under a high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and a transmission electron microscopy (TEM). (Figure 4.1) According to the images, Pd NSs have lateral size of 7.2 ± 0.8 nm (Figure 4.1b) and thickness of about 1.5 nm (Figure 4.1d).

Figure 4.1 a) HAADF-STEM and b-d) TEM images of the synthesized Pd NSs. Insets: a) Scheme of a typical hexagonal nanosheet. The lateral size is defined as the diagonal length (L). b) Statistical analysis of lateral size of Pd NSs measure by TEM. c) HRTEM image of a typical Pd NS.

After the seed-mediated growth, the obtained Pd@Ru NSs were characterized by HAADF-STEM and TEM as well. (Figure 4.2) The products are uniform NSs (Figure 4.2a) with lateral size of 7.8 ± 0.7 nm (Figure 4.2b), which is slightly larger than pure Pd NSs (Figure 4.1b). The lattice fringes with an interplaner spacing of 0.23 nm were identified from the aberration-corrected HAADF-STEM image of a single flat NS (Figure

4.2d), which is equivalent to pure Pd NS (Figure 4.1c). This interplaner spacing corresponds to the 1/3(422) planes of face-centered-cubic (fcc) Pd.^[6] Figure 4.2e shows the side view of a Pd@Ru NS composed of 9-12 atomic layers. The interplaner spacing is measured to be 0.23 nm again, and it can be indexed to the {111} planes of fcc Pd. Some crystal defects, such as twins and stacking faults, are observed (Figure 4.2e) due to the lattice mismatch (3.6%) between Pd and Ru.^[23] The formation of Pd@Ru core-shell structure was confirmed by the energy-dispersive X-ray spectroscopy (EDS) elemental mapping of a single NS vertically oriented on the TEM copper grid (Figure 4.2f).

Figure 4.2 a) TEM, c) HAADF-STEM and d,e) aberration-corrected HAADF-STEM images of Pd@Ru NSs. b) Statistical analysis of lateral size of Pd@Ru NSs measured in (a). f) STEM-EDS elemental mapping of a typical Pd@Ru NS. g) Schematic illustration of the synthetic process of Pd@Ru NSs.

The EDS was used to estimate the elemental composition of Pd@Ru NSs as well. According to the EDS spectrum (Figure 4.3), the atomic ratio of Pd to

Ru is approximately 86.8/13.2, which is quite close to the result measured by an inductively coupled plasma optical emission spectrometry (ICP-OES) 88.3/11.7.

Figure 4.3 A representative EDS spectrum of Pd@Ru NSs, proving that the atomic ratio of Pd to Ru is 86.8/13.2. The additional Cu signal arises from the TEM copper grid.

The electronic states of Pd and Ru atoms in Pd NSs and Pd@Ru NSs were investigated by the X-ray photoelectron spectroscopy (XPS). As shown in Figure 4.4a and b, a positive shift of 0.85 eV in the binding energy of Pd can be observed in the Pd@Ru NSs (336.06 eV for Pd(0) 3d_{5/2} and 341.35 eV for Pd(0) 3d_{3/2}) compared to the Pd NSs (335.21 eV for Pd(0) 3d_{5/2} and 340.50 eV for Pd(0) 3d_{3/2}). This shift indicates that the deposition of Ru atoms induced the change of the electronic property of Pd.^[24,25] The binding energies of Ru 3d_{5/2} and Ru 3d_{3/2} are measured to be 280.45 eV and 284.62 eV respectively (Figure 4.4c), which suggests the formation of metallic Ru in the Pd@Ru NSs.^[25,26] Besides, the Ru 3p_{3/2} peak centered at 461.94 eV (Figure 4.4d) further confirms the metallic state of Ru in the Pd@Ru NSs.^[26]

Figure 4.4 a) Pd 3d XPS spectrum of Pd NSs. b) Pd 3d, c) Ru 3d and d) Ru 3p XPS spectra of Pd@Ru NSs.

Several more control experiments have been done to study the formation mechanism of Pd@Ru NSs. It has been found that no product could be obtained when the reaction was conducted without the pre-synthesized Pd NSs. The pre-synthesized Pd NSs can serve as seeds for Ru deposition because they are capable of decreasing the nucleation energy barrier of Ru atoms. Then the Pd NSs simultaneously provide the heterogeneous nucleation sites for the subsequent epitaxial growth of Ru.^[27,28] In addition, the amount of Ru(acac)₃ precursor was increased for comparison. However, the thickness of Pd@Ru NSs would not increase any more (Figure 4.5), and the Pd/Ru atomic ratio remained the same.

Figure 4.5 TEM images of Pd@Ru NSs obtained using the same procedure but with addition of different amount of Ru(acac)₃. a) 8 mg, and b) 16 mg of Ru(acac)₃.

For a single Pd@Ru NS, if Pd core was completely covered by Ru monolayer, the molar percentage of Ru was theoretically calculated to be 31.8% (Appendix A.2). However, as mentioned above, the actual molar percentage of Ru is around 11.7% measured by ICP-OES, which is much lower than the theoretical value. This indicates the incomplete coverage of Ru on the surface of Pd NSs. Submonolayered Ru decorated Pd NSs enables the dual exposure of Ru and Pd atoms on the surface of Pd@Ru NSs. Based on the characterization results, it is believed that the underpotential deposition (UPD) process is responsible for the formation of Pd@Ru NSs (Figure 4.2g). The UPD is widely applied to deposit a monolayer of metal atoms on a foreign metal substrate, in which the standard reduction potential of the substrate is much more positive than that of the deposited metal.^[23,29] In this case, the standard reduction potential of Pd²⁺/Pd pair (0.95 V) is much more positive than that of Ru³⁺/Ru pair (0.45 V),^[30] which meets the requirement for the UPD process.

4.3.2 Catalytic performance

As known, Pd-based nanostructures are excellent catalysts for various chemical reactions.^[6,31,32] As a proof-of-concept application, the Pd@Ru NSs were used as catalysts for the reduction of 4-nitrophenol to

demonstrate their structural advantage in the catalysis. This reaction was conveniently monitored with a UV-Vis spectrometer by measuring the distinctive absorption of the reactant 4-nitrophenol and the product 4-aminophenol. Prior to the catalysis, the addition of NaBH₄ induced the formation of 4-nitrophenolate anions under alkaline condition, which has a characteristic absorption peak at 400 nm.^[33] This peak gradually decayed upon the proceeding of the reduction reaction. Meanwhile, the formation of 4-aminophenol product was proven by the appearance and growth of a new peak at 300 nm (Figure 4.6a and b). The intensity of normalized absorption peaks at 400 nm for both Pd@Ru NSs and Pd NSs were recorded and plotted as a function of reaction time (Figure 4.6c) to study the reaction kinetics. The faster decay for the Pd@Ru NSs indicates their superior catalysis activity towards the reduction of 4-nitrophenol. As excessive amount of NaBH₄ was present in both catalytic reactions, the reaction rate was merely determined by the adsorption of 4-nitrophenol on the surface of catalysts, following the pseudo-first-order kinetics.^[34,35] Hence, the plot of logarithm of absorption versus reaction time (Figure 4.6d) can be fitted linearly. The slopes, i.e. the rate constant (k) for the catalysis, were calculated to be 0.221 and 0.163 for Pd@Ru NSs and pure Pd NSs respectively, which further confirms the excellent catalytic performance of the Pd@Ru NSs.

Figure 4.6 Comparison of the catalytic activities of a) Pd@Ru NSs and b) Pd NSs in the reduction of 4-nitrophenol. c) Normalized absorption (against the initial value at reaction time of 0 min) at 400 nm for 4-nitrophenol as a function of time. d) Plots of $-\ln(\text{absorption})$ versus reaction time generated from (c), where the normalized absorption at 400 nm was recorded.

The pure Ru NSs were synthesized based on a previously reported method^[36] for comparative study (Figure 4.7a and b). Under exactly the same reaction conditions, the decay of absorption peak at 400 nm was quite slow (Figure 4.7c and d), indicating their weak catalytic activity. The rate constant of the pure Ru NSs was calculated to be 0.011 (Figure 4.7e), which is far more less than that of the Pd@Ru NSs as well as the pure Pd NSs. Figure 4.7f shows a control experiment without adding any catalysts. The reduction reaction cannot proceed without the catalysts.

Figure 4.7 a,b) TEM images of Ru NSs synthesized c) The catalytic activities of Ru NSs in the reduction of 4-nitrophenol. d) Normalized absorption (against the initial value at reaction time of 0 min) at 400 nm for 4-nitrophenol as a function of time. e) Plots of $-\ln(\text{absorption})$ versus the reaction time generated from (d), where the normalized absorption at 400 nm was recorded. f) Control experiment in the reduction of 4- nitrophenol (without catalyst).

Furthermore, the semi-hydrogenation of 1-octyne was also used as a model reaction to investigate the catalytic activity and selectivity of the obtained Pd@Ru NSs. Different from the reduction of 4-nitrophenol, the reaction was monitored with gas chromatography (GC). At each fixed time interval during the hydrogenation process, aliquots of samples were taken and examined by GC to study the reaction kinetics. The conversion of 1-octyne

against time by using Pd@Ru NSs and Pd NSs as catalysts were plotted in Figure 4.8a. It is clear that 1-octyne could be fully converted only after 40 mins with the Pd@Ru NSs as catalysts, while around 60% conversion was achieved for the pure Pd NSs under the same reaction conditions. As known, 1-octyne can be partially hydrogenated to 1-octene, and then fully reduced to n-octane. During the catalytic reactions, both products were obtained. Figure 4.8b shows the yield of 1-octene is much higher than that of n-octane in both reactions. However, the yield of 1-octene with the Pd@Ru NSs as catalysts grew faster compared to that for the Pd NSs, thus demonstrating higher catalytic activity of the Pd@Ru NSs.

Figure 4.8 Comparison of the catalytic properties of Pd@Ru NSs and Pd NSs in the semi-hydrogenation of 1-octyne. a) Plots of conversion of 1-octyne versus reaction time. b) Plots of yield of 1-octene and n-octane versus reaction time by using Pd@Ru NSs and Pd NSs as catalysts. The error bars are obtained based on three independent catalytic reactions.

The selectivity towards 1-octene can be calculated based on the yields of two products. Figure 4.9 shows the selectivity measured at different conversion rates of 1-octyne. As observed, the Pd@Ru NSs and the Pd NSs showed quite similar selectivity towards 1-octene at the same conversion rate of 1-octyne, generally above 90%. Hence, despite the enhanced catalytic activity, the Pd@Ru NSs does not compromise the selectivity contributed by the Pd NSs.

Figure 4.9 1-Octene selectivity versus 1-octyne conversion by using Pd@Ru NSs and Pd NSs as catalysts. The error bars are obtained based on three independent catalytic reactions.

The enhanced catalytic activity of the Pd@Ru NSs was confirmed in the reduction of 4-nitrophenol and the semi-hydrogenation of 1-octyne, which might be owing to their ultrathin 2D structure,^[7,8] crystal defects like twins and stacking faults,^[37-39] and the synergistic effect between different components.^[23,40,41] First of all, the ultrathin 2D structure ensures the Pd@Ru NSs possess very large surface area, i.e. large contact area with reactants. Besides, the incomplete coverage of submonolayered Ru on few-layer Pd NSs enables dual exposure of high-density unsaturated atoms on the surface,^[7,8] thus induces the synergistic effect for the catalysis.^[23] Secondly, there are some previous report about that the electronic structure and the surface activity of metal nanostructures can be modulated by the presence of the crystal defects like twins and stacking faults as shown in Figure 4.2e, which may result in improved catalytic activity.^[37,42] Thirdly, the deposition of submonolayered Ru on the Pd NSs changes the electronic structure of Pd, which was confirmed by the XPS characterization (Figure 4.4), therefore the catalytic activity may be improved.^[24,25]

4.4 Conclusion

In summary, for the first time, the sub-monolayered Ru decorated-ultrathin Pd NSs have been successfully synthesized, based on a seed-mediated growth method. The underpotential deposition (UPD) process is responsible for the formation of Pd@Ru NSs. The as-synthesized novel bimetallic Pd@Ru NSs exhibit excellent catalytic properties towards the reduction of 4-nitrophenol and the semi-hydrogenation of 1-octyne as compared to the pure Pd NSs and Ru NSs. It is believed that this synthetic strategy with precise control of sub-monolayered Ru on ultrathin Pd NSs could be universally applicable to various similar metallic nanostructures, which might have promising catalytic applications.

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Chapter 5

Ultrathin Pd Nanosheets immobilized on 2D Porphyrinic MOFs for Enhanced Photo-oxidation performance

2D noble metal/porphyrinic MOF composite was synthesized via a seed-mediated growth method. Owing to the synergistic effect between the photothermal effect of Pd and the light-harvesting ability of the porphyrinic MOF Cu-TCPP, the composite exhibits superior catalytic performance than pure Pd NSs in the photo-oxidation of benzyl alcohol under high light irradiation intensity. Furthermore, the catalytic activity of the composite can be altered upon different light irradiation intensities.

5.1 Introduction

In current chemical industry, selective oxidation of alcohols to aldehyde in the presence of oxygen is a very important process for the production of many fine chemicals.^[1,2] Noble metal NPs and noble metal-based composites have been considered as effective catalysts for such reactions.^[3-7] These catalysts often require harsh reaction conditions such as high temperature and high oxygen pressure, which is not favored for the recyclability of catalysts as well as the operation safety of the reactions. In this context, compositing noble metal with photosensitizer becomes a possible solution to catalyze the reactions under relatively mild conditions.

Recently, metal-organic frameworks have drawn growing attention owing to their unique porous structure, enormously high surface area and great flexibility for versatile applications.^[8-11] Within the MOF family, porphyrinic MOFs exhibit excellent light-harvesting ability.^[12] They have been applied as photosensitizers in various chemical reactions.^[13-15] On the other hand, Pd nanostructures were intensively reported as promising catalysts for alcohol oxidation.^[16-19] Moreover, Pd benefits from photothermal effect under light irradiation owing to surface plasmon resonance (SPR),^[20-22] which can possibly promote the catalysis reactivity. The integration of Pd and porphyrinic MOF may induce a synergistic effect, thus enhance the catalytic performance for alcohol oxidation under light irradiation.

Based on this hypothesis, 2D Pd/Cu-TCPP (TCPP = tetrakis(4-carboxyphenyl)porphyrin) NSs were prepared *via* a seed-mediated growth method. Cu-TCPP is a previously reported 2D MOF nanosheet formed by the paddlewheel metal nodes, i.e., $\text{Cu}_2(\text{COO})_4$, and TCPP ligands.^[23] Compared to 3D architecture, 2D morphology ensures the contact between two components without hindering the diffusion of chemicals. Compared

with Cu-TCPP and Pd NSs, the Pd/Cu-TCPP composite NSs showed enhanced catalytic performance in the photo-oxidation of benzyl alcohol, as shown in Figure 5.1.

Figure 5.1 Pd/Cu-TCPP for enhanced photocatalytic oxidation of benzyl alcohol.

5.2 Experimental section

5.2.1 General information

Chemicals were all purchased from Sigma-Aldrich (ACS grade) and used as received unless otherwise noted. Ethanol (absolute, 99.9%), acetone (99.9%) and ethyl acetate (99%) were purchased from Merck (Nordic European Centre, Singapore). The low-magnification TEM measurement was performed on a JEOL JEM-2100F operated at 200 kV. The energy dispersive X-ray spectroscopy (EDS) spectrum of sample was measured using a JEOL JSM-7600F operated at 15 kV. Inductively coupled plasma optical emission spectrometry (ICP-OES) was performed on a Dual-view Optima 5300 DV ICP-OES system. The UV-Vis spectrum of the sample suspension was recorded using Shimadzu UV-2700 UV-Vis spectrophotometer. X-ray diffraction (XRD) patterns were recorded to study the crystal structure with a Shimadzu XRD-6000 Diffractometer

using nickel-filtered Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). A 300W xenon lamp (MAX-302, Asahi Spectra Company, Led.) with adjustable current was used as the light source for photocatalysis reactions. The reactants and products in the photo-oxidation of benzyl alcohol were analyzed with a gas chromatograph (Agilent, 6890N) equipped with a HP-5 column (Agilent) and a flame ionization detector (FID).

5.2.2 Pd nanosheets

The ultrathin Pd NSs were synthesized using a modified method following a previous report.^[24] Firstly, PVP (MW=29000, 30 mg), CA (170 mg), CTAB (60 mg), and Pd(acac)₂ (16 mg) were dissolved in DMF (10 mL) and magnetically stirred for 1 h for homogeneous mixture. The resulting orange-red solution was transferred into a 50 mL flask, and flushed with N₂ gas for 20 min. After W(CO)₆ (100 mg) was added into the solution, the flask was sealed under N₂ atmosphere and heated at 80 °C in oil bath for an hour. Eventually, the product was precipitated by acetone (30 mL), and further separated by centrifugation at 6000 rpm for 5 min. The mixture of ethanol (5 mL) and acetone (40 mL) was used to wash the product. A high speed centrifugation at 12000 rpm for 10 min was required for separation. The obtained Pd NSs were re-dispersed in ethanol (5 mL).

5.2.3 Pd/Cu-TCPP nanosheets

The synthesis method for Cu-TCPP^[23] was slightly modified to obtain Pd/Cu-TCPP NSs. In a 20mL capped vial, Cu(NO₃)₂·3H₂O (1.8 mg, 0.0075 mmol) and Trifluoroacetic acid (1.0 M $\times$ 5 μ L) were mixed with the suspension of pre-synthesized Pd NSs (1.1mg/mL, 0.5mL) in 6 mL of the mixture of DMF and ethanol (V:V=3:1). Then TCPP (2.0 mg, 0.0025 mmol) dissolved in 2 mL of the mixture of DMF and ethanol (V:V=3:1) were added dropwisely under stirring. After that, the solution was sonicated

for 10 min. The vial was heated to 80 °C and then kept for 3 h for the reaction. The resulting brownish red nanosheets were washed twice with ethanol and collected by centrifuging at 8,000 r.p.m. for 10 min. Finally, the obtained Pd/Cu-TCPP nanosheets were redispersed in 3mL of ethyl acetate (EA).

5.2.4 Photo-oxidation of benzyl alcohol

In a 5 mL glass vial, benzyl alcohol (20 μ L) was added into the EA suspension of Pd/Cu-TCPP NSs (0.7 mg/mL, 3mL). Then the reactor was perfectly sealed with a silicon stopper, and the residual air was expelled by flushing oxygen through a needle several times. After flushed one more time with oxygen, the reaction was kept at 1 atm of oxygen and 75 °C for 8 hours to allow the catalytic reaction to proceed. The system was simultaneously irradiated by a 300W xenon light source, whose power can be tuned from 0% to 100% conveniently.

5.3 Results and Discussion

5.3.1 Characterization

Ultrathin Pd NSs were synthesized at first. They were observed under a transmission electron microscopy (TEM). (Figure 5.2) According to the images, the Pd NSs have quite uniform lateral size, and their thickness is around 1.5 nm (Figure 5.2d).

Figure 5.2 a) DF-STEM and b-d) TEM images of Pd NSs.

After the seed-mediated growth, the obtained Pd/Cu-TCPP NSs were observed under a TEM as well. (Figure 5.3) The large scale image (Figure 5.3a) indicates the uniform dispersion of Pd NSs on a large Cu-TCPP NS. These Pd NSs have a lateral size of 8.2 ± 0.6 nm. (Figure 5.3d) The interplaner spacing is measured to be 0.23 nm (Figure 5.3c), and it can be indexed to the $\{111\}$ planes of fcc Pd.

Figure 5.3 a, b) TEM images of Pd/Cu-TCPP. c) HRTEM image of Pd NSs. d) Statistical analysis of lateral size of Pd NSs.

The AFM image of Pd/Cu-TCPP NSs (Figure 5.4a) further confirmed the 2D morphology of the composite. The thickness of numbers of NSs were measured in the AFM image and statistically calculated to be 13.0 ± 1.4 nm. (Figure 5.4b)

Figure 5.4 a) AFM image of Pd/Cu-TCPP NSs. b) Statistical analysis of the thickness of Pd/Cu-TCPP NSs measured in AFM image.

The energy dispersive X-ray spectroscopy (EDS) was used to estimate the elemental composition of Pd/Cu-TCPP NSs as well. According to the EDS spectrum (Figure 5.5), the weight ratio of Cu to Pd is approximately 55.2/44.8, which is quite close to the result measured by an inductively coupled plasma optical emission spectrometry (ICP-OES) 54.8/45.2. Based on the structure of Cu-TCPP, the loading content of Pd is around 13.6 wt%.

Figure 5.5 EDS spectrum of Pd/Cu-TCPP.

The XRD pattern of Pd/Cu-TCPP NSs (Figure 5.6a) was collected to further confirm the composition. The small peak at 9° and the large peak at 19° are

quite consistent with XRD pattern of Cu-TCPP NSs.^[23] Three relatively sharp peaks at 40°, 47° and 68° respectively can be indexed to fcc Pd precisely. According to the UV-Vis spectra of Pd/Cu-TCPP, Cu-TCPP and Pd NSs (Figure 5.6b), Pd NSs only have weak broad absorption in visible wavelength range. On the other hand, Cu-TCPP NSs show two broad absorption bands. Thus the composite Pd/Cu-TCPP NSs have strong absorption in visible range as well. It is expected that Pd/Cu-TCPP may take advantage of light-harvesting ability from Cu-TCPP in photocatalysis reactions.

Figure 5.6 a) XRD pattern and b) UV-Vis spectra of Pd/Cu-TCPP, Cu-TCPP and Pd NSs.

5.3.2 Catalytic performance

The photocatalytic activity of Pd/Cu-TCPP NSs in oxidation of benzyl alcohol was examined and compared with bare Cu-TCPP NSs and freestanding Pd NSs. (Figure 5.7a) Bare Cu-TCPP had no activity for such reactions. On the other hand, Pd and Pd-based complexes were applied as catalysts for alcohol oxidation for decades.^[7,25-27] However, harsh reaction conditions, such as high pressure and temperature, are often required. For this case, Pd NSs showed very limited catalytic activity at atmospheric pressure. The conversion of benzyl alcohol was only around 15% after 8 hours of reactions. Moreover, they would form aggregates during the reaction, which is highly undesirable for the activity and stability of

catalysts. The Pd/Cu-TCPP composite NSs exhibited superior catalytic activity than Pd NSs. The conversion of benzyl alcohol reached over 30% within 8 hours, which suggests a synergistic effect between Pd NSs and Cu-TCPP. The influence of light intensity was also investigated as shown in Figure 5.7b. The Pd/Cu-TCPP NSs had the lowest catalytic activity in dark. The ultimate conversion rate is below 6%. With increasing light intensity, their catalytic performance was promoted a lot. This phenomenon indicates that light intensity plays a crucial role in the photo-oxidation reaction.

Figure 5.7 a) Photocatalytic performance of Pd/Cu-TCPP, bare Cu-TCPP and Pd NSs in oxidation of benzyl alcohol under 100% light irradiation intensity. b) Catalytic activity of Pd/Cu-TCPP under different light irradiation intensity (100% of power, 50% of power and dark).

After 8 hours of reaction, the catalysts were collected by centrifugation and then washed by ethanol. In the presence of 2D MOF NSs, Pd NSs could be conveniently re-dispersed into solvent and thus recycled for further catalysis. Otherwise freestanding Pd NSs tend to aggregate into large particles. The catalytic performance for 3 cycles was recorded in Figure 5.8. It is clear that the catalytic activity was only compromised a little for the second and third cycle, which suggests the Pd/Cu-TCPP NSs have good catalytic stability for at least 3 cycles of catalysis reactions.

Figure 5.8 Cyclability of Pd/Cu-TCPP (Each cycle takes 8 hours).

After three cycles of catalysis, the Pd/Cu-TCPP NSs were observed under TEM again. (Figure 5.9) It seems the Cu-TCPP NSs were partially damaged by high temperature and light irradiation. However, there was no isolated Pd NSs or NPs present on the image, which means the adhesion between Pd NSs and Cu-TCPP was still very strong.

Figure 5.9 TEM image of Pd/Cu-TCPP after 3 cycles of catalysis.

Based on the enhanced catalytic performance, it can be concluded that there is a synergistic effect between Pd NSs and Cu-TCPP. In the presence of photosensitizers, molecular dioxygen O_2 in nature can be activated into

singlet oxygen $^1\text{O}_2$, which is a powerful oxidant in the reactions.^[28-31] Porphyrinic MOFs were recently reported as efficient photosensitizers for singlet oxygen formation.^[32-34] Besides, the photoexcitation of noble metal nanoparticles (e.g. Pt, Pd, Au) would result in the generation of singlet oxygen as well.^[2,35,36] Hence, the integration of Cu-TCPP and Pd NSs promotes the photo-oxidation catalysis. The electron transfer scheme of the composite is proposed as shown in Figure 5.10. Due to the semiconductor-like property of Cu-TCPP and the surface plasmon resonance (SPR) of Pd, the electron flow at the interface is determined by two competing process: Schottky junction and plasmonic effect.^[37-40] With 100% light intensity, more electrons in the valence band of Cu-TCPP are excited to the conduction band, and then flow to Pd. A net electron flow from Cu-TCPP to Pd results in electron-rich surface of Pd, which promotes the activation of O_2 to $^1\text{O}_2$. Hence, the photocatalytic activity of Pd/Cu-TCPP NSs is twice larger than that of pure Pd NSs. However, at 50% light intensity, Schottky junction and plasmonic effect seem to reach a balance. The catalytic activity of composite is only slightly larger than that of pure Pd. Moreover, when the reaction is carried out in dark, no photoelectrons can be generated without light. Thus molecular dioxygen O_2 cannot be activated into singlet oxygen $^1\text{O}_2$, which results in poor activity.

Figure 5.10 Proposed electron transfer scheme of Pd/Cu-TCPP.

5.4 Conclusion

In summary, a 2D noble metal/porphyrinic MOF composite, which is referred to as Pd/Cu-TCPP nanosheet, was prepared in this work. Owing to the light harvesting ability of Cu-TCPP and the photothermal plasmonic effect of Pd, the composite NSs exhibit superior catalytic activity in the photo-oxidation of benzyl alcohol than individual components. The catalytic activity can be enhanced with increasing light irradiation intensity. Based on the experimental results, the electron transfer scheme was proposed. It is reasonable to believe that the synergistic effect between Cu-TCPP and Pd can promote the formation of singlet oxygen, thus increase the catalytic activity of the composite.

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Chapter 6

Engineering Channel of Metal-Organic Frameworks to Enhance the Catalytic Selectivity of NPs/MOF Composite

A method was developed to tune the pore size of NPs/MOF composite. Amino groups attached on ligands were modified with alkyl chains of different lengths through post synthetic modification, and thus the pore size can be adjusted. All the intrinsic and modified NPs/MOF composites were employed respectively as heterogeneous catalysts for the hydrogenation of olefins (triphenylethylene, trans-stilbene, cyclooctene). Impressively, the modified NPs/MOF composites showed enhanced size selectivity corresponding to the increased alkyl chains lengths, until Pt/UiO-66-AM5 blocked most of reactants outside.

6.1 Introduction

As a relatively new type of crystalline porous solids, metal-organic frameworks (MOFs) drew lots of attention in recent decades.^[1] They are hybrid organic-inorganic supermolecular materials whose extended networks are formed by nodes of metal ions or clusters of metal ions coordinated to bi- and multinodal rigid organic linkers.^[2,3] Compared to zeolites, MOFs can be achieved through numerous combinations of metal clusters and organic linkers. Up to now, more than 20,000 different MOFs have been designed and reported worldwide.^[4] They can be easily functionalized through modification of organic ligands.^[5] With light weight, high specific surface area and outstanding flexibility, MOFs are considered as good candidates in applications of gas storage,^[6,7] separation^[8], sensing,^[9] photocatalysis^[10] as well as chemical catalysis.^[2,11-14] In recent years, encapsulation of metal NPs, such as Au^[15], Pd^[16-18], Pt^[19,20] and Ru^[21], into MOFs were frequently reported^[22,23]. The unique porous nature of MOFs influences the activity and selectivity of the nanoparticle catalysts while still maintains transport of reactant and product ^[24-26].

To date, there are two main strategies for encapsulation of metal NPs into MOFs. In traditional encapsulation strategies, metal precursors are impregnated, followed by reduction process within the pores and channels of MOFs^[16,27-29]. However, there are several limitations in this approach. Firstly, it is hard to completely embed all NPs since they can attach on external surface of MOFs, which will affect catalytic selectivity of composites. Secondly, it is challenging to control sizes, shapes or locations of NPs. Hence, a new encapsulation strategy was developed by Huo's group^[24] in 2012, in which pre-synthesized NPs stabilized by polyvinylpyrrolidone (PVP) serve as nucleation sites for MOF, so that the size, shape and spatial distribution of encapsulated NPs could be controlled. Currently this strategy has been successfully extended to NPs including Pt,

Au^[24] and Pd^[20], incorporated into MOFs such as ZIF-8^[24], UiO-66 and MIL-53^[20]. With these strategies, a large variety of NPs/MOF catalysts were prepared.

However, the most reported NPs/MOF catalysts showing good selectivity were based on the idea that using the prepared MOFs with different pore diameters to match the molecular sizes for the selective catalysis. This strategy loses the intrinsic flexibility of MOFs in catalytic reaction. With high chemical variety, channel environment of MOFs, such as aperture size, hydrophobicity or acidity, can be conveniently tailored through post-synthetic modification (PSM)^[5] or other approaches to fulfill the requirements of different chemical reactions.

Herein, I would like to report an example demonstrating the possibility of tuning pore size of functional NPs/MOF composites based on the requirement of catalytic reaction by post synthetic modification. Amino groups attached on ligands were modified with alkyl chains of different lengths and thus the pore size can be adjusted. All the intrinsic and modified NPs/MOF composites were employed respectively as heterogeneous catalysts for olefin hydrogenation (Figure 6.1), and the modified ones exhibited increased size selectivity.

Figure 6.1 The selective catalysis of modified Pt/UiO-66-AMn composites.

6.2 Experimental section

6.2.1 General information

Commercial reagents were purchased from Sigma-Aldrich (ACS grade) and used as received unless otherwise noted. Morphology of UiO-66-NH₂ was characterized by scanning electron microscope (SEM) images taken by a JEOL JSM-7600 field-emission SEM with accelerating voltage of 5 kV. Transmission electron microscope (TEM) images taken by a JEOL JEM 2010F at an accelerating voltage of 200 kV were applied to confirm encapsulation of Pt NPs. X-ray diffraction (XRD) patterns were recorded to study the crystal structure with a Bruker AXS D8 Advance Diffractometer using nickel-filtered Cu K α radiation (λ = 1.5406 Å). Inductively coupled plasma optical emission spectrometry (ICP-OES) was performed on a Dual-view Optima 5300 DV ICP-OES system. Modified UiO-66-NH₂ products were examined by PerkinElmer Frontier FT-IR to confirm the presence of attached groups. Nitrogen adsorption/desorption isotherms were collected by Micromeritics ASAP 2020 to obtain Brunauer-Emmett-Teller (BET) surface area and porosity information. After catalytic hydrogenation, ¹H NMR spectra of products were collected by NMR Bruker AV400 (400MHz) spectrometer.

6.2.2 PVP-stabilized Pt NPs

3 nm PVP-stabilized Pt NPs were prepared according to previous work of Zhang's group.^[24] PVP (133 mg, Mw=29,000), methanol (180 mL), and aqueous solution of H₂PtCl₆ (20 mL, 6.0 mM) were mixed and stirred in a flask (500 ml) for 3 hours at 110 °C under air. Then excess methanol was evaporated by a rotary evaporator under reduced pressure until only 5 mL solution was left. Acetone was used to precipitate Pt NPs in the remaining solution. And the NPs were collected by centrifugation at 8,000 rpm for 5

minutes. The product was intensively washed with chloroform and hexane to remove excess free PVP. All Pt NPs were finely dispersed in N,N-Dimethylmethanamide (DMF, 2 mL) to obtain a Pt concentration of 11.7 mg/mL according to the initial amount of H_2PtCl_6 .

6.2.3 Pt/UiO-66-NH₂ composite

In this experiment, 5 mL DMF solution of ZrCl_4 (20 mM) and 5 mL DMF solution of 2-Amino-1,4-Benzenedicarboxylate (BDC-NH₂, 20 mM) were mixed well in a 20 mL glass vial. Then 1.37 mL acetic acid and 80 μL DMF solution of Pt NPs were sequentially added. The vial was kept at 120 °C for 24 hours without stirring. Products were finally collected by centrifugation at 6000 rpm for 3 minutes and washed intensively with DMF and methanol respectively. The obtained composite had Pt content of 2.1 wt% (ICP-OES).

6.2.4 PSM of Pt/UiO-66-NH₂ composite

Three types of alkyl anhydride were used to modify UiO-66-NH₂, which were respectively acetic anhydride, butyric anhydride and hexanoic anhydride. In a typical experiment, 60 mg UiO-66-NH₂ (~0.2 mmol-NH₂) was suspended in 2 mL chloroform, and then one equivalent of anhydride was added. The reaction was kept at 55 °C for 24 hours with continuous stirring. Upon collection by centrifugation, the products were washed firstly with chloroform, and then soaked in methanol for 3 days with methanol replaced every 24 hours to extract by-products and solvent from the pores. The modified MOFs were denoted as UiO-66-AM1 (UiO-66-NH-COCH₃), UiO-66-AM3 (UiO-66-NH-CO(CH₂)₂CH₃) and UiO-66-AM5 (UiO-66-NH-CO(CH₂)₄CH₃) respectively.

6.2.5 Catalytic olefin hydrogenation

Hydrogenation of olefins (triphenylethylene, trans-stilbene, cyclooctene) was chosen to test the catalytic selectivity of modified Pt/Uio-66-NH₂ composites. In the experiment, catalyst (10 mg) was loaded into a 5 mL glass vial. Then the reactor was perfectly sealed with a silicon stopper, and the residual air was expelled by flushing hydrogen through a needle several times. Ethyl acetate (EA, 3 mL) solution of olefins was injected into reactor, and it required sonication for 10 minutes to produce homogeneous suspension of catalyst in EA. After flushed one more time with hydrogen, the reaction was kept at 1 atm of hydrogen and 35 °C for 24 hours to allow hydrogenation reaction of olefins to proceed.

6.3 Results and Discussion

6.3.1 Characterization

The UiO-66-NH₂ still maintain the well morphology and crystal structure by PSM. Transmission electron microscopic (TEM) images of intrinsic Pt/Uio-66-NH₂ (Figure 6.2a) showed identical morphology with typical UiO-66, which is regular octahedron crystal (200 nm) with smooth surface. Pt NPs were successfully encapsulated at the center of octahedron crystals, which proved the effectiveness of encapsulation strategy. After modification in chloroform solution, no obvious change in morphology can be observed from Pt/Uio-66-AM1, Pt/Uio-66-AM3 and Pt/Uio-66-AM5. (Figure 6.2b-c)

Figure 6.2 TEM images of a) Pt/UiO-66-NH₂, b) Pt/UiO-66-AM1, c) Pt/UiO-66-AM3 and d) Pt/UiO-66-AM5.

XRD patterns (Figure 6.3a) showed that Pt/UiO-66-NH₂ exhibits a completely identical crystal structure of UiO-66. Modified samples showed no loss of crystal structure. The XRD peaks of Pt could not be identified because they are of low concentration. FT-IR spectra of all the samples were collected and compared in Figure 6.3b. The reaction between UiO-66-NH₂ and the anhydrides would result in formation of amides. The bands at 1673 cm^{-1} of the modified samples are corresponded to C=O stretching in secondary amide.^[30] In addition, another band at 1300 cm^{-1} accompanies C-N-H bending and C-N stretching.^[31] The two bands which were not seen in UiO-66-NH₂ exhibit the presence of amide group. For modified samples UiO-66-AM3 and -AM5, several bands in the range of $2850\text{--}2990\text{ cm}^{-1}$ were witnessed, which represent sp^3 C-H stretching in aliphatic compounds. The result makes sense because long chain anhydrides introduce -CH₂-groups into MOF during modification process.

Figure 6.3 a) Powder XRD pattern and b) FT-IR spectra of Pt/Uio-66-NH₂ and three modified composites.

Nitrogen adsorption/desorption isotherms (Figure 6.4a) at 77K were plotted, and the isotherm plots for Pt/ Uio-66-NH₂ and three modified composites exhibit similar shapes. Steep increases in nitrogen uptake were observed in very low relative pressure region, indicating physical adsorption in micropores. When micropores were filled, low slop region in middle of isotherms showed multilayer adsorption. Pore size distribution of the samples were illustrated in Figure 6.4b. With increasing alkyl chain length, pore width was reduced gradually from approximately 5.5 Å to 5.2 Å.

Figure 6.4 a) Nitrogen adsorption-desorption isotherms at 77 K and b) pore size distribution of Pt/Uio-66-NH₂ and three modified composites.

Calculated results of BET surface area were listed and compared in Table 6.1. BET surface area of intrinsic Uio-66 is 1492 m²·g⁻¹. When Pt NPs were

loaded, this composite experiences lower surface area ($1340 \text{ m}^2.\text{g}^{-1}$) due to the presence of Pt and PVP.^[20] In this case, Pt/UiO-66-NH₂ certainly has even lower surface area ($1222 \text{ m}^2.\text{g}^{-1}$) because of additional amino groups. With increasing length of attached functional groups, modified MOFs should have decreasing surface area. But Pt/UiO-66-AM1 and Pt/UiO-66-AM3 showed quite comparable BET surface area. This can be explained by reduced conversion of ligands in PSM process for long chain anhydride. In 2010, Garibay and coworkers digested modified MOFs and collected their ¹H NMR spectra. Then they were able to calculate conversion of amino groups to amides by comparing integrated peak areas of unmodified and modified ligands.^[32] It turned out conversion decreased with increasing chain lengths of anhydrides due to the hindered diffusion in micropores. In this study, it is reasonable to consider that less butyric anhydride would react with BDC-NH₂ compared to acetic anhydride. Eventually, similar BET surface areas and micropore volumes were obtained and Pt/UiO-66-AM5 has the lowest surface area among the four samples with the longest attached functional groups.

Table 6.1 BET surface areas of Pt/UiO-66-NH₂ and three modified composites.

Sample	BET Surface Area ($\text{m}^2.\text{g}^{-1}$)
Pt/UiO-66-NH ₂	1222
Pt/UiO-66-AM1	929
Pt/UiO-66-AM3	855
Pt/UiO-66-AM5	679

After hydrogenation experiments, all the four NPs/MOF composites were collected and characterized by TEM characterization again. Their results showed no obvious change in both morphology and crystallinity (Figure 6.5), which proved the stability and reliability of the catalysts.

Figure 6.5 TEM images of a) Pt/UiO-66-NH₂. b) Pt/UiO-66-AM1. c) Pt/UiO-66-AM3. d) Pt/UiO-66-AM5 after hydrogenation experiments.

6.3.2 Catalytic performance

The catalytic selectivities of the four samples were tested in liquid-phase hydrogenation of triphenylethylene, trans-stilbene and cyclooctene. As listed in Table 6.1, all four composites showed barely no catalytic activity for hydrogenation of triphenylethylene, indicating that the size of triphenylethylene molecules exceeds the composites apertures, namely, C=C double bonds could not contact with Pt NPs encapsulated inside the MOFs. The lack of catalytic activity for three modified composites is another proof evidencing that no NPs were located at the MOFs' external surface .

Table 6.2 Catalytic performance of Pt/Uio-66-NH₂ and three modified composites.

Sample	Conversion of Triphenylethylene (%)	Conversion of Trans-stilbene (%)	Conversion of Cyclooctene (%)

Pt/Uio-66-NH ₂	<1	49	51
Pt/Uio-66-AM1	0	13	22
Pt/Uio-66-AM3	0	5	15
Pt/Uio-66-AM5	0	4	4

As trans-stilbene (5.6 Å) is smaller in size than triphenylethylene (5.8 Å), it was capable of diffusing into the MOF composites and then being hydrogenated. Comparing conversion data of these four samples, a clear trend could be found: with increasing lengths of the attached functional groups, conversions of trans-stilbene were reduced from 49% to 4% due to retarded diffusions of trans-stilbene into micropores. Hydrogenation of cyclooctene (5.5 Å) showed a similar trend, but higher conversion as a result of its smaller size. Conversions of cyclooctene and trans-stilbene was plotted in Figure 6.6. The ratio between cyclooctene conversion and trans-stilbene conversion could be considered as selectivity towards cyclooctene. A clear trend of improved selectivity was witnessed with increasing alkyl chain lengths until Pt/Uio-66-AM3 exhibited highest selectivity. Pt/Uio-66-AM5 showed very low catalytic performance due to a restricted diffusion of reactants caused by long alkyl chain on ligands, showing it is not an ideal catalyst for hydrogenations of cyclooctene and trans-stilbene in this study.

Figure 6.6 Size-selective hydrogenation catalytic properties of four NPs/MOF composites.

6.4 Conclusion

In summary, this chapter presented aperture size modification of NPs/MOF composites by utilizing chemical variety of MOFs. Modified NPs/MOF composites showed enhanced size selectivity in olefin (triphenylethylene, trans-stilbene, cyclooctene) hydrogenation corresponding to the increased alkyl chains lengths, until Pt/UiO-66-AM5 blocked most of reactants outside. This study revealed advantages of MOFs as supporting materials for heterogeneous catalysis: by utilizing their incredible chemical variety, environments of pores and channels can be conveniently tailored to fulfil the requirements of different chemical reactions.

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Chapter 7

Discussion and Future Work

This chapter summarizes the whole thesis. Based on the accomplished three projects, the hypothesis can be proved that noble metal-based nanocomposites exhibit superior catalytic performance than pure metal nanostructures owing to synergistic effect between the components and introduced properties from the functional materials. The Discussion part summaries the novel outcomes achieved. At last, some future works are proposed. Taking advantage of the flexibility of MOFs, the hydrophobicity and acidity of the noble metal/MOF composites can be further modified to fulfill requirements of different chemical reactions.

7.1 Discussion

This thesis mainly focuses on the synthesis of noble metal-based nanocomposites for their enhanced catalytic performance. Three projects in total are involved. Ultrathin bimetallic NSs, 2D noble metal/MOF NSs and 3D noble metal NPs/MOF composites are fabricated respectively. Their catalytic performances are examined in reactions including reduction of 4-nitrophenol, hydrogenation of olefins as well as photo-oxidation of benzyl alcohol.

In the first project, a synthetic route of ultrathin bimetallic core-shell NSs was successfully established where the core is incompletely covered by the shell. The composite NSs showed superior catalytic activity than the individual component. The results prove the hypothesis that coupling noble metal with another component may induce a synergistic effect, which can promote the catalytic activity.

Noble metal NSs was supported by 2D MOF NSs in the second project. Porphyrinic MOF NSs not only served as supporting material, but also introduced photo-electronic properties into the material. Thus the composite exhibited good performance in the photocatalysis reaction. These outcomes reflect that combining noble metal with some functional materials, such as MOFs, can introduce some additional properties, thus enhance the catalytic activity. Moreover, supporting materials can promote the dispersion and stability of noble metal nanostructures, so the catalysts can be recycled for several times.

Owing to the flexibility of MOFs, pore size of noble metal NPs/MOF core-shell composite was varied through post-synthetic modification in the third project. The catalytic selectivity of the composite was enhanced due to physical constraint. This project further proves that functional materials can

be altered conveniently to enhance the catalytic selectivity.

Based on the research we have done, it can be concluded that noble metal-based nanocomposites, such as bimetallic core-shell nanosheets and NPs/MOF composites, provide a better option for catalytic reactions in terms of stability, selectivity as well as activity.

7.2 Future Work

7.2.1 2D noble metal/metal chalcogenide NSs

Chalcogenide materials are usually semiconductors, which can contribute to photocatalytic reactions. Banin *et al.*^[1] synthesized Pt-CdSe hybrids, and managed to control morphology by tuning pH conditions of the growth solution. Compared with nanorods, Pt-CdSe nanonets showed superior photocatalytic activity. The nanonet morphology enabled denser Pt surface coverage, and thus resulted in more efficient charge separation, which could produce more catalytic sites for the redox reactions. Rogach and coworkers^[2] discussed the effect of Pt cluster size on photocatalytic activity of Pt-CdS nanorods in hydrogen evolution reaction. They found subnanometer sized Pt clusters exhibited remarkable performance, even though they are less in amount compared to large Pt clusters. Based on the rich experience in 2D materials synthesis, Zhang's group demonstrated the epitaxial growth of Pd, Pt and Ag nanostructures on MoS₂ nanosheet.^[3] As shown in Figure 7.1, Pt NPs exhibited major orientations of (111) and (101). The Pt-MoS₂ hybrids showed superior electrocatalytic performance in the hydrogen evolution reaction compared with Pt/C with the same Pt amount, which could be attributed to the defined orientations at the interface.

Figure 7.1 a) TEM image of Pt-MoS₂ hybrid nanosheet. b) Enlarged TEM image of Pt NPs on MoS₂ nanosheet. c) SAED pattern of the Pt-MoS₂ hybrid nanosheet. d–f) HRTEM images of Pt NPs on MoS₂ nanosheet. Inset in (f): photograph of the Pt-MoS₂ solution. (Reprinted with permission from ref. 3)

Besides the semiconducting properties, chalcogenide materials may poison the noble metal catalysts such as Pt and Pd. For most of case, catalyst poisoning is undesirable because it leads to loss of catalytic activity. However, when noble metal/metal chalcogenide composites are fabricated into 2D structure, noble metal catalysts are only partially poisoned, which might allow selective intermediates to be isolated and final products with desirable stereochemistry to be achieved. For next step, I intend to design 2D noble metal/metal chalcogenide NSs for enhanced catalytic selectivity.

7.2.2 Hydrophobic/hydrophilic noble metal NPs/MOF composites for enhanced catalytic selectivity

The introduced long alkyl chain by PSM process not only tunes pore size of MOF, but also brings hydrophobic properties into the material. Using the same approach, Nguyen and coworkers modified IRMOF-3 and MIL-53(Al)-NH₂ with alkyl chains of various lengths.^[4] Contact angle measurements were used to examine the hydrophobic/hydrophilic nature of

materials. Unmodified IRMOF-3 and MIL-53(Al)-NH₂ are highly hydrophilic with contact angle of 0. However, when attached alkyl chain length increased to 4 and above, modified IRMOF began to show hydrophobic ($90^\circ < \text{contact angle} < 150^\circ$) properties, while MIL-53(Al)-NH₂ was turned into superhydrophobic (contact angle $> 150^\circ$) material. This hydrophobic modification could enhance moisture stability of MOFs, and introduce special physical and chemical properties. Hydrophobic MOFs are quite potential materials in selective gas adsorption,^[5,6] but they can possibly be applied in chemical catalysis as well.

Knoevenagel condensation is an important reaction in synthesis of many fine chemicals. This reaction can be catalyzed by bases or Lewis acids. As materials containing metal centers, a number of MOFs show catalytic activity for Knoevenagel condensation, including MIL-100(Al), Cu₃(BTC)₂(H₂O)₃, UiO-66.^[7] Generally, the catalytic activity of UiO-66 is the lowest among them due to fewer basic sites. However, with the introduction of amino groups, amount of basic sites are increased.^[7] Zr(IV) site could also possibly form bifunctional acid-base pair with amino groups in its proximity.^[8] Therefore, UiO-66-NH₂ showed superior catalytic activity than UiO-66.

According to study by Canivet and coworkers, the catalytic activity of MOFs for Knoevenagel condensation was also related to hydrophobic/hydrophilic nature of catalytic environment.^[9] In their case, a MOF called SIM-1 was modified with dodecylamine. The newly obtained SIM-2(C₁₂) showed dramatically increased catalytic activity for Knoevenagel condensation, as shown in Figure 7.2. The difference was explained by hypothesis: water molecules are removed in Knoevenagel condensation reactions, the hydrophobic environment hinders water adsorption on metal centers, so more reactants are able to adsorb on catalysts.

Figure 7.2 Time-dependent formation of product of Knoevenagel condensation. (Reprinted with permission from ref.9)

If this hypothesis holds true, the modified MOFs with alkyl chain would possibly show higher catalytic activity for Knoevenagel condensation than unmodified UiO-66-NH₂ due to their hydrophobic pore environment. Furthermore, with encapsulated noble metal NPs, more catalytic sites will be introduced. This will be a great example that engineering hydrophobic/hydrophilic environment of MOFs can optimize their catalytic properties, which further proves tailored MOF can be designed for various chemical reactions.

7.2.3 Acidic noble metal NPs/MOF composites for multiple catalytic sites

As a class of versatile materials, MOFs can be functionalized with strongly acidic groups, such as sulfonic acid. With such modification, Brønsted acid sites are introduced into MOF structure, while Brønsted acids are important catalysts for reactions like hydrolysis, esterification, acetalization and so on.^[10] With the presence of both Brønsted acid sites and Lewis acid sites, acid functionalized MOFs are expected to work as excellent solid acid catalysts with selectivity and reusability.

Sulfonic acid-functionalized MIL-101 (HSO₃-MIL-101) was prepared and studied by several groups as catalyst for cellulose hydrolysis,^[11] acetalization of aldehydes with diols,^[12] etc. The catalyst turned out to be highly stable and efficient, combining the advantages of homogeneous and heterogeneous catalysts.

Combining acid-functionalized MOFs with noble metal NPs can create multiple catalytic sites within the composites. The catalytic activity and selectivity can be examined by alcoholysis of epoxides, as shown in Figure 7.3.^[13]

Figure 7.3 Scheme of alcoholysis of epoxides. (Reprinted with permission from ref. 13)

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Appendices

A.1 Definition of conversion, yield, and selectivity in catalytic reactions

$$\text{Conversion} = \frac{\text{Moles of reactant consumed}}{\text{Moles of reactant fed in system}} \times 100\% \quad (\text{S1})$$

$$\text{Yield} = \frac{\text{Actual moles of specific product}}{\text{The maximum moles of specific product (fully produced)}} \times 100\% \quad (\text{S2})$$

$$\text{Selectivity} = \frac{\text{Moles of desired product}}{\text{Moles of reactant consumed}} \times 100\% \quad (\text{S3})$$

A.2 Calculation of molar percentage of Ru in the Pd@Ru NS with complete coverage of monolayered Ru

Figure A.1 Scheme of the hexagonal nanosheet.

The Pd@Ru NSs have approximately hexagonal shape with an average lateral size (L) of about 7.8 nm and thickness (h) of about 1.9 nm, so the Pd@Ru NSs have an average edge length (a) of about 3.9 nm.

As the atomic radii of Pd and Ru are very close, in order to simplify the calculation without compromising the accuracy, I may calculate the molar percentage of Ru in the Pd@Ru NSs which was completely covered with monolayered Ru atoms.

The total surface area of top and down facets in one Pd@Ru NS is: $S = 3\sqrt{3} \times 3.9^2 = 79.03 \text{ nm}^2$.

The total surface area of side facets in one Pd@Ru NS is: $S = 6 \times 3.9 \times 1.9 = 44.46 \text{ nm}^2$.

The volume of one Pd@Ru NS is: $V = \frac{3\sqrt{3}}{2} \times 3.9^2 \times 1.9 = 75.08 \text{ nm}^3$.

The average Pd atoms density in the (111) facet is $1.53 \times 10^{15} / \text{cm}^2$, and the average Pd atoms density in the (110) facet is: $0.93 \times 10^{15} / \text{cm}^2$.^[2,3] In the hexagonal nanosheet, the top and down facets can be considered as the (111) facets, while the side facets can be considered as the (110) facets. Hence, the total number of surface atoms is $(79.03 \times 10^{-14} \times 1.53 \times 10^{15}) + (44.46 \times 10^{-14} \times 0.93 \times 10^{15}) = 1.622 \times 10^3$.

As the density of Pd crystal is 12.023 g/cm^3 , the mass of one Pd@Ru NS is $75.08 \times 10^{-21} \times 12.023 = 9.027 \times 10^{-19} \text{ g}$.

Since Pd has a molar mass of 106.42 g/cm^2 , the total number of Pd atoms in a Pd@Ru NS can be calculated, i.e. $(9.027 \times 10^{-19}/106.42) \times 6.02 \times 10^{23} = 5.106 \times 10^3$.

When the surface of Pd NS is completely covered with monolayer Ru atoms, the molar percentage of Ru in a Pd@Ru NS can be calculated to be $(1.622 \times 10^3)/(5.106 \times 10^3) \times 100\% = 31.8\%$, which is higher than 13.2% and 11.7% measured by EDS (Figure S3) and ICP-OES, respectively. Therefore, in the synthesized Pd@Ru NSs, the surface of Pd NSs was only covered with sub-monolayered Ru.

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