Electronic and local structures of Pt-based bimetallic alloy and core-shell systems

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Abstract

This thesis investigates the electronic structure of Pt for catalysis applications. The importance of the Pt 5d band is discussed in terms of the bonding capability of Pt. The oxygen reduction reaction in proton exchange membrane fuel cells is chosen as the catalytic reaction model to illustrate the effect of Pt 5d states on Pt-O interaction. Pt-based bimetallic systems are introduced as a solution for the high price and limited resources of Pt. Despite lower usage of Pt, the tuning capability to optimize the Pt 5d band in bimetallic catalysts is supposed to provide superior catalytic activity. Advanced synchrotron X-ray techniques including normal X-ray absorption fine structure (XAFS), X-ray ptychography, and high energy resolution fluorescence detected (HERFD) X-ray absorption/emission spectroscopy (XAS/XES) are combined with laboratory characterization techniques including transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and X-ray powder diffraction (XRD) to study the behavior of Pt upon alloying or forming core-shell structures with 3d transition metals.

Three Pt-based bimetallic systems are studied, including Pt-Ni bulk alloys, Pt-Ni nanoparticles (NPs), and Pt-Cu NPs. Pt-Ni bulk alloys are synthesized as model compounds to study the many-body effect, charge redistribution, and local structure of Pt upon alloying. It is found that Pt gains 5d electrons, resulting in more symmetric Pt 4f XPS peaks when diluted in Ni, while Ni loses 4p and 4d electrons, resulting in an increase of K-edge XAS whiteline (WL) intensity, more symmetric Ni 2p XPS peaks, and stronger shake-up satellites. The downshifting of the Pt valence states and upshifting of Ni valence states are also observed with ultraviolet photoelectron spectroscopy (UPS) and density functional theory (DFT) calculations. Pt-Ni NPs, as the Pt-Ni systems in nanoscale, are used to track the evolution process including the alloying and de-alloying of Pt during the synthesis of the bimetallic systems. It is found that Pt goes through five distinct stages, i.e. core frame, tight network, outer frame, thin skin, and particulate shell. The electronic and local structures at each stage are tracked with XAS. Pt-Cu NPs are in the form of core-shell or alloy NPs, with a very low amount of Pt either on the surface or in the bulk. For the 8-nm Cu@Pt core-shell NPs, several monolayers of Pt are deposited on the Cu core, exhibiting good controllability by the polyol reduction method.
The advantages of HERFD-XAS/XES are demonstrated in studying the Pt 5d band of Pt-Ni and Pt-Cu bimetallic systems. In the valence-to-core (VTC) XES experiments, the widths of the VTC emission lines and energy transfers show the shrinking and downshifting of the Pt valence band upon alloying with Ni. For HERFD-XAS, significantly narrowed WLs, enhanced near-edge XAS features, and easily removable background have enabled detailed analysis of the WL peaks with high accuracy. Combining the HERFD-XAS results for Pt-Ni and Pt-Cu bimetallic systems, Pt foil, and Pt NPs, a general linear relationship between the WL areas of Pt L$_3$- and L$_2$-edges is established. Physically, this linear relationship indicates that the unoccupied Pt 5d$_{5/2}$ and 5d$_{3/2}$ states also have a linear relationship. Experimentally, this finding suggests that measuring the Pt L3-edge alone will provide enough information to study the unoccupied Pt 5d states of Pt-based metallic systems.

Keywords

Bimetallic, platinum, nickel, copper, core-shell, alloy, synchrotron, X-ray absorption spectroscopy, X-ray emission spectroscopy, X-ray photoelectron spectroscopy, valence-to-core emission
Summary for Lay Audience

Platinum is an excellent catalyst in many chemical reactions. However, because of the high price and limited production, it is desirable to reduce the usage of platinum while maintaining high performance of the catalysts. To achieve this goal, one needs to target the key factor for catalytic activity, which is the valence band of platinum, and apply controllable modifications.

In this thesis, the chemical reaction in a hydrogen fuel cell is used to illustrate the connection between the electronic structure of platinum and its catalytic activity. Bimetallic systems combining platinum and a cheap transition metal, as a promising solution, have been studied in detail to reveal the change of platinum electronic structure. In specific, platinum-nickel bulk alloys, platinum-nickel nanoparticles, and platinum-copper nanoparticles are synthesized and characterized by advanced synchrotron X-ray techniques. These synchrotron X-ray techniques have great advantages over traditional lab techniques in studying the fundamental properties of materials including electronic structure, chemical environment, and crystal structure.

As a result, it is found that platinum attracts electrons from first-row transition metals upon alloying, while the valence band of platinum shrinks and shifts to lower energy. On the other hand, the shape of the unoccupied electron states above the valence band is found to follow a linear relationship between the two types of platinum 5d states. This linear relationship is established by combining the results from different bimetallic systems and thus is considered generally valid. Other than the physical implication, this finding also provides guidance for future experiments and data analysis.
Co-Authorship Statement

Chapter 3 contains materials from a previously published manuscript. Dr. Tsun-Kong Sham is co-authored and he played a major role in revising the content presented in this thesis.

In Chapter 3, the bulk alloys were synthesized by Jim Garret at the Brockhouse Institute of Materials Research. The lab X-ray photoelectron spectroscopy measurements were performed by Danielle Covelli and Ramaswami Samynaiken at Saskatchewan Structural Sciences Centre. The density functional theory calculation was conducted by Dr. Yun-Mui Yiu.

In Chapter 4, the X-ray photoelectron spectroscopy measurements were performed by Dr. Mark Biesinger at Surface Science Western. The transmission electron microscopy was conducted at Biotron, Western University.

In Chapter 5, the transmission electron microscopy was conducted at Biotron, Western University.

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<tr>
<td>APS</td>
<td>Advanced Photon Source</td>
</tr>
<tr>
<td>bcc</td>
<td>Body-centered cubic</td>
</tr>
<tr>
<td>CCWT</td>
<td>Continuous Cauchy wavelet transform</td>
</tr>
<tr>
<td>CLS</td>
<td>Canadian Light Source</td>
</tr>
<tr>
<td>CN</td>
<td>Coordination number</td>
</tr>
<tr>
<td>EXAFS</td>
<td>Extended X-ray absorption fine structure</td>
</tr>
<tr>
<td>fcc</td>
<td>Face-centered cubic</td>
</tr>
<tr>
<td>FY</td>
<td>Fluorescence yield</td>
</tr>
<tr>
<td>hcp</td>
<td>Hexagonal close packed</td>
</tr>
<tr>
<td>HERFD</td>
<td>High energy resolution fluorescence detected</td>
</tr>
<tr>
<td>HXPES</td>
<td>Hard X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>ORR</td>
<td>Oxygen reduction reaction</td>
</tr>
<tr>
<td>PEMFC</td>
<td>Polymer electrolyte membrane fuel cell</td>
</tr>
<tr>
<td>SBCA</td>
<td>Spherically bent crystal analyzer</td>
</tr>
<tr>
<td>SDD</td>
<td>Silicon drift detector</td>
</tr>
<tr>
<td>STXM</td>
<td>Scanning transmission X-ray microscopy</td>
</tr>
<tr>
<td>UPS</td>
<td>Ultraviolet photoelectron spectroscopy</td>
</tr>
<tr>
<td>VB</td>
<td>Valence band</td>
</tr>
<tr>
<td>VTC</td>
<td>Valence to core</td>
</tr>
<tr>
<td>WL</td>
<td>Whiteline</td>
</tr>
<tr>
<td>WT</td>
<td>Wavelet transform</td>
</tr>
<tr>
<td>XANES</td>
<td>X-ray absorption near-edge structure</td>
</tr>
<tr>
<td>XAS</td>
<td>X-ray absorption spectroscopy</td>
</tr>
<tr>
<td>XES</td>
<td>X-ray emission spectroscopy</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
</tbody>
</table>
Chapter 1

1. Introduction

1.1. Pt-based electrochemical catalysts

Pt is considered the best catalyst for many industrial chemical reactions because of its unique electron configuration. One application under extensive research is fuel cell catalysts. Fuel cells are an environmentally friendly and promising alternative power source for buildings, vehicles, and extreme situations/areas. Compared with fossil fuel consumption, a fuel cell using H\(_2\) and O\(_2\)/air directly converts chemical energy into electricity, with its by-products only consisting of water and heat. Other than renewability and cleanliness, the efficiency of fuel cells is much higher than combustion engines. These advantages of fuel cells have drawn attention from researchers as well as entrepreneurs. Currently, multiple types of fuel cells have been developed for various applications. According to the US department of energy (DOE) \(^1\), a brief comparison between different types of fuel cells is shown in Table 1-1. In this thesis, the study is focused on Pt-based catalysts for polymer electrolyte membrane fuel cells (PEMFC, also known as proton exchange membrane fuel cells).

\[
\begin{align*}
2H_2 + O_2 & \rightarrow 2H_2O \\
H_2 & \rightarrow 2H^+ + 2e^- \\
O_2(g) + 4H^+ + 4e^- & \rightarrow HOO^* + 3H^+ + 3e^- \rightarrow H_2O(l) + \text{HO}^* + H^+ + e^- \rightarrow 2H_2O(l) \\
O_2(g) + 2H^+ + 2e^- & \rightarrow HOO^* + H^+ + e^- \rightarrow H_2O_2(l)
\end{align*}
\]

In a typical PEMFC (as shown in Figure 1-1), H\(_2\) and O\(_2\) are the fuel gases fed into the anode and cathode, respectively, with a certain back pressure. These two gases combine through chemical reactions (the total reaction shown in Eq. 1.1) to produce water, electricity, and heat. At the anode, the H\(_2\) molecules are decomposed into protons (in the form of H\(_3\)O\(^{+}\))
on the surface of a Pt-based catalyst. This reaction is called hydrogen oxidation reaction (HOR), as shown in Eq. 1.2. At the cathode, the adsorbed oxygen molecules are decomposed into single oxygen atoms or elongated to form O-O species on the catalyst (can be the same as the catalyst at the anode). The protons from the anode travel through the PEM and combine with the oxygen species at the cathode, which is the so-called oxygen reduction reaction (ORR) \(^2\). This step can go through two different paths shown as the four-electron path to produce water, and the two-electron path to produce \(\text{H}_2\text{O}_2\) in Figure 1-2, with the corresponding reactions in Eqs 1.3 and 1.4, respectively. The reaction path is determined by the catalyst at the cathode. More specifically, the dynamics and kinetics of each step are determined by the binding strength between the adsorbate species and the catalyst, and the association/dissociation energies of atoms/molecules. In other words, the bonding states and

<table>
<thead>
<tr>
<th>Fuel Cell Type</th>
<th>Electrolyte</th>
<th>Operating Temperature (^\circ)C</th>
<th>Stack Size</th>
<th>Electrical Efficiency</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer Electrolyte Membrane (PEMFC)</td>
<td>Perfluorosulfonic acid</td>
<td>&lt; 120</td>
<td>&lt;1 kW - 100 kW</td>
<td>60% (H(_2)); 40% (reformed fuel)</td>
<td>Backup power, Portable power, Distributed generation, Transportation, Specialty vehicles</td>
</tr>
<tr>
<td>Alkaline (AFC)</td>
<td>Aqueous KOH in a porous matrix, or alkaline polymer membrane</td>
<td>&lt; 100</td>
<td>1 - 100 kW</td>
<td>60%</td>
<td>Military, Space, Backup power, Transportation</td>
</tr>
<tr>
<td>Phosphoric Acid (PAFC)</td>
<td>(\text{H}_3\text{PO}_4) in a porous matrix or in a polymer membrane</td>
<td>150 – 200</td>
<td>5 - 400 kW</td>
<td>40%</td>
<td>Distributed generation</td>
</tr>
<tr>
<td>Molten Carbonate (MCFC)</td>
<td>Molten carbonates in a porous matrix</td>
<td>600 – 700</td>
<td>300 kW - 3 MW</td>
<td>50%</td>
<td>Electric utility, Distributed generation</td>
</tr>
<tr>
<td>Solid Oxide (SOFC)</td>
<td>Yttria stabilized zirconia</td>
<td>500 – 1000</td>
<td>1 kW - 2 MW</td>
<td>60%</td>
<td>Auxiliary power, Electric utility, Distributed generation</td>
</tr>
</tbody>
</table>

Table 1-1. Comparison of fuel cells
Figure 1-1. Schematic of a typical fuel cell showing the hydrogen oxidation reaction (HOR) at the anode and oxygen reduction reaction (ORR) at the cathode.

Figure 1-2. Schematic of the two reaction paths for ORR: the four-electron path producing H$_2$O and the two-electron path producing H$_2$O$_2$. 
anti-bonding states between the adsorbates the catalyst play the most significant role in determining the catalytic activity. An optimal ORR catalyst ought to have an ideal binding strength of O species on the surface, thus to have a good balance in dissociating the O₂ (higher binding energy tends to dissociate the O₂ more efficiently), protonation, and releasing of the final products, as depicted in Figure 1-3(a). For transition metal catalysts where the valence band is mainly composed of d (3d, 4d, 5d) states, the coupling between the O species and the catalyst is made through O 2p states and d states. This results in significantly different activity between d-band metals, among which Pt is known as the best element for ORR. On the Pt surface, the O 2p states hybridize with the Pt 5d states to form the bonding orbitals (Pt-A) and anti-bonding orbitals (Pt-A)⁺. A highly simplified model is shown in Figure 1-3(b). The filling extent of the (Pt-A)⁺ determines the binding strength of the O species on the Pt. To understand the Pt-A interaction, the adsorption of O₂ on Pt is explained in detail in the following. In literature, three binding models of O₂ on the Pt surface are reported, i.e. the Yeager model (also called bridge model)³, Griffith model⁴, and Pauling model⁵⁻⁷, as shown in Figure 1-3(c). For each model, some selected orbital coupling between Pt and O₂ are presented. In the Yeager model, The two oxygen atom dock on two adjacent Pt atoms. The Pt 5d₂ orbitals interact with both the filled π and partially filled π* orbitals of the O₂. In the Griffith model, both oxygen atoms are adsorbed on the same Pt atom, with the O₂ internuclear axis lying parallel to the Pt surface. The filled O₂ π orbitals interact with the Pt 5d₂ orbital while O₂ π* orbitals interact with Pt 5dₓz,yz orbitals. In the Pauling model, only one end of the O₂ molecule docks on a Pt atom, with the internuclear axis of O₂ lying around 60 degrees to the normal direction (z direction for Pt) of the Pt surface. The filled O₂ σ orbitals interact with the Pt 5d₂ orbital while the O₂ π* orbitals interact with Pt 5dₓz,yz orbitals. To understand the charge transfer between Pt and O₂, one needs to consider the configuration of O₂ molecular orbitals (see Figure 1-4(a)). The σ and π bonding orbitals are fully filled while the anti-bonding orbitals π* are partially filled. When the σ and π orbitals of O₂ are interacting with Pt, electrons tend to transfer from O₂ to Pt. On the other hand, when π* orbitals of O₂ interacts with Pt, electrons tend to transfer from Pt to O₂. An example of a π-type bonding orbital (Pt-A) formed by the coupling of O₂ π* and Pt 5dₓz is shown in Figure 1-4(b). In this case, Pt 5dₓz donates to O₂ π*. As a result, the binding strength between the two oxygen atoms decreases. The binding strength between O₂ and Pt, however, increases.
Figure 1-3. (a) Volcano-type activity showing the highest catalytic activity at optimal adsorbate binding strength. (b) Hybridization of Pt 5d states with adsorbate states forming bonding states (Pt-A) and anti-bonding states (Pt-A)*. (c) Three Pt-O₂ adsorption models including the Yeager model, Griffith model, and Pauling model, with selected interacting orbitals between O₂ and Pt.
Herein, it is clear that the bonding orbitals (Pt-A) between Pt and O₂ are not necessarily formed by the molecular bonding orbitals of O₂. Also note that the abovementioned orbital couplings shown in Figure 1-3(c) and 1-4(b) are incomplete. In other words, more than ten of such orbital couplings can exist for each adsorption model because of the complexity of the molecular orbitals. In addition, all three models can exist simultaneously during the ORR reaction, while the Griffith and Pauling models are preferred. While these models are useful to describe the adsorption configurations, they do not represent the reaction path for ORR. For the d-band center theory using the position of d-band as the descriptor (as described in Figure 1-3(a and b)), all reaction steps of the ORR are taken into consideration. Generally, on an optimized catalyst, the ORR reaction path described in Eq 1.3 would have two rate determining steps (e.g. HOO° formation in Step 1 and HO° formation in Step 3) instead of one (the O₂ binding strength is either too strong or weak). Pure Pt among all elements shows the best ORR activity (closest to the ideal scenario) as well as a good stability. Pt NPs loaded on carbon, therefore, became the first generation of the commercial ORR catalyst. Pt itself, however, is a noble metal with very high price and limited exploitable
resource on earth. To achieve more affordable products, improvement on the catalyst design is necessary. Regarding the overall activity of fuel cell catalysts, Two effective strategies can be applied:

(1) Nanoengineering to achieve nanosized catalysts. Nanosized structures can significantly enlarge the reactant-catalyst interface, and thus improve the overall activity by orders of magnitudes with the same amount of catalysts. Modern Pt catalysts are mostly designed as nanoparticles at the size of sub-10 nm, dispersed on a conducting substrate. Metallic nanoparticles can be synthesized via a wide range of methods including laser ablation, salt reduction, thermal decomposition, ligand removal of organometallics, and photolysis and radiolysis.10

(2) Valence band modification. The modification of the valence states is a direct way to tune the catalytic activity of a single active site (Pt atom). A straightforward way is to induce heterogeneous elements to form alloy or layered structures such as core-shell structures with a thin Pt shell as the reaction interface. Metallic core-shells NPs are normally synthesized by reduction of metal salts in an aqueous environment with reducing agents such as sodium borohydride, hydrazine, oleylamine, and polyols, in sequential processes.

These two strategies are usually combined to better control the properties of the catalysts. PtCo alloy NPs (on carbon support) at the size of a few nanometers, for example, as one of the most advanced commercial ORR catalysts is used in Mirai, a new fuel cell vehicle developed by Toyota. Expectations for the fuel cell industry in the near future is briefly discussed in the following.

Current commercial Pt catalysts include Pt/C as the first generation and Pt-M (M=Co, Ni, etc.) alloy nanoparticles as the second generation ORR catalysts. Extraordinary performance has been reported for bimetallic catalysts for ORR. For example, ordered Pt3Co and PtCo NPs have been reported to have high catalytic activity and stability with slow decay for both ORR and membrane electrode assembly (MEA) tests. However, because of the high price and limited source of Pt, more advanced catalysts with high efficiency and lower usage of Pt are required. Modern research of the electrode catalysts focuses on two respects regarding the use of platinum group metals (PGM): PGM-free catalysts as substitute for
Pt and highly active and stable low-PGM catalysts.\textsuperscript{22-24} So far, Pt-based bimetallic nanostructures have shown much (order of magnitude) higher activity and stability than any other candidate. In the near future, low-PGM catalysts would be the most promising option for large-scale production.

In April 2020, the US DOE released the FY 2019 Progress Report for the DOE Hydrogen and Fuel Cells Program\textsuperscript{25}. In the Fuel Cell Research and Development (R&D) subprogram, key objectives for fuel cells are summarized in Table 1-2. Meanwhile, the objectives for hydrogen infrastructures as another essential part are also established by the Infrastructure and Systems Research and Development (R&D) subprogram, including expectation for hydrogen liquefying techniques, and hydrogen delivery and dispensing cost ($7/kg by 2025).

<table>
<thead>
<tr>
<th>Application</th>
<th>Electrical Efficiency</th>
<th>Durability</th>
<th>Mass Production Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heavy-duty trucks</td>
<td>68% (ultimate 72%)</td>
<td>25000 hours (ultimate 30000 hours)</td>
<td>$80/kW by 2030 (ultimate $60/kW)</td>
</tr>
<tr>
<td>Automotive</td>
<td>65%</td>
<td>5000 hours (ultimate 8000 hours)</td>
<td>$40/kW by 2025 (ultimate $30/kW)</td>
</tr>
<tr>
<td>Combined heat and power (CHP) systems</td>
<td>50% (90% CHP efficiency)</td>
<td>80000 hours</td>
<td>$1500/kW (natural gas) $2100/kW (biogas)</td>
</tr>
</tbody>
</table>

1.2. Bimetallic alloys and core-shell nanoparticles

As mentioned above, inducing a transition metal into Pt is a simple and effective way to improve the ORR activity. To achieve nanosized bimetallic NPs, metal salts are normally reduced in an aqueous environment by the reducing agent and capping agent. Depending on the synthesizing environment (temperature, pH, ligands, reducing capability, etc.) and procedures (time, single/multi step, annealing, etc.), one can obtain NPs with various morphologies and elemental distributions with the same metal precursors. Typically, core-shell NPs and alloy NPs are the two most commonly studied bimetallic systems, as shown in Figure 1-5. In a core-shell structure\textsuperscript{11} where the two different ingredients form an interface, Pt feels a compressive strain when coupled with an element with a smaller lattice size, or a
tensile strain in the case of a larger lattice size. When the Pt is compressed, the higher extent of overlapping leads to the broadening of the Pt valence (5d) band. With the same filling proportion of the valence band, the center of the valence band will shift to lower position relative to the Fermi level. Consequently, the anti-bonding states (Pt-A)* between Pt and the adsorbate tend to lower and have a higher filling extent. This is the so-called strain effect. In an alloy structure, the two metals are mixed either in an ordered or disordered arrangement. The valence states of the two elements interact with each other, leading to redistribution of the states. This is the so-called ligand effect. In bimetallic NPs, these two effects normally are present simultaneously and hard to distinguish.

Figure 1-5. Schematic of core-shell and alloying structures obtained by inducing transition metals.

1.3. Application of synchrotron X-ray techniques on nanomaterials

Modern synchrotron X-ray techniques have been widely used in the characterization of nanomaterials, especially for complicated systems such as core-shell NPs. Because of the small size and high surface to bulk atomic ratio, NPs are normally a mixture of two or more different structures, with each only consisting of very thin repeating patterns. It is hence a challenge for traditional laboratory techniques such as X-ray powder diffraction (XRD), which requires certain amount of crystallite to provide enough signal. Moreover, the electronic structure and chemical information, in specific, can only be obtained with synchrotron X-ray techniques in most cases. Synchrotron X-ray techniques cover a wide range of advanced detecting techniques, among which X-ray absorption spectroscopy (XAS),
scanning transmission X-ray microscopy (STXM), X-ray ptychography, and X-ray emission spectroscopy (XES) are utilized in this thesis. XAS as the most fundamental synchrotron X-ray technique detects the electronic structure and local environment of a specific element. STXM and X-ray ptychography as microscopic techniques provides spatial as well as elemental information for NPs. XES is a band sensitive technique, providing the capability to track the change of the electron band. These techniques are explained in detail in the following chapter.

1.4. Outline of the thesis

The outline of the thesis is as follows. Chapter 1 provides the induction of Pt-based bimetallic materials as the electrocatalyst for fuel cell applications. Chapter 2 introduces the synchrotrons, beamlines, and X-ray techniques used in this thesis. Chapter 3 discusses the electronic and local structures of Pt-Ni alloys, with a focus on the Pt electronic states near the Fermi level. Chapter 4 discusses the alloying and dealloying process of Pt-Ni bimetallic nanoparticles during the synthesizing process. Chapter 5 investigates the electronic and local structures of Cu@Pt core-shell nanoparticles with a Cu core and an ultrathin Pt skin. Chapter 6 introduces a high energy resolution X-ray absorption/emission technique in the application of the Pt-based bimetallic systems. Chapter 7 summarizes the study in this thesis.

1.5. References


(3) Yeager, E.; Razaq, M.; Gervasio, D.; Razaq, A.; Tryk, D. The electrolyte factor in O₂ reduction electrocatalysis; Department of Chemistry, Case Western Reserve University, Cleveland Ohio 1993.


(8) Hansen, H. A.; Rossmeisl, J.; Nørskov, J. K. Surface Pourbaix diagrams and oxygen reduction activity of Pt, Ag and Ni (111) surfaces studied by DFT. *PCCP* **2008**, *10*, 3722-3730.


Chapter 2

2. Synchrotron Instrumentation

2.1. Synchrotron overview

Since the first X-ray was discovered by German physicist Wilhelm Röntgen in 1895, X-ray science has thrived in many disciplines including physics, chemistry, materials science, biology, medical science, and so on. As high energy (typically 100 eV – 100 keV) electromagnetic waves, X-rays possess short wavelengths (0.01 – 10 nm) and strong penetrating capability (depending on the energy and the material). Short wavelengths allow for measurements at atomic scale. Other than the size appropriateness, almost all elements have absorption edges (abrupt change of light absorption) and light emission in the X-ray energy range. These features can serve as elemental fingerprints in material characterization.

For scientific research, synchrotron as a bright and collimated X-ray source has been developed to provide advanced characterization techniques. A synchrotron is a device that accelerates electrons to nearly the speed of light and produces highly polarized light in a continuous energy range from infrared light (IR) to X-ray (synchrotron light) when the electrons are accelerated by their trajectory being bent by bending magnets. Compared with traditional X-ray sources, synchrotron X-rays have several advantages:

(1) Wide tunability. Synchrotron light as continuum electromagnetic waves consists of photons ranging from IR to hard X-rays. This continuity allows for the tunability of the X-ray energy to investigate the absorption edge of a specific element.

(2) High brilliance (also called brightness) and low emittance. Synchrotron light is typically characterized by its brilliance (with the unit photons/s/mm²/mrad²/0.1%bandwidth), in other words, the higher brilliance, the higher flux of photons of a given wavelength on a tiny spot with small divergence. This is usually accompanied by low emittance, in other words, the product of source cross section and solid angle of emission is small. This high brilliance of a synchrotron ensures the sufficient angular resolution for diffraction experiments, high spatial resolution for microscopy, and enough signal strength for small amounts of samples.
(3) High extent of polarization. Synchrotron light is generated when the relativistic electrons are accelerated. In a synchrotron, this controlled acceleration results in highly polarized light. Linear, circular, or elliptical polarization can be achieved based on the capability of the device. Polarized X-rays provide probing capability of oriented features such as π orbitals on a highly ordered surface.

(4) Time structure. Synchrotron light has its time structure because of the use of the radio frequency cavity, which synchronize the electron bundles at relativistic domain (this is also how synchrotron is named). The light pulses are typically separated by dark intervals at the scale of a hundred nanoseconds (depending on the specifications of the synchrotron), which enables study of dynamics.

(5) Coherence. Synchrotron light is generated with certain extent of coherent properties, including lateral (spatial) coherence and longitudinal (temporal) coherence. Coherent X-rays can be utilized in many X-ray imaging techniques such as radiology, holography, and ptychography.

2.2. Synchrotron facilities

Synchrotron light was first observed at a 70 MeV synchrotron accelerator at the General Electric Research Laboratory in 1947. After that, four generations of synchrotrons have been developed (excluding free electron lasers, which are sometimes categorized as the fourth generation synchrotron). A brief history of synchrotrons is described followed by the introduction of the hardware in a typical synchrotron.

The first-generation synchrotrons were constructed by altering the storage ring of particle accelerators. Tantalus, designed and built by Rowe and collaborators in the Synchrotron Radiation Center (SRC) in Wisconsin, achieved its first light in 1968. This is the first storage ring dedicated to the production of synchrotron radiation, with a circumference of only 9.38 m and an energy of 240 MeV $^{1-2}$. Other first-generation synchrotrons including large storage rings were also built around the world, such as the 2.5-GeV SPEAR ring at the Stanford Linear Accelerator Center (SLAC), 3.5-GeV DORIS ring at Deutsches Elektronen Synchrotron (DESY), and 10-GeV Cornell Electron Storage Ring (CESR) at Cornell University. These synchrotrons were constructed as electron-positron colliders, which have low beam currents and low synchrotron radiation output.
The second-generation synchrotrons were designed and dedicated for synchrotron radiation production using electrons as the charged particles in the storage ring, instead of colliders. The brightness and efficiency thus had been greatly improved. New synchrotrons were constructed, such as the famous National Synchrotron Light Source (NSLS) at the Brookhaven National Laboratory (BNL) and the 1-GeV storage ring Aladdin replacing Tantalus, while some other first-generation synchrotrons were upgraded, such as Stanford Synchrotron Radiation Laboratory (SSRL) at SLAC and HASYLAB (Hamburger Synchrotronstrahlungslabor) at DESY.

The third generation took another leap in brightness by incorporating undulators and wigglers as the electron accelerating devices, or in other words, synchrotron light generators. Wigglers and undulators are both called insertion devices because they are inserted into the straight sections between two bending magnets. Coherence, spatial resolution, and temporal resolution had also been significantly enhanced. The third-generation synchrotrons are the major synchrotrons in operation today, including the 6-GeV European Synchrotron Radiation Facility (ESRF), 7-GeV Advanced Photon Source (APS) at Argonne National Laboratory, 8-GeV SPring-8 (largest in the world) in Harima Science Garden City in Japan, 1.9-GeV Advanced Light Source (ALS) at Berkeley, 2.9-GeV Canadian Light Source (CLS), and so on.

The next (fourth) generation synchrotrons are represented by the diffraction-limited storage rings (DLSR), with MAX-IV being the first facility, followed by upgrades of ESRF, APS, ALS, Swiss Light Source (SLS), and SPring-8, as well as new constructions in Brazil, China, and so on. The major improvement lies in the horizontal emittance (by 1 – 2 orders of magnitude) by using a series of miniaturized bending magnets (thanks to the advancement of computer numerical control of machining and improved vacuum technology).
In a typical synchrotron as shown in Figure 2-1, Electrons emitted from a heated cathode are first accelerated in the linear accelerator (LINAC) to a high speed, with energy of hundreds of MeV. They are then injected into the booster ring to reach 99.9999985% the speed of light by further acceleration. These electron bundles with the energy at the order of GeV are finally transferred to the storage ring, where they are kept cycling for hours or even days. The direction of the electron beam is controlled by bending magnets located at the turning sections, where the synchrotron radiations are generated by the highly relativistic electrons. The insertion devices including wiggler and undulators are brighter and more coherent X-ray sources than bending magnets, locating at the straight sections (not shown in the figure). The synchrotron radiation generated from bending magnets, wigglers, and undulators has different characteristics because of the arrangement and strength of magnets, as shown in Figure 2-2. Bending magnets and wigglers produce synchrotron light with a broad and continuous spectrum over the whole energy range, while undulators produce a series of sharp peaks depending on the gap between magnets (not the gap shown in Figure 2-2(a)). Accordingly, when scanning the energy, an undulator has to adjust the gap in real-time. The production of synchrotron radiations costs loss of energy for electrons, and thus decrease the speed. The radiofrequency (RF) cavity provides the compensation of the energy loss as

Figure 2-1. Schematic of a synchrotron. The blue curve represents the electron path. The yellow lines represent the synchrotron radiation. The synchrotron ring is reprinted from EPSIM 3D/JF Santarelli, Synchrotron Soleil. Copyright © EPSIM 3D/JF Santarelli, Synchrotron Soleil.
well as regulation of electron bundles by applying an oscillating electromagnetic field. The synchrotron radiation is an intense, continuous (IR to hard X-ray), highly collimated, and polarized light, as mentioned above. These characteristics allow for a wide range of advanced characterization techniques at the end stations.

Figure 2-2. (a) Configurations of magnets for bending magnets, wigglers, and undulators, with (b) their corresponding characteristics of synchrotron radiations.

2.2.1. Canadian Light Source (CLS)

Canadian Light Source (CLS) is a third-generation synchrotron located in Saskatoon, Saskatchewan, Canada. CLS is equipped with a 2.9 GeV storage ring with a circumference of 170.88 m and a maximum current of 220 mA. The horizontal and vertical emittances are 18 and 0.09 nm-rad, respectively. Since the formal open of the CLS in 2005, the number of operational beamlines has been increased to 15 through Phase-I to Phase-IV construction and upgrade, covering a wide range of applications.

2.2.2. Advanced Photon Source (APS)

Advanced Photon Source (APS) is a third-generation synchrotron located at Argonne National Laboratory, 30 miles southwest of Chicago, Illinois, USA. The APS consists of a 7.0-GeV storage ring and a 450-MeV linear accelerator as the injector. The ring has a circumference of 1,104 m, with an operating ring current of 100 mA and the effective emittance of 3.1 nm-rad. Currently, the APS consists of 34 sectors with a total of more than
50 beamlines covering nearly every scientific discipline, from materials science to biology, chemistry, environmental, geological, and planetary science, and fundamental physics.

2.3. Beamlines

The beamlines related to this thesis are briefly introduced in the following.

2.3.1. Beamline Sector 20-BM at APS

The Sector 20-BM beamline at APS uses the beam source generated from the bending magnet. The beamline uses the Si(111) monochromator with an energy resolution of $1.4 \times 10^{-4}$, from 2.7 to 32.7 keV \(^9\). The available X-ray techniques include X-ray absorption fine structure (XAFS), micro-fluorescence, micro-XAFS, micro-diffraction, time-resolved X-ray excited optical luminescence (TRXEOL), and diffraction anomalous fine structure, covering the disciplines of material science, environmental science, and chemistry. Most of the hard X-ray XAFS in this thesis is completed at the 20-BM beamline.

2.3.2. Beamline Sector 20-ID at APS

The Sector 20-ID beamline at APS uses an undulator as the beam source, with a flux approximately two orders of magnitude higher than that of the BM beamline. Two types of monochromators are available, i.e. Si(111) with an energy resolution of $1.4 \times 10^{-4}$ for the energy range of 2.7 – 32.7 keV, and Si(311) with an energy resolution of $0.3 \times 10^{-4}$ for the energy range of 8 – 50 keV \(^10\). The X-ray techniques include XAFS, X-ray Raman scattering (XRS), resonant X-ray emission spectroscopy (RXES), micro-XAFS, confocal X-ray microscopy, micro-fluorescence, micro-XRD, and time-resolved XAFS. The XES experiment in this thesis is completed at the 20-ID beamline.

2.3.3. Soft X-ray microcharacterization beamline (SXRMB) at CLS

The SXRMB at CLS is a medium energy X-ray beamline covering the energy range of 1.7 – 10 keV using a bending magnet X-ray source. Two sets of monochromators can be selected based on the energy requirement: InSb(111) with an energy resolution of $3.3 \times 10^{-4}$ for 1.7 – 3.7 keV and Si(111) with an energy resolution of $1.0 \times 10^{-4}$ for 2 – 10 keV. InSb(111) provides higher flux while Si(111) has higher energy resolution. \(^11\) Four endstations are available at the SXRMB: (1) The solid state endstation is designed for bulk analysis of solid samples, such as pellets and powders. Samples are placed under a vacuum of $10^{-7}$ torr, the
endstation is optimized for lower energy edges such as Si, P, and S. (2) The microprobe station provides a 10 μm × 10 μm beam spot for mapping experiments. Micro-XAS can also be performed on specific spots using the microprobe. (3) The ambient table is designed for bulk analysis of a wide range of samples under a flow of inert gases (typically helium). (4) Hard X-ray photoelectron spectroscopy (HXPES) utilizes the variable energy capability of synchrotron radiation, offering depth-profiling photoelectron analysis of materials. In this thesis, the HXPES of Pt-Ni nanoparticles was conducted at the HXPES endstation.

2.3.4. Soft X-ray spectromicroscopy (SM) at CLS

The Spectromicroscopy (SM) beamline uses an Apple II type undulator to provide an intense beam in the 130 – 2700 eV energy range. An infinity-corrected plane grating monochromator (PGM) with a vertical dispersion plane is designed to provide an energy resolution of 1.0 – 3.3 × 10^{-4}. The SM beamline is equipped with imaging capability for many disciplines such as polymer science, environmental science, biological applications, and energy materials. Imaging techniques include scanning transmission X-ray microscopy (STXM) in either ambient or cryogenic condition, photoemission electron microscope (PEEM) using X-ray or ultraviolet source, and X-ray Ptychography.

2.4. Detection modes

XAS beamlines are normally equipped with multiple detecting modes (detectors) to accommodate different experiment requirements and collect different types of signals for sample analyses. The most common detecting modes are introduced in the following. In most cases, multiple detecting modes can be applied simultaneously, as shown in Figure 2-3.

![Figure 2-3. Optical path of synchrotron X-rays at the endstation showing the three detecting modes.](image)
2.4.1. Fluorescence yield (FY)

FY mode collects the X-ray fluorescence ($I_f$) emitted from the sample when excited by the incident X-ray ($I_0$). The fluorescence detector (shown as the cylinder in Figure 2-3) is normally aligned 45 degrees to the sample and 90 degrees to the incident beam. These angles, however, can be flexible based on the experiment setup and sample requirement (at a very low angle for surface detection, for example). Because of the deep penetrating depth, FY mode is considered bulk sensitive. For a limited amount of sample (less than a milligram), FY mode is the best option to obtain enough signal. Thick samples (elementally dense), however, suffer from the self-absorption effect, by which the emitted X-ray is re-absorbed by the sample, causing distortion of the XAS features. For low Z elements using soft X-rays, the self-absorption effect tends to be more severe.

2.4.2. Transmission

Transmission signal ($I_t$) measures the light intensity after the incident X-ray ($I_0$) has been partially absorbed by the sample. The intensity is measured by ionization of the inert gas (selection of the gas is based on the X-ray energy to be measured) in the ion chamber (shown as rectangles in Figure 2-3). Transmission mode is also bulk sensitive because the X-ray penetrates the whole sample. Meanwhile, thick samples (from electron density perspective) are likely to block the X-ray from penetrating and thus are not suitable for transmission mode. For nanomaterials in the form of powder, a uniform sample is expected for the XAS experiment to avoid the pinhole effect, which causes unstable intensity and compromises the absorption features. Compared with FY mode, transmission signals can bypass the self-absorption effect, and thus provide a more reliable signal. In addition, the sample thickness information (from an elemental perspective) is also embedded in an unnormalized absorption spectrum.

2.4.3. Total electron yield (TEY)

TEY mode measures the total electron yield including photoelectrons, auger electrons, and secondary electrons ejected from the sample by monitoring the current compensation ($I_e$). Because electrons are charge carriers with low mass, the traveling trajectories of electrons are severely affected by electromagnetic fields. As a result, TEY mode can only measure the surface of samples. The probing depth depends on the electron inelastic mean free path (IMFP)\textsuperscript{16}, or in other words, the kinetic energy of electrons and density of the sample. The
electron IMFP in Ni (a sample composition in Chapters 3 and 4) is shown in Figure 2-4, from which electrons with 10000 eV kinetic energy can only escape from around 9 nm of Ni without losing the chemical information. The probing depth is typically a few times of the IMFP for TEY mode.

![Figure 2-4. IMFP of electrons in Ni with kinetic energy ranging from 50 to 10000 eV.](image)

2.5. Synchrotron X-ray techniques

2.5.1. X-ray absorption spectroscopy (XAS)

When light interacts with matter, the incident photons can be either absorbed, scattered, or transmitted. The relationship between the intensities of the incident ($I_0$) and transmitted ($I_t$) lights follow the Lambert-Beer Law (Eq. 2.1), concerning the sample thickness $t$ and absorption coefficient $\mu$. Physically, the absorption coefficient depends on the energy level as well as the electron density, qualitatively following the trend described in Eq. 2.2, where $\rho$ is the sample density, $Z$ is the atomic number, $A$ is the atomic mass, and $E$ is the X-ray energy. Generally, the X-ray absorption (versus $E$) of a sample increases abruptly at the edge (excitation from the core level to an unoccupied bound/quasi-bound state or the continuum) and decreases gradually afterward until meeting another absorption edge (from the same or another element), following the change of the cross section $\sigma$ (versus $E$). For experiments collecting signal in FY or TEY detecting modes, i.e. the fluorescence yield ($I_f$) or electron yield ($I_e$), as mentioned above, $\mu$ is expressed as the yield to $I_0$ ratio (based on the fact that the yield is proportional to the absorption), as shown in Eq. 2.3. This equation holds when
affecting factors such as the self-absorption effect is small. The fluorescence intensity is also affected by the emission angle, effective sampling volume (instead of the actual sample thickness), etc.

\[ \frac{I_t}{I_0} = e^{-\mu t} \]  

(2.1)

\[ \mu = \sigma \cdot \rho \approx \frac{\rho Z^4}{AE^3} \]  

(2.2)

\[ \mu \propto \frac{I_{f,e}}{I_0} \]  

(2.3)

\[ \lambda = \frac{h}{p} = \frac{h}{\sqrt{2m(E - E_0)}} \]  

(2.4)

By scanning across the absorption edge of a specific element using a continuous X-ray energy source, one can obtain the absorption spectrum. This technique is called X-ray absorption spectroscopy (XAS) or X-ray absorption fine structure (XAFS). It is usually conducted in a synchrotron utilizing the continuity and tunability of the intense X-ray. In a hard X-ray absorption spectrum, typically, two regions including the X-ray absorption near edge structure (XANES or NEXAFS, from -20 to +50 eV) and extended X-ray absorption fine structure (EXAFS, above +50 eV) are analyzed, corresponding to the near-edge region and high energy region, respectively. In a soft X-ray absorption experiment, normally only the XANES region will be collected due to the closeness of edges (from the same element or different elements) in energy. \( \chi(E) \), representing \( \mu t \), is analyzed in the following to extract the information of the electronic structure and local structure (chemical environment).

While XANES and EXAFS are extracted from the same adsorption spectra, the origin of each is fundamentally different. When core electrons are excited by the incident X-ray and become photoelectrons, they propagate as De Broglie waves with the wavelengths described by Eq. 2.4, where \( h \) is the Planck constant, \( p, m, \) and \( E - E_0 \) are the momentum, mass, and kinetic energy of the electron, respectively. Low \( KE \) photoelectrons tend to be scattered multiple times within the local domain and dominantly contribute to the XANES, while high \( KE \) photoelectrons tend to dominate the EXAFS by single scattering. A simplified scattering
picture of photoelectrons is shown in Figure 2-5. Generally, the XANES region and EXAFS region are analyzed separately.

Figure 2-5. (a) Multiple scattering contributing to XANES and single scattering contributing to EXAFS.

In the XANES region, the X-ray absorption is dominated by the dipole-allowed \((\Delta l = \pm 1, \Delta j = \pm 1, 0)\) transition of core electrons to unoccupied bound/quasi-bound states or the continuum. As a result, the absorption edge position \((E_0)\) is sensitive to the oxidation state, that is, the more electron loss, the harder the excitation, and thus the higher energy the edge. Pre-edge features are sensitive to local symmetry due to the crystal field splitting (e.g., tetragonal vs octahedral) and orbital hybridization (e.g., K-edge for Fe vs Fe\(_2\)O\(_3\)), which generate unoccupied dipole-allowed states at an energy lower than the vacuum level (edge). Moreover, the WL peak (the major peak following the edge jump) area is sensitive to the number of dipole-allowed unoccupied states. Mathematically, the electron transition rate \(P_{i\rightarrow f}\) from the initial state \(|\psi_i\rangle\) (with energy \(E_i\)) to the final state \(|\psi_f\rangle\) (with energy \(E_f\)) is described by Fermi’s golden rule in Eq. 2.5, where \(H'\) is the interaction Hamiltonian operator between the electromagnetic field and the electron, and \(\rho\) is the density of states. For the specific case of electrons excited by X-ray, the interaction Hamiltonian \(H'\) is proportional to \(\hat{e} \cdot \hat{r} e^{i\hat{k} \cdot \hat{r}}\), where \(\hat{e}\), \(\hbar \hat{k}\), \(\hbar \omega\) are the X-ray’s electric polarization vector, momentum, and energy, respectively, and \(\hat{r}\) is the position vector. The transition rate is thus expressed in Eq. 2.6.
Because of the high sensitivity of chemical environments, XANES is extensively used in the analysis of oxidation state, chemical components, occupation of molecular orbitals, local symmetry, and so on. For example, at Fe K-edge, higher oxidation will lead to a higher energy shift of the absorption edge and higher whiteline (WL) intensity. A linear combination fitting of the XANES region can semi-quantify different Fe species such as Fe, FeO, and Fe$_2$O$_3$. Meanwhile, the pre-edge region is sensitive to 3d-p hybridization between Fe and the ligand atoms, although 1s $\rightarrow$ 3d transitions are dipole-forbidden. As a result, tetrahedral Fe will have a higher pre-edge peak than octahedral Fe. Other than geometry (symmetry), the pre-edge multiplet features also information of spin state, oxidation state, and bridging ligation $^{17}$. In a fast-growing area, in-situ/operando measurement of chemical reactions, XANES is also a commonly used X-ray technique to track the chemical change, intermediate products, and structural evolution in real-time during a reaction.

EXAFS measures the modulation of the absorption coefficient as a function of photon energy beyond the XANES region to as much as 1000 eV above the edge. The EXAFS modulation is usually expressed in k-space, through a transformation of the electron kinetic energy to wavenumber, as described by Eq. 2.7. Physically, core electrons are excited to continuum states (photoelectrons) with excess kinetic energy (KE). The photoelectrons propagate as De Broglie waves and are scattered by the surrounding atoms, as discussed above. The outgoing electron waves interfere with the backscattered waves, resulting in the EXAFS modulation. The well-developed model for the EXAFS modulation is shown in Eq. 2.8 $^{18-19}$.
\[
\chi(k) = \sum_j \left[ N_j S_0^2 f(k, \theta) e^{-2R_j / \lambda_e(k)} e^{-2k^2 \sigma_j^2} \frac{1}{kR_j^2} \right] \sin \left[ 2kR_j + \delta(k) \right] \]

(2.8)

where \( N_j \) is the coordination number (CN) of atom type \( j \); \( S_0^2 \) is amplitude reduction term due to the many-body effects; \( f(k, \theta) \) is the atomic scattering amplitude; \( e^{-2R_j / \lambda_e(k)} \) is the amplitude damping term due to the electron escape depth \( \lambda_e \); \( e^{-2k^2 \sigma_j^2} \) is the Debye-Waller factor, that is, the amplitude damping term due to thermal motion; \( R_j \) is the interatomic distance between the absorber atom and the scatterer atom; \( \delta(k) = 2\delta_a(k) + \delta_b(k) \): is the phase shift function attributed to the absorber \( \delta_a(k) \) and the back-scatterer \( \delta_b(k) \). In a typical EXAFS fitting, \( N_j, S_0, \sigma_j^2, \) and \( R_j \) are the variable parameters to quantitatively obtain the CN and interatomic distances for the elements of interest. Qualitatively, one can use the Fourier transform of the EXAFS to obtain the R-space, from which it is visually plausible to identify the crystal structure of crystalline materials. The actual interatomic distances, however, can only be obtained from the EXAFS fitting because of the phase shift \( \delta(k) \), which causes the R-space features to shift towards lower interatomic distances.

EXAFS is a powerful tool to examine the local structure of materials, regardless of crystallinity because of the short-range scattering (within a few atomic shells). The interatomic distance \( R \), as the most reliable parameter with a resolution of around 0.02 Å, can be used to track a slight change of bonding distances. For example, the Pt-Pt bond length upon alloying with different elements or different compositions can be accurately determined by EXAFS fitting. Another example is molecule-like catalysts such as M-N-C (M is a 3d transition metal) structures. The M-N and M-C bonding distances are significant for the adsorption of species on the M atom. This type of structures is usually very difficult to determine but can be examined with EXAFS. At beamlines equipped with quick-EXAFS capability (full EXAFS spectrum collection in seconds or even milliseconds), EXAFS is also applied to in-situ/operando measurements to track structural changes of materials during a chemical reaction or atmospheric/thermal treatments.
2.5.2. Scanning transmission X-ray microscopy (STXM)

STXM is a spectromicroscopic technique, by which it means the soft X-ray absorption spectra can be embedded in X-ray mapping. This is done by X-ray scanning through the whole region of interest (ROI) at each energy point (normally across the absorption edge). In the STXM endstation, a Fresnel zone plate with an outer zone width ($\Delta r_n$) of 25 nm was utilized to focus the X-ray beam at the focal length of 0.83 mm. The diffraction/spot size limited spatial resolution ($1.22 \times \Delta r_n$) is about 30 nm. The sample was raster-scanned in two dimensions, with a point (0D) detector (Scintillator + PMT/PD) placed after the sample to collect the transmission signal in real space. Although with the “transmission” term in the name, STXM is normally equipped with an FY detector and sometimes also an optical detector. Therefore, several detecting modes are available depending on the requirement of the samples. XAS coupled with microscopy is a powerful tool to study heterostructures, especially when composed of different elements. For example, the interaction of drug molecules with drug carriers can be revealed by studying the XAS at different regions of the composite at nanoscale \(^{20}\).

2.5.3. X-ray ptychography

\[ \text{Figure 2-6. Schematic of X-ray Ptychography} \] \(^{21}\).

X-ray Ptychography is a lensless X-ray imaging technique combining STXM and coherent diffraction imaging (CDI) \(^{22}\). At the X-ray Ptychography endstation (shared with STXM), the X-ray beam from the monochromator travels through the pinhole (5 μm) and the sample, generating the coherent speckle diffraction pattern on the detector, as shown in Figure 2-6 \(^{21}\). Unlike STXM, Ptychography records the signal in reciprocal space with a 2D pixelated
CCD. An iterative algorithm is developed to retrieve the absorption (real part) and phase shift coefficient (imaginary part) information. A sub-10 nm resolution of the final images can be achievable after computational reconstruction. Similar to STXM, with the tunable property of the synchrotron X-ray, the spatial distribution of elements through the whole nanostructures can be revealed by selecting the X-ray energy below and above the absorption edges of the interested elements.

Figure 2-7. Dipole allowed X-ray emission followed by excitation of 1s core holes.

Darker color indicates relatively higher emission intensity. Each orbital is label with two equivalent notation on the left axis and right axis, respectively.

2.5.4. X-ray emission spectroscopy (XES)

When a core electron is excited by the incident X-ray (or other processes such as electron bombardment), a core hole is left behind. The decay of the core hole is completed by the transition of an electron from a higher energy level, emitting an X-ray photon. This X-ray emission process is illustrated in Figure 2-7. When 1s core holes are created, multiple X-ray emission channels exist simultaneously, with the strongest (highest probability) one being Kα1 emission (2p3/2 → 1s), followed by Kα2 (2p1/2 → 1s), Kβ1 (3p3/2 → 1s), and Kβ2 (3p1/2 → 1s). Decay channels from higher energy states and dipole-forbidden states are
The shape of the X-ray emission spectrum, in principle, shows the structure of the band (occupied) from which electrons decay, with core-hole lifetime and instrumental broadening. Because the creation of the core holes is directly related to the X-ray absorption, one can monitor an X-ray emission channel as a function of the incident X-ray energy to obtain the XAS. This is the FY detection mode discussed above.

In the case where the core holes are filled by electrons from the valence band, the X-ray emission is specifically termed valence-to-core (VTC) emission. For transition metals, VTC emission can only be detected with a high energy resolution experiment setup because the intensity is very weak compared with other emission lines. VTC emission, however, is an important technique because the valence electrons play the most important role in chemical bonding and chemical reactions. XES is a fast developing technique for applications in chemistry, material sciences, biology, and environmental sciences. Chemical information including orbital splitting, spin and oxidation states, as well as the local symmetry are embedded in the XES. In Chapter 6, XES with a high energy resolution setup is conducted on Pt alloys to study the change of Pt valence band upon alloying with 3d transition metals.

2.6. Summary of beamlines and X-ray techniques

The beamlines and corresponding X-ray techniques used in this thesis are summarized in Table 2-1.

<table>
<thead>
<tr>
<th>Beamline</th>
<th>Technique</th>
<th>Material System</th>
<th>Chapter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sector 20-BM, CLS@APS</td>
<td>XAS</td>
<td>Pt-Ni alloys</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pt-Ni NPs</td>
<td>4</td>
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<tr>
<td></td>
<td></td>
<td>Pt-Cu NPs</td>
<td>5</td>
</tr>
<tr>
<td>Sector 20-ID, CLS@APS</td>
<td>HERFD-XAS</td>
<td>Pt-Ni alloys</td>
<td>3, 6</td>
</tr>
<tr>
<td></td>
<td>HERFD-XES</td>
<td>Pt-Cu NPs</td>
<td>5, 6</td>
</tr>
<tr>
<td>SXRMB, CLS</td>
<td>HXPES</td>
<td>Pt-Ni NPs</td>
<td>4</td>
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<tr>
<td>SM, CLS</td>
<td>X-ray Ptychography</td>
<td>Pt-Ni NPs</td>
<td>4</td>
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</tbody>
</table>
2.7. References


Chapter 3

3. Pt-Ni Alloy Systems

3.1. Introduction

Platinum has been widely studied for its outstanding catalytic performance in various chemical reactions in renewable fuel conversion, oil industry, environmental protection, and so forth. However, due to the high price and limited reserves of platinum, catalysts with higher efficiency and lower cost are demanded by the market. Introducing a non-noble metal into the catalyst is one of the promising solutions to Pt-based catalysts. So far, Pt-M (M is a transition metal) bimetallic nanocrystals have been reported as efficient electrocatalysts for methanol oxidation reaction \(^1\)-\(^2\), hydrolytic hydrogenation \(^3\) and oxygen reduction reaction (ORR) \(^4\)-\(^6\), attributed to the shifted d-band center of active sites (mostly Pt) which affects the binding energy (BE) of adsorbate molecules \(^7\). These bimetallic systems usually contain or consist of disordered and inhomogeneous alloy structures, due to which the analysis of the physical and chemical properties becomes challenging but essential to articulate. Pt has unoccupied density of state (DOS) of 5d\(^{5/2}\) character just above the Fermi level; in Pt-Ni alloys, for example, the charge redistribution due to hybridization of the Pt 6s, 5d and Ni 4s, 4p and 3d ultimately determines the electronic structure of the alloy hence its catalytic behavior. Extensive X-ray photoelectron spectroscopy (XPS) studies of these nano bimetallic systems have been reported in recent years, the charge redistribution and many-body effect, however, are commonly ignored or ill interpreted. In this study, we focus on these issues by studying bulk Pt-Ni alloys. The interaction of the XPS core level and the valence band (VB) of the two alloying components Pt and Ni revealed from these measurements is discussed in the following sections.

3.2. Experimental and theoretical methods

3.2.1. Synthesis of Pt-Ni alloys

Bulk Pt-Ni alloys with different Pt:Ni atomic ratios were prepared according to the phase diagram \(^8\). Stoichiometric amount of Pt and Ni (3:1, 1:1, and 1:3 atomic ratio) were arc melted repeatedly in vacuum to form homogeneous solutions. The alloys were then vacuum-
sealed in an ampoule, followed by the annealing process at 400 °C for 72 hours. The three Pt-Ni alloys are henceforth labeled as Pt$_3$Ni, PtNi, and PtNi$_3$, as shown in Figure 3-1(a).

![Figure 3-1. (a) As-synthesized Pt-Ni alloys. (b) XRD spectra of alloy samples and reference metals. The Pt data was obtained from the standard Pt pattern (JCPDS 65-2868).](image)

3.2.2. X-ray characterizations and density functional theory calculations

The crystallographic information of the alloys was obtained using a Rigaku RU200BVH X-ray diffractometer with a Co Kα X-ray source ($\lambda = 1.789$ Å), as shown in Figure 3-1(b). The (111), (200), and (220) peaks show a clear shift to lower angles relative to the Ni face-centered cubic (fcc) structure as the Pt content increases in the alloys, while the fcc cubic structure is preserved. Both Pt and Ni are fcc structure in the Fm$\overline{3}$m space group. The lattice constants calculated from the X-ray powder diffraction (XRD) pattern using an fcc structure are 3.52, 3.66, 3.74, 3.85, and 3.92 Å for Ni, PtNi$_3$, PtNi, Pt$_3$Ni, and Pt, respectively, indicating a Vegard’s law behavior.

To probe the change of d-band states as well as the local structure, the X-ray absorption fine structure (XAFS) including the X-ray absorption near edge structure (XANES) region and extended XAFS (EXAFS) were collected at Beamline 20-BM at the Advanced Photon Source (CLS@APS) and analyzed with ATHENA and ARTEMIS. The spectra of the alloy samples (powder, 10 ~ 50 microns) were recorded in fluorescence yield mode (FY). The XANES and EXAFS results in energy and R-space, respectively (Figure 3-4) indicate that both Pt and Ni in all the alloys are in metallic state as judged from the negligible threshold
shift from the pure element. This suggests that the bulk of alloys is not oxidized, while the surface oxides had little contribution to the spectra in these measurements. In Figure 3-2(a), alloy samples show less intense Pt L3-edge WLs than Pt foil, indicating the $2p_{3/2} \rightarrow 5d_{5/2,3/2}$ transition has access to less available $5d_{5/2}$ holes (Pt 5d holes are dominantly $5d_{5/2}$), that is, that Pt gains 5d electrons in the alloys. In the meanwhile, extra resonances (compared with Pt foil) beyond the WL at ~11576 and ~11588 eV, and blue shifted peaks (~11595 eV) are observed because of a contracted Pt lattice in the presence of Ni atoms and the multiple scattering involving both Pt and Ni neighboring atoms, because Ni has a higher backscattering amplitude in the low k region than Pt. On the other hand, Ni K-edge XANES show increased WL intensity ($Ni \ 1s \rightarrow 4p$) as the Pt/Ni ratio increases (Ni becomes more diluted), Figure 3-2(b), indicating a loss of p electrons from Ni 4sp band, while the multiple scattering resonances above the WL are red-shifted because of an expanded lattice compared with bulk Ni. Pt-Pt and Ni-Pt characteristics are also enhanced and shifting to larger values in R-space (Figure 3-2(c and d)) as the Pt content increases. The first shell fitting parameters for the EXAFS are shown in Table 3-1 and fitted curves in Figure 3-3. The amplitude reduction factor $S_0^2$ at each edge was obtained by fitting the spectrum of the reference metal with its standard crystal structure (coordination number on the first shell). For each alloy, Pt L3-edge and Ni K-edge were fitted simultaneously with the constrain that Pt-Ni and Ni-Pt have the same bonding distance. 13 independent parameters (maximum allowed: 20) are used in each fit. The fitted interatomic distances are summarized with the XRD result in Figure 3-4, verifying the increasing size as the Pt content increases. Note that the Pt-Pt and Ni-Ni bond lengths do not strictly follow Vegard’s law, but tend to stay at their pure material values, indicating some local disorder. The ratios of the Pt and Ni CN agree with the alloy composition, while the total CNs for both Pt sites (7.3, 7.5, and 8.4 for Pt3Ni, PtNi, and PtNi3, respectively) and Ni sites (8.7, 8.0, and 6.2 for Pt3Ni, PtNi, and PtNi3, respectively) were smaller than expected because of some self-absorption effect using the FLY detection mode and the disordered nature of the alloys.
Figure 3-2. XAFS spectra of alloys and pure metals. (a and b): XANES at Pt L₃- and Ni K-edges, respectively. (c and d): Fourier transform of the EXAFS in R-space at Pt L₃- and Ni K-edges, respectively, with a k² weighing. (e and f): k-space at Pt L₃- and Ni K-edges, respectively, with a k² weighing. Note that the Ni foil spectrum intensity in (d and f) is divided by 2 for visual comparison.
Figure 3-3. First-shell EXAFS fitting of Pt L₃-edge (left column) and Ni K-edges (right column) for Pt-Ni alloys. The fitted k ranges were set to be 2 – 12.5 Å⁻¹ for Ni K-edge and 2 – 14 Å⁻¹ for Pt L₃-edge.
Figure 3-4. Calculated averaged bond lengths from XRD results using an fcc structure and bond lengths fitted from EXAFS results.

Table 3-1. Fitting parameters for Pt L3-edges and Ni K-edges EXAFS for Pt-Ni alloys.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Path</th>
<th>CN</th>
<th>Bond Length (Å)</th>
<th>$\sigma^2$ (Å²)</th>
<th>$\Delta E_0$ (eV)</th>
<th>R-factor ($10^{-3}$)</th>
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<td>Pt-Pt</td>
<td>12</td>
<td>2.765 ± 0.002</td>
<td>0.0046 ± 0.0002</td>
<td>7.63 ± 0.26</td>
<td>3.08</td>
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<td>Ni foil</td>
<td>Ni-Ni</td>
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<td>6.95 ± 0.23</td>
<td>0.06</td>
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<td>Pt-Pt</td>
<td>5.2 ± 0.6</td>
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<td>0.0050 ± 0.0005</td>
<td>7.38 ± 0.52</td>
<td>0.98</td>
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<td>Pt-Ni</td>
<td>2.1 ± 0.5</td>
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<td>Ni-Ni</td>
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<td>Ni-Pt</td>
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<td>Ni-Ni</td>
<td>3.9 ± 0.4</td>
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<td>0.0069 ± 0.0007</td>
<td>4.93 ± 0.23</td>
<td>0.41</td>
</tr>
<tr>
<td>PtNi3</td>
<td>Pt-Pt</td>
<td>1.9 ± 0.6</td>
<td>2.664 ± 0.006</td>
<td>0.0040 ± 0.0013</td>
<td>7.59 ± 0.49</td>
<td>0.24</td>
</tr>
<tr>
<td></td>
<td>Pt-Ni</td>
<td>6.5 ± 0.4</td>
<td>2.570 ± 0.003</td>
<td>0.0052 ± 0.0004</td>
<td>7.59 ± 0.49</td>
<td>0.24</td>
</tr>
<tr>
<td></td>
<td>Ni-Ni</td>
<td>4.6 ± 0.2</td>
<td>2.536 ± 0.002</td>
<td>0.0071 ± 0.0005</td>
<td>5.09 ± 0.27</td>
<td>0.24</td>
</tr>
<tr>
<td></td>
<td>Ni-Pt</td>
<td>1.6 ± 0.3</td>
<td>2.570 ± 0.003</td>
<td>0.0070 ± 0.0017</td>
<td>5.09 ± 0.27</td>
<td>0.24</td>
</tr>
</tbody>
</table>
Figure 3-5. XPS and UPS spectra of as-prepared samples. (a) Ni 2p\textsubscript{3/2} XPS spectra of samples. Red dotted line: experiment result; black line: fitted curve; blue area: fitted Ni 2p\textsubscript{3/2}; pink area: satellite peak Sat. 1; green area: satellite peak Sat. 2; and cyan line: Shirley-type background. (b) Pt 4f XPS spectra of samples. Red dotted line: experiment result; black line: fitted curve; blue area: Pt 4f\textsubscript{7/2}; pink area: Pt 4f\textsubscript{5/2}; and cyan line: Shirley background. (c) Normalized VB of samples measured by UPS. The vertical solid lines show the narrowing of the Pt 5d apparent spin-orbit splitting and the shift of the 5d band centroids (relative to Pt metal) away from the Fermi level, and Ni 3d band centroid (relative to Ni metal) towards the Fermi level. (d) Extracted Ni 2p\textsubscript{3/2} and (e) Pt 4f\textsubscript{7/2} main peaks with fitted $\alpha$.

Charge redistribution of Pt and Ni in alloys is also studied using XPS conducted on a Kratos AXIS Supra XPS equipped with an Al K\textalpha\ (1486.6 eV) X-ray source and a UV discharge source for ultraviolet photoelectron spectroscopy (UPS). Pt 4f and Ni 2p spectra were collected with a pass energy of 20 eV and an energy step of 0.05 eV. The sample surfaces were cleaned with a high flux Ar\textsuperscript{+} monatomic ion source inside the XPS chamber right before the XPS measurement. The source was run using a beam energy of 500 eV for 1 minute on each sample to remove surface contamination and oxides without causing damage.
The spectra were aligned and calibrated to the Fermi level of 0 BE. The results are shown in Figure 3-5 where Ni 2p and Pt 4f main peaks were fitted with CasaXPS. Note that for the Ni 2p doublets, only the more intense 2p$_{3/2}$ is used for further analysis. A Shirley background and the Doniach–Sunjic, Gaussian–Lorentzian DS$(\alpha, n)GL(m)$ line shape (see Appendix A) were used to fit the asymmetric Ni 2p and Pt 4f main peaks caused by the many-body effect, which is associated with the presence of narrow unoccupied d states at the Fermi level (e.g., the Au 4f$_{7/2}$ peak is nearly symmetric and Au has a fully occupied d band, while Pt exhibits an asymmetric DSc line shape because of the presence of unoccupied d states just above the Fermi level) $^{10}$. Ni 2p shake-up satellites labelled as Sat.1 and Sat.2 were fitted with GL(30) line shape. From Figure 3-5(a), four trends in the Ni 2p spectra are observed as the Pt content increases: (1) the Ni 2p$_{3/2}$ main peaks of the alloys (852.57, 852.46, 852.38, and 852.32 eV for Ni foil, PtNi$_3$, PtNi, and Pt$_3$Ni, respectively) shift to lower BE. (2) The 2p main peaks become more asymmetric as indicated by the asymmetric parameters $\alpha$ (0.115, 0.130, 0.160, and 0.180 for Ni foil, PtNi$_3$, PtNi, and Pt$_3$Ni, respectively) in the DS profile $^{10}$ in Table 3-2. This is also clearly shown in the normalized peaks in Figure 3-6(a). (3) Shake-up satellites Sat. 1 (856.49, 855.55, 854.85, and 853.84 eV for Ni foil, PtNi$_3$, PtNi, and Pt$_3$Ni, respectively) and Sat. 2 (858.61, 858.11, 857.72, and 857.25 eV for Ni foil, PtNi$_3$, PtNi, and Pt$_3$Ni, respectively) shift to lower BE, with a decreasing energy difference from the main peak, namely $\Delta E_1$ (3.92, 3.09, 2.47, and 1.52 eV for Ni foil, PtNi$_3$, PtNi, and Pt$_3$Ni, respectively) and $\Delta E_2$ (6.04, 5.65, 5.34, and 4.93 eV for Ni foil, PtNi$_3$, PtNi, and Pt$_3$Ni, respectively). (4) The area proportions of Ni 2p$_{3/2}$ main peaks (92.80, 88.89, 88.04, and 85.80% for Ni foil, PtNi$_3$, PtNi, and Pt$_3$Ni, respectively) decrease, while those of Sat. 1 (1.27, 3.45, 3.93, and 5.73% for Ni foil, PtNi$_3$, PtNi, and Pt$_3$Ni, respectively) and Sat. 2 (5.94, 7.66, 8.04, and 8.47% for Ni foil, PtNi$_3$, PtNi, and Pt$_3$Ni, respectively) increase. On the other hand, as the Pt is more diluted in Ni, the Pt 4f peaks (see Figure 3-5(b and e), Table 3-3, and Figure 3-6) shift to higher BE (Pt 4f$_{7/2}$ at 71.08, 71.10, 71.19, and 71.31 eV for Pt, Pt$_3$Ni, PtNi, and PtNi$_3$, respectively), while the line shape becomes more symmetric ($\alpha = 0.135, 0.115, 0.085$, and 0.072 for Pt, Pt$_3$Ni, PtNi, and PtNi$_3$, respectively).
Table 3-2. XPS fitting parameters for Ni 2p\(_{3/2}\) peaks. Satellite peaks are fitted with GL(30) line shape.

<table>
<thead>
<tr>
<th></th>
<th>2p(_{3/2}) (eV)</th>
<th>Asymmetric Line Shape</th>
<th>FWHM (eV)</th>
<th>%</th>
<th>Sat. 1 (eV)</th>
<th>%</th>
<th>ΔE(_1) (eV)</th>
<th>Sat. 2 (eV)</th>
<th>%</th>
<th>ΔE(_2) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>852.57</td>
<td>DS(0.115,0)GL(75)</td>
<td>0.99</td>
<td>92.80</td>
<td>856.49</td>
<td>1.27</td>
<td>3.92</td>
<td>858.61</td>
<td>5.94</td>
<td>6.04</td>
</tr>
<tr>
<td>PtNi(_3)</td>
<td>852.46</td>
<td>DS(0.130,0)GL(75)</td>
<td>0.93</td>
<td>88.89</td>
<td>855.55</td>
<td>3.45</td>
<td>3.09</td>
<td>858.11</td>
<td>7.66</td>
<td>5.65</td>
</tr>
<tr>
<td>PtNi</td>
<td>852.38</td>
<td>DS(0.160,0)GL(75)</td>
<td>0.92</td>
<td>88.04</td>
<td>854.85</td>
<td>3.93</td>
<td>2.47</td>
<td>857.72</td>
<td>8.04</td>
<td>5.34</td>
</tr>
<tr>
<td>Pt(_3)Ni</td>
<td>852.32</td>
<td>DS(0.180,0)GL(75)</td>
<td>0.89</td>
<td>85.80</td>
<td>853.84</td>
<td>5.73</td>
<td>1.52</td>
<td>857.25</td>
<td>8.47</td>
<td>4.93</td>
</tr>
</tbody>
</table>

Table 3-3. XPS fitting parameters for Pt 4f\(_{7/2,5/2}\) peaks.

<table>
<thead>
<tr>
<th></th>
<th>4f(_{7/2}) (eV)</th>
<th>Asymmetric Line Shape</th>
<th>FWHM (eV)</th>
<th>4f(_{5/2}) (eV)</th>
<th>Asymmetric Line Shape</th>
<th>FWHM (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PtNi(_3)</td>
<td>71.31</td>
<td>DS(0.072,0)GL(75)</td>
<td>0.76</td>
<td>74.66</td>
<td>DS(0.072,0)GL(75)</td>
<td>0.76</td>
</tr>
<tr>
<td>PtNi</td>
<td>71.19</td>
<td>DS(0.085,0)GL(75)</td>
<td>0.75</td>
<td>74.54</td>
<td>DS(0.085,0)GL(75)</td>
<td>0.76</td>
</tr>
<tr>
<td>Pt(_3)Ni</td>
<td>71.10</td>
<td>DS(0.115,0)GL(75)</td>
<td>0.74</td>
<td>74.45</td>
<td>DS(0.115,0)GL(75)</td>
<td>0.75</td>
</tr>
<tr>
<td>Pt</td>
<td>71.08</td>
<td>DS(0.135,0)GL(75)</td>
<td>0.74</td>
<td>74.43</td>
<td>DS(0.135,0)GL(75)</td>
<td>0.76</td>
</tr>
</tbody>
</table>

Figure 3-6. Normalized Ni 2p\(_{3/2}\) (a) and Pt 4f\(_{7/2,5/2}\) (b) XPS spectra. As the Pt: Ni ratio increased, both Ni 2p and Pt 4f line shapes tended to be more asymmetric, indicating the Pt 5d electron loss and Ni 3d electron gain upon alloying.
Figure 3-7. Experimental and simulated Pt L₃-edge XANES for Pt-Ni alloys and corresponding crystal structures used in WIEN2k. Purple ball: Ni; Cyan ball: Pt.

Theoretical calculation of the XANES spectra at the Pt L-edge and Ni K-edge and the DOSs at the VB of these Pt-Ni alloys have been done using WIEN2K ¹¹ based on the density functional theory (DFT) ¹²-¹³. The linearized augmented plane wave (LAPW) method and the generalized gradient approximation (GGA) have been used. ¹⁴ The theoretical spectra are shown together with the experimental XANES of Pt₃Ni, PtNi, and PtNi₃ in Figure 3-7(a, c, e), and with corresponding crystal models illustrated in Figure 3-7(b, d, f) and described in Appendix B, respectively. These crystal structures are built based on the predefined bimetallic compositions and bond lengths from EXAFS fitting results. The total DOS (with Gaussian line broadening of 0.02 Ry) at the VB with contributions from each element just below the Fermi level and the experimental VB from UPS are plotted in Figure 3-8. From the total DOS of Pt and Ni, it is apparent that Ni has higher occupancy of energy states closer to the Fermi level than that of Pt. It is also apparent from the calculated DOS that both Pt and Ni total DOS push each other away upon alloying. In the meanwhile, Ni d bands (centroid)
shifts toward the Fermi level while the Pt d band centroid is further away from the Fermi level. This trend is the same as the core BE shift discussed below. Note that the calculated DOSs do not reflect the difference between Pt 5d and Ni 3d cross sections at the UPS energy. In the following, charge redistribution and many-body effect of Pt-Ni alloys are discussed based on the experimental and DFT results.

Figure 3-8. The VB measured by UPS in (a, c, e), and calculated DOS with partial contributions of Pt and Ni in (b, d, f) for Pt₃Ni, PtNi, and PtNi₃, respectively.

\[
A_3 = C_0N_0E_3 \left( R_{5d}^{2p3/2} \right)^2 \cdot \left( \frac{6h_{5/2} + h_{3/2}}{15} \right) \tag{3.1}
\]

\[
A_2 = C_0N_0E_2 \left( R_{5d}^{2p1/2} \right)^2 \cdot \left( \frac{h_{3/2}}{3} \right) \tag{3.2}
\]

\[
h_{5/2} = \frac{1}{2C_3} \left( \frac{E_2}{E_3} A_3 - A_2 \right) \tag{3.3}
\]

\[
h_{3/2} = \frac{3}{C_2} (A_2) \tag{3.4}
\]
3.3. Discussion

We analyzed the XANES (unoccupied DOS) and XPS (occupied DOS) results below. The WLs of Pt L$_3$- and Ni K-edges, corresponding to Pt 2p$_{3/2} \rightarrow 5d_{5/2,3/2}$ and Ni 1s $\rightarrow$ 4p transitions, are shown in Figure 3-2(a and b), respectively. A reduction in Pt L$_3$-edge WL intensity is observed for all alloy samples relative to the Pt foil, indicating a decrease of Pt 5d holes. In other words, Pt gains 5d electrons in the alloy. Note that Pt 2p $\rightarrow$ 6s transitions are also allowed by the dipole transition rule; this contribution, however, is relatively negligible and broad because of the matrix element and the band effect (6s is free electron like), and commonly neglected in the WL analysis. Thus the WL is dominated by Pt 2p$_{3/2} \rightarrow 5d_{5/2,3/2}$ transitions. On the other hand, all alloy samples show more intense Ni K-edge WLs relative to the Ni foil, suggesting a loss of Ni 4p electrons from the 4sp band. The Pt 5d$_{5/2}$ and 5d$_{3/2}$ holes, h$_{5/2}$ and h$_{3/2}$, are qualitatively estimated by calculating the WL areas of Pt L$_3$-edge ($A_3$) and L$_2$-edge ($A_2$) using Eq. 3.1 and 3.2 \cite{16, 20}, where $C_o = 4\pi^2\alpha/3$ and where $\alpha$ is the fine structure constant. $N_0$ is the atomic density of Pt, $1.12 \times 10^{23}$ atoms·cm$^{-3}$. $E_{3,2}$ are the threshold energy of Pt L$_3$- and L$_2$-edges (11564 and 13273 eV, respectively). $R_{5d}^{2p_{3/2,1/2}}$ are the radial dipole-moment matrix elements for Pt 2p$_{3/2} \rightarrow 5d$ and 2p$_{1/2} \rightarrow 5d$ transitions. By assuming $R_{5d}^{2p_{3/2}} = R_{5d}^{2p_{1/2}}$, Eqs. 3.1 and 3.2 can be rearranged to simplify the expressions (for normalized spectra) of h$_{5/2}$ and h$_{3/2}$, as shown in Eqs. 3.3 and 3.4, where $C_3$ and $C_2$ are constants estimated using the theoretically calculated bulk Pt values h$_{5/2} = 1.000$ and h$_{3/2} = 0.344$ in literature \cite{16}. This procedure is often necessary to get quantitative results because the 5d hole DOS in Pt is not evenly distributed among the 5d$_{5/2}$ and 5d$_{3/2}$ states because in high Z elements such as Au and Pt, the spin orbit interaction is strong ($\sim$ 1 eV in atom yielding an apparent spin–orbit 5d band doublet with $\sim$ 3 eV separation in the VB). In Pt metal, the 5d holes are of largely d$_{5/2}$ character and the 5d$_{3/2}$ states are nearly full. Dipole selection rules ($\Delta l = \pm 1, \Delta j = 0, \pm 1$) couples the 2p$_{3/2}$ to 5d$_{5/2,3/2}$ and 2p$_{1/2}$ to 5d$_{3/2}$. Hence, the Pt L$_3$-edge WL is intense while the Pt L$_2$-edge WL is very weak in the Pt metal. Practically, the WL area $A_j$ is determined by fitting the Pt L$_3$-edge XANES with an arctangent background and Gaussian peaks (see Figure 3-9), while $A_2$ is calculated correspondingly using the L$_2$-edge. It is worth mentioning that in previous studies on Au-Pt and Au-Cu alloys \cite{20-21}, $A_{2,j}$ were determined by subtracting the XANES of pure Au from the edges of interest, which is less reliable in this
case because of the strong scattering background from Ni in low k. The calculated Pt 5d holes are 1.059, 0.976, and 0.746 for Pt$_3$Ni, PtNi, and PtNi$_3$, respectively, showing a decreasing trend as Pt is more diluted in Ni.
Figure 3-9. Gaussian fitting for the calculation of Pt 5d holes. Blue areas in (a, c, e, and g): $A_3$ calculated from Pt L$_3$-edge XANES WLs, for Pt, Pt$_3$Ni, PtNi, and PtNi$_3$, respectively. Blue areas in (b, d, f, and h): $A_2$ calculated from Pt L$_2$-edge XANES WLs, for Pt, Pt$_3$Ni, PtNi, and PtNi$_3$, respectively.
We can also investigate the d holes from the DS asymmetric peak shape \(^1\) observed in all Pt 4f\(_{5/2,7/2}\) and Ni 2p\(_{3/2}\) XPS peaks because of unfilled d band states just above the Fermi level. The XPS results in Figure 3-5(a and b) show that as the Ni content increases, the Pt 4f peaks become less asymmetric, indicating that the unfilled portion of the Pt 5d states is partially filled upon alloying, which agrees with the XANES results. In contrast, Ni 2p main peaks becomes more asymmetric as the Pt content increases, indicating more unfilled Ni 3d states become available. The asymmetries are further analyzed with DS line shape expressed in Eqs. 3.5 and 3.6 \(^2\),

\[
f(E) = \frac{\Gamma(1 - \alpha) \cos \left[ \frac{\pi \alpha}{2} + (1 - \alpha) \arctan \left( \frac{E}{\gamma} \right) \right]}{(\gamma^2 + E^2)^{\frac{1-\alpha}{2}}}
\]

\[
\alpha = \sum_l \frac{q_l^2}{2(2l + 1)}
\]

where \(\Gamma\) is a gamma function, \(\gamma\) is the life time of the hole state, and \(\alpha\) is the singularity index associated with the asymmetry, in terms of the Friedel sum rule \(^3\), \(l\) is the angular momentum quantum number, and \(q_l\) is the partial screening charge at the Fermi level. In practice, the DOS above the Fermi level is not a constant or with a regular shape. The many-body line shape \(f(E)\), however, is not very sensitive to this shape. With this validity, it is possible to extract the information of the unoccupied states at the Fermi level through \(\alpha\). Note that for actual XPS peaks fitting, the gamma function is a constant for a given \(\alpha\) and thus ignored, and a further implementation with a combination of Lorentzian and Gaussian profiles is included (detailed description in Appendix A). Herein, we assume that the DOS at the Fermi level is dominated by d \((l = 2)\) states for both Pt and Ni. The fitting and calculated result is shown in Figure 3-5(d and e) and Table 3-4. As the Ni content increases (Pt more diluted in Ni), Pt 5d holes decrease (1.162, 1.072, 0.922, and 0.848 for Pt, Pt\(_3\)Ni, PtNi, and PtNi\(_3\), respectively). On the other hand, Ni 3d holes increase as the Pt content increases (Ni more diluted in Pt, 1.072, 1.140, 1.265, and 1.342 for Ni, PtNi\(_3\), PtNi, and Pt\(_3\)Ni respectively). The calculated result from XPS asymmetric peaks matches well with the WL calculation, considering the assumption made in both cases.
Table 3-4. Calculation of Pt 5d holes at the Fermi level using the Pt L₃,₂-edge XANES WLs and Pt 4f XPS peaks, and Ni 3d holes using Ni 2p₃/₂ XPS peaks.

<table>
<thead>
<tr>
<th></th>
<th>Pt L₃-edge and L₂-edge WLs</th>
<th>Pt 4f XPS</th>
<th>Ni 2p₃/₂ XPS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A₃</td>
<td>A₂</td>
<td>h₅d₅/₂</td>
</tr>
<tr>
<td>Pt</td>
<td>2.358</td>
<td>0.593</td>
<td>1.000*</td>
</tr>
<tr>
<td>Pt₃Ni</td>
<td>1.700</td>
<td>0.606</td>
<td>0.707</td>
</tr>
<tr>
<td>PtNi</td>
<td>1.704</td>
<td>0.438</td>
<td>0.722</td>
</tr>
<tr>
<td>PtNi₃</td>
<td>1.520</td>
<td>0.143</td>
<td>0.663</td>
</tr>
</tbody>
</table>

* Data from theoretical calculation in REF 16.

While the direction of electron transfer from the XANES WLs and XPS line shape results (Ni losses 3d and 4p electrons and Pt gains 5d electrons) is in line with the electronegativity (Pt higher than Ni), anomalous BE shift of Pt and Ni XPS peaks are observed, as shown in Figure 3-5(a and b), and Table 3-2 and 3-3. Intuitively, the BE of Pt peaks are expected to be lower upon alloying with more Ni because of more electrons screening the nucleus and thus less Coulombic attraction to the core electrons, while Ni peaks shift to higher energy upon alloying with more Pt. The experiment, however, gave the opposite result (Pt 4f₇/₂ peaks at 0.02, 0.11, and 0.23 eV for Pt₃Ni, PtNi, and PtNi₃, respectively, with respect to Pt metal; Ni 2p₃/₂ peaks at −0.11, −0.19, and −0.25 eV for PtNi₃, PtNi, and Pt₃Ni, respectively, with respect to Ni metal). This anomalous shift is likely attributed to two factors: (1) VB redistributed relative to the Fermi level (BE is measured relative to the Fermi level). Pt 5d centroids are pushed away (~ 0.5 eV for PtNi₃) from while the Ni 3d centroids are closer (~0.3 eV for Pt₃Ni) to the Fermi level, as shown in the UPS result in Figure 3-5(c). DFT results in Figure 3-8 also show a similar but exaggerated trend. This indicates that the redistribution of DOS dominates the screening effect arising from the DOS at the Fermi level, which screens more effectively than the DOS away from the Fermi level. (2) Pt diluted in Ni is screened by less polarizable Ni relative to Pt. Another noticeable finding is the narrowing of the Pt 5d spin-orbit splitting when diluted in Ni. This suggests that the downshifting of the d-band center in these alloys originates from the downshifting of the DOS, rather than simple broadening of the VB, which can be achieved by the compressive strain effect on Pt. In other words, Pt-based alloys and Pt-skinned nano structures (e.g., core-shells) are utilizing two
different mechanisms to shift the d-band center, albeit similar effect on the adsorbate (e.g. H₂, O₂) in the catalytic process²⁵.

In addition to the asymmetric line shape, the many-body effect is analyzed by the Ni 2p₃/₂ satellites peaks Sat. 1 and Sat. 2 (with an energy separation ΔE₁ and ΔE₂, respectively, from the main peak), which are found to have an apparent shift along with the varying Pt/Ni ratio, as shown in Figure 3-5(a) and Table 3-2. The Ni 2p₃/₂ main peak and the ca. 6 eV satellite peak Sat. 2 have been well studied, corresponding to the one-hole final state c⁻¹3d¹⁰⁴s (c⁻¹ is the photo-excited core hole) and two-hole final state c⁻¹3d⁹⁴s²²⁶. The subtle satellite peak Sat. 1 at ca. 3 eV is assigned to the 3d → 4s interband transition, as predicted and demonstrated in literature²⁷-²⁹. It is found that both Ni satellites shift toward the main peak (ΔE₁ and ΔE₂ decrease) and the intensity of both (area percentage) increases with the Pt content (from Ni to Pt₃Ni). Essentially, the separation ΔE between the satellites and main peaks is the energy difference between the different final states. When the Ni d band is narrowed and pushed towards the Fermi level, smaller difference between 3d¹⁰⁴s and 3d⁹⁴s² is reasonably expected. In the meanwhile, the increase of the Ni satellite intensities upon alloying with Pt is associated with the more localized Ni d band, resulting in more sluggish relaxation of electrons to fill the d hole (main peak intensity decreases relatively)²⁶,³⁰. Moreover, this trend is in good agreement with reported Ni alloyed with more electropositive elements (Mg, Al, Ti, Cr, Ta, In, etc.)³¹ and more electronegative elements (Pd and Au)³².

In the DFT calculation, these more localized Ni valence states are shown as narrower Ni total DOS shifting towards the Fermi level in Figure 3-8.

3.4. Conclusions

In summary, the many-body effect, charge redistribution, and local structure were studied on fcc Pt–Ni alloys prepared by the vacuum arc melting method. It is found that Pt gains 5d electrons, resulting in more symmetric Pt 4f XPS peaks when diluted in Ni, while Ni loses 4p and 3d electrons, resulting in an increase of K-edge WL intensity, more asymmetric Ni 2p XPS peaks, and stronger shake-up satellites. These trends are in good agreement with the fact that Pt is more electronegative than Ni. However, anomalous XPS core level shift for both Ni and Pt was observed in contrast to electronegativity considerations; this discrepancy is attributed to the DOS redistribution and screening effects upon alloying. DOS closer to the Fermi level screens better. It thus points to the effect of not only charge transfer but how the
transferred charge is redistributed in the VB. In the meanwhile, both UPS experiment and DFT calculation indicates that both Pt and Ni valence states tend to be narrower upon alloying with the other metal, while Ni DOS is pushed closer to the Fermi level and Pt DOS in the opposite direction. This suggests different mechanisms for Pt-based alloys and Pt-skinned nano structures, such as core@shell, in manipulating the position of d-band center, while both lead to a similar effect on adsorbates on Pt for chemical reactions. The fundamental and trending information in the local and electronic structures for transition metal alloys presented here is expected to help articulate complex bimetallic systems for catalysis and will serve as a guide for design of alloy-based nano-systems for various applications.

3.5. References


(4) Zhao, X.; Chen, S.; Fang, Z.; Ding, J.; Sang, W.; Wang, Y.; Zhao, J.; Peng, Z.; Zeng, J. Octahedral Pd@ Pt_{1.8}Ni core–shell nanocrystals with ultrathin PtNi alloy shells as active catalysts for oxygen reduction reaction. J. Am. Chem. Soc. 2015, 137, 2804-2807.


(13) Kohn, W.; Sham, L. J. Self-consistent equations including exchange and correlation effects. Phys. Rev. 1965, 140, 1133-&.


Chapter 4

4. Alloying and De-alloying of Pt-Ni Bimetallic Nanoparticles

4.1. Introduction

Pt-M composites, where M is a 3d transition metal (Fe, Ni, Co, etc.), as a low Pt usage catalyst have been studied as catalysts for many important industrial processes such as oxygenate reforming $^1$ and oxygen reduction reaction (ORR) $^2$. Limited by the high price and low production of Pt, modern catalysts are normally designed as nanocomposites rather than bulky composites. Nano-sized Pt-M alloys have been reported to have much higher catalytic activity over monometallic Pt $^3$-$^4$. The enhancement is mainly attributed to the strain effect induced by a change of the lattice constant $^5$-$^6$ and ligand effect induced by the interaction with the neighboring atoms $^7$-$^8$. Both effects can change the coupling of the adsorbate states with Pt states, which leads to stronger or weaker binding strength of the adsorbates. The binding strength finally determines the overall catalytic activity $^9$. Among the Pt-M bimetallic nanoparticles (NPs), Pt-Ni alloys have shown several to tens of folds higher activity than commercial Pt/C catalyst towards ORR both experimentally $^{10}$-$^{11}$ and theoretically $^9$. Pt-Ni NPs thus are also a candidate for a later generation of commercial ORR catalyst in fuel cells. The long-term stability of Pt-Ni NPs, however, suffers from the dissolving of the 3d transition metal when exposed in acidic environment $^{12}$. An effective solution is core-shell nano structures containing a 3d metal or alloy core with a Pt skin. This structure can improve the stability while maintaining the tunability of the composition, lattice constant, and chemical property $^{13}$. Pt-Ni core-shell structures have been reported with different morphologies, such as rhombic dodecahedrons with Pt edges, NPs with a few Pt mono layers, and particulate Pt skin on Pt-Ni alloys $^{14}$-$^{16}$. The formation and properties of these core-shell NPs, however, are not clearly explained in literature because of the complexity of these systems. The complexity originates from the heterogeneity between the core and the shell, while the alloy system itself is complicated. In the previous Chapter, Pt-Ni alloys have been studied as model systems to reveal the physical and chemical properties of Pt upon alloying. In this Chapter, the structural evolution of PtNi$_x$@Pt core-shell NPs along with their physical properties are studied. It is found that Pt-Ni NPs can undergo all the aforementioned morphologies in a single synthesizing process through alloying and de-
alloying of the Pt content. This evolution process, powered by the different surface energies and atomic radii between Pt and Ni, is divided into five stages with distinct structural features. At each stage, the electronic and local structures are discussed.

4.2. Experimental section

4.2.1. Synthesis of PtNi\textsubscript{x} bimetallic nanoparticles

The Pt-Ni bimetallic NPs were synthesized by hot-injection method. Oleylamine was used as the solvent, reducing agent, and capping agent\textsuperscript{17}. Typically, 10 ml of oleylamine (98%, Sigma-Aldrich) was preheated to 250 °C with N\textsubscript{2} protection (20 ml·min\textsuperscript{-1}) in a three-necked round bottom flask in a silicone oil bath, as seen in Figure 4-1. 1:1 atomic ratio of Pt and Ni precursors, in other words, 20.8 mg of K\textsubscript{2}PtCl\textsubscript{4} (99.9%, Alfa Aesar) with 11.9 mg NiCl\textsubscript{2}·6H\textsubscript{2}O (99.9%, Sigma-Aldrich) were dissolved in 1 ml of oleylamine and heated to 120 °C. The precursors were then injected into the hot oleylamine with a syringe. The whole pot of the mixture was extracted from the hot oil and cooled down after controlled crystal growth time, i.e., 10, 20, 40, 60, and 120 min after injection. The mixture was washed with ethanol and hexane with 1:1 ratio, sonicated, and centrifuged. The NPs underwent the washing process for four times before re-dispersed in hexane for storage, and labeled as PtNi\textsubscript{x}-10, 20, 40, 60, 120, respectively. To study the Pt and Ni elemental distribution at different stages, the bimetallic NPs were etched in 0.5 M HCl solution at room temperature for two hours to remove the Ni content. Note that the etched samples were only for transmission electron microscope (TEM) characterization.

![Figure 4-1. Experimental setup for synthesis of PtNi\textsubscript{x} bimetallic NPs.](image-url)
4.2.2. Characterization

The morphology of bimetallic NPs at different evolution stages were confirmed using a Philips CM10 TEM. The TEM was equipped with a LaB$_6$ filament operated at 80 kV. The pristine and etched bimetallic NPs were compared to reveal the Pt structure inside the particles.

Laboratory X-ray photoelectron spectroscopy (XPS) and synchrotron-based hard X-ray photoelectron spectroscopy (HXPES) were used to probe the elemental composition of the bimetallic NPs at different depths. According to the inelastic mean free path (IMFP) of electron from the NIST database\(^\text{18}\) (normally the detecting depth is considered three times the IMFP), lab-based XPS using an Al Ka X-ray source (1486.6 eV) probes a depth of ca. 3 nm from the surface of PtNi$_x$ NPs, therefore is considered as surface sensitive. To qualitatively study the bulk composition, HXPES was done at the Soft X-ray Microcharacterization Beamline (SXRMB) at the Canadian Light Source (CLS). Two energies (3000 and 7000 eV) were chosen to probe the Ni 2p and Pt 4f states for the PtNi$_x$ NPs, as comparison to the lab-based XPS. From the NIST database, 3000 and 7000 eV incident X-rays can probe depths of ca. 9 nm and 18 nm (three times the IMFP), respectively, for these heavy metal NPs.

X-ray absorption spectroscopy (XAS) including near-edge X-ray absorption fine structure (NEXAFS or XANES) and extended X-ray absorption fine structure (EXAFS) were used to study the electronic and local structures of Pt as well as Ni element in the bimetallic NPs. The X-ray absorption spectra at Pt L$_3$- and L$_2$-edges, and Ni K-edges were recorded at the synchrotron beamline (CLS@APS, Sector 20-BM) and processed with ATHENA and ARTEMIS\(^\text{19}\).

To investigate the core-shell structure of PtNi$_x$-120, two types of X-ray microscopy were utilized, that is, normal-mode scanning transmission X-ray microscopy (STXM)\(^\text{20}\) and X-ray ptychography. Compared with visible-light and electron microscopy, X-ray microscopy has the advantages of high resolution and deep detecting depth at the same time. For normal STXM, a Fresnel zone plate with an outer zone width of 25 nm was utilized to focus the X-ray beam at the focal length of 0.83 mm, with a final spatial resolution of about 30 nm. The sample was raster-scanned in two dimensions, with a point (0D) detector placed after the sample to collect the transmission signal in real space. X-ray ptychography is a lensless X-
ray imaging technique combining STXM and coherent diffraction imaging (CDI)\textsuperscript{21}. The X-ray beam from the monochromator travels through a 5 μm pinhole and the sample, generating the coherent speckle diffraction pattern on the detector. Compared with STXM, ptychography records the signal in reciprocal space with a 2D pixelated CCD. The absorption (real part) and phase (imaginary part) information are retrieved by applying an iterative algorithm. After reconstruction, final images with sub-10 nm resolution can be achieved. Similarly, with the tunable property of the synchrotron X-ray, the chemical information and spatial distribution of elements within the energy range can be revealed throughout the whole NP.

4.3. Results and discussion

The morphology of PtNi\textsubscript{x} samples at different evolution stages are shown in the TEM images in Figure 4-2. From PtNi\textsubscript{x}-10 to PtNi\textsubscript{x}-120, the nanostructure clearly shows distinct features at each evolution stage, both in shape and elemental distribution. PtNi\textsubscript{x}-10 particles have a size of 40 – 50 nm, while all other samples are between 80 – 100 nm with a slow increase of size over time, which may indicate that the evolution of the NPs in the bulk is accompanied by further deposition of metal atoms on the surface. The corresponding etched samples are shown in the bottom row. Note that due to the etching process with strong acid, any exposing Ni content is expected to be removed, while Pt is resistant to the etching. From the TEM image of etched PtNi\textsubscript{x}-10 (Figure 4-2(a)), the Pt frame is clearly seen in the core of the NPs. As the growth time extends to 20 min, the Pt content becomes a highly porous structure throughout the whole particle (Figure 4-2(b)), followed by the subsequent segregation of the Pt frame on the outer edges of PtNi\textsubscript{x}-40 (Figure 4-2(c)). At 60 min, the Pt has spread over the whole surface of the NPs, protecting the Ni content in the core. Thus, no obvious change can be observed from the TEM image of etched PtNi\textsubscript{x}-60 compared with the unetched one (Figure 4-2(d)). At 120 min, the bimetallic NPs show a core-shell structure with a particulate Pt surface and a PtNi\textsubscript{x} alloy core (Figure 4-2(e)), which is confirmed with XRD and EXAFS in later discussion. These surface particles are not observed at any prior stage, meaning that they directly grow on the Pt-covered NP surface rather than originate from the adhesion of pre-formed particles. In other words, these surface particles can function as robust active sites when used as catalysts. In addition, large surface area is expected based on the size (ca. 8 nm) of the surface particles. The formation of the Pt core
frame in PtNi\textsubscript{x}-10 and the Pt outer frame in PtNi\textsubscript{x}-40 has been reported by Niu \textit{et al} \textsuperscript{14}, attributing to a combined effect of atomic radii difference and surface energy difference between Pt and Ni. Herein, a more complete migration and segregation path for Pt is shown for the bimetallic core-shell PtNi\textsubscript{x} NPs: 1) formation of Pt core frame; 2) diffusion of Pt from core to surface; 3) thickening of Pt edges on the surface; 4) Pt spreading over the whole particle surface; 5) formation of a thorny Pt surface resulting in PtNi\textsubscript{x}@Pt core-shell NPs. It is worth mentioning that the precursors concentration and the oil bath temperature have great influence on the growth time to reach each evolution stage, as well as an impact on the overall crystal structure.

![Figure 4-2. TEM results of (a) PtNi\textsubscript{x}-10, (b) PtNi\textsubscript{x}-20, (c) PtNi\textsubscript{x}-40, (d) PtNi\textsubscript{x}-60, and (e) PtNi\textsubscript{x}-120. The upper row shows the as-synthesized NPs while the bottom row the corresponding samples etched with 0.5 M HCl for 2 hours at room temperature. The scale bar represents 50 nm in each image.](image)

The lab XPS results for all samples as well as HXPES results for selected samples (PtNi\textsubscript{x}-10, 20, and 120) are shown in Figure 4-3. The Pt 4f XPS spectra are aligned by the 4f\textsubscript{7/2} metallic Pt at 71.0 eV and the Ni XPS 2p spectra by the 2p\textsubscript{3/2} peak of metallic Ni at 852.6 eV. Slight shifts between different samples are not analyzed in detail because of the complexity of the systems. Mainly the element distribution is discussed in the following. At first glance,
one can easily see the quality (signal to noise) of spectra is quite different at different X-ray energies, that is, the higher energy (from 1486.6 to 3000 and finally 7000 eV), the worse spectra. This is because of the X-ray absorption cross section decays dramatically above the binding energy of a certain electron energy level. For each X-ray energy, the unnormalized XPS signal intensity ratio between Pt 4f and Ni 2p qualitatively indicates the distribution of each element in the depth profile. Comparing Lab XPS results in Figure 4-3(a and b), PtNi_{10} NPs show the lowest Pt intensity and highest Ni intensity among all samples because of the Pt frame in the core of NPs, while PtNi_{120} NPs show the opposite trend because of the thick Pt shell on the surface. The NPs at evolving stages, i.e. PtNi_{20}, 40, and 60 NPs, show spectra features lying between the PtNi_{10} and PtNi_{120}. Note that PtNi_{60} NPs show low Pt intensity relative to Ni, suggesting that the Pt skin at this stage is very thin. Meanwhile, it is obvious that the Pt is robust against oxidation whether existing in the bulk or on the surface. Ni, on the other hand, is oxidized to a greater or lesser extent for all samples (on or near the surface considering the probing depth of XPS), among which PtNi_{10} NPs have the highest ratio of oxidized Ni to metallic Ni (2p_{3/2} peak at 852.6 eV) because of lack of Pt on the surface to protect Ni from being oxidized. The oxidized Ni is evidenced by the Ni^{2+} 2p_{3/2} peak at ca. 856 eV and satellite peaks at ca. 862 eV, which show enhanced many-body effect compared to metallic Ni. For the HXPES results for PtNi_{10}, 20, and 120, a similar trend of elemental distribution is observed. Meanwhile, when the X-ray energy is increased from 3000 eV (Figure 4-3(c)) to 7000 eV (Figure 4-3(e)), the IMFP of the photoelectrons increases, in other words, we are probing a deeper depth, the core Pt frame for PtNi_{10} NPs becomes observable for HXPES even with a much lower X-ray cross section. Considering the morphology and depth profile, both the Lab XPS and HXPES results agree well with the TEM results. Judging from the binding energy, the spectral pattern and the probing depth, the Pt remains essentially metallic throughout and the core Ni is metallic while the surface Ni is oxidized.
Figure 4-3. XPS results for Pt 4f levels (a, c, e) at the incident X-ray energies of 1486.6, 3000, and 7000 eV, respectively, and Ni 2p levels (b, d, f) at 1486.6, 3000, and 7000 eV, respectively. X-ray at 1486.6 eV is the Al Kα source in a lab XPS. XPS at 3000 and 7000 eV use the synchrotron X-ray source at SXRMB.
The XRD pattern of PtNi\(_x\)-120 is compared with Pt, Ni metals, and Pt-Ni alloys (see details in Chapter 3), as shown in Figure 4-4. It is obvious that the diffraction pattern at each constructive plane appeared as a continuous (e.g., \(2\theta\) from 46.7° to 49.2° for (111)) region rather than a well-defined peak, compared with the metals and alloys. This indicates that there might be a continuous (from the perspective of elemental composition) transition region from the core to the shell. To semi-quantitatively analyze the composition, the Pt content vs lattice size for the metal and alloy standards is summarized in Figure 4-5, using a linear fit. Herein, the plane distances \(d\) (and thus the lattice sizes) were obtained by the Bragg’s equation, i.e. \(n\lambda = 2d \cdot \sin(\theta)\), where \(n=1\) for the first order diffraction, \(\lambda = 1.790\ \text{Å}\) for Co K\(_\alpha\) X-ray source, and \(\theta\) is the diffraction angle. From the fitted equation (labeled in red in Figure 4-5), the diffraction pattern (\(2\theta\) from 46.7° to 49.2°) of the nanocomposite corresponds to the lattice size range of 3.72 – 3.91 Å (first shell bond length of 2.63 – 2.76 Å) and Pt content of 46% – 93%, roughly from PtNi to Pt.

![Figure 4-4. XRD patterns of PtNi\(_x\)-120 sample compared with Pt, Ni, and Pt-Ni alloys. The fitted fcc lattice sizes are labelled.](image)
Figure 4-5. Linear relationship between the Pt content and lattice size for fcc structures. The fitted line and equation are labeled in red.

Figure 4-6. PtNi$_x$-120 NPs under electron microscopy and X-ray microscopies:
(a) TEM image with a magnified single particle in the inset; (b) Averaged image obtained from normal STXM mode; (c and d) X-ray Ptychography in amplitude and phase, respectively, below Ni L$_3$-edge (845 eV); (e and f) X-ray Ptychography in amplitude and phase, respectively, above Ni L$_3$-edge (853 eV).
X-ray microscopic techniques including normal STXM and X-ray ptychography at the SM beamline are also conducted on PtNi\(_x\)-120 NPs, as shown in Figure 4-6. Note that the TEM image in Figure 4-6(a) is not showing the same NPs as in other images but similar specimens from the same batch. X-ray microscopy provides spatial distribution based on the resolution of the techniques. For normal STXM, the spatial distribution is ca. 30 nm. Considering that the size of PtNi\(_x\)-120 NPs is around 100 nm, this resolution is not enough to resolve the core-shell structure, as shown in Figure 4-6(b). In comparison, X-ray ptychography with an 8 nm resolution can distinguish between the core and shell, as shown in Figure 4-6(c and e) for X-ray energy below and above Ni L\(_3\)-edge, respectively. Note that the microscopy is collecting the transmission signal. When the X-ray energy is below the Ni L\(_3\)-edge, the absorption cross sections for both Ni and Pt are low, the image thus obtained shows the thickness distribution of the bimetallic particles. A darker color corresponds to larger thickness, which can be either the core of the particles or overlapping areas of multiple particles. At X-ray energy above the Ni L\(_3\)-edge, because of the abrupt increase of the absorption cross section for Ni, the dark color indicates the position of Ni element regardless of the thickness. As a result, the Ni exists mainly in the core of the NPs, as shown in Figure 4-6(e). This agrees well with the TEM, XRD, and XPS results.

The electronic and local structures of Pt and Ni are investigated using XAS. The XANES and Fourier transformed EXAFS in R-space are shown in Figure 4-7, and corresponding k-space in Figure 4-8 and 4-9. The Pt L\(_3\)-edge spectra of all samples in Figure 4-7(a) are calibrated by positioning the Pt L\(_3\)-edge energy of the reference Pt foil at 11564 eV. The Ni K-edge spectra of all samples in Figure 4-7(b) are calibrated by positioning the Ni K-edge energy of the reference Ni foil at 8333 eV. From the 1\(^{st}\) derivative peaks (edge positions) in Figure 4-7(c and d), the Pt and Ni in all samples were in metallic state, with no obvious shift of the edge positions. It is worth mentioning that the XAS were conducted in FY mode, in which case the surface as well as the bulk signal were recorded due to the large detecting depth. Therefore, possible small amount of oxides on the surface would be negligible relative to the strong bulk signal. Focusing on the Pt L\(_3\)-edge WL intensity in Figure 4-7(a), one can observe that all PtNi\(_x\) NPs have lower WL intensity than that of the Pt foil. This is because Pt attracts electrons from Ni upon alloying, the Pt d band narrows and gains d charge as demonstrated in Chapter 3. For Ni K-edges in Figure 4-7(b), no clear trend is observed.
Figure 4-7. Normalized XANES at (a) Pt L₃-edge and (b) Ni K-edge, with their first derivatives in (c and d), respectively, and Fourier transformed EXAFS at (e) Pt L₃-edge and (f) Ni K edge. The magnified WLs at Pt L₃-edges are shown in the inset in (a). Pt and Ni foil spectra were collected in transmission mode. Bimetallic NPs spectra were collected in FY mode.
Figure 4-8. k-space of Pt L3-edge with a $k^2$ weighting for (a) Pt foil, (b) PtNix-10, (c) PtNix-20, (d) PtNix-40, (e) PtNix-60, and (f) PtNix-120, respectively.

Figure 4-9. k-space of Ni K-edge XAS with a $k^2$ weighting for (a) Ni foil, (b) PtNix-10, (c) PtNix-20, (d) PtNix-40, (e) PtNix-60, and (f) PtNix-120, respectively.
relating to the Pt alloying and de-alloying except that all Ni K-edge WLs for bimetallic NPs are higher than that of Ni foil because of charge transfer from Ni to Pt. Another observation from XAS is that the scattering peaks of PtNi\textsubscript{x} NPs shift to higher energy relative to the Pt foil at Pt L\textsubscript{3}-edge, and the scattering peaks shift to lower energy relative to the Ni foil at Ni K-edge. These shifts directly reflect the lattice size change of the NPs relative to reference foils as are the neighboring atoms on average. In Figure 4-7(e), the Pt L\textsubscript{3}-edge EXAFS in R-space show that the Pt chemical environment changes dramatically at each evolution stage through alloying and de-alloying processes. A dominating Pt-Pt feature (split peaks at 2.1 and 2.6 Å) is visually observable only for PtNi\textsubscript{x}-120 NPs. For other samples this feature is mitigated because of the considerable amount of Pt-Ni bonds. Notice that the reference foils have higher intensity in R-space compared with the bimetallic NPs. This phenomenon is attributed to two reasons: (1) the spectra for reference foils were collected in transmission mode while the bimetallic NPs in FY mode, which suffers from self-absorption effect; and (2) the reference foils have higher crystallinity than the NPs.

Detailed information is extracted through the first-shell EXAFS fitting using ARTEMIS\textsuperscript{19}. The amplitude reduction factor S\textsubscript{0}\textsuperscript{2} at each edge was obtained by fitting the spectrum of the reference metal with its standard crystal structure (coordination number on the first shell). For each alloy, Pt L\textsubscript{3}-edge and Ni K-edge were fitted simultaneously with the constrain that Pt-Ni and Ni-Pt have the same bonding distance. 13 independent parameters (maximum allowed: 19) are used in each fit. The fitted curves are shown in Figure 4-10 for Pt L\textsubscript{3}-edge, Figure 4-11 for Ni K-edge, and the fitted parameters in Table 4-1. It is worth mentioning that in EXAFS fitting with a correct model, the interatomic distance is the most reliable parameter while the fitted CN of each species/shell can be affected by the detection mode, self-absorption effect, many-body effect\textsuperscript{22}, and the Debye-Waller factor. These factors will affect the overall intensity of the signal and thus lead to unreliable fitted CNs, unless with a well-defined model, in EXAFS fitting. It is therefore not trustworthy to determine the crystal structure from the fitted CNs. Instead, the curve shape of Fourier transformed EXAFS in R-space is more reliable to reveal the crystal structure. In the PtNi\textsubscript{x} bimetallic NPs, all samples show a similar crystal structure, in other words, fcc-like structure, mimicking that of the Ni foil, as shown in Figure 4-7(f). The fitted Pt-Pt bond lengths (2.765, 2.694, 2.691, 2.693, 2.696, and 2.739 Å for Pt foil, PtNi\textsubscript{x}-10, PtNi\textsubscript{x}-20, PtNi\textsubscript{x}-40, PtNi\textsubscript{x}-60, and PtNi\textsubscript{x}-120,
Figure 4-10. Fourier Transformed Pt L$_3$-edge EXAFS results in R-space with a $k^2$ weighting and the fitting results for (a) Pt foil, (b) PtNi$_x$-10, (c) PtNi$_x$-20, (d) PtNi$_x$-40, (e) PtNi$_x$-60, and (f) PtNi$_x$-120, respectively.

Figure 4-11. Fourier Transformed Ni K-edge EXAFS results in R-space and the fitting results for (a) Ni foil, (b) PtNi$_x$-10, (c) PtNi$_x$-20, (d) PtNi$_x$-40, (e) PtNi$_x$-60, and (f) PtNi$_x$-120, respectively.

PtNi$_x$-120, respectively.
Table 4-1. First-shell EXAFS fitting parameters for as-synthesized PtNi$_x$ bimetallic NPs and reference foils.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Bond</th>
<th>CN</th>
<th>Bond (Å)</th>
<th>$\sigma^2$ (Å$^2$)</th>
<th>$\Delta E_0$ (eV)</th>
<th>R-factor ($10^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt foil</td>
<td>Pt-Pt</td>
<td>12</td>
<td>2.765 ± 0.002</td>
<td>0.0046 ± 0.0002</td>
<td>7.63 ± 0.26</td>
<td>0.41</td>
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<tr>
<td>Ni foil</td>
<td>Ni-Ni</td>
<td>12</td>
<td>2.492 ± 0.002</td>
<td>0.0061 ± 0.0002</td>
<td>6.95 ± 0.23</td>
<td>0.06</td>
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<td>PtNi$_x$-10</td>
<td>Pt-Pt</td>
<td>4.4 ± 0.9</td>
<td>2.694 ± 0.007</td>
<td>0.0058 ± 0.0009</td>
<td>6.21 ± 0.72</td>
<td>0.96</td>
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<tr>
<td></td>
<td>Pt-Ni</td>
<td>5.1 ± 0.6</td>
<td>2.586 ± 0.005</td>
<td>0.0070 ± 0.0009</td>
<td>6.21 ± 0.72</td>
<td>0.96</td>
</tr>
<tr>
<td></td>
<td>Ni-Ni</td>
<td>6.0 ± 0.6</td>
<td>2.516 ± 0.007</td>
<td>0.0085 ± 0.0008</td>
<td>2.79 ± 0.93</td>
<td>0.96</td>
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<tr>
<td></td>
<td>Ni-Pt</td>
<td>0.5 ± 0.8</td>
<td>2.586 ± 0.005</td>
<td>0.0041 ± 0.0090</td>
<td>2.79 ± 0.93</td>
<td>0.96</td>
</tr>
<tr>
<td>PtNi$_x$-20</td>
<td>Pt-Pt</td>
<td>3.6 ± 0.9</td>
<td>2.691 ± 0.007</td>
<td>0.0051 ± 0.0011</td>
<td>6.64 ± 0.74</td>
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<td>Pt-Ni</td>
<td>6.3 ± 0.7</td>
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<td>0.0068 ± 0.0007</td>
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<td>Ni-Ni</td>
<td>7.7 ± 0.4</td>
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<td></td>
<td>Ni-Pt</td>
<td>0.9 ± 0.3</td>
<td>2.583 ± 0.005</td>
<td>0.0051 ± 0.0011</td>
<td>4.18 ± 0.38</td>
<td>0.20</td>
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<td>PtNi$_x$-40</td>
<td>Pt-Pt</td>
<td>4.3 ± 1.0</td>
<td>2.693 ± 0.014</td>
<td>0.0069 ± 0.0017</td>
<td>7.18 ± 0.95</td>
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<td>Pt-Ni</td>
<td>5.6 ± 0.8</td>
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<td>Ni-Ni</td>
<td>6.9 ± 0.4</td>
<td>2.508 ± 0.003</td>
<td>0.0072 ± 0.0003</td>
<td>4.12 ± 0.50</td>
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<tr>
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<td>Ni-Pt</td>
<td>0.5 ± 0.7</td>
<td>2.577 ± 0.007</td>
<td>0.0039 ± 0.0094</td>
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<tr>
<td>PtNi$_x$-60</td>
<td>Pt-Pt</td>
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<td>Pt-Ni</td>
<td>4.9 ± 0.8</td>
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<td>0.0074 ± 0.0013</td>
<td>6.80 ± 0.78</td>
<td>1.17</td>
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<td>Ni-Ni</td>
<td>5.4 ± 0.9</td>
<td>2.543 ± 0.006</td>
<td>0.0103 ± 0.0016</td>
<td>3.34 ± 0.80</td>
<td>1.17</td>
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<td>Ni-Pt</td>
<td>2.3 ± 0.9</td>
<td>2.605 ± 0.007</td>
<td>0.0076 ± 0.0033</td>
<td>3.34 ± 0.80</td>
<td>1.17</td>
</tr>
<tr>
<td>PtNi$_x$-120</td>
<td>Pt-Pt</td>
<td>6.9 ± 0.6</td>
<td>2.739 ± 0.003</td>
<td>0.0056 ± 0.0005</td>
<td>6.22 ± 0.44</td>
<td>0.51</td>
</tr>
<tr>
<td></td>
<td>Pt-Ni</td>
<td>2.7 ± 0.6</td>
<td>2.608 ± 0.007</td>
<td>0.0088 ± 0.0019</td>
<td>6.22 ± 0.44</td>
<td>0.51</td>
</tr>
<tr>
<td></td>
<td>Ni-Ni</td>
<td>6.4 ± 0.7</td>
<td>2.543 ± 0.007</td>
<td>0.0108 ± 0.0009</td>
<td>3.56 ± 0.74</td>
<td>0.51</td>
</tr>
<tr>
<td></td>
<td>Ni-Pt</td>
<td>2.1 ± 0.7</td>
<td>2.608 ± 0.007</td>
<td>0.0063 ± 0.0022</td>
<td>3.56 ± 0.74</td>
<td>0.51</td>
</tr>
</tbody>
</table>

respectively) show that Pt-Pt bonds for all bimetallic NPs exhibit different extent of compression relative to Pt foil. The final product PtNi$_x$-120 among all NPs shows the least Pt-Pt compression because of the thick Pt shell. The Pt-Ni bond lengths (2.586, 2.583, 2.577,
2.605, and 2.608 Å for PtNi\textsubscript{x}-10, PtNi\textsubscript{x}-20, PtNi\textsubscript{x}-40, PtNi\textsubscript{x}-60, and PtNi\textsubscript{x}-120, respectively) as well as the Ni-Ni bond lengths (2.492, 2.516, 2.518, 2.508, 2.543, and 2.543 Å for Ni, PtNi\textsubscript{x}-10, PtNi\textsubscript{x}-20, PtNi\textsubscript{x}-40, PtNi\textsubscript{x}-60, and PtNi\textsubscript{x}-120, respectively) are not following the trend of Pt. Further analysis is associated with the extent of alloying for Pt and Ni in the bimetallic NPs.

\[ J_{Pt} = \frac{P_{\text{observed}}}{P_{\text{random}}} \times 100\% \]  
(4.1)

\[ J_{Ni} = \frac{R_{\text{observed}}}{R_{\text{random}}} \times 100\% \]  
(4.2)

The extent of alloying is calculated using Eqs 4.1 and 4.2. \( J_{Pt} \) is the alloying extent of Pt. \( P_{\text{observed}} = \frac{CN_{Pt-Ni}}{\sum CN_{Pt-\text{i}}} \) is the proportion of Ni CN surrounding Pt atoms. Similarly, \( J_{Ni} \) is the alloying extent of Ni. \( R_{\text{observed}} = \frac{CN_{Ni-Pt}}{\sum CN_{Ni-\text{i}}} \) is the proportion of Pt CN surrounding Ni atoms. \( P_{\text{observed}} \) and \( R_{\text{observed}} \) are divided by the corresponding values \( P_{\text{random}} \) and \( R_{\text{random}} \) of standard random alloy stoichiometry. For the standard, it is assumed that \( P_{\text{random}} = R_{\text{random}} = 0.5 \) for PtNi alloy (Note that for PtNi alloy, \( P_{\text{random}} = 0.53 \), \( R_{\text{random}} = 0.51 \) in the previous study. \( ^8 \)) The calculated results are summarized in Table 4-2. It is observed that the alloying extent of Pt remains high until the last stage (PtNi\textsubscript{x}-120), with the highest value occurring at PtNi\textsubscript{x}-20, as seen from the calculated \( J_{Pt} \) (107, 127, 113, 103, and 56% for PtNi\textsubscript{x}-10, 20, 40, 60, and 120, respectively). When \( J \) is more than 100%, it means Pt has more Pt neighbors than expected based on the stoichiometry. This trend is in good agreement with the Pt-Pt bond lengths. The alloying extent of Ni, \( J_{Ni} \) (96, 21, 14, 60, and 49% for PtNi\textsubscript{x}-10, 20, 40, 60, and 120, respectively), on the other hand, does not follow that of Pt. The lowest \( J_{Ni} \) occurs at the sample PtNi\textsubscript{x}-40, where the shortest Ni-Ni bond is observed. The Ni-Ni bond lengths generally agrees with the \( J_{Ni} \) trend, except for PtNi\textsubscript{x}-10. In the case of PtNi\textsubscript{x}-10, \( J_{Ni} \) is 96% but the Ni-Ni bond is 2.516, not significantly expanded by Pt. This may be caused by a significant CN\textsubscript{Ni-Pt} contribution at the interface with the Pt core frame. Other than the Ni-Pt frame interface the Ni is relatively pure, as seen from the TEM image in Figure 4-2(a).
Table 4-2. Extent of alloying for Pt and Ni in PtNi\textsubscript{x} bimetallic NPs calculated with the fitted CNs.

<table>
<thead>
<tr>
<th>Sample</th>
<th>N\textsubscript{Pt-Pt}</th>
<th>N\textsubscript{Pt-Ni}</th>
<th>N\textsubscript{Ni-Ni}</th>
<th>N\textsubscript{Ni-Pt}</th>
<th>P\textsubscript{observed}</th>
<th>R\textsubscript{observed}</th>
<th>J\textsubscript{Pt}</th>
<th>J\textsubscript{Ni}</th>
</tr>
</thead>
<tbody>
<tr>
<td>PtNi\textsubscript{x-10}</td>
<td>4.4</td>
<td>5.1</td>
<td>6.0</td>
<td>5.5</td>
<td>0.537</td>
<td>0.478</td>
<td>107%</td>
<td>96%</td>
</tr>
<tr>
<td>PtNi\textsubscript{x-20}</td>
<td>3.6</td>
<td>6.3</td>
<td>7.7</td>
<td>0.9</td>
<td>0.636</td>
<td>0.105</td>
<td>127%</td>
<td>21%</td>
</tr>
<tr>
<td>PtNi\textsubscript{x-40}</td>
<td>4.3</td>
<td>5.6</td>
<td>6.9</td>
<td>0.5</td>
<td>0.566</td>
<td>0.068</td>
<td>113%</td>
<td>14%</td>
</tr>
<tr>
<td>PtNi\textsubscript{x-60}</td>
<td>4.6</td>
<td>4.9</td>
<td>5.4</td>
<td>2.3</td>
<td>0.516</td>
<td>0.299</td>
<td>103%</td>
<td>60%</td>
</tr>
<tr>
<td>PtNi\textsubscript{x-120}</td>
<td>6.9</td>
<td>2.7</td>
<td>6.4</td>
<td>2.1</td>
<td>0.281</td>
<td>0.247</td>
<td>56%</td>
<td>49%</td>
</tr>
</tbody>
</table>

4.4. Conclusions

The evolution process of PtNi core-shell NP formation including the alloying and de-alloying of Pt in PtNi\textsubscript{x} bimetallic NPs is studied through five stages. The resulting NPs are analyzed with electron and X-ray techniques including TEM, XRD, XPS, XAS, and X-ray Ptychography. The electronic and local structures at each of the five stages are discussed. At the first stage PtNi\textsubscript{x-10}, the Pt exists as a core frame surrounded by Ni. At the second stage PtNi\textsubscript{x-20}, Pt diffuses throughout the whole NPs and forms a tight Pt network filled by Ni. Pt reaches the highest alloying extent (highest Pt-Ni interaction). At the third stage PtNi\textsubscript{x-40}, an outer frame is formed on the edges of the NPs. Ni at this stage reaches the lowest alloying extent (lowest Pt-Ni interaction, highest Pt-Pt interaction). At the fourth stage PtNi\textsubscript{x-60}, the Pt spreads over the surface of the bimetallic NPs, protecting the Ni in the bulk. High alloying extent for both Pt and Ni is observed. At the final stage PtNi\textsubscript{x-120}, a thick Pt shell is formed on the surface. Particulate Pt with size of ca. 8 nm are grown on the outermost layer to provide a large surface area. The Pt-Pt bond length is slightly shorter than Pt foil but higher than any other stage. The core is believed to be composed of a PtNi-like alloy structure with a continuous transition region linking the Pt shell. This study shows the spontaneous formation of PtNi@Pt core-shell structure with a particulate Pt surface during the aqueous synthesis. The Pt shell increases the oxidation resistance of Ni while benefiting from the lattice control provided by the alloy core.
4.5. References


Chapter 5

5. Cu@Pt Core-Shell Nanoparticles

5.1. Introduction

In a proton exchange membrane fuel cell (PEMFC) using hydrogen and oxygen as fuels, oxygen reduction reaction (ORR) at the cathode is the most sluggish process (six orders of magnitudes slower than then hydrogen oxidation reaction at the anode) that requires highly efficient catalysts. Although decades of effort have been devoted in fuel cell researches, Pt-based catalysts, so far, is still the only candidate with sufficiently high performance to be used in a fuel-cell-driven vehicle. Fundamentally, this is attributed to the unique 5d configuration of Pt. During the ORR, the coupling of Pt 5d states with the oxygen states determines the dissociation of O₂ and selection of products (H₂O and H₂O₂). As a result, a volcano-type activity towards the adsorbate binding strength is normally observed. In the current market, Two generations of commercial catalysts including Pt and Pt-M (M is a 3d transition metal) alloy NPs have been developed for fuel cells. For the first generation, Pt nanoparticles at around 3 nm are loaded on carbon substrate. The large specific surface area of NPs is utilized to provide more active sites compared with bulk Pt. Pt-M alloy NPs. The second generation commercial product further reduce the usage of Pt by introducing an affordable transition metal while tuning the d-band states of Pt by ligand effect. Whereas, drawbacks have been reported in these alloy systems. One restriction is that the specific active area decreases when the M atoms (instead of Pt) are exposed as part of the alloy surface. As a result, the total mass and volume of the catalyst must be significantly increased to maintain high power output. Another drawback is the leaching of the exposing M species in acidic environments, compromising the lifetime of the catalysts. These factors have hindered the commercialization of Pt-M alloy catalysts from large scale production. To develop next-generation Pt-based catalysts, current research is focused on the M@Pt (M is an affordable metal or alloy) core-shell NPs, where Pt only exists as an ultrathin shell to minimize the Pt usage. In these M@Pt core-shell NPs, Pt with the ultrathin structure not only suffers from the ligand effect, as discussed for the alloy case, but also the strain effect induced by the M core. For the ligand effect, the Pt 5d states are redistributed to accommodate the M states. For the strain effect, the 5d band of Pt is tuned by
compressing/expanding the Pt lattice. Both effects can be utilized to optimize the binding energy of surface species. In addition, the M core is protected by Pt from leaching or oxidizing. This type of core-shell NPs is a promising candidate for ORR catalysts in fuel cells in the near future, from the perspective of lowering the usage of Pt while maintaining high specific power output (normalized by both the mass and the volume) and reasonable lifetime (>10000 h). In this study, Cu as an earth abundant and affordable element is chosen to be the core material for Cu@Pt core-shell NPs. Similar Pt-Cu bimetallic systems have been reported in literature 5-9, for example, Cu₃Pt nanoframes for ORR 6, Cu@Pt core-shell NPs for ethanol oxidation 7, PtCu NPs for CO oxidation 8, and Cu@Pt/ Pt@Cu core-shell NPs for NOₓ reduction 9. High performance has been achieved. However, the detailed physical properties including the electronic structure and local structures are not clear in previous studies because of the complexity of the core-shell systems. Moreover, current Pt-based core-shells still meet the challenge in synthesizing uniform and well-performing products in an affordable way. In this chapter, the Cu@Pt core-shell NPs were synthesized in a well-controlled reaction path, i.e. polyol reduction 10-13 in the presence of PVP55000. In this method, ethylene glycol (EG) is chosen as the solvent, reducing agent and capping agent, while PVP55000 mainly functions as an additional capping agent to limit the particle size. During the synthesis, the ethylene glycol is kept at the boiling state, thus to provide a very stable temperature and reducing environment. For synthesis requiring higher temperature, polyols such as diethylene glycol (DEG), triethylene glycol (TEG), and polyethylene glycol (PEG) can be used. 14 The properties of the NPs were examined with electron spectroscopy and X-ray spectroscopy to evaluate the synthesizing method and results.

5.2. Experimental section

5.2.1. Synthesis of bimetallic/monometallic NPs

The Cu@Pt bimetallic core-shell NPs were synthesized by reduction of the Pt precursor Pt(acac)₂ and Cu precursor Cu(acac)₂ in EG with the presence of PVP55000. In specific, 20 mg of Cu(acac)₂ and 116 mg of PVP55000 were dispersed into 32 ml of EG in a 50 ml round bottom flask. The mixture was then heated to the boiling point (197 °C) and kept refluxing for 20 min. The red suspension was then cooled down to below 100 °C before 7.7 mg of Pt(acac)₂ (accompanied by 1 ml EG) was added into the mixture. The mixture was heated to boiling again and kept refluxing for 1 hour to obtain a dark suspension. The solid was
washed with de-ionized water and ethanol using a centrifuge for three times. After washing, the final product was kept in ethanol, labeled as Cu@Pt_{0.25} (0.25 indicate the Pt/Cu ratio in the precursors). Because of the fast reduction rate of Cu precursor and slow reduction of Pt precursor, the Cu precursor was completely reduced to form the Cu core NPs in the first refluxing process while Pt only forms a very thin layer on Cu in the second refluxing process. For Cu@Pt_{0.5}, the amount of Pt precursor was changed to 15.4 mg without any other change of conditions. For comparison, Cu NPs, Pt NPs, and CuPt NPs were also synthesized to provide structural and electronic information. For Cu NPs, only the first refluxing process with the Cu precursor was applied. For Pt NPs, only the Pt precursor was added into the mixture, and the refluxing time was set to be two hours. For CuPt NPs, both the Cu and Pt precursors were put into the solvent at the same time for reflux for one hour.

5.2.2. Characterization

The sizes and morphology of bimetallic and monometallic NPs are confirmed by TEM (Philips CM10). The crystal structures were examined with XRD using a Co Kα X-ray source. The electronic and local structures were investigated using synchrotron X-ray techniques including normal XAS and high energy resolution fluorescence detected (HERFD)-XAS (see Chapter 6). The metallic bonding distances and coordination numbers are extracted by EXAFS fitting using ARTEMIS\textsuperscript{15}. 

15. ARTEMIS is a program for the analysis of EXAFS data.
Figure 5-1. TEM images of samples (a) Cu NPs, (b) Cu@Pt\textsubscript{0.25}, (c) Cu@Pt\textsubscript{0.5}, (d) CuPt NPs, and Pt NPs.
5.3. Results and Discussion

The morphology and size of the samples are confirmed by TEM images, as shown in Figure 5-1. Pt NPs, Cu@Pt$_{0.25}$, and Cu@Pt$_{0.5}$ all show uniform particles at the size of 8 – 9 nm. In contrast, Cu NPs in Figure 5-1(a), show a slightly smaller size (7 – 8 nm) while the CuPt NPs (3 – 5 nm) in Figure 5-1(d) are obviously smaller than other NPs. The crystal structures of the bimetallic NPs are determined by XRD using a Co K$_\alpha$ X-ray source. The results are presented in Figure 5-2. For the Cu@Pt$_{0.25}$ and Cu@Pt$_{0.5}$ core-shell NPs, the fcc structure of Cu is preserved without any obvious peak shift compared with Cu NPs. Additional broad and weak peaks attributed to the Pt shell, however, exist at slightly larger angle compared with the Pt (111) peak, indicating the reduced lattice size of the ultrathin Pt layer on the Cu core. Moreover, shoulders at the lower angle side of Cu(111) peaks are also observed, which are believed to be the alloy structure between the Cu core and Pt shell. Further evidence from EXAFS confirms that Pt is not in the form of isolated particles from Cu, as discussed in the next section. CuPt NPs, on the other hand, do not show obvious Pt
peaks. Meanwhile, a stronger shoulder (broadened peak) with a weaker Cu(111) peak are observed for CuPt NPs. This indicates higher extent of alloying structure in CuPt NPs compared with Cu@Pt core-shell NPs. Note that all three Pt-Cu bimetallic samples exhibit a combination of different structures instead of a single phase.

The electronic and local structures of Pt and Cu in the bimetallic NPs are studied by XAS. No oxidation (absorption edge shift or metal-oxygen bond) is observed in all E-spaces and R-spaces in Figure 5-3, confirming the metallic state of Pt and Cu in all NPs. For Cu K-edge XAS, as shown in Figure 5-3(a), all samples except CuPt NPs are highly consistent with Cu foil. This is because the transmission signal (as well as the FY signal) are collecting the information from the whole sample particles, which are mostly composed of a relatively thick Cu core with or without an ultrathin Pt layer. CuPt NPs, on the other hand, exhibits a slight shift of the modulation towards lower energy at the EXAFS region, indicating a slightly larger lattice size. This is the evidence that small amount of Pt has been inserted into the Cu lattice during the synthesis, forming an alloy structure. From R-space in Figure 5-3(c) and k-space in Figure 5-3(e), the preservation of the fcc structure is more obvious, with only a slight decrease of the peak intensity. It is worth mentioning that the nano-sized particles (Cu NPs) lead to lower overall CN compared with the Cu foil because of the higher proportion of Cu atoms on the particle surface. The Cu@Pt0.25 and Cu@Pt0.5 core-shell as well as the CuPt NPs additionally suffer from the effect of lattice nonuniformity because of the different sizes of Pt and Cu atoms. With higher amount of Pt or greater extent of mixing (CuPt NPs), the CN of Cu sites decreases (12, 10.7, 10.7, 10.3, and 9.8 for Cu foil, Cu NPs, Cu@Pt0.25, Cu@Pt0.5, and CuPt NPs, respectively), as shown in the EXAFS fitting parameters in Table 5-1 (fitted curves in Figure 5-4 and Figure 5-5). Meanwhile, a slight increase of the Cu-Cu bond length only happens for the sample CuPt NPs where Pt is inserted into the Cu lattice in the bulk. Note that the Cu-Pt path is not included in the fitting because of its negligible contribution to the overall spectra. For the Pt L3-edge, the change of the chemical environment surrounding Pt accompanied by the Pt content is dramatic, as seen in the E-space in Figure 5-3(b), R-space in Figure 5-3(d), and k-space in Figure 5-3(f). The Pt-Pt scattering peaks become more visually undistinguishable as the Pt amount decreases (especially for Cu@Pt0.25 and CuPt NPs), with the corresponding Pt-Pt bond lengths (2.765, 2.763, 2.727, 2.692, 2.693 Å for Pt foil, Pt NPs, Cu@Pt0.5, Cu@Pt0.25, and CuPt NPs,
Figure 5-3. XAFS spectra of Pt-Cu bimetallic systems and pure metals. (a and b): XANES at Cu K- and Pt L$_3$-edges, respectively. (c and d): Fourier transform of the EXAFS at Cu K- and Pt L$_3$-edges, with a $k^2$ weighing. (e and f): k-space at Cu K- and Pt L$_3$-edges, respectively, with a $k^2$ weighing. The Cu K-edge spectra were collected in transmission mode and the Pt L$_3$-edge in FY mode.
respectively) affected more significantly by Cu. Note that the 2.727 Å bond distance for Pt is desirable for ORR according to the d-band center theory, where a slightly shorter Pt-Pt bond will decrease the Pt 5d band center and thus weakens (optimizes) the binding strength of the surface oxygen species. The ratio of Pt-Pt CN and Pt-Cu CN (surrounding Pt) also shows an obvious change (6.5:4.5, 3.9:7.6, and 4.2:7.4 for Cu@Pt0.5, Cu@Pt0.25, and CuPt NPs, respectively). Meanwhile, the Pt-Cu bond lengths (2.604, 2.611, and 2.611 Å for Cu@Pt0.5, Cu@Pt0.25, and CuPt NPs, respectively) and the total CNs (12, 11.1, 11.0, 11.5, and 11.6 for Pt foil, Pt NPs, Cu@Pt0.5, Cu@Pt0.25, and CuPt NPs, respectively) exhibit no statistical trend because the Pt-Cu bond length and total CN are not directly linked to the Pt concentration or the atomic distribution in the NPs.

Table 5-1. First-shell EXAFS fitting parameters for Pt foil, Pt NPs, Cu@Pt0.25, Cu@Pt0.5, and CuPt NPs. The k range was set to be 2.5 – 14 Å⁻¹.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Path</th>
<th>CN</th>
<th>Bond Length (Å)</th>
<th>σ² (Å²)</th>
<th>ΔE₀ (eV)</th>
<th>R-factor (10⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt foil</td>
<td>Pt-Pt</td>
<td>12*</td>
<td>2.765 ± 0.002</td>
<td>0.0046 ± 0.0002</td>
<td>7.63 ± 0.26</td>
<td>0.31</td>
</tr>
<tr>
<td>Pt NPs</td>
<td>Pt-Pt</td>
<td>11.1 ± 0.6</td>
<td>2.763 ± 0.009</td>
<td>0.0060*</td>
<td>7.64 ± 1.19</td>
<td>1.28</td>
</tr>
<tr>
<td>Cu foil</td>
<td>Cu-Cu</td>
<td>12*</td>
<td>2.539 ± 0.005</td>
<td>0.0086 ± 0.0006</td>
<td>2.98 ± 0.83</td>
<td>0.17</td>
</tr>
<tr>
<td>Cu NPs</td>
<td>Cu-Cu</td>
<td>10.7 ± 0.6</td>
<td>2.538 ± 0.004</td>
<td>0.0084 ± 0.0005</td>
<td>2.99 ± 0.60</td>
<td>0.11</td>
</tr>
<tr>
<td>Cu@Pt0.25</td>
<td>Pt-Pt</td>
<td>3.9 ± 0.6</td>
<td>2.692 ± 0.012</td>
<td>0.0060 ± 0.0001</td>
<td>6.19 ± 0.75</td>
<td>0.13</td>
</tr>
<tr>
<td>Cu@Pt0.25</td>
<td>Pt-Cu</td>
<td>7.6 ± 0.8</td>
<td>2.611 ± 0.005</td>
<td>0.0073 ± 0.0008</td>
<td>6.19 ± 0.75</td>
<td>0.13</td>
</tr>
<tr>
<td>Cu@Pt0.25</td>
<td>Cu-Cu</td>
<td>10.7 ± 0.7</td>
<td>2.539 ± 0.004</td>
<td>0.0086 ± 0.0005</td>
<td>2.80 ± 0.60</td>
<td>0.11</td>
</tr>
<tr>
<td>Cu@Pt0.25</td>
<td>Cu-Pt</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cu@Pt0.5</td>
<td>Pt-Pt</td>
<td>6.5 ± 1.0</td>
<td>2.727 ± 0.009</td>
<td>0.0059 ± 0.0010</td>
<td>5.86 ± 1.00</td>
<td>0.35</td>
</tr>
<tr>
<td>Cu@Pt0.5</td>
<td>Pt-Cu</td>
<td>4.5 ± 0.9</td>
<td>2.604 ± 0.008</td>
<td>0.0064 ± 0.0014</td>
<td>5.86 ± 1.00</td>
<td>0.35</td>
</tr>
<tr>
<td>Cu@Pt0.5</td>
<td>Cu-Cu</td>
<td>10.3 ± 0.6</td>
<td>2.539 ± 0.004</td>
<td>0.0087 ± 0.0005</td>
<td>2.70 ± 0.61</td>
<td>0.13</td>
</tr>
<tr>
<td>Cu@Pt0.5</td>
<td>Cu-Pt</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CuPt NPs</td>
<td>Pt-Pt</td>
<td>4.2 ± 1.3</td>
<td>2.693 ± 0.010</td>
<td>0.0060 ± 0.0015</td>
<td>6.95 ± 0.80</td>
<td>0.07</td>
</tr>
<tr>
<td>CuPt NPs</td>
<td>Pt-Cu</td>
<td>7.4 ± 0.9</td>
<td>2.611 ± 0.005</td>
<td>0.0072 ± 0.0009</td>
<td>6.95 ± 0.80</td>
<td>0.07</td>
</tr>
<tr>
<td>CuPt NPs</td>
<td>Cu-Cu</td>
<td>9.8 ± 0.8</td>
<td>2.544 ± 0.006</td>
<td>0.0089 ± 0.0008</td>
<td>2.41 ± 0.82</td>
<td>0.13</td>
</tr>
<tr>
<td>CuPt NPs</td>
<td>Cu-Pt</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

* Preset values
Figure 5-4. First-shell EXAFS fitting of Pt L₃-edges for samples (a) Pt NPs, (b) Cu@Pt₀.₂₅, (c) Cu@Pt₀.₅, and (d) CuPt NPs.

Figure 5-5. First-shell EXAFS fitting of Cu K-edges for samples (a) Cu NPs, (b) Cu@Pt₀.₂₅, (c) Cu@Pt₀.₅, and (d) CuPt NPs.
Figure 5-6. Wavelet transform of Pt L₃-edges for Pt foil, Pt NPs, Cu@Pt₀₂₅, Cu@Pt₀₅, and CuPt NPs. The EXAFS signals are amplified with a k² weighing. The two dashed line represents the Pt-Cu and Pt-Pt scattering, respectively.
Continuous Cauchy wavelet transform (CCWT) \(^{17}\) is also conducted on the Pt L\(_3\)-edge EXAFS for the samples, as shown in Figure 5-6. Wavelet transform (WT) is often used in signal processing to separate the time domain and frequency domain. In the case of EXAFS, the signal is visualized in three-dimension: the wavevector \((k)\), the uncorrected interatomic distance \((R + \Delta R)\), and WT modulus (corresponding to the decomposition of the EXAFS amplitude terms). Compared with Fourier transform of EXAFS, WT has the additional \(k\)-space resolution to resolve the scattering amplitude maximum at different wavenumbers. The different scattering amplitudes are used to distinguish the backscattering species based on that different elements scatter differently \(^{18-19}\). For Pt foil and Pt NPs in Figure 5-6, the first-shell Pt-Pt scattering feature shows the main scattering maximum at \(k = 10.3\ \text{Å}^{-1}\), with the relatively weak signal at \(k = 7.5\ \text{Å}^{-1}\) (corresponding to the peak at 2.1 Å in R-space). This weak intensity peak for Pt foil and Pt NPs is the splitting feature of the Pt-Pt scattering caused by Ramsauer-Townsend effect \(^{20-21}\). For Pt-Cu bimetallic systems including Cu@Pt\(_{0.25}\) and Cu@Pt\(_{0.5}\) core-shells, and CuPt NPs, the CCWT amplitude is dominated by the Pt-Cu scattering signal. A weak Pt-Pt feature is observed in Cu@Pt\(_{0.5}\). These results are in excellent agreement with the EXAFS fitting results.

**Table 5-2. Pt and Cu thickness information calculated with Pt L\(_3\)-edge jump EJ\(_{\text{Pt}}\) and Cu K-edge jump EJ\(_{\text{Cu}}\) from transmission signal.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>EJ(_{\text{Pt}})</th>
<th>EJ(_{\text{Cu}})</th>
<th>T(_{\text{NPs}}) (nm)</th>
<th>T(_{\text{Pt}}) (nm)</th>
<th>T(_{\text{Cu}}) (nm)</th>
<th>Pt composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu@Pt(_{0.25})</td>
<td>0.056</td>
<td>0.327</td>
<td>8</td>
<td>0.90</td>
<td>6.96</td>
<td>2.0 layers on surface</td>
</tr>
<tr>
<td>Cu@Pt(_{0.5})</td>
<td>0.098</td>
<td>0.387</td>
<td>8</td>
<td>1.19</td>
<td>6.55</td>
<td>2.6 layers on surface</td>
</tr>
<tr>
<td>CuPt NPs</td>
<td>0.048</td>
<td>0.134</td>
<td>4</td>
<td>0.73</td>
<td>3.05</td>
<td>18 at.% in bulk</td>
</tr>
</tbody>
</table>
Figure 5-7. Proposed simplified near-surface structures for Cu@Pt$_{0.25}$, Cu@Pt$_{0.5}$, and CuPt NPs. Pt atoms are represented by gray circles and Cu by orange circles.

The thicknesses of Pt and Cu for bimetallic NPs are estimated based on the EXAFS fitting results and raw transmission spectra (not shown) at Pt L$_{3}$-edge and Cu K-edge, as shown in Table 5-2. The edge jumps are directly extracted from the transmission spectra, that is, 0.056, 0.098, and 0.048 at Pt L$_{3}$-edge for Cu@Pt$_{0.25}$ Cu@Pt$_{0.5}$, and CuPt NPs, respectively, and 0.327, 0.387, and 0.134 at Cu K-edge for Cu@Pt$_{0.25}$ Cu@Pt$_{0.5}$, and CuPt NPs, respectively. The total thickness of bimetallic NPs are assumed to be 8 nm, based on the TEM results. The thickness ratios of Pt and Cu are estimated by the cross sections at Pt L$_{3}$-edge and Cu K-edge. The obtained thickness of Pt is 0.90 and 1.19 nm for Cu@Pt$_{0.25}$ and Cu@Pt$_{0.5}$, respectively, corresponding to 2.0 and 2.6 layers (using (111) planes) on the surface. For CuPt NPs, the Pt is estimated to be ca. 18% atoms in bulk. Proposed simplified 2D schematics of these NPs are shown in Figure 5-7.

5.4. Conclusions

Cu@Pt core-shell NPs have been successfully synthesized with a polyol reduction method in the presence of PVP$_{55000}$. The pure Cu core covered by an ultrathin Pt shell has been confirmed with electron and X-ray microscopies. The Pt shell thickness was found to be 2.0 monolayers for Cu@Pt$_{0.25}$ and 2.6 monolayers for Cu@Pt$_{0.5}$. In CuPt NPs, Pt was inserted into the Cu lattice, composing 18% of the total atoms in the NPs. For core-shell structures, Pt-Pt bonds were compressed to different extent depending on the amount of Pt on the
surface, while the Cu core showed no observable change. For the alloy NPs, the Pt-Pt bond length was significantly compressed, while Cu-Cu was slightly elongated because of the Pt insertion. The charge transfer from Cu to Pt was confirmed from the XAS result. Combining the CNs and thickness information, models for the surface configurations of these Pt-Cu bimetallic NPs are proposed. This study confirms the controllability of the polyol reduction method for a wide range of tunable physical properties of the bimetallic NPs, hence chemical properties as well. It is possible to establish protocols for affordable synthesizing methods of NPs based on controlled Pt-Pt interaction for the requirement of catalytic reactions.

5.5. References


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(13) Fievet, F.; Lagier, J.; Figlarz, M. Preparing monodisperse metal powders in micrometer and submicrometer sizes by the polyol process. MRS Bull. 1989, 14, 29-34.


Chapter 6

6. High Energy Resolution Fluorescence Detected (HERFD) XAS/XES for Pt-based Bimetallic Systems

6.1. Introduction

In recent years, HERFD-XAS/XES has been developed as a powerful tool to study the electronic structure for materials in various disciplines such as biological science and catalysis. HERFD-XAS/XES is a high energy resolution X-ray emission technique detecting secondary processes of X-ray absorption. Compared with the FY mode of normal XAS using a silicon drift detector (SDD), with an energy resolution on the order of hundred eV, HERFD-XAS/XES detects a well-resolved emission line with sub-lifetime broadening (typically less than one to a few eV). The secondary processes are described by the modified Kramers-Heisenberg formula as Eq. 6.1,

\[
F(\Omega, \omega) = \sum_f \left| \sum_n \frac{\langle f | T_2 | n \rangle \langle n | T_1 | g \rangle}{E_g - E_n + \Omega - i\Gamma_n/2} \right|^2 \\
\times \frac{\Gamma_f/2\pi}{(E_g - E_f + \Omega - \omega)^2 + \Gamma_f^2/4}
\] (6.1)

where \( |g\rangle, |n\rangle, \) and \( |f\rangle \) are the ground state, intermediate states, and final states corresponding to the system energies \( E_g, E_n, \) and \( E_f, \) respectively; \( T_1 \) and \( T_2 \) are the transition operators; \( \Omega \) and \( \omega \) are the incident photon energy and emission photon energy, respectively; \( \Gamma_n \) and \( \Gamma_f \) are the lifetime broadening of the intermediate states (with a core hole) and final states (depending on the emission line), respectively. The corresponding processes are illustrated in Figure 6-1. It should be mentioned that \( \Omega - \omega \) is the energy loss which is a constant below threshold where \( \omega, \) the RIXS, exhibits a dispersion but \( \Omega - \omega \) increases as \( \Omega \) increases above the threshold when \( \omega \) becomes characteristic fluorescence. It should also be noted that secondary processes including X-ray fluorescence are not a true measurement of but are proportional to the absorption coefficient in the hard X-ray range.
Figure 6-1. Illustration of detection of secondary processes involving intermediate states. $\Omega$ is the incident energy and $\omega$ is the emission energy.

Figure 6-2. Schematic of core-hole lifetime and instrumental broadening in RIXS planes of Pt shown as (a) emission energy $\omega$ vs incident energy $\Omega$ and (b) incident energy $\Omega$ vs energy transfer $\Omega - \omega$. 
\[ \Gamma_{app} \approx \frac{1}{\sqrt{(1/\Gamma_n)^2 + (1/\Gamma_f)^2}} \]  
(6.2)

\[ f_V \approx 0.5346f_L + \sqrt{0.2166f_L^2 + f_G^2} \]  
(6.3)

Theoretically, the coupling of the intermediate state \( \Gamma_n \) and final state \( \Gamma_f \) lifetime broadenings is expressed in Eq. 6.2\(^4\), giving the apparent measured peak broadening, \( \Gamma_{app} \). Note that this mathematic relationship will result in a \( \Gamma_{app} \) smaller than both \( \Gamma_n \) and \( \Gamma_f \), enabling the sub-lifetime detection in secondary processes. For more practical estimation, the observed broadening also includes the instrumental contributions, that is, the incident beam broadening \( E_{INC} \) and the emission line broadening \( E_{EMI} \). \( E_{INC} \) is determined by the monochromator of the beamline, in other words, the resolution of the incident beam, usually ranging from a few tenths of eV to a few eV for hard X-ray. \( E_{EMI} \) is determined by the detecting setup at the end station. In the case of HERFD setup using a spherically bent crystal analyzer (SBCA) in a Rowland circle\(^8\)-\(^10\). The instrumental broadening \( E_{INC} \) and \( E_{EMI} \) are treated as Gaussian profiles while the intrinsic lifetime broadening \( \Gamma_n \) and \( \Gamma_f \) as Lorentzian profiles. Empirically, the Voigt-type broadening \( f_V \) is calculated when the Gaussian-type broadening \( f_G \) is convoluted with the Lorentzian-type broadening \( f_L \), as shown in Eq. 6.3\(^11\).

The estimation of the final lifetime broadening \( \Gamma \) is decomposed into three steps:

1. The coupling of the final state lifetime broadening with detector broadening, \( \Gamma_{FIN} \), is obtained by the convolution of the Lorentzian-type \( \Gamma_f \) with the Gaussian-type \( E_{EMI} \) using Eq. 6.4.

2. The apparent broadening \( \Gamma_{app} \) is obtained by coupling the intermediate state lifetime broadening \( \Gamma_n \) and the final state lifetime broadening \( \Gamma_{FIN} \) using Eq. 6.5.

3. The final broadening \( \Gamma \) is obtained by convoluting the \( \Gamma_{app} \) with the incident beam broadening \( E_{INC} \) using Eq. 6.6.

\[ \Gamma_{FIN} = 0.5346f_f + \sqrt{0.2166f_f^2 + E_{EMI}^2} \]  
(6.4)
\[
\Gamma_{app} = \frac{1}{\sqrt{(1/\Gamma_n)^2 + (1/\Gamma_{FIN})^2}} \quad (6.5)
\]

\[
\Gamma = 0.5346\Gamma_{app} + \sqrt{0.2166\Gamma_{app}^2 + E_{INC}^2} \quad (6.6)
\]

In this study, the HERFD-XES is conducted for the valence-to-core (VTC) emission (L_\beta 5) near the Pt L_3-edge for Pt-Ni alloys. Starting with the ground state \(2p_{3/2}^4 5d_{3/2}^x 5d_{5/2}^y 6s^z\), the hard X-ray photon excites the Pt atom into the intermediate states with a \(2p_{3/2}\) hole, that is, \(2p_{3/2}^3 5d_{3/2}^{x+1} 5d_{5/2}^y 6s^z\), \(2p_{3/2}^2 5d_{3/2}^x 5d_{5/2}^{y+1} 6s^2\), or \(2p_{3/2}^2 5d_{3/2}^x 5d_{5/2}^y 6s^{z+1}\) at dipole-allowed resonances. The core-hole lifetime of intermediate states refers to the lifetime of the \(2p_{3/2}\) hole. The \(2p_{3/2}\) core-hole is then filled by the \(5d_{3/2, 5/2}\) electron in the valence band (L_\beta 5 emission), leaving behind the \(5d_{3/2, 5/2}\) hole which determines the final state lifetime broadening. HERFD-XAS at Pt L_3- and L_2-edges is also conducted to obtain high-resolution absorption spectra. For the Pt L_3-edge XAS, the L_\alpha 1 emission line is chosen. The intermediate states are the same as the L_\beta 5 emission while the final state hole is changed to \(3d_{5/2}\), with a much longer lifetime. For the Pt L_2-edge monitoring the L_\beta 1 emission, the intermediate state and final state core-holes are \(2p_{1/2}\) and \(3d_{3/2}\), respectively. It is worth mentioning that the narrowing of the emission lines in the HERFD setup not only sharpens and enhances the features but also lowers the background signal at the XANES region. For example, the L_\beta 1 (\(3d_{3/2} \rightarrow 2p_{1/2}\)) emission line is not separable from the tail of the L_\beta 2 (\(3d_{5/2} \rightarrow 2p_{1/2}\)) emission line in normal SDD. When the excitation energy rises across the L_2 edge, the L_\beta 2 signal decreases (as other background channels should). This involvement of the L_3 excitation will not significantly change the shape of the L_2 XANES, but induce a varying background which shifts the WL peak and those closely following (in the absorption intensity axis). The HERFD setup exclusively looking at the interested emission line provides more accurate spectra for quantitative analysis of the XANES region.

The calculated results of the lifetime broadening for Pt L_\alpha 1, L_\beta 1, and L_\beta 5 emission lines are summarized in Table 6-1. \(\Gamma_n\) and \(\Gamma_f\) values are extracted from the FEFF code \(^{12}\). Note that the VTC emission final state lifetime broadening is considered negligible and set to be 0. The
incident beam broadening $E_{INC}$ is calculated using the Si(311) monochromator setup with an energy resolution of $0.3 \times 10^{-4}$ (this value is $1.4 \times 10^{-4}$ for VTC emission using the Si(111) monochromator), providing a broadening of 0.35 eV for Pt L₃-edge and 0.4 eV for Pt L₂-edge. The detector broadening $E_{EMI}$ is estimated to be 3 eV based on the elastic scattering signal. This empirical calculation method gives the final lifetime broadening of 3.40, 3.86, and 3.40 eV for Pt L₁, L₂, and L₂ emission lines, respectively. The practical values, however, may vary based on the optimization of the optical path.

![Figure 6-3. HERFD-XAS/XES setup. Left: Illustration of the Rowland circle. Right: Experiment setup at the CLS®APS Sector 20-ID beamline.](image)

![Table 6-1. Intrinsic, instrumental, and final broadening for Pt L₁, L₂, and L₂ emission lines.](table)

<table>
<thead>
<tr>
<th>Absorption Edge</th>
<th>Emission Line</th>
<th>$\Gamma_\text{a}$ (eV)</th>
<th>$\Gamma_\text{f}$ (eV)</th>
<th>$E_{INC}$ (eV)</th>
<th>$E_{EMI}$ (eV)</th>
<th>$\Gamma_\text{FIN}$ (eV)</th>
<th>$\Gamma_{app}$ (eV)</th>
<th>$\Gamma$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt L₃</td>
<td>Lₐ₁ (M₅-L₃)</td>
<td>5.08</td>
<td>2.40</td>
<td>0.35</td>
<td>3.00</td>
<td>4.48</td>
<td>3.36</td>
<td>3.40</td>
</tr>
<tr>
<td>Pt L₂</td>
<td>Lₐ₁ (M₄-L₂)</td>
<td>5.91</td>
<td>3.13</td>
<td>0.40</td>
<td>3.00</td>
<td>5.01</td>
<td>3.82</td>
<td>3.86</td>
</tr>
<tr>
<td>Pt L₃</td>
<td>Lₐ₅ (V-L₃)</td>
<td>5.08</td>
<td>-</td>
<td>1.62</td>
<td>3.00</td>
<td>3.00</td>
<td>2.58</td>
<td>3.40</td>
</tr>
</tbody>
</table>

The HERFD experimental setup composed of a PILATUS 100K-S 2D detector (DECTRIS Ltd., Switzerland), an SBCA ¹³−¹⁵, and the sample with the geometry defined by a
Rowland circle ($\Phi \approx 0.5$ m), is shown in Figure 6-3. Because of the high energy resolution requirement, an SBCA is designed only for a narrow range of emission energies. Pt L$_{\alpha 1}$ uses the Si(800) diffraction planes while Pt L$_{\beta 1}$ and L$_{\beta 5}$ use Si(911). For HERFD-XES (Pt L$_{\beta 5}$, VTC), the data was collected by a raster scan with a 0.5 eV step for both the excitation energy (11550 – 11580 eV) and emission energy (11550 – 11580 eV). During the scan, the 2D detector moves vertically according to the angle of SBCA, which selects the emission energy. For HERFD-XAS, the emission energy is tuned to the peak energy of the emission line (Pt L$_{\alpha 1}$ for Pt L$_3$-edge and Pt L$_{\beta 1}$ Pt L$_2$-edge) for each sample and the 2D detector is at a fixed position. Note that the emission energy (Pt L$_{\alpha 1}$ for example) is not a constant among alloy and reference samples. In other words, the emission line of a sample can have a slight energy shift relative to that of the Pt foil. This is caused by the screening effect of the redistributed charge $\delta$, which occurred when the element is placed in different chemical environment $^{16-17}$. Depending on the proportion of $\delta$ penetrating into the core levels and the shapes of the core level wavefunctions, the core levels experience screening of the positive nucleus to varying degrees. In the case of Pt-Ni alloys where Pt atoms attracts negative charge from Ni atoms, the screening effect on the Pt 2p levels is stronger than that on the Pt 3d levels. As a result, the Pt L$_{\alpha 1}$ emission line, that is, Pt 3d$_{5/2}$ $\rightarrow$ 2p$_{3/2}$, moves to a lower energy with respect to pure Pt. For HERFD-XAS experiments collecting only the XAS at a certain emission energy instead of a 2D plane (incident energy vs emission energy), the chemical shift must be taken into account. It should be mentioned that for the HERFD-XES (VTC) shown in Figure 6-2 above and Figure 6-5 in the following section, the emission line is affected not only by the abovementioned chemical shift, but also directly by the redistribution of the valence states. These two factors contribute to the emission line shift as well as the pattern in the 2D plane, and the anomaly of XPS peak shifts in Chapter 3.
6.2. Results and discussion

6.2.1. HERFD-XAS for PtNi alloys

Figure 6-4. HERFD-XAS at Pt L$_{3,2}$-edges compared with SDD results (normal FY mode).

Figure 6-5. Raw spectra of Pt L$_{3}$- and L$_{2}$-edges collected in transmission mode. The spectra are aligned by setting the edge energy to 0 eV.

The HERFD-XAS are compared with the normal FY mode results in Figure 6-4. Note that all the HERFD spectra are calibrated according to standard Pt threshold values (11564 eV for Pt L$_{3}$-edges and 13273 eV for Pt L$_{2}$-edges). The spectroscopic (normal FY mode) trends have
been analyzed in Chapter 3. The HERFD series show the same trend but with significantly enhanced XANES features for analysis. The Pt L₃- and L₂-edges are fitted with a Voigt-type profile as the WL peak and an error function as the background. Note that because of the narrow lifetime broadening, the commonly used arctangent background (as seen in Chapter 3) is not a good option for HERFD-XAS in this case. The widths of the WL peaks and error function backgrounds are constrained by the calculated core-hole lifetime broadening in Table 6-1, that is, 3.40 eV for A₃ and 3.86 eV for A₂. Note that for Pt NPs in the next section, the A₃ width is not constrained because of the broadened WL peak arising from the large proportion (estimated around 23%) of surface atoms in the whole Pt NPs. Semiquantitative WL analysis is carried out using the Eqs. 6.7 and 6.8 (equivalent to Eqs. 3.1 and 3.2), where the density of Pt, \( N₀ = 0.112 \times 10^{24} \) atoms/cm³, the radial components of the dipole moment matrix elements \( R_{5d}^{2p_{1/2}} = R_{5d}^{2p_{3/2}} = R_{5d}^{2p} = 3.103 \times 10^{-11} \) cm, \( \alpha \) is the fine structure constant, \( E_{3,2} \) are the Pt L₃,2 edge energies, i.e. 11564 and 13273 eV, respectively. The transitions to 6s states are neglected because of the low density of states and negligible radial dipole moment matrix element. Instead of using the literature values of Pt 5d holes \( h_{5/2} \) (1.000) and \( h_{3/2} \) (0.344) \(^{18} \), the ratio of \( h_{5/2}/h_{3/2} \) (Eq. 6.9) of Pt foil is used as the initial condition along with a preset number of total 5d holes, \( n_{Pt} \) (Eq. 6.10), which is the only variable.

\[
A_3 = (4/3)\pi^2\alpha N_0 E_3 \left( R_{5d}^{2p_{3/2}} \right)^2 \cdot \left( \frac{6h_{5/2} + h_{3/2}}{15} \right) \tag{6.7}
\]

\[
A_2 = (4/3)\pi^2\alpha N_0 E_2 \left( R_{5d}^{2p_{1/2}} \right)^2 \cdot \left( \frac{h_{3/2}}{3} \right) \tag{6.8}
\]

\[
\frac{h_{5/2}}{h_{3/2}} = \frac{1}{2C} \left( \frac{5E_2}{E_3} A_3 - A_2 \right) = \frac{1}{6} \left( \frac{5E_2 A_3}{E_3 A_2} - 1 \right) \tag{6.9}
\]

\[h_{5/2} + h_{3/2} = h_{Pt} \text{ (preset value)} \tag{6.10}\]

The fitting of WL areas \( A_3 \) (5.306, 4.935, 4.661, and 4.228 for Pt foil, Pt₃Ni, PtNi, and PtNi₃, respectively) and \( A_2 \) (2.718, 2.575, 2.282, and 2.098 for Pt foil, Pt₃Ni, PtNi, and PtNi₃, respectively) for Pt foil and alloys are shown in Figure 6-6. A clear decreasing trend is
observed as the content of Ni increases. In Table 6-2, the calculated Pt 5d holes for the Pt-Ni alloys (1.087, 1.007, and 0.917 for Pt₃Ni, PtNi, and PtNi₃ respectively) are summarized with a preset Pt 5d hole number \( h_P \) of 1.162, which is from the XPS calculation in Chapter 3 (calculations with other initial values are shown in Figure 6-11). The calculated Pt 5d hole numbers exhibit an almost linear relationship with the Ni concentration in the alloys. In other words, every 25% increase of the Ni content leads to around 0.08 increase of electron filling in the Pt 5d character of the alloy d band.

Note that the uncertainty of 5d hole estimation lies on the assumptions and limitations as the following:

1. Processing error. The WL areas \( A_1 \) and \( A_2 \) are empirically determined. They are sensitive to the background function and lifetime broadening. This process can contribute to around 5% of uncertainty for HERFD-XAS WLs. For normal FY or transmission mode, this uncertainty can be as large as 20% because of the broadening.

2. Theoretical error. The difference between the radial dipole moment matrix elements \( R_{5d}^{2p_{1/2}} \) and \( R_{5d}^{2p_{3/2}} \) is neglected.

3. Theoretical error. Transitions from 2p to 6s states are neglected.

4. Experimental error. The emission line energy for HERFD-XAS has to be optimized for each sample, which may induce error.

Table 6-2. Calculated Pt 5d holes from the WL areas of Pt L₃- and L₂-edges for Pt-Ni alloys and comparison with Pt foil. \( h_P \) is set to be 1.162.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( A_3 )</th>
<th>( A_2 )</th>
<th>( h_{5/2} )</th>
<th>( h_{3/2} )</th>
<th>( h_{5d} )</th>
<th>( \Delta h_{5d} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt foil</td>
<td>5.306</td>
<td>2.718</td>
<td>0.732</td>
<td>0.430</td>
<td>1.162</td>
<td></td>
</tr>
<tr>
<td>Pt₃Ni</td>
<td>4.935</td>
<td>2.575</td>
<td>0.679</td>
<td>0.408</td>
<td>1.087</td>
<td>-0.075</td>
</tr>
<tr>
<td>PtNi</td>
<td>4.661</td>
<td>2.282</td>
<td>0.645</td>
<td>0.361</td>
<td>1.007</td>
<td>-0.155</td>
</tr>
<tr>
<td>PtNi₃</td>
<td>4.228</td>
<td>2.098</td>
<td>0.585</td>
<td>0.332</td>
<td>0.917</td>
<td>-0.245</td>
</tr>
</tbody>
</table>
Figure 6-6. WL fitting for Pt L$_3$- and L$_2$-edges to extract the WL areas $A_3$ (a, c, e, g) for Pt foil, Pt$_3$Ni, PtNi, and PtNi$_3$, respectively, and $A_2$ (b, d, f, h) for Pt foil, Pt$_3$Ni, PtNi, and PtNi$_3$, respectively. The experimental data, fitted curves, and error function background are labeled with red dotted lines, black solid lines, and purple solid lines, respectively. The extracted Voigt-type $A_3$ and $A_2$ are labeled as the blue area.
6.2.2. HERFD-XES (VTC) for PtNi alloys

The VTC emission, as the name suggests, originates from the valence electrons combining with core holes, emitting a fluorescence photon, in which case, the energy of the emitted X-ray would be very close to the excitation energy which will also appear in the spectrum as an elastically scattered peak, as shown in Figure 6-7. A clear trend of increasing intensity of the elastic scattering is observed as the concentration of Ni increases. This is because Ni mainly contributes to elastic X-ray scattering instead of absorption at the X-ray energy near Pt L-edges. In PtNi$_3$, the elastic scattering signal is strong enough to partially overlap with the VTC emission, while it is negligible in Pt$_3$Ni. Focusing on the excitation-emission energy distribution of the VTC emission, one can see different emission patterns near the absorption edge for the alloys even though all Pt are in metallic state (excluding PtO$_2$). The emission pattern tends to be more symmetric because of higher occupation of 5d states. In the meanwhile, the emission center shift to lower energy as Pt is surrounded by more Ni, as indicated by the yellow dash line in the middle column of Figure 6-7. Detailed analysis is discussed in the following section. Note that the Pt 5d$_{3/2}$ and 5d$_{5/2}$ band are not resolved in the VTC emission spectra because the 5d splitting is smaller than the energy resolution mentioned above.

The XES spectra near Pt L$_3$-edge are extracted and shown in Figure 6-8. The energy transfer $\Delta E$ (3.3, 2.8, 2.9, 3.3, and 3.6 eV for PtO$_2$, Pt, Pt$_3$Ni, PtNi, and PtNi$_3$, respectively), or the centroid of the d band of Pt character shifts away from the Fermi level as Pt is surrounded by more Ni, as shown in Figure 6-8(a-e) This is in line with the results in Chapter 3, that is, that the occupied Pt 5d states are pushed away from the Fermi level upon alloying with Ni. The XES spectra for each sample at the resonance maximum is summarized in Figure 6-8(f). The XES spectra are fitted with a 3.0 eV wide Gaussian peak and the VTC signal. Also in good agreement with XPS results, the Pt VTC emission lines, hence the band widths, are exhibiting a narrowing trend (7.2, 7.1, 7.0, 6.2 eV for Pt, Pt$_3$Ni, PtNi, and PtNi$_3$, respectively) as Ni content increases. Note that the VTC width for Pt in PtO$_2$ is 5.9 eV, smaller than any other sample. This narrowing in the oxide, however, originates from a different mechanism than the Pt-Ni alloy systems. Since the valence band provides the electron for the VTC emission, charge transfer from Pt to oxygen will have a direct effect of reducing the width of occupied states. In the case of the alloy systems, charge (occupied
Figure 6-7. HERFD-XES(VTC) for (a) PtO₂, (b) Pt, (c) Pt₃Ni, (d) PtNi, and (e) PtNi₃.

Left column: energy transfer vs incident photon energy. Middle column: incident energy vs emission energy. Right column: 3D view of incident energy vs emission energy. The yellow dotted line indicates the emission energy of the resonance maximum for pure Pt.
to be continued
DOS) redistribution dominates the charge transfer (from Ni to Pt). While these two mechanisms both lead to the narrowing of the occupied 5d band, they are accompanied by distinctly different behaviors because of the opposite trend in the number of unoccupied states. For PtO₂, the number of Pt 5d holes significantly increase, resulting in much stronger many-body effect and asymmetry in emission lines (for both electron emission and X-ray emission).
6.2.3. HERFD-XAS for Pt-Cu bimetallic nanoparticles

The HERFD-XAS at Pt L₃- and L₂-edges for Pt-Cu has also been conducted with the previously described HERFD setup. Similarly, the Pt L₃-edge was detected with the Pt Lα₁ emission line and the Pt L₂-edge with Lβ₁ emission line. The obtained HERFD spectra are shown in Figure 6-9 in comparison with those from normal FY mode. A₃ and A₂ are extracted, as shown in Figure 6-10, to calculate the number of Pt 5d holes for samples. The results are summarized in Table 6-3.

Figure 6-9. XAS detected with normal FY mode at (a) L₃-edge and (b) L₂-edge in comparison with HERFD-XAS at (c) L₃-edge and (d) L₂-edge, respectively, for Pt-Cu bimetallic nanoparticles and references.
Figure 6-10. WL fitting for Pt L₃- and L₂-edges to extract the WL areas A₃ (a, c, e, g, i) for Pt foil, Pt NPs, Cu@Pt₀.₂₅, Cu@Pt₀.₅, and CuPt NPs, respectively, and A₂ (b, d, f, h, j) for Pt foil, Pt NPs, Cu@Pt₀.₂₅, Cu@Pt₀.₅, and CuPt NPs, respectively. The experimental data, fitted curves, and error function background are labeled with red dotted lines, black solid lines, and purple solid lines, respectively. The extracted Voigt-type A₃ and A₂ are labeled as the blue area.
Table 6-3. Calculated Pt 5d holes from the WL areas at Pt L3- and L2-edges for Pt-Cu bimetallic systems and comparison with Pt metal. \( h_{Pt} \) is set to be 1.162.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( A_3 )</th>
<th>( A_2 )</th>
<th>( h_{5/2} )</th>
<th>( h_{3/2} )</th>
<th>( h_{5d} )</th>
<th>( \Delta h_{5d} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt foil</td>
<td>5.306</td>
<td>2.718</td>
<td>0.732</td>
<td>0.430</td>
<td>1.162</td>
<td></td>
</tr>
<tr>
<td>Pt NPs</td>
<td>5.420</td>
<td>2.719</td>
<td>0.749</td>
<td>0.430</td>
<td>1.179</td>
<td>0.017</td>
</tr>
<tr>
<td>Cu@Pt0.25</td>
<td>3.580</td>
<td>1.633</td>
<td>0.499</td>
<td>0.259</td>
<td>0.758</td>
<td>-0.404</td>
</tr>
<tr>
<td>Cu@Pt0.5</td>
<td>4.075</td>
<td>1.677</td>
<td>0.573</td>
<td>0.265</td>
<td>0.838</td>
<td>-0.324</td>
</tr>
<tr>
<td>CuPt NPs</td>
<td>3.400</td>
<td>1.451</td>
<td>0.477</td>
<td>0.230</td>
<td>0.706</td>
<td>-0.456</td>
</tr>
</tbody>
</table>

\[
A_2 = 0.6608A_3 - 0.7967 \quad (6.11)
\]

\[
A_3 = CE_3 \left( \frac{6h_{5/2} + h_{3/2}}{15} \right) \quad (6.12)
\]

\[
A_2 = CE_2 \frac{h_{3/2}}{3} \quad (6.13)
\]

\[
h_{5/2} = (0.1153A_3 + 0.0181)h_{Pt} \quad (6.14)
\]

\[
h_{3/2} = (0.0901A_3 - 0.1086)h_{Pt} \quad (6.15)
\]

\[
h_{5d} = (0.2054A_3 - 0.0905)h_{Pt} \quad (6.16)
\]

\[
h_{5/2} = 1.2804h_{3/2} + 0.1572h_{Pt} \quad (6.17)
\]

With the preset \( n_{Pt} = 1.162, A_3 \) (5.306, 5.420, 3.580, 4.075, and 3.400 for Pt foil, Pt NPs, Cu@Pt0.25, Cu@Pt0.5, and CuPt NPs, respectively) and \( A_2 \) (2.718, 2.719, 1.633, 1.677, and 1.451 for Pt foil, Pt NPs, Cu@Pt0.25, Cu@Pt0.5, and CuPt NPs, respectively) result in Pt 5d holes of 1.179, 0.758, 0.838, and 0.706 for Pt NPs, Cu@Pt0.25, Cu@Pt0.5, and CuPt NPs, respectively. Compared with the Pt-Ni alloys, these Cu@Pt core-shell and alloy NPs have higher amount of charge transfer to Pt because of the lower Pt amount on/in Cu.
Combining the 5d hole calculations for Pt-Ni alloys and Pt-Cu systems, the relationship between \( A_3, A_2, \) and 5d holes is plotted in three dimensional in Figure 6-11(a). An almost linear relationship between \( A_3 \) and \( A_2 \) is observed, as shown in Figure 6-11(b) and Eq. 6.11. By associating the Eq. 6.11 with the Eqs 6.12 and 6.13 (derived from Eqs. 6.7 and 6.8), the expressions for \( h_{5/2} \) and \( h_{3/2} \) can be determined as Eqs. 6.14 and 6.15, and the total number 5d holes \( h_{5d} \) as Eq. 6.16. In these general expressions, \( n_Pt \) is the preset total number of 5d holes for Pt metal, the \( A_3 \) is the only variable to determine the \( h_{5/2}, h_{3/2}, \) and \( h_{5d} \). This is an important finding in two aspects: (1) Physically, \( h_{5/2} \) and \( h_{3/2} \) also have a linear relationship (a constant \( h_{5/2}/h_{3/2} \) ratio with a certain energy range above the Fermi level) upon alloying with other metals (Cu and Ni in this case), as described in Eq. 6.17 and illustrated in Figure 6-11(d). In other words, if one slice the unoccupied Pt 5d band, the 5d\( _{5/2} \) to 5d\( _{3/2} \) DOS ratio remains constant near the Fermi level, regardless of the change of the overall band shape. Moreover, at \( h_{3/2} = 0 \) (assuming that the relationship is still valid), \( h_{5/2} \) equals to a constant value, that is, \( 0.1572h_{Pt} \). (2) Experimentally, detecting \( A_3 \) alone will provide enough information to calculate the number of unoccupied \( h_{5/2}, h_{3/2}, \) and \( h_{5d} \). Consider that most ex-situ and in-situ experiments only study the Pt L\( _3 \)-edges to obtain XANES and EXAFS information for Pt-based catalysts, this finding will certainly provide more access to the physical properties of the materials.

6.3. Conclusions

The advantages of HERFD-XAS and XES have been demonstrated in studying the Pt 5d band of Pt-Ni and Pt-Cu bimetallic systems. In the VTC XES experiments, the widths of the VTC emission lines and energy transfers show the shrinking and downshifting of the Pt valence band upon alloying with Ni. Different emission patterns are observed because of chemical shifts and valence states redistribution upon alloying. For HERFD-XAS, significantly narrowed WL, enhanced XANES features, and easily removable background have enabled detailed analysis of the WL peaks with higher accuracy. Pt L\( _2 \)-edge is found to have an obvious WL, which is normally neglected in normal XAS measures. Combining the HERFD-XAS results for Pt-Ni and Pt-Cu bimetallic systems, Pt foil, and Pt NPs, a linear relationship between the WL areas of Pt L\( _3 \)- and L\( _2 \)-edges is established. This area linear relationship indicates that the unoccupied Pt 5d\( _{5/2} \) and 5d\( _{3/2} \) states, i.e. \( h_{5/2} \) and \( h_{3/2} \), also
Figure 6-11. Summary of Pt 5d holes from HERFD-XAS WL calculations. (a) Calculations using the initial 5d hole number $h_{Pt}$ of 1.344, 1.162, and 1 for Pt foil. (b) Linear relationship between $A_2$ and $A_3$. (c) Linear relationship between total 5d hole number and $A_3$. $h_{Pt}$ is set to be 1.162. (d) An illustration of the unoccupied 5d states for Pt in generation situations. Note that the downshifting of the occupied 5d states is not shown.

have a linear relationship. This finding demonstrates that measuring the Pt L$_3$-edge alone will provide enough information to study the unoccupied 5d states of Pt in Pt-based alloys. A
detailed picture for unoccupied Pt 5d states and a calculation model for based on Pt L₃-edge WL area is proposed. Considering the morphological and compositional variance in these bimetallic systems, these linear relationships are believed to be reliable in general cases including Pt-based bimetallic, trimetallic, and even high entropy systems with complicated components.

6.4. References


(2) Bauer, M. HERFD-XAS and valence-to-core-XES: new tools to push the limits in research with hard X-rays? PCCP 2014, 16, 13827-13837.


Chapter 7

7. Conclusions and Future Work

7.1. Conclusions

This thesis investigates the electronic structure of Pt for catalysis applications. The importance of the Pt 5d band is discussed in terms of the bonding capability of Pt. Oxygen reduction reaction is chosen as the catalytic reaction model to illustrate the effect of Pt 5d states on the several Pt-O bonding types. Pt-based bimetallic systems are introduced as a solution for the high price and limited resources of Pt. Despite lowering usage of Pt, bimetallic catalysts can achieve higher performance thanks to the tuning capability to optimize the Pt 5d band (Chapter 1). Advanced synchrotron X-ray techniques including XAFS, X-ray ptychography, and HERFD-XAS/XES are introduced as powerful tools to study the electronic and local structures (Chapter 2). Pt-Ni bimetallic bulk alloys are synthesized as model compounds to investigate the behavior of Pt upon alloying with transition metals (Chapter 3). It has been found that Pt gains 5d electrons while Ni loses 4p and 3d electrons upon alloying. These charge transfers result in the change of asymmetry of XPS peaks as well as the WL intensities for both Pt and Ni. In the meanwhile, the downshifting and narrowing of Pt valence states are observed. In addition to bulk alloys, Pt-Ni bimetallic NPs are studied in Chapter 4. By obtaining the product at different synthesizing stages (from 10 min to 2 hours), the evolution of Pt inside the bimetallic NPs is investigated. It has been found that at each stage, Pt forms a completely different structure. In detail, a Pt core frame is formed at the beginning, followed by Pt diffusion from inside to the surface. A thickened Pt outer frame is then observed before a thin Pt layer covers the entire NP. At the final stage, tiny Pt NPs at ca. 8 nm are grown on the original NP, composing the protective Pt shell with a high specific area for chemical reactions, while the core is believed to be a PtNi-like alloy structure. From the perspective of practical applications, Cu@Pt core-shell NPs with an ultrathin Pt shell are also synthesized with a polyol reduction method (Chapter 5). Using transmission mode XAS, the Pt shell thickness has been found to be 2.0 monolayers for Cu@Pt_{0.25} and 2.6 monolayers for Cu@Pt_{0.5}. Because of the low Pt amounts on the Cu core, the electronic and local structure of Pt undergo significant change by the ligand effect.
and strain effect. More in-depth study of the Pt 5d states has been carried out by utilizing the HERFD-XAS/XES technique (Chapter 6). From VTC XES, the downshifting and narrowing of the Pt 5d valence states upon alloying have been experimentally visualized, showing a good agreement with the UPS and DFT results in Chapter 3. For HERFD-XAS, significantly narrowed WL, enhanced XANES features, and easily removable background have enabled detailed analysis of the WL peaks with high accuracy. By combining the HERFD-XAS results for Pt-Ni and Pt-Cu bimetallic systems, Pt foil, and Pt NPs, a linear relationship between the unoccupied Pt 5d_{5/2} and 5d_{3/2} states has been established. This correlation is believed to be generally valid for Pt in fcc systems.

7.2. Future work

Core-shell structure with a thin Pt shell is a promising solution for high-performance and affordable catalysts for fuel cells among other applications. The cost of synthesizing core-shell structures, however, is still an obstacle in the way to large-scale commercialization. The choice of precursors as well as the synthesizing path are essential to the overall cost of the final product. Meanwhile, testing the reliability of the products can be tedious and complicated because of the countless possibilities of morphology and composition for materials in nanoscale. Using the HERFD-XAS/XES techniques described in this thesis, one will be able to experimentally examine the Pt 5d band, which is the most important factor in bimetallic systems for catalysis. The linear relationships developed in this thesis for Pt L\textsubscript{3} and L\textsubscript{2}-edge WL areas as well as 5d holes can be a powerful tool for systematic study.

This 5d hole model developed in chapter 6, however, is based on fcc or fcc-like crystal systems, whether for Pt-Ni and Pt-Cu bimetallic systems or pure Pt metal. Considering the directional characteristics of 5d orbitals, it is possible that other Pt atoms in other crystal systems may exhibit a different linear relationship. To obtain Pt in different crystal systems, one may simply dope Pt into other metals such as Fe (bcc) and Co (hcp).

Further improvement is also proposed in terms of 5d hole calculations. XPS and XAS WL calculation are based on different assumptions and have different limitations. For XPS calculation in Chapter 3, the 6s hole scattering effect is neglected in determining the asymmetric parameter of the core level peaks. For normal mode XAS, strict rules in WL peak extraction have to be established because of the large uncertainty attributed to the
background removal from broadened XANES features. The more reliable analysis using HERFD-XAS can serve as the calibration to standardize the normal mode XAS and XPS calculations. Meanwhile, for HERFD experiments, experimental errors from optimization of the analyzer angle has to be carefully handled. A higher energy resolution setup (compared with the 3-eV resolution in this thesis) is also expected to provide more detailed VTC XES to study the valence band structure.

This fundamental study bridges Pt-based bimetallic systems with their electronic properties. For future study, performance tests including electrochemical activity and stability tests are expected to be conducted on these bimetallic systems, using techniques such as rotating disk electrodes, membrane electrode assembly, and in-situ XAS. This will further bridge the material performance with their electronic properties, and hence guide the material design for different applications.
Appendices

Appendix A. Fitting model for XPS asymmetric peaks

The XPS asymmetric peaks are fitted with the Doniach-Sunjic profile: \( DS(\alpha,n)GL(m) \)
with

\[
DS(x: \alpha, F, E) = \frac{\cos\left[\frac{\pi\alpha}{2} + (1 - \alpha)\arctan\left(\frac{x - E}{F}\right)\right]}{(F^2 + (x - E)^2)^{(1-\alpha)/2}}
\]

\[
GL(x: F, E, m) = \exp\left(-4ln2(1 - m)\frac{(x - E)^2}{F^2}\right)/(1 + 4m\frac{(x - E)^2}{F^2})
\]

where \( \alpha \) is the asymmetric parameter, \( E \) is the peak position, \( F \) is the half-width at half-
maximum (HWHM) of the Lorentzian convoluted, \( n \) is the width of a Gaussian convoluted
with the Doniach-Sunjic profile, and \( m \) is an integer defining the percentage of the Gaussian
in the Gaussian-Lorentzian product GL(m). These line shape functions are available in
CasaXPS and explained in the manual.
Appendix B. Crystal models for XANES and valence band calculations by WIEN2k

The crystal structures for the model Pt-Ni alloys are described and depicted in the following:

(a) \( \text{Pt}_3\text{Ni} \): 

The crystal structure for the model \( \text{Pt}_3\text{Ni} \) is described in Figure 3-7 (b).

The space group is #221, Pm-3m.

The lattice constants: \( a = b = c = 3.850 \text{ Å}; \alpha = \beta = \gamma = 90^0 \).

The atomic sites: Pt at \( (\frac{1}{2}, 0, \frac{1}{2}) \); Ni at \( (0, 0, 0) \).

(b) \( \text{PtNi} \): 

The crystal structure for the model \( \text{PtNi} \) is described in Figure 3-7 (d). It is modelled from a supercell 2x1x1 of fcc Pt with the substitution of 4 Ni for 4 Pt.

The space group is #25, Pmm2.

The lattice constants: \( a = b = 3.741 \text{ Å}, c = 7.482 \text{ Å}; \alpha = \beta = \gamma = 90^0 \).

The atomic sites: \( \text{Pt at (0, 0, 0), (0, 0, \frac{1}{2}), (\frac{1}{2}, 0, \frac{1}{4}), (\frac{1}{2}, 0, \frac{3}{4});} \)

\( \text{Ni at (0, \frac{1}{2}, \frac{1}{4}), (0, \frac{1}{2}, \frac{3}{4}), (\frac{1}{2}, \frac{1}{2}, 0) (\frac{1}{2}, \frac{1}{2}, \frac{1}{2}).} \)

(c) \( \text{PtNi}_3 \): 

The crystal structure for the model \( \text{PtNi}_3 \) is described in Figure 3-7 (f).

The space group is #221, Pm-3m.

The lattice constants: \( a = b = c = 3.660 \text{ Å}; \alpha = \beta = \gamma = 90^0 \).

The atomic sites: Ni at \( (\frac{1}{2}, 0, \frac{1}{2}); \text{Pt at (0, 0, 0).} \)
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Elucidating the Many-Body Effect and Anomalous Pt and Ni Core Level Shifts in X-ray Photoelectron Spectroscopy of Pt–Ni Alloys

Author: Jiatang Chen, Yun Mui Yiu, Zhiqiang Wang, et al
Publication: The Journal of Physical Chemistry C
Publisher: American Chemical Society
Date: Jan 1, 2020

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Presentations:

1. “Tracking the Electronic and Local Structures of Pt-Ni Bimetallic Alloys and Core-Shell Nanoparticles with Synchrotron X-ray Techniques” Poster Presentation,