IMAGING OF NANOPARTICLES AND
NANOCRYSTAL INTERACTIONS WITH OXIDE SURFACES

BY

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DISSERTATION

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ABSTRACT

Surfaces and interfaces have a major impact on the structure and properties of materials, especially in nanostructures, including supported metal nanoparticles (NPs) used as catalysts in chemical industries and environmental remediation. For example, oxide supported gold NPs demonstrate outstanding chemical activity in selective oxidation of CO at low temperatures, and strong support effect is believed to be involved in the enhancement of their catalytic activities. The interfaces formed by the Au NPs and their supports are heterogeneous. In homogeneous materials, another type of interfaces is formed at grain boundaries. Such interfaces play a critical role in materials’ microstructure development. Recent advances in electron microscopy have significantly improved our capability for studying interfaces. Here we extend the interfacial study to two types of samples, one sample is Au NPs supported on rutile (TiO$_2$) surface and the other is transformation of Pt icosahedral NPs. In both cases, information obtained by innovative electron microscopy reveals atomic interfacial interactions at unprecedented details.

In our study on the Au/TiO$_2$ catalyst, we systematically examined the interfacial effects on the structure of Au NCs and the interface using aberration corrected scanning transmission electron microscopy (AC-STEM). Results show that by high temperature annealing, Au NCs supported on stepped TiO$_2$ (110) surfaces develop an approximate and preferred epitaxial relationship with Au(111)||TiO$_2$(110). The interfacial interaction can modify the shape of the NCs, and introduce significant strain in Au NCs near the surface steps. This strain is seen relaxed in Au layers away from the interface. By measuring the shape parameters, an interfacial energy of $\gamma_{\text{int}} \sim 0.48$ J/m$^2$ is calculated for Au NCs on
TiO$_2$ (110) surface steps. This value is smaller than that for Au NCs on flat TiO$_2$ (110) surfaces, which explains the stability of the interface.

To examine the heterogeneous interface in three-dimensions, we further developed the depth-sectioning technique using STEM. Using this, we obtained conclusive evidences of interfacial Au atoms formed on the rutile (TiO$_2$) (110) surfaces by activation using high temperature (~500$^\circ$C) annealing in air. Results show that the interface between Au nanocrystals and TiO$_2$ (110) surfaces consists of a single atomic layer with Au atoms embedded inside the Ti-O plane. The number of interfacial Au atoms is estimated from ~1 to 8 in an interfacial atomic column. Direct impact of interfacial Au atoms is observed on an enhanced Au-TiO$_2$ interaction and the reduction of surface TiO$_2$.

To determine the TiO$_2$ surface structure and interface oxidation state, we performed atomic resolution imaging of the Au/TiO$_2$ (110) interface using both annular bright field (ABF) STEM and chromatic aberration ($C_c$) corrected TEM. Direct interpretable images of oxygen columns are achieved, together with gold and titanium atomic columns. We located the bridging oxygen atoms on the surface and at the interface, and observed interfacial oxygen vacancies as well. Interfacial Au atoms near the vacant oxygen atomic column are seen shifting downwards, indicating a stronger Au-Ti bonding where oxygen is reduced. These experimental results suggest that Au NCs on TiO$_2$ promote interfacial restructuring, reduction of the oxide surface and stabilization of the NCs by pinning metal atoms onto the oxide surfaces, all critical to catalysis.

To explore the scientific opportunities provided by fast imaging in environmental TEM, two studies have been carried out, including the behavior of Au catalyst on top of Si nanowires in heating environment, and the transformation of Pt icosahedral NPs in
reactive gases. Upon heating the Au NP on a Si nanowire, we captured the initial kinking of the Au NP and the following atomic diffusion of Au on Si NW surface. In reactive gases, the catalytic Pt icosahedral NPs transform into a FCC single crystal. We captured the dynamics employing both chemical triggering and collective atomic motion. In both studies, the processes were monitored using a fast electron camera at 2.5 ms time resolution. The results provide critical insights to nanoparticle catalyst behaviors with improvement in both time resolution and spatial resolution.
To my families.
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TABLE OF CONTENTS

CHAPTER 1: INTRODUCTION

1.1. Objectives

1.2. Experimental Approach

1.3. Background and Motivations

1.3.1. Au NCs supported on Metal Oxide Surface

1.3.2. Pt NPs for Oxygen Reduction Reaction

1.4. Organization of This Thesis

1.5. References

CHAPTER 2: HIGH RESOLUTION TRANSMISSION ELECTRON MICROSCOPY AND SCANNING TRANSMISSION ELECTRON MICROSCOPY

2.1. Transmission Electron Microscopy

2.1.1. Basic Principles

2.1.2. High Resolution Electron Microscopy (HREM)

2.2. Scanning Transmission Electron Microscopy

2.2.1. Image Formation in STEM

2.2.2. Probe Formation and Lens Aberrations

2.2.3. Aberration Correction

2.2.4. Contrast Mechanisms in HAADF STEM

2.2.4.1. Intensity of HAADF STEM Images from Kinematic Scattering
CHAPTER 5: OXYGEN STATE CHANGE IN THE INTERFACE OF GOLD NANOCRYSTAL SUPPORTED ON RUTILE SURFACE

5.1. Introduction...............................................................91
5.2. Experimental............................................................93
5.3. Results...........................................................................93
5.3.1. Interfacial States of TiO₂..............................................95
5.3.2. Interfacial Spacing.....................................................98
5.3.3. Interfacial Energy......................................................100
5.4. Conclusions..............................................................102
CHAPTER 6: SCIENTIFIC OPPORTUNITIES IN ENVIRONMENTAL ELECTRON MICROSCOPY USING FAST ELECTRON DIRECT DETECTION CAMERA

6.1. Au Nanoparticle Kinking and Au Atomic Diffusion on Si Nanowire

6.2. Transformation of Pt Icosahedral Nanoparticles into FCC Single Crystal

6.3. References

CHAPTER 7: CONCLUSIONS AND FUTURE PERSPECTIVES

7.1. Conclusions

7.2. Future Perspectives

7.3. References
Nanoparticles made of noble metals are important catalysts in major industries. For example, Pd-Au bimetallic catalysts are used to treat diesel engine exhaust gas by Fiat[1]. The same material is used by DuPont to treat ground water (to transform organic chlorinated compounds) in USA. Au NPs with the support of PET (polyethylene terephthalate) nonwoven fabric and alumina woven mash are used to purify air in Japan [2]. Oxide supported Au NPs are also employed in commercial plants to produce methyl methacrylate [3]. The opportunity and possibility that can be brought by metal nanoparticle catalyst are thus extensively discussed in literature; research focusing on the preparation and installation methods and their applications to various other fields, such as electronics, optics and medical diagnosis continues to attract large interest.

1.1. Objectives

A major part of this thesis describes a body of work carried out in a research project that was designed to address the following major questions associated with metal NPs catalysis using the model system of Au NPs supported by rutile (TiO$_2$) surface:

1) What is the equilibrium crystal shape in 3D for NPs down to nanometer scale?

As commonly accepted, the 3D equilibrium crystal shape is determined by minimizing the surface and interface energies. This is obtained by using the Wulff construction or modified Wulff construction (Wulff-Kaishew theorem) for isolated and supported metal NPs, respectively. Without interfacial strain, the Wulff-Kaishew theorem predicts self-similarity of equilibrium crystal shapes regardless
of crystal sizes. In nanometer scale, is this theorem kept or influenced by the atomic structure and interaction?

2) What is the surface and interface energy of supported NPs?

Assuming that the surface and interface are uniform as in liquids or perfect crystals, the energy cost in creating a surface or interface is quantified as the surface and interfacial energy. With surface roughness, the surface is usually regarded as a new plane with different orientation in large scale to calculate the surface energy. For metal NPs, within a few nanometers, the surface roughness only gives one or very few atomic steps, while the other parts are still flat. Then what is the modified interfacial energy? Does this correlate more to the energy of flat interface or to the atomic step defect?

3) What is the reconstructed interfacial structure at atomic scale?

Widmann et al. reported that the reducible interfaces could provide moving oxygen and oxygen vacancies to facilitate the reaction of selective oxidation of CO as well as stabilizing the Au NCs [4]. The local oxidation state could be examined if oxygen atoms could be detected and imaged. Once the atomic structure is determined with information about oxygen atom locations, the effect of reducible surface during reaction could be better understood. If oxygen vacancy is created at the interface, what is the reconstructed interfacial structure then? And how does this influence the Au atoms from the NP close to the interface.

4) How does the reconstructed interface affect the free energy?

With DFT calculation, interfacial energies and interfacial spacing could be
computed for different oxidation states and with different atomic registry in the Au/oxide interface [5]. Experimentally with various structures observed, the interfacial spacing could be directly measured and interfacial energies calculated. Comparing the values with theoretical calculation could provide insights about the structural properties.

The other part of this thesis is to observe the structural behaviors of metal NPs under reactive environment. The questions we seek to address are how do the structure of catalytic nanoparticles change and under what conditions during chemical reaction. The NPs we choose to study is Au NPs on Si nanowires, and Pt icosahedral NPs. Au NPs are used as catalyst to grow Si nanowires. It is found that change of growth conditions like temperature and pressure will lead to change of the nanowire morphology. Observation on the behavior of Au NPs on Si nanowires at different temperature therefore brings insight on the physics behind the phenomenon. The Pt icosahedral NPs belong to a class of structures called multiple-twinned particles (MTPs). MTPs attract special interest in nanoscience and technology because of their unusual atomic packing, non-crystallographic symmetry and outstanding catalytic activity for oxygen reduction reaction (ORR). Large MTPs can be grown from small seeds under controlled conditions [6, 7]. However, they are unstable compared to the bulk FCC structure [8-10], at certain condition, the MTPs will transform to FCC crystals, the transformation mechanism remains controversial.

1.2. Experimental Approach

To achieve the above objectives requires new developments in experimental characterization techniques. To obtain structural information of the NP and at the interface, 3D imaging and light atom detection (for oxygen) are needed. In electron microscopy,
atomic resolution imaging is obtained using (scanning) transmission electron microscopy (S)TEM, thanks to recent progress in aberration correctors[11-20]. However, these images are 2D projections; constructing 3D structure from the projected images is still a major challenge. A popular imaging technique in studying interfacial structures is cross-sectional Z-contrast imaging. (Details of image contrast mechanisms are discussed in Chapter 2.) This technique is extremely useful in improving image contrast in examining the interface between light and heavy materials, because of the Z-dependent chemical contrast. The use of aberration corrector also provides large convergence angle in forming a sharp electron probe. This large angle significantly reduces the depth of focus of the probe, which enhances the sensitivity in detection of atom positions along beam direction. Thus it is possible to reconstruct the 3D atomic structure from 2D image series acquired at different focus, which shares the same principle as the 3D tomography using depth sectioning in optical microscopy[18, 21-24].

The other challenge in revealing the atomic structure comes from the deficiency for Z-contrast to detect light atoms. Because of the weak interactions between light elements and electrons, the scattered electrons can hardly be collected by high angle annular dark field (HAADF) detector for Z-contrast imaging. For the same reason conventional TEM imaging cannot efficiently image oxygen atoms due to the deficiency of information transfer. Thus it is difficult to characterize oxygen atoms at the interface. This obstacle is recently overcome by the development on annular bright field (ABF) detector in STEM and chromatic aberration (C\text{c}) correction in TEM. With ABF detector collecting electrons scattered to lower angles to image light elements and C\text{c} correction enhancing the contrast transfer in high resolution electron microscopy (HREM), both techniques are capable to
image light elements at atomic resolution (details in the results chapters)[16, 25, 26].

While atomic structures can be imaged using advanced electron microscopy, capturing dynamic processes of NP catalyst requires \textit{in situ} TEM study with a gas or liquid atmosphere introduced into the sample chamber and a heating stage to control the temperature. This function is realized using specially designed differential pumping systems equipped on the environmental TEM (E-TEM) along with a heating tungsten wire to hold the nanoparticles[27]. The TEM sample thus can be directly exposed to the electron beam under different gas environment at selected temperatures.

The structural dynamics of nanoparticles usually involve processes taking place and lasting for only several msecs or even shorter time. Capturing this fast process is beyond the capability of normal TEM camera. Using a new generation camera with more sensitive detector, shorter exposure time and faster processer, the time resolution is improved to above msec, which enables the high speed high resolution imaging of particle during chemical reaction[28].
1.3. Background and Motivations

![Volcano plot correlating catalytic activity for H2 oxidation (temperature for 50% conversion) and the strength of the metal-oxygen bond (redrawn after ref[29]).](image)

**Figure 1.1. Volcano plot correlating catalytic activity for H2 oxidation (temperature for 50% conversion) and the strength of the metal-oxygen bond (redrawn after ref[29]).**

The catalysts we studied are supported Au NCs and Pt icosahedral NPs. The catalytic activity of metal NPs has different origins. For Pt and Pd NPs, active atoms locate on the low coordination sites; exposing surfaces and facets with such sites by controlling the shapes and sizes are thus important [30-33]. One example is the recent work on icosahedral Pt NPs with only \{111\} surfaces, which demonstrated to enhance the activity for oxygen reduction reaction (ORR) [6]. Au, which was long believed to be inert in chemical reactions, surprisingly shows catalytic activity when made into different forms including Au clusters having only a few atoms[34, 35], nanoporous Au sponge[36], and supported Au NPs[29, 37-39]. The catalytic behavior of Au clusters with only a few atoms is attributed to their properties in co-adsorption of reactant molecules[34, 35]. While the nanoporous Au catalysis is proposed to share the same mechanism as supported Au nanoparticles[40]. This is because the residual Ag left on the surface during synthesis can be oxidized to AgO.
clusters during catalytic reaction, which is inversely supported by Au and forms a new heterogeneous metal-oxide interface. Figure 1.1 shows the activity of different metal oxide catalysts plotted in terms of temperature for 50% conversion ($T_{1/2}$) of 1.0 vol% hydrogen in air at an hourly volume speed of 2E4 h$^{-1}$mL (g cat.)$^{-1}$ and the enthalpy of metal oxide formation per gram-atom of oxygen[29]. The enthalpy indicates how strong the metal-oxygen bond is[41, 42]. Lower $T_{1/2}$ represents higher catalytic activity. On the right of the volcano, the activity drop due to stronger bond between metal and oxygen slows the rate of oxygen donation from metal oxides. On the left, the very weak metal-oxygen bond slows the oxygen uptake process from the gas phase, thus limits the oxidation rate. Au has the weakest bond with oxygen in Figure 1.1. Thus, by preparing metal oxide supported Au NPs, the combined system then inherits both the strong metal-oxygen bond to fast uptake oxygen from gas from the support and the weak one for higher rate of oxygen donation by Au. Using this principle, the supported Au NPs could theoretically be made catalytically very active.

**1.3.1. Au NCs supported on Metal Oxide Surface**

Au NCs supported on oxide surface can be prepared by coprecipitation, co-sputtering and alloying of Au and the metal component of the support [43, 44], or by deposition of Au/Au compounds on oxide supports [19, 44]. With Au NPs smaller than 5 nm in diameter on metal oxides, such as TiO$_2$, MgO, Fe$_x$O$_y$ and CeO$_2$, it is found that the catalytic activity is significantly enhanced [37, 38]. Especially, Au/TiO$_2$ catalysts are remarkably active in selective oxidation of CO to CO$_2$ at 203 K [29]. This discovery attracted fundamental interest in research as well as from industry, because to build products with higher efficiency and reduced environmental pollution is always the ultimate goal in market for
lower energy cost and cleaner processes. Before Au NPs were used, supported Pt and Pd NCs were employed as the major catalysts in automobile emission systems. The lower activity of Pt group catalysts for CO oxidation below 473 K leads to the “cold start-up” issue with excessive CO exhaustion due to incomplete fuel combustion [45]. The low temperature working condition for supported Au NPs makes them perfect substitutes to eliminate CO in the emission system. It is also brought to the attentions that converting CO into CO$_2$ helps avoid poisoning the electrodes for fuel cell applications using methanol or hydrocarbons. Besides, supported Au NPs are found to be active in catalyzing selective epoxidation of propene[46], ethyne hydrochlorination[47], etc.

Understanding the mechanism in catalytic activity of supported Au NPs is therefore benefiting in applications as well as finding new scientific principles to create more active catalysts. The studies on supported Au NC catalysis have been reviewed extensively [29, 37, 42, 47-53]. From these studies, the uniqueness of supported Au NPs lies on its nature of heterojunction. The formation of a heterogeneous interface brings not only the advantages of both Au and the support, but also the more important support effects. These effects could influence the support and the NPs in multiple ways.

One effect is that the metal – support interaction could change the atomistic structures of nanoparticles. The structures of NPs are critical for their catalytic properties. The proposed active sites involves atoms at the corners, vertex, and near the interface; their availability largely depends on the shape and structure of nanoparticles [31-33]. Extensive fundamental research has been performed on metal nanoparticles [8, 9, 54-58] and shown that the equilibrium shapes of large metal nanoparticles are governed by the principles of surface/interface energy minimization. For isolated metal NPs, the shapes are in the form
of Wulff construction [54], with supports, the interaction changes the surface energy into interfacial energy and thus the shape of NPs are truncated into Winterbottom construction [55]. When supported by imperfect surfaces, the surface defects will also limit the mobility of NPs and introduce defects, such as twin boundaries, in the NPs. Twin boundaries themselves in isolated NPs are also not uncommon [8, 9, 56-58]. This modification of NP shapes and structures thus could change the catalytic activity related to sites with different coordination.

One other important effect is that the state of interface could be changed and deviates significantly from the original surface structure of the support. Widmann proposed that the reducible interfaces could provide moving oxygen and oxygen vacancies that are necessary to enhance the reaction rate and stabilize the Au NCs [4]. In DFT calculation, different oxidation states in the Au-TiO$_2$ interface result in various interfacial spacing and energy [5], which directly influence the stability of the system. More evidence that highlighted the role of interface in catalysis is reported by Tadahiro Fujitani, who studied the H$_2$-D$_2$ exchange reaction catalyzed by Au NPs on TiO$_2$ (110) surfaces [59]. In Figure 1.2, the rate of HD formation by catalyst increases exponentially when the diameter of Au NPs decreases. The turnover frequency, on the other hand, remains a constant value, meaning that the rate of HD formation per perimeter gold atom shows no dependence on the diameter of the gold NPs. This further illustrates that the rate of reaction catalyzed by Au is proportional to the length of perimeter. Atoms near the perimeter are thus possible active locations for hydrogen dissociation[41].
Figure 1.2. Rates of $\text{H}_2$-$\text{D}_2$ exchange on $\text{Au/TiO}_2$(110) model catalysts as a function of the mean diameter of gold nanoparticles (redrawn from ref[59])

In studies on the effect of NC structures and interfaces on catalyst, electron microscopy has shown promising capability to provide detailed structures at atomic resolution with valuable information that other techniques can hardly offer [48]. From TEM images of Au/CeO$_2$ multilayers, Zhou et al demonstrated a remarkable scaling relationship between the length of the Au-CeO$_2$ interface and the CO oxidation reactivity[60]. In revealing the surface and interface structure, Shibata et al demonstrated a success in imaging the reconstructed TiO$_2$ (110) surface and Au/TiO$_2$ interface induced by electron beam. For reaction dynamics, Kuwauchi [39] et al captured the body shift and rotation of Au NC on oxygen terminated CeO$_2$ surface in reactive gas using in situ environmental TEM.

These observations using electron microscopy are beneficial in that upon determining
the interfacial structure and capturing the reaction dynamics, information like heat of formation, strain, electronic structures and their evolution during reaction could then be clear. An image relating the structure to the catalytic activity could then be made possible.

1.3.2. Pt NPs for Oxygen Reduction Reaction

Reducing oxygen gas in an acidic environment is a major step in fuel cell using oxygen and hydrogen. Electrocatalysts for oxygen reduction reaction (ORR) therefore play a crucial role in developing cost effective proton exchange membrane fuel cells. Recent exploration has resulted in various types of electrocatalysts including metal and alloy nanocrystals [61], perovskite [62], carbon-based materials [63], transition metal oxide, carbide [64], transition metal chalcogenide [65] and macrocyclic compound [66, 67]. Pt based nanoparticles are among the most practical materials for use in strong acidic media thanks to the high activity and stability. Theoretical calculations on Pt nanoparticles indicate that specific types of surface structures, alloying with non-Pt metals and strain could all contribute to enhancement of the activity [7, 68, 69], by facilitating the adsorption of oxygen gas molecules, scission of O-O bonds on the surface, and formation of surface-absorbed hydroxyl groups. Pt alloy NCs of different sizes, shapes and compositions are then made in order to meet the requirements for optimized properties. It has been reported that Pt alloy icosahedral NPs, especially Pt$_3$Ni with sizes of 15 - 36 nm, with {111} enclosure surfaces demonstrate largely improved ORR area activity and mass activity comparing to others[7]. The strain on the {111} facets induced by multiple twin boundaries in icosahedral symmetry is believed as the major factor that leads to the improvement. However it is found that under a certain circumstances the icosahedral structure will be lost during ORR. It is thus intriguing to study the shape and structure evolution of Pt and Pt
alloy icosahedral NPs to help better understand the reaction dynamics, which might further help improve the design of fuel cell electrocatalysts.

As the icosahedral NPs each has 20 identical FCC single crystal tetrahedrons with their faces joint, the system also provides an ideal model for study on grain growth in polycrystalline metals and alloys. Observing how the twin boundaries and grain boundaries change could provide informative insight on several important questions in materials science, including grain boundary migration, grain growth, and icosahedral phase transformation.

1.4. Organization of This Thesis

In what follows, we describe an electron microscopy based approach to the characterization of the atomic structure of nanoparticles, their interfaces and the in situ study on nanoparticle behaviors. Results are presented after Chapter 2 on introduction of basic concepts and operations in (S)TEM. Chapter 3 is quantification of the epitaxial relationships of Au NCs supported on stepped TiO$_2$ (110) surfaces with different miscut angles, their equilibrium shapes, interfacial geometries, strain and a measurement of the interfacial energy using selected NCs supported on low miscut TiO$_2$ (110) surfaces. This is followed by Chapter 4 reporting on the observation of interfacial Au atoms embedded inside the TiO$_2$ surface. Quantitative study on the numbers of Au atoms and their locations in 3D is shown in details which could be fitted with theoretical results reported by simulation groups. In Chapter 5, we represent the detection of interfacial oxygen atoms, determination of oxygen states at the interface, and discussion on the influence of different interfacial state on the Au NPs’ shape and interfacial energy. In Chapter 6, using the newly developed fast in-situ electron microscopy, we report the success in observation of Au NP
kinking and Au diffusion on the surface of Si nanowires, as well as observing the transformation of large Pt icosahedral (Ic) nanoparticles (36 nm in diameter) into FCC single crystal after exposing to partial oxygen pressure at elevated temperature. Our microscopy data at 2.5 ms time resolution provides new insights into nanostructure behaviors that are critical to many areas of materials science. Conclusions are in Chapter 7 along with discussions on future perspectives.
1.5. References


http://www.gatan.com/products/tem-imaging-spectroscopy/k2-camera


CHAPTER 2

HIGH RESOLUTION TRANSMISSION ELECTRON MICROSCOPY AND
SCANNING TRANSMISSION ELECTRON MICROSCOPY

Transmission electron microscopy is a major characterization tool for materials research. The microscopy resolution in general depends on the radiation wavelength. For optical microscopes, the resolution as defined by the minimum distinguishable distance is diffraction limited to $0.61\lambda/NA$, where $NA$ is the numerical aperture and $NA=\sin\theta$ in air. For the optical wavelength $\lambda = 550$ nm and $\sin\theta = 1$ for a large numerical aperture, the resolution is about 336 nm. To resolve structures smaller than this requires techniques using a smaller wavelength. The invention of transmission electron microscopes (TEM) thus came from this idea by employing electrons with a short de Broglie wavelength. For example, when accelerated to 200 keV in energy, the electron wavelength is 0.0025 nm [1-3].

In a conventional TEM, the resolution of ~0.2 nm is achieved at the 200 kV acceleration voltage, which is much larger than the 0.0025 nm wavelength. The resolution is limited by the lens aberrations and the small numerical aperture to work with these aberrations. Recent development of aberration correction has significantly improved the resolution to sub-angstrom (<0.1 nm) in high resolution electron microscopy (HREM). In scanning transmission electron microscopy (STEM), the use of aberration correctors enables the formation of a sharp electron probe of less than 0.1 nm in diameter. By using a high-angle annular dark field (HAADF) detector, electrons scattered to high angles can be collected and used to form images of atomic columns with intensity depending on the atomic number ($Z$) [4]. When equipped with energy dispersive spectrometer (EDS) and
electron energy loss spectrometer (EELS), the sub-angstrom probe makes it possible to acquire quantitative information from an atomic column related to its composition, thickness and electronic structure.

In this chapter, the basic concepts and principles of TEM and STEM are first provided, with discussions on TEM and STEM image formation. Aberration correction and its impact on electron microscopy are briefly described. The focus is on HAADF-STEM and HREM, since both are major tools employed in the experimental studies described in this thesis.

2.1. Transmission Electron Microscopy

2.1.1. Basic Principles

Figure 2.1(a) shows the schematic of electron optics in a TEM. Electrons are emitted from either a thermionic electron source or a field emission gun, and accelerated by DC electric field to 60–300 keV in energy. The electron beam is then focused by electromagnetic lenses. A group of condenser lenses located above the specimen and after the electron gun make up the illumination system. Together, they are used to converge and spread the beam in order to control the electron illumination on the sample. A condenser lens aperture helps to remove electrons propagating at high angles that experience the most significant lens aberrations and to control the beam angle as well as to make a parallel beam. Within the illumination system, there are a group of coils used as deflectors to shift and tilt the electron beam [5].

In a modern TEM, the sample area is placed inside the objective lens; the field above the sample acts as the final condenser lens in STEM, while the field below is used to form images in TEM. Both the image resolution and the smallest probe that can be formed are
limited by the aberrations of the objective lens in an uncorrected TEM. The dominant objective lens aberration is the spherical aberration ($C_s$). After the first image formed by the objective lens, intermediate and projector lenses placed after the objective lens further magnify the image in the image mode and project the image onto the viewing screen or an electron camera. In diffraction mode, the intermediate and projector lenses project the image at the back focal plane (BFP) of the objective lens onto the screen, thus form diffraction patterns.

Figure 2.1. A schematic of the TEM components (a) and the ray diagram (b) of electron paths in objective lens area.

Figure 2.1(b) shows the function of the objective lens in a ray diagram that illustrates the electron illumination and formation of the diffraction pattern at the back focal plane and image at the selected area aperture plane. When a parallel electron beam is transmitted through crystalline materials, parallel crystal planes of different orientations diffract the
electrons to certain distinct angles defined as Bragg angles in the so-called Bragg reflection. These electrons travelling along the same direction then converge to the same point in the BFP of the objective lens. This process is shown by the ray paths in Figure 2.1(b). In diffraction mode, this plane is magnified and projected to the screen. Beneath the BFP, the electrons from the same object point converge to the same point in the image plane of the objective lens. This is the plane being used for the selected area aperture.

An objective aperture can be inserted in the BFP in imaging mode. When the aperture is centered to allow only the central beam to pass through, bright field (BF) images are formed. When only the direct beam is used for imaging, the image shows diffraction contrast, where areas diffracting strongly appear dark. When the aperture selects one or several of the diffracted beams for imaging, dark field (DF) images are formed. In a DF image, areas that diffract electrons strongly in the selected directions appear bright. For HREM, a large objective aperture is used to select several beams to allow the interference among the direct and diffracted beams. The interference offers the lattice images or atomic resolution images under favorable imaging conditions.

In diffraction mode, a selected area aperture located in the objective lens image plane is sometimes used to select a certain area of the sample to form a diffraction pattern, which is the so-called selected area electron diffraction (SAED). Sharp diffraction spots will form when the illuminating electron beam is parallel. When illuminated with a convergent beam, convergent beam electron diffraction (CBED) patterns are formed with diffraction disks instead of sharp diffraction spots, these disks show intensity variations inside. The intensity variation carries detailed structural information about the sample. By changing the beam convergent angle and beam size, different disk sizes and areas of different sizes can be used.
to measure structure factors as well as the sample thickness [6, 7].

2.1.2. High Resolution Electron Microscopy (HREM)

To form atomic resolution images in HREM, thin specimens must be aligned along a major zone axis orientation. The electron beam is parallel to the optic axis, so the electron wave function can be described as a plane wave, $\psi_0(r)$. The electron interaction with a thin specimen modifies the electron wave function, which is described by the specimen transmission function ($T$). The wave function of electrons exiting the specimen is then:

$$\psi_{\text{exit}}(r) = T[\psi_0(r)]$$

which is called the electron exit wave function. This exit wave function is then imaged by the objective lens. In an electron electromagnetic lens, two major aberrations exist, the chromatic aberration ($C_c$) and spherical aberration ($C_s$). With the chromatic aberration, electrons of different energy are focused to different planes. With the spherical aberration, the off-axis electrons experience a stronger magnetic force than the center electrons and are deflected more strongly. This results in focusing the off-axis electrons at a plane before the imaging plane for electrons close to the optical axis. The lens aberrations modify the electron wave function. The result is an angle dependent phase shift, which can be described by the Fourier components of the wave function formed at the BFP of the objective lens:

$$\psi_t(k) = \psi_{\text{exit}}(k) \exp(-i\chi(k)) = \psi_{\text{exit}}(k) P(k),$$

here $k$ is the electron wave vector in the reciprocal space, $\psi_t(k)$ is the wave function at the BFP, $\psi_{\text{exit}}(k)$ is the Fourier transform of the exit wave function and $\chi(k)$ is the phase introduced by lens aberrations. Without aberration corrector, $\chi(k)$ can be written in:
\[ \chi(k) = \chi_s(k) + i\chi_c(k), \]

\[ \chi_s(k) = \pi\lambda k^2 \left( \frac{1}{2} C_s \lambda^2 k^2 + df \right), \]

\[ \chi_c(k) = -\frac{1}{2} (\pi\lambda \Delta_E)^2 k^4, \]

where \( \chi_s(k) \) describes the effect of spherical aberration, \( df \) is the lens defocus, \( \chi_c(k) \) is the chromatic aberration, \( C_s \) is the spherical aberration coefficient, and \( \Delta_E \) is the spread of electron energy. The energy spread comes from the electron source, the interaction with specimen, and the instability of high voltage and objective lens current:

\[
\Delta_E = C_c \left[ \left( \frac{\Delta E}{V_{accelerate}} \right)^2 + \left( \frac{\Delta V_{accelerate}}{V_{accelerate}} \right)^2 + 4 \left( \frac{\Delta I_{obj}}{I_{obj}} \right)^2 \right]^{1/2}.
\]

Therefore the quality of HREM images can be improved by using a stable electron source, by improving the stability of high voltage and lens current and by using thinner specimen or using an energy filter.

The electron wave function at the BFP of the objective lens then propagates to the image plane, which is the inverse Fourier transform of the wave function at BFP. The intensity of the image recorded equals the squared complex amplitude of the wave function:

\[
I_{HREM}(r) = |FT^{-1}(\psi_i(k))|^2 = |FT^{-1}(\psi_{exit}(k) P(k))|^2 = |\psi_{exit}(r) \otimes P(r)|^2,
\]

where \( P(r) \) is the point spread function (PSF) in HREM. The PSF is affected by lens aberrations and defocus. With a thin specimen, the convolution of the exit wave function with the PSF results in a broadening effect. The resolution of images in HREM is thus determined by the PSF. For a conventional TEM at 200 kV, the resolution could be better than 0.2 nm, and with image corrector, it could be improved to better than 0.1 nm.
2.2. Scanning Transmission Electron Microscopy

In STEM, an electron probe is formed by converging the electron beam on the sample using the condenser lenses, including objective lens pre-field [5]. The probe is rastered over a selected area of the sample, as shown in Figure 2.2. Either the transmitted or scattered electrons are detected for bright field or dark field image formation. The image magnification is determined by the scanned area, instead of the lens magnification as in TEM. The pixel intensity in a STEM image is the collected signal from the detector during the acquisition time while the probe was at a given sample position. The acquisition time is called the dwell time. When an electron energy loss spectrometer is used to detect the electrons, different loss mechanisms can be distinguished, enabling both composition analysis and the study of local electronic structures.

In this section, the principles of STEM image formation are first introduced, followed by discussions on probe formation, the limit of the spherical aberration, and aberration correction in the effort to overcome this limitation. The incoherent imaging mechanisms for Z-contrast using a HAADF detector in STEM are discussed at the end.

![Fig 2.2. Principles of STEM HAADF and BF imaging](image)
2.2.1. Image Formation in STEM

The formation of an electron probe in STEM is enabled by the pre-field of the objective lens, which images the crossover formed by the condenser lenses with a large demagnification [5]. The probe is aligned to be parallel to the optical axis at each point when scanning over the sample. This function is realized by pivoting the beam at the front focal plane (FFP) of the objective lens (Figure 2.3(a)) by using the double deflection coils above the upper pole piece of the objective lens. At each scanning point, a stationary CBED pattern is generated in the BFP of the objective lens, as shown in Figure 2.3(b). To collect the electrons diffracted to different angles, the STEM detectors work in the diffraction mode and select parts of the CBED pattern. By using different parts of the diffraction pattern to form a real space image, information related to different aspect of electron scattering can be acquired. A semiconductor device or a scintillator-photomultiplier type detector is used as the STEM detector, the latter is very sensitive and capable of single electron detection.

In STEM BF imaging, a small disk detector is centered on the optical axis. The size of the detector is chosen to cover only the central part of the CBED pattern[5]. By using a large condenser aperture to form the electron probe, the CBED disks overlap, the BF detector could thus collect both the central disk and the overlapping diffraction disks. The image contrast in this condition is equivalent to HREM image contrast from the principle of reciprocity[8]. STEM BF images are thus coherent phase contrast images[8, 9]. When the center beam is blocked by a beam stopper, the bright field detector is converted into the so-called annular bright field (ABF) detector, which provides the possibility to image light elements like oxygen and hydrogen[10, 11].
Annular dark field (ADF) imaging uses an annular detector, which has a hole in the middle of the detector and is centered on the optical axis (Figure 2.2). This detector collects electrons scattered to the detector with inner and outer cut-off angles, which are determined by the detector geometry. With electrons passing through the center detector hole, the BF image can be acquired simultaneously with an ADF image. The ADF detector is designed with large inner and outer cut-off angles, when used at a large camera length, it serves as the high-angle annular dark field (HAADF) detector, which collects electrons scattered to high angles by the sample. At the high angles, the electrons are mostly scattered by phonons, which are less coherent and diffraction contrast is thus minimized by averaging the signal over the detector area. Incoherent imaging with characteristic intensity dependence on atomic number (Z) is thus obtained, which is the so called Z-contrast.
2.2.2. Probe Formation and Lens Aberrations

In the incoherent imaging mode, the resolution of STEM is determined by the size of electron probe. The probe size is limited by diffraction from the aperture and spherical aberration in the probe forming lenses[12]. To form an electron probe, a circular aperture is used to limit the passing of a convergent beam. The result is an Airy pattern in the objective plane[12] in the diffraction limit. The Airy pattern has a central maximum with concentric side lobes. The diameter of the first minimum of the Airy pattern

\[ \delta_D = 0.61 \frac{\lambda}{\alpha} \]  \hspace{1cm} 2.2.1

is then defined as the size of the probe. In Equation 2.2.1, \( \alpha \) is the convergence semi-angle of the electron beam. To form a smaller probe and achieve better resolution in STEM therefore requires a larger convergence angle. The aperture, however, cannot be too large, because high angle electrons experience significant lens aberrations. Similar to HREM, the effect of lens aberrations in STEM introduces a phase shift to the incident electron wave function for a conventional objective lens,

\[ \chi(\alpha) = \frac{2\pi}{\lambda} \left( \frac{1}{4} C_s \alpha^4 - \frac{1}{2} df \alpha^2 \right). \]  \hspace{1cm} 2.2.2

This results in broadening of the electron probe. By changing the defocus, \( df \), to minimize the phase shift, the possible smallest probe size is then

\[ \delta_0 = 0.43C_s^{1/4}\lambda^{3/4}, \]  \hspace{1cm} 2.2.3

when \( \alpha = \left( \frac{4\lambda}{C_s} \right)^{1/4} \), without aberration correction. To further improve the resolution of STEM then requires the lens aberration correction.
2.2.3. Aberration Correction

Two major aberrations limit the performance of magnetic round lenses, chromatic aberration and spherical aberration[13]. Chromatic aberration originates from electrons with different energy in an electron beam, which are focused in different planes by the objective lens. This is one of the major limiting factor in HREM however not in STEM[14]. Spherical aberration originates from the stronger magnetic field away from the lens center. The off axis electrons are therefore deflected more strongly than electrons travelling along the optical axis. This results in the off axis electrons being focused at an earlier plane than the central part. As shown in Figure 2.4, a point in the object is not focused into a point on the same plane, but forms a disk defined by the envelope of all the electron rays. The smallest disk is called the disk of least confusion, whose radius $\delta_s$ is defined by [12]

$$\delta_s = \frac{1}{4} C_3 \alpha^3$$  \hspace{1cm} 2.2.4

where $C_3$ is the third order spherical aberration coefficient. The aberration coefficient is always positive in round lens. In STEM, the probe size is limited by the spherical aberration as well as by the probe forming aperture, as discussed above. From Equation 2.2.4, a smaller probe could benefit from a smaller convergence angle, which offsets the advantage of using a large convergence angle in the diffraction limit. It is thus necessary to correct the spherical aberration to achieve the smallest possible electron probe with the largest convergence angle. Current designs of aberration corrected S/TEM compensate the aberration by using multipole magnetic lenses, for example, hexapole lenses, that produce negative spherical aberration. The combination with the positive aberrations from the objective lens then results in a zero spherical aberration. So far, two types of aberration correctors have succeeded, which are the so-called quadruple-octupole corrector and the
hexapole corrector [13, 15, 16]. With the aberration corrected, the electrons are more precisely brought to a common focus.

Figure 2.4. The ray diagram of electrons focused by a lens with spherical aberration. Electrons travel through outer parts of the lens away from the optical axis will be focused at earlier plane.

The components and ray diagram of electrons in an aberration corrector made of hexapoles (sextupoles) are shown in Figure 2.5. The corrector consists of a telescopic round-lens doublet and two sextupoles. Incorporating multipole elements brings extra aberrations into the electron optics. To minimize these aberrations requires symmetric configuration of the electromagnetic fields and paraxial trajectories, since higher degree of symmetry cancels more aberrations. This is achieved by placing the identical multipole elements symmetrically with respect to the mid-plane of the corrector. The elements can be excited symmetrically or anti-symmetrically with respect to the planes. In Figure 2.5, one sextupole locates at the front focal plane of the first lens and the other at the back focal plane of the second lens. These focal planes are conjugated and they image the first sextupole with magnification \( M = -1 \) onto the second sextupole. This configuration cancels
out all second-order path deviations introduced by the first sextupole. The remaining is third order aberrations of the same nature as those of round lenses, while with negative sign. This negative spherical aberration is proportional to the square of the sextupole strength. The corrector therefore can compensate the spherical aberrations of the round lenses.

**Figure 2.5.** Arrangement of the sextupole corrector and the objective lens by means of a telescopic transfer doublet resulting in an electron optical aplanat. (redrawn after [16].)

The use of aberration corrector brings the possibility of forming an electron probe with a large aperture in STEM; sub-angstrom resolution STEM imaging can therefore be achieved [17]. The large convergence angle also provides stronger beam intensity and shorter depth of focus[18-22]. With the probe size being comparable to atoms, it is also possible to identify chemical compositions at atomic resolution using energy dispersive spectra or electron energy loss spectra. In TEM mode, aberration correction provides better control of contrast transfer function and higher signal noise ratio, which enables the
imaging of light elements, such as oxygen atoms in oxide materials [23].

2.2.4. Contrast Mechanisms in HAADF-STEM

The advantage of HAADF STEM is its contrast sensitive to Z and its nature of incoherent imaging. The definition of incoherent imaging originates from self-luminous objects. In 1896, Lord Rayleigh proposed that illuminating a sample over a wide range of angles could make the sample effectively a self-luminous object[24]. Therefore no interference between radiation from different parts of the object could take place[4]. The image formation is thus an incoherent process. The intensity of the image can be described as a convolution[4]:

\[ I_{\text{incoherent}} = |P'(r)|^2 \otimes |\psi(r)|^2 \]

where \( P'(r) \) is the probe function and \( \psi(r) \) is the object potential function.

In HREM, a parallel beam is employed to illuminate the sample. The image intensity given in Equation 2.1.7 is \( I_{\text{HREM}}(r) = |\psi_{\text{exit}}(r) \otimes P(r)|^2 \). This is the equation for coherent imaging, which can be written as

\[ I_{\text{coherent}} = |P(r) \otimes \psi(r)| \cdot |P^*(r) \otimes \psi^*(r)|. \]

In HREM the phase of the point spread function could change rapidly at different focus and the phase of exit wave function is influenced by the sample thickness. The contrast reversals with different focus and sample thickness are frequently observed. In incoherent imaging, this relationship does not apply.

In this section, to illustrate the contrast mechanism in HAADF STEM, we considered three parts of electrons scattered by the object. Kinematic scattering is discussed first, which assumes a thin sample is used and the electrons are scattered only once. To explain the nature of atomic resolution Z-contrast imaging in HAADF STEM, the effect of multiple
scattering, the so called dynamical scattering is introduced then, employing a Bloch-wave approach. The kinematic and dynamical scattering in STEM only cover the coherent part of the imaging electrons; while incoherent electrons are the major portion utilized for HAADF imaging. The last part considers the thermal diffuse scattering (TDS), which is the incoherent scattered electrons collected by the ADF detector.

2.2.4.1. Intensity of HAADF STEM Images from Kinematic Scattering

As explained in the previous section, electrons traveling at an angle to the optical axis carry a phase shift of $\chi(k_i)$ caused by the magnetic lens aberrations, compared to electrons traveling parallel to the optical axis, $k_i = 0$. This additional phase in a conventional objective lens could be written in [4):

$$\chi(k_i) = \pi \lambda C_1 |k_i|^2 + \frac{1}{2} \pi \lambda^3 C_3 |k_i|^2.$$  \hspace{1cm} 2.2.7

where $C_1$ is identical to defocus $df$, $C_3$ is the lens aberration and $\lambda$ is the wavelength of electrons. With aberration corrector, $C_3$ could be corrected and higher-order aberrations therefore should be included in equation 2.2.7 [25]. The amount of aberrations in general increases with the angle from the optical axis, it is thus beneficial to limit only the central portion of the electron beam to pass through the probe forming aperture and effectively reduce the effects of lens aberrations. During STEM imaging, the probe is scanned across the sample and scattered by the sample. Coherent Bragg diffraction gives the well-defined CBED pattern that is seen in the detector plane. The CBED disk size is determined by the beam convergence angle, which is defined by the probe forming aperture.
Figure 2.6. A schematic of the electron scattering geometry for STEM imaging from a coherently formed electron probe. BF and ADF detectors collect different parts of the CBED pattern. The red arrow lines indicate the process of two incident plane waves being scattered into the same final wave.

With a large convergence angle, electrons interact with the sample from a wide range of angles, using a detector collecting the electrons scattered to high angles will eliminate the interference of electrons scattered from different parts of the sample. This meets the requirement of incoherent imaging according to Lord Rayleigh. In incoherent imaging, the intensity is formed by a convolution of the probe function with the object function. With an ADF detector, the image intensity forms by collecting the electrons falling on to the detector, which could be expressed by integration of the intensity over a detector function $D(k_f)$:
\[
\tilde{I}(Q) = \int D(k_f) \int A(k_i - q/2)A^*(k_i + q/2) \\
\cdot \psi(k_f - k_i + q/2)\psi^*(k_f - k_i - q/2) dk_i dk_f,
\]

2.2.8

noticing that there is a shift of \(q/2\) when writing down the equation[4], where \(k_i \pm q/2\) represents the electrons interfering to form the CBED pattern. In Equation 2.2.8, the integration over \(k_i\) is within \(A(k_i - q/2)A^*(k_i + q/2)\), meaning that the overlap of aperture functions is limited in a region determined by \(q\). A much larger value of \(D(k_f)\) than the aperture size therefore reduces the dependence of integration over \(k_f\) on \(k_i\). The smaller dependence thus allows the integration in Equation 2.2.8 to be separated. The Equation can then be written as:

\[
\tilde{I}_{ADF}(q) = \int A(k_i - q/2)A^*(k_i + q/2) \, dk_i \\
\times \int D(k_f)\psi(k_f - k_i + q/2)\psi^*(k_f - k_i - q/2) \, dk_f \\
= T(q)\tilde{O}(q)
\]

2.2.9

\(\tilde{O}(q)\) here represents the Fourier transform of the object function. \(T(q)\) is called optical transfer function (OTF) in incoherent imaging, which is the inverse Fourier transform of \(A(k_i)\) corresponds to the probe function of \(P(r_0)\). In real space the intensity of ADF image therefore is

\[
I_{ADF}(r_0) = |P(r_0)|^2 \otimes O(r_0),
\]

2.2.10

with \(O(r_0)\) representing the object in real space. It can be seen that Equation 2.2.10 carries the character of intensity from incoherent imaging as in Equation 2.2.5. So with a detector geometry having a large enough annular detection area, HAADF STEM imaging is in the
form of incoherent imaging.

2.2.4.2. Intensity of HAADF STEM Images from Dynamical Scattering

The above derivation of HAADF STEM image intensity considers only kinematic diffraction, which means that electrons collected by the detector are only scattered once by the sample. However the samples used in STEM are usually more than 10 nm thick, allowing multiple scattering events to take place during electron-sample interaction. Therefore the contribution of dynamical scattering in HAADF STEM image intensity must be considered. In the approach using Bloch waves considering only the coherent electrons, it is shown that only the electrons in 1s states in real space is collected by the HAADF detector. The electron distribution in different Bloch states around atoms in a lattice is shown in Figure 2.7. The 1s states are seen highly localized at the atomic position, so the image intensity also peaks on the atomic columns. The electrons scattered to higher angles correspond to the ones interacting strongly with the states having high transverse kinetic energy. A column with heavy atoms thus scatters more electrons for imaging than light elements, which is why the intensity depends on \( Z \)\[4, 26\]. In dynamical scattering, the intensity in HAADF STEM images therefore shows atomic resolution and dependence on \( Z \).

![Figure 2.7](image)

*Figure 2.7. The distribution of the first three Bloch states of electrons around atoms in a lattice. (Redrawn after [10].)*
2.2.4.3. Thermal Diffuse Scattering

The major portion of detected electrons in HAADF STEM are incoherently scattered electrons rather than coherent ones. Thermal diffuse scattering (TDS) from atom vibrations in crystal in this case contributes dominantly to the incoherent electrons scattered to high angles. The vibration of atoms in crystal lattice is quantized in the form of phonons. The electrons scattered by phonons result in a diffuse intensity background in electron diffraction, which is the origin of the word ‘diffuse’ in TDS[27]. Thermal diffuse scattered electrons have random phases. Even though the scattering mechanism is different from the kinematic and dynamic process as described in previous sections, incoherent electrons also lead to Z dependent intensity peaks on atomic columns.

In an event of electron scattering by phonons, the electrons are ‘absorbed’ in the way they penetrate the crystal lattice and scattered to high angles. Adsorption is used here because the electrons are lost from the coherent part of electrons in this process. Similar to dynamic coherent electron diffraction, the high angle electrons scattered by phonons in this process are also from the highly localized 1s Bloch states at atomic positions. The intensity is therefore dependent on Z and locates on atomic positions as well. In the coherent electron part on the HAADF detector, the intensity primarily from the 1s states can be shown as [4],

\[ I_{\text{coherent}}(t) \propto e^{-\sigma t} [1 - \cos(\zeta t)], \tag{2.2.11} \]

where \( t \) is thickness. \( \sigma \) is the absorption coefficient determining the absorption of the wave function, \( \zeta \) is the phase change rate of the wave function along the depth of the sample, defined as the thickness frequency for the 1s states. For TDS, Equation 2.2.11 can be integrated over the sample thickness, the intensity from TDS is
\[ I_{TDS}(t) \propto (1 - e^{-\sigma t}) - (1 + \frac{\sigma^2}{\xi^2})^{-1} \frac{\sigma}{\xi} e^{-\sigma t} \sin(\zeta t) + \frac{\sigma^2}{\xi^2} (1 - e^{-\sigma t} \cos(\zeta t)) \]  

Therefore with large thickness \((t)\), the value of \(e^{-\sigma t}\) is smaller, in turn the sinusoidal part diminishes and the intensity approaches 1. In Figure 2.8 the intensity with different thickness is plotted for coherent electrons and TDS electrons. The total intensity is also plotted,

\[ I_{ADF}(t) = I_{TDS}(t) + \alpha I_{coherent}(t). \]

The TDS part becomes dominant after the thickness reaches 20 nm\[4\]. With normal TEM samples, the thickness can easily exceed 20 nm; the intensity on ADF detector is thus dominated by TDS electrons.

\[ \text{Figure 2.8. The intensity of ADF image and the parts from coherent electrons and thermal diffuse scattering. (Replotted after [12].)} \]
2.3. References


CHAPTER 3

INTERACTION OF NANOMETER-SIZED GOLD NANOCRYSTALS WITH RUTILE (110) SURFACE STEPS REVEALED AT ATOMIC RESOLUTION*

3.1. Introduction

The interaction between surface steps and nanocrystals (NCs) represents a challenging problem in the study of structural physics at nanometer-scale interfaces. In a NC, hundreds to thousands of atoms bond together by atomic forces are attracted by atoms on the support surface. The presence of surface steps can greatly influence the collective behavior of atoms in the NC. Interactions with surface steps are found in the early stage of thin-film growth and in supported catalysts made of small nanoparticles. In thin-film growth, numerous studies have reported preferential nucleation on surface steps (for an example, see Kern, Le Lay [1]). In catalysis, metal nanoparticles, each a few nm in diameter, are dispersed across the support surface. The interaction with supports can greatly influence the chemical activity and selectivity of the catalyst[2, 3]. Model systems that have been studied by surface science techniques are mostly 2D surfaces. This geometry, easily accessible by a number of characterization techniques, underlies much of the progress that has been made in this area (for a review, see [3]). Going beyond flat 2D surfaces will bridge the gap between the model and experimental systems involving rough or faceted surfaces with terraces, atomic steps or ledges and kinks.

Recent development in aberration corrected (AC) scanning transmission electron microscopy (STEM) in the form of Z-contrast imaging obtained using a high angular annular dark field (HAADF) detector[4-7] allows an observation of individual atoms in projection [8] and a determination of the NC shape and its interfacial energy [9]. To resolve crystalline interfaces at atomic resolution, interfacial atoms must be aligned in atomic columns. This can be achieved in epitaxial interfaces with their well-defined crystal orientation relationships. Direct visualization of individual atomic columns at interfaces has been extremely fruitful for the study of interfacial atomic and electronic structure [10-13].

Here we report a study of Au NCs supported on vicinal (stepped) rutile (TiO\textsubscript{2}) (110) surfaces using AC-STEM. We selected this system for study because gold nanoparticles supported on TiO\textsubscript{2} have been intensively investigated for their size-dependent chemical activities [14-17]. Smaller Au nanoparticles (<5nm) become chemically active [14-19] for selective conversion of carbon monoxide to carbon dioxide at room temperature or below. The smaller nanoparticles are beneficial because they contain a higher number of low coordinated atoms and exposed interfacial sites, which have been proposed as active sites for chemical reaction[7, 20]. The rutile (110) surface is a popular choice for studying Au-TiO\textsubscript{2} catalysts [21-24] for its structural stability [14]. The Au nanoparticles we study are epitaxial NCs formed by thermal annealing.

We study the interaction between Au NCs and the TiO\textsubscript{2} (110) surface by examining the interface in the cross-sectional sample viewing geometry. This method is sensitive to the interfacial atomic structure of very small NCs [9, 25, 26]. Using this approach, we have quantified the epitaxial relationships of Au NCs supported on stepped TiO\textsubscript{2} (110) surfaces.
with different miscut angles. We find the approximate \( \text{Au}(111) || \text{TiO}_2(110) \) orientation relationship as most dominant, while other orientation relationships are also seen. The equilibrium shapes of the Au NCs can be described using the truncated Wulff construction modified by the interface. Influence of the support surface steps on the NC structure is also examined by measuring the strain inside the Au NCs and calculating the interfacial energy. Severe strain is found near the steps and relaxes away from the interface. The interfacial energy computed using selected NCs supported on low miscut TiO\(_2\) (110) surfaces is lower than the energy of Au NCs on flat TiO\(_2\)(110), suggesting a more stable junction. These measurements provide a detailed picture of the interaction between NCs and TiO\(_2\) (110) surface steps. Insights obtained here from studying model vicinal surfaces have the potential to significantly enhance our understanding of early stage thin-film growth and real catalyst.

In what follows, we first describe the experimental methods employed for this study. This is followed by the results and discussion section, in which we describe and discuss our measurement results of NC orientation, shape, strain and interfacial energy. After the conclusion, we provide an appendix describing the experimentally observed orientation relationship based on the concept of coincidence site lattice (CSL).

### 3.2. Experimental Methods

The Au NCs on vicinal surfaces are prepared using the previously reported synthesis technique [9, 27] that enables high resolution AC-STEM investigation. A single crystal TiO\(_2\) (rutile) of (001) orientation (EPI-polished, obtained from MTI Corporation, Richmond, CA, USA) is used as the substrate. Before Au deposition, the TiO\(_2\) crystal was thinned, polished, and perforated by ion milling at 5 KeV, after which a hole is created in
the center. The crystal was then annealed at 1000 °C in air to form TiO$_2$ (110) edge facets [14]. The crystal was then annealed at 1000 °C in air to form TiO$_2$ (110) edge facets. The facets are of different types around the hole. The annealing also helps the reduced surfaces due to ion milling to be fully re-oxygenated [14]. Au was deposited onto the prepared facets at room temperature using an e-beam evaporator using a slow deposition rate of 0.033 nm/min. Using a quartz monitor, we measured the deposited thickness of the film to be 0.4 nm. The sample was then annealed at elevated temperatures (400-500 °C) to promote the formation of epitaxial NCs before loading it into the microscope.

A JEOL 2200FS STEM with a CEOS probe Cs corrector and annular dark-field (ADF) detector was used for atomic resolution Z-contrast imaging. The microscope was operated at 200kV. The performance of this microscope was described in [28]. This microscope is installed in the Center for Microanalysis of Materials at University of Illinois.

3.3. Results and Discussions

3.3.1. Rotation of Epitaxial Au Nanocrystals on Stepped TiO$_2$ (110) Surfaces

Figure 3.1 (a)-(c) show three Z-contrast images of the Au NCs (from 3.3 nm to 5.7 nm in width) formed on vicinal, stepped, TiO$_2$ (110) surfaces with the $\Sigma$9 phase boundary (a detailed analysis of phase boundaries observed in Au on TiO$_2$ (110) is described in Appendix). The images were taken along the TiO$_2$ [001] and Au [110] zone axis directions. Both atomic columns in the Au NCs and Ti columns in TiO$_2$ are clearly resolved. The atoms at the interface could be seen by changing the contrast and brightness range in the image display. These atoms appear dark in the image because of the wedge-shaped substrate as well as the shape of NCs. The brighter contrast of Au compared to the duller contrast of Ti is due to the Z-contrast difference obtained using a high inner cutoff angle.
for the ADF detector used for STEM image acquisition. Oxygen columns in the substrate are not seen because of the low atomic number of oxygen. Both Au and Ti atomic columns are resolved here because of the approximately epitaxial relationship categorized as \( \text{Au(111)}_{[-110]} \parallel \text{TiO}_2(110)_{[001]} \), which gives \( \text{Au}(11 \overline{1}) \parallel \text{TiO}_2(110) \) and \( \text{Au}[1 \overline{1}0] \parallel \text{TiO}_2[001] \). These relationships have been reported as the preferred epitaxial relationship for Au NCs formed on flat TiO\(_2\) (110) surfaces [9, 20, 25]. For Au NCs supported on surface steps, the epitaxial relationship is only approximate because of a small rotation of the Au (111) plane normal from the TiO\(_2\) (110) plane normal direction, while Au [-110] appears to be parallel to TiO\(_2\) [001].
Figure 3.1. (a-c) Atomic-resolution HAADF-STEM images of Au NCs of different sizes in approximate epitaxial relation of \( \text{Au}(11-1) || \text{TiO}_2(110) \). The images were recorded along the \( \text{TiO}_2[001] \), or \( \text{Au}[110] \), zone axis. The \( \text{TiO}_2 \) appears in a square lattice. The red boxes mark the identified CSL unit cells in \( \text{Au} \) and \( \text{TiO}_2 \) lattices respectively. (d) A schematic illustration of an Au NC on vicinal surfaces. Parameters used to describe the vicinal surface structure are also marked in (d), including tilt axis \( \vec{n}_T \), two angles here associated with surface miscut and nanocrystal rotation. The vectors \( \vec{n}_{\text{cusp}} \) and \( \vec{n}_v \) denote the plane normals of the “cusped” and vicinal surfaces.

The morphology of the supported Au NC as seen in Figure 3.1(a)-(c) is schematically illustrated in Figure 3.1(d). The parameters used to describe the interfacial morphology are labeled as: 1) the tilt axis marked as \( \vec{n}_T \), 2) the view direction (\( \text{TiO}_2 \) [001]),
3) the miscut angle, $\theta_v$, which characterizes the orientation of the vicinal surface, and 4) the planes normal of the “cusped” and vicinal surfaces, $\vec{n}_{cusp}$ and $\vec{n}_v$, respectively[29]. In this study, we focus on cases viewed along the TiO$_2$ (001) direction (which is also the tilt axis $\vec{n}_T$), where $\vec{n}_{cusp}$ represents the TiO$_2$ (110) surface normal. To measure the miscut angle of TiO$_2$ (110) surfaces, we need to identify interfacial atoms and their position. This is achieved using the image analysis techniques described in ref.[30]. For a determination of the gold NC orientation, the rotation angles are measured using the (111) spots observed in the FFT (fast Fourier transform) spectrum of the atomic resolution NC image.

In Figure 3.1(a), the miscut angle from the TiO$_2$ (110) surface is measured at 7.4°. The Au (110) is rotated by 4.9°. With this small rotation angle, the Au (111) planes as seen in the image are nearly parallel to the TiO$_2$ (110) planes. At the interface, the gold atomic plane is seen as deformed following the TiO$_2$ (110) terraces with noticeable atomic vacancies near the surface step. On the flat part of the interface, 4 titanium atomic columns at a length of 1.03 nm coincide with 5 Au atomic columns at a length of 1.07 nm. A similar match is observed in Figure 3.1(b) with a NC rotation angle of 0.46° on a 7.2° miscut surface and in Figure 3.1(c) with a NC rotation angle of 5.7° on a 9.7° miscut surface.

To elucidate the relationship between the NC rotation and the miscut angle of the stepped surfaces, we plot the measured Au (111) plane rotation angle ($\theta_{Au}$) versus the measured TiO$_2$ (110) surface miscut angle ($\theta_v$), as shown in Figure 3.2(a). The results of Figure 3.2(a) show that the gold NC rotation angle is smaller than the surface miscut angle on low-miscut TiO$_2$ (110) surface. Most of the observed gold NCs have rotation angles of 5° or smaller. There are also significant variations in the observed rotation angles. While one may expect that low miscut surfaces lead to low NC rotation angles and the NC rotation
increases with the surface miscut, this is not the case. The rotation angle distribution appears flat relative to the surface miscut angles. The rotation angles do not appear strongly affected by the sizes of the NCs either, as shown in Figure 3.2(b).

**Figure 3.2.** The measured NC rotation angles for different NCs are plotted (a) as a function of the substrate miscut angle, (b) as a function of the NC width.

### 3.3.2. Equilibrium Shapes of Au NC on Stepped TiO$_2$ Surfaces

The gold NCs observed were formed by annealing. Previous studies show that the annealed NCs are expected to exhibit some forms of equilibrium shapes [31, 32]. The equilibrium shape found in the Au NCs supported on a flat TiO$_2$ (110) surface was reported by Shankar et al. [9]. The experimental NC shapes can be approximately fitted based on the Wulff construction[33]. For supported NCs, the Wulff construction is truncated due to the NC-substrate interaction. For epitaxial Au NCs on TiO$_2$ (110), the NC equilibrium shapes are quantified by the distance between the center and top ($h$), total height ($H = 2h - \Delta h$), with $\Delta h$ for the truncated height, and width ($w$) [9].
We extended the above shape model to the analysis of NCs supported on vicinal TiO$_2$ surfaces. The parameters used to quantify the shapes are illustrated in Figure 3.4(d). Measurements were carried out for the shape parameters based on the aberration corrected STEM images. Figure 3.3(b) plots the height versus width for NCs with the $\Sigma 9$ heterophase grain boundary (similar to those shown in Figure 3.1). Here we focus on the NCs sitting on one or two TiO$_2$ surface steps with a small rotation angle (<6°). As described before, these NCs are characterized by the deformed Au (111) plane at the interface, which approximately follows the rutile (110) surface terraces. These NCs, as we see in Figure 3.3(b), have similar shapes in term of the height and width ratio. Because of the conformity of the Au (111) lattice plane to TiO$_2$ (110) surface, their shapes can be described approximately using the model developed for Au NCs on the flat TiO$_2$ (110) surface.
Figure 3.3. (a) Histogram of the NC rotation angle distribution. The Au NCs included here have a small rotation angle less than 6°. (b) A plot of the measured NC height versus the measured width. (c) A plot of $\Delta h/h$ versus NC width for the measured Au NCs. The width of the NCs included in the measurement ranges from 2.7 to 6.3 nm. (d) A plot of $(dh-h)/h$ vs. $1/a_{int}$, for details, see text.

In the plot of Figure 3.3(b), the NC height ranges from 1.5 nm to 4.5 nm. The width of these NCs is distributed from 2.5 nm to 6.5 nm. For an equilibrium shaped self-standing NC without truncation, the height and width are related to each other by the following equation[9]: $h_{111} = cw = \frac{1}{\sqrt{6}} w \approx 0.41 w$. The constant $c$ in case of supported NCs is determined by the interfacial interaction. Difference in the NC shapes can be measured by comparing the coefficient $c$ and its deviation from the ideal case of 0.41. The previous
study found that Au NCs on TiO$_2$ (110) flat surface have a coefficient $c$ with the value of 0.49[9]. Compared to this value, our slope of 0.64 for the NCs observed on vicinal rutile (TiO$_2$) surfaces is much larger. The increased height and width ratio indicates that NCs on the low miscut vicinal surfaces have a different equilibrium shape compared to the flat surface case.

3.3.3. Interfacial Strain of Au NC on Low Miscut TiO$_2$ Surfaces

On flat TiO$_2$ surfaces, Au NCs with the epitaxial relationship of Au(111)[-110]||TiO$_2$(110)[001] have a ~2.3% misfit strain between the lattice planes of Au(220) and TiO$_2$(002). Previous report suggested that this misfit strain had little effect on the Au NC shapes[9]. In the cases studied here, the interaction with surface steps are expected to lead to interfacial strain, which could influence the equilibrium shapes and deviation from the self-similar NC shape [32, 34-38]. However, the linear correlation between the height and width seen for the observed NCs on surface steps show a good self-similarity in the NC shapes and suggest that the surface step effect on Au NC shapes is limited to local interfacial strain.

To provide a quantitative assessment of strain inside the Au NCs, we use a recently developed lattice analysis method, called TeMA, based on the analysis of atomic resolution images using template matching [39]. In this method, first an image of the atomic column is obtained by spatial averaging over a group of atomic columns recorded in the Z-contrast image. Then, this image is used as template to detect and locate the position of individual atomic columns with sub-pixel precision. The measured atom column positions are then used to calculate the projected strain (in 2D) at atomic resolution. To overcome the scan noise, which is often present in experimental STEM images, we used the substrate (TiO$_2$) as a reference to measure and correct the scan noise. Details of this procedure are reported
in ref.[39]. After the correction, the substrate (TiO$_2$) lattice is $a=b=3.25$ Å, $\alpha=90^\circ$, and the 2D Au lattice along Au [001] zone axis in average is measured as: $a=2.52$ Å, $b=2.48$Å, $\alpha=109.6^\circ$. For comparison, the standard values for the 2D gold lattice along [001] zone axis is: $a=b=2.50$Å, $\alpha=109.5^\circ$. Figure 3.4 (a) indicates the displacement of atomic columns from the average lattice sites (indicated by small circles); the displacement vector of each atomic column is indicated by a line for both Au and Ti. The line originates from the average lattice site and ends at the location of the atomic column determined from the Z-contrast image. The original image used for the displacement measurement is shown in Figure 3.1(c); deformation can be seen directly in the image for the interfacial atomic columns near the surface steps. In the magnified image taken at the interfacial region shown in (b), large displacements of 0.65Å are seen at the interfacial Au layer. Here, atoms move horizontally on the terrace and displace vertically near the steps. The interfacial displacement reduces in atomic layers away from the interface, especially for these at 3 layers away or more. Displacement of Ti atoms is also seen, but small compared to the position shift of Au atoms in the NC. Figure 3.4 (c) to (e) show the strain map for $\varepsilon_{xx}$, $\varepsilon_{yy}$ and $\varepsilon_{xy}$, calculated from the displacement map. In these strain maps, the Au NC is under compression in x direction ($\varepsilon_{xx}$) near the surface step and a small tensile strain is seen in regions near the top, bottom left and bottom right corners of the NC. Surface Au atoms on left and right sides are under a small compression. In y direction, the strain ($\varepsilon_{yy}$) is modulated by the interface, expansion is seen where Au and TiO$_2$ terraces are in contact. The shear strain ($\varepsilon_{xy}$) map shows a change from positive to negative shear strain near the surface step. The large strain is seen next to the surface step close to -4.9%, while the strain seen on the NC surface is only about 0.7%.
**Figure 3.4.** a) Au atomic displacements measured from the atomic resolution image shown in Figure 3.1(c). The Au atom positions in an undistorted lattice are marked by circles, while the lines indicate the amount and direction of measured atomic displacements (for details, see text). The magnified region near the interface is shown in (b). (c-e) Strain maps for the Au NC calculated based on the measured displacements for normal stain in x ($\varepsilon_{xx}$) and y ($\varepsilon_{yy}$) direction and shear strain ($\varepsilon_{xy}$). The strain maps for the TiO$_2$ substrate are not shown here.
3.3.4. Interfacial Energy of Au NC on Low Miscut TiO$_2$ Surfaces

Based on the observed shape similarity among Au NCs on low miscut vicinal TiO$_2$ (110) surfaces, we measured the interfacial energy and triple line energy by applying the modified Wulff-Kaischew theorem [1, 9, 40]. The Wulff-Kaischew principle describes how the equilibrium shape of a supported NC is related to the surface and interfacial energies independent of the NC size by the equation:

$$\frac{\Delta h - h}{h} = \frac{\gamma_{TiO_2} - \gamma_{Int}}{\gamma_{Au}}$$  \hspace{1cm} (3.1)

where $\gamma$ refers to the surface and interface energies, $h$ and $\Delta h$ are NC geometry parameters as defined in 3.2, $\Delta h$ can be calculated as $\Delta h = 2h - H$. The equation contains the ratio of $\Delta h/h$, which describes the amount of dewetting with the value of 0 in the case of complete dewetting.

At the interface of a supported Au NC, there is a solid-solid-vapor triple junction. The triple line energy, which is the excess energy of the line at the triple junction, should also be considered in determining the equilibrium shape of supported Au NCs. The Wulff-Kaischew theorem after adding the triple line energy factor into Equation 3.1 becomes[9]:

$$\frac{\Delta h - h}{h} = \frac{\gamma_{TiO_2} - \gamma_{Int}}{\gamma_{Au}} - \frac{\tau_{Int}}{\gamma_{Au}} \frac{d\ell_{Int}}{dA_{Int}}$$  \hspace{1cm} (3.2)

where $d\ell_{Int}/dA_{Int}$ is the “geometric factor”, which can be rewritten in terms of measureable quantities as[9]:

$$\left(\frac{d\ell_{Int}}{dA_{Int}}\right)_{112} = \frac{2\sqrt{3}}{a_{Int}} = \frac{2\sqrt{3}}{\left(w + \frac{2\Delta h}{\tan \theta}\right)}$$  \hspace{1cm} (3.3)

where $\tan \theta = 1.633$. The derivation of Equation 3.3 is given in ref [9].

To calculate the interfacial energy, we focus on the group of Au NCs on low miscut TiO$_2$ surfaces, which includes 27 Au NCs with the $\Sigma 9$ phase boundary. A histogram of
their rotation angles is plotted in Figure 3.3(a). As it is shown, the rotation angles range from 0° to 6° and a majority of these NCs are distributed around the 3° rotation angle.

In Figure 3.3(d), we plot \((\Delta h - h)/h\) versus “1/\(a_{\text{Int}}\)” with the data measured from the 27 NCs. If we assumes a linear relationship between the measured dewetting factor \(dh/h\) and the geometrical factor based on the self-similar NC shape, \(\gamma_{\text{Int}}\) and \(\tau_{\text{Int}}\) then can be extracted from the slope and intercept if we know \(\gamma_{\text{Au(111)}}\) and \(\gamma_{\text{TiO}_2(110)}\).

To study the conformity of NC dewetting over the NC shape for all NCs included in the analysis, we plot the distribution of the \(dh/h\) value with particle size in Figure 3.3(c). This plot shows that there are significant fluctuations in dewetting among different Au NCs. We have attempted to fit the plot with a linear function to investigate the trend of \(dh/h\) with width increment, as shown in the figure. However the value of R-square is too small (0.15); there is no strong statistical evidence for the size dependence of particle shape here. Thus, the self-similar NC shape represents a reasonable average among Au NCs observed on the low miscut TiO\(_2\) (110) surfaces.

The deduction of the interfacial energy is based on Equation 2, where \(\frac{\Delta h - h}{h}\) vs. \(\frac{dA_{\text{Int}}}{dA_{\text{Int}}}\) is fitted with a linear curve, and \(\frac{\gamma_{\text{TiO}_2} - \gamma_{\text{Int}}}{\gamma_{\text{Au}}}\) is the intercept \(b\). Then, \(\gamma_{\text{Int}}\) is computed from \(\gamma_{\text{Int}} = \gamma_{\text{TiO}_2} - b\gamma_{\text{Au}}\) with \(b\) measured to be -0.12±0.09. Calculation of interfacial energy thus requires the surface energies for both Au and TiO\(_2\) (\(\gamma_{\text{Au}}\) and \(\gamma_{\text{TiO}_2}\)).

In the previous analysis\([9]\), \(\gamma_{\text{Au(111)}}=1.283\ \text{J/m}^2\) is used following Vitos et al \([41]\) and \(\gamma_{\text{TiO}_2(110)}=0.33\ \text{J/m}^2\)\([20]\). Assuming the same values, the triple line energy is measured to be \(9.1\pm1.8 \times 10^{-10}\ \text{J/m}\) and the interfacial energy to be \(0.48\pm0.12\ \text{J/m}^2\) from Figure 3. The
interfacial energy is lower than the previous result of gold NCs on flat surfaces at 0.61±0.06 J/m² [9].

The triple line energy measured at 9.1±1.8 ×10⁻¹⁰ J/m for Au NCs on stepped TiO₂ (110) surfaces is larger than the value of 4.5±1.3 ×10⁻¹⁰ J/m reported earlier for Au NCs on flat TiO₂ (110) surfaces. The value of triple line energy also depends on the surface energy of Au (γ_{Au}). A full account of the increase in the triple line energy, thus, requires a delineation of the change in surface energy.

The interfacial energy can be expressed as \( \gamma_{Int} = \gamma_{Au} + \gamma_{TiO_2} - \gamma_{Bond} \), where \( \gamma_{Bond} \) is the free energy associated with the bonding between the Au NC and the substrate [42]. Lower interfacial energy suggests a larger bonding energy and stronger interaction here.

With steps introduced at the interface both \( \gamma_{TiO_2} \) and \( \gamma_{Au} \) are expected to change. The surface energy of a miscut surface of angle \( \theta \) can be approximately written as

\[
\gamma(\theta) = \gamma(0) \cos \theta + \frac{\beta}{h} \sin \theta
\]

3.4

where \( \beta \) is the energy associated with the surface step that includes the energy for creating an isolated step on the nominal surface and the interaction energy between surface steps [43, 44]. A simple approximation for the step energy is to consider step as a small facet and its energy given by the surface energy of the corresponding nominal surface. Because of the miscut angle is small (less than 18°), the correction from the step energy is expected to be small too. The correction for surface steps will change the values of the measured interfacial and triple line energies, but will not significantly alter the conclusion reached above.
3.4. Conclusions

Using atomic resolution Z-contrast imaging, we have succeeded in elucidating the interaction of Au NCs with stepped rutile (TiO\textsubscript{2}) (110) surfaces by observing the approximate epitaxial orientation relationships, rotation of Au NCs, and in the case of vicinal TiO\textsubscript{2} (110) surfaces, by measuring interfacial and triple line energies. The main results are: 1) surface steps induces a small rotation in the NCs in an amount less than the surface miscut angle, 2) there are significant strain near the surface steps inside Au NCs, and 3) the shape of Au NCs on low miscut surfaces is approximately similar. Compared to Au NCs on flat surfaces, our measurements show a large height/width ratio, lowered interfacial energy and increased triple line energy for NCs observed on surface steps.

3.5. Coincidence Lattice and Heterophase Grain Boundary of Au Nanocrystals on Vicinal TiO\textsubscript{2} (110) Surfaces

The cases discussed in text are for Au NCs on TiO\textsubscript{2} (110) surfaces with a small miscut angle (18° or less). Figure 3.5 shows cases where the miscut is large or where other epitaxial relationships are observed. In Figure 3.5 (a), the gold NC with a 17.80° rotation is on a 18.43° miscut TiO\textsubscript{2} (110) surface. The Au NC is 3 nm wide and has a flat (111) interfacial layer of gold. This flat gold layer over stepped TiO\textsubscript{2} surface leaves the interfacial space between the bottom of the NC and the rutile surface steps relatively empty. In Figure 3.5 (b) and (c), the observed Au NCs exhibit two approximate epitaxial relationships of Au(110)[001]∥TiO\textsubscript{2}(110)[−110] and Au(001)[−110]∥TiO\textsubscript{2}(110)[1−110]. In Figure 3.5 (b), the (110) planes of the Au NC reside on a surface with a miscut angle of 9.3° and the NC itself rotates away from the TiO\textsubscript{2} [110] surface normal by 9.3°. The NC in Figure 3.5 (b) has
small Au (001) facets together with Au (111) and (110) facets. In comparison, the NCs observed in Figure 3.1 have facets of (111) and (110) planes. The Au (110) plane has a lower packing density compared to the Au (111) plane and the Au bottom (110) plane is seen as flat at the interface. The Au NC in Figure 3.5 (c) has (001) top and bottom facets as seen above the vicinal TiO$_2$ surface. The bottom (100) plane is seen to be flat as well and its plane normal rotates $13.4^\circ$ from the TiO$_2$ (110) direction on a stepped surface of a $19.5^\circ$ miscut angle. The NC in Figure 3.5 (b) also contains a defect; a twin boundary is seen at the top of the NC as marked by the red line.

**Figure 3.5.** Atomic-resolution HAADF-STEM images of Au NCs. (a) An Au NC with (111) bottom facet resides on a high miscut TiO$_2$ surface. (b) A supported Au NC on TiO$_2$ surface steps with an approximate epitaxial relationship of Au(110)[001]||TiO$_2$(110)[$\bar{1}$10]. (c) A supported Au NC on TiO$_2$ surface steps in an approximate epitaxial relationship of Au(001)[$\bar{1}$10]||TiO$_2$(110)[$\bar{1}$10]. The red lines indicate defects inside the Au NCs in (b) and (c). The arrow marks the position where the defect originates from. Red boxes mark the CSL unit cells in Au and TiO$_2$ lattices.
The epitaxy and interfacial structure can be rationalized based on the concept of coincidence site lattice (CSL) cells [45, 46] and the CSL lattice model for heterophase grain boundaries in crystalline solids. Because CSL is never perfect in across a heterophase grain boundary, we use the ‘fit-misfit’ model developed in above references. In this model, the interfacial boundary has partial lattice matching across the hetero phase junction and regions of ‘misfit’ as boundary line defects possessing dislocation/boundary step character [46]. For the NCs in Figure 3.1, since 5 gold repeats along the (111) direction match 4 titanium columns in the TiO$_2$ (110) direction, we built a gold 5×5 CSL cell in the Au NC lattice first and defined this cell as M$_1$. In the TiO$_2$ lattice, we selected a titanium 4×4 lattice cell defined as M$_2$, which has a similar size to M$_1$. Both M$_1$ and M$_2$ are labeled by red boxes in the STEM figures and the schematic of the overlapped lattices is depicted in Figure 3.6. Since M$_1$ and M$_2$ are of similar size and shape, either one can be regarded as the unit cell shared by both lattices, from which this type of interface is calculated to be a $\Sigma$ 9 boundary.

By analyzing the lattice cell in TiO$_2$ based on the atomic resolution image and overlapping on top of the gold lattice, we also measured the rigid body shift between the two crystals. In the images of Figure 3.1(a), (b), and (c) here, each gold NC is shifted from the TiO$_2$ with a distance of 2.55 Å, 2.05 Å and 1.46 Å, respectively.
Figure 3.6. A schematic of the CSL unit cells. Au atoms are in yellow with red cell and titanium atoms in blue with black cell. The overlapped cells show the small rotation and mismatch between the two CSL cells.

Following the same analysis as described above, we found that the NC in Figure A3.1 (a) has a $\sum 6$ interfacial boundary with a 5×4 Au CSL cell and a 4×3 Ti CSL cell selected as $M_1$ and $M_2$. In Figure A3.1(b), we selected a 5×2 gold CSL cell $M_1$ and a 4×2 titanium CSL cell $M_2$, which indicates a $\sum 4$ boundary. In Figure 3.5(c), a 4×4 gold lattice cell and a 3×3 titanium lattice cell are selected and thus the interface is a $\sum 5$ boundary.

Overall, we observed the following CSLs of $\sum 9$, $\sum 6$, $\sum 4$ and $\sum 5$ for the heterophase grain boundary between Au NCs and TiO\textsubscript{2} vicinal surfaces. Among these coincidence site lattices, $\sum 9$ is the most popular; it is observed on low miscut TiO\textsubscript{2} (110) surfaces. The $\sum 6$ and $\sum 5$ tend to be observed on TiO\textsubscript{2} (110) surfaces with large miscut angles.
3.6. References


CHAPTER 4

DIRECT OBSERVATION OF INTERFACIAL AU ATOMS
ON TiO₂ IN THREE-DIMENSIONS*

4.1. Introduction

The major challenge in the study of metal nanoparticles as heterogeneous catalysts is to correlate the composition and atomic-scale structure of catalysts with their chemical reactivity. A striking example is Au, which becomes chemically active as the catalyst for oxidation of CO or LT-WGS (low-temperature water gas-shift) reactions in the form of nanoparticles, when their sizes decrease to ~4 nm in diameter[1-4]. Since Au is inert in bulk form, delineating the role(s) played by its atomic-scale structures is thus critical to understand Au catalysis. The accumulated experimental and theoretical evidences show that the catalytic activity and selectivity of gold for oxidation are controlled by three major factors; the type of metal oxide supports[2, 5-8], size of the Au nanoparticles[2, 9], and the Au-support contact structure[10-12]. All three factors can be influenced by the catalyst preparation method[13]. Several mechanisms have been proposed to explain the dramatic size-dependent chemical activities of gold with a focus on Au nanoparticles or their interactions with the support. In the former category, the proposed mechanisms include the role of low-coordination surface Au atoms[14-17] or quantum size effect[18-20], while mechanisms involving the interface include interfacial charge transfer[6, 17, 21], strong support interaction[12, 22-24], strain[25] and interfacial Au atoms[26].

Interface, in general, has a large impact on the nanoparticle’s morphology and strain[22, 24, 25, 27, 28], as well as on the so-called perimeter atoms of the nanoparticles[12, 29]. In addition, strong “support effect” is observed where reducible oxides have demonstrable advantage over non-reducible ones for Au catalysts[2, 3, 30, 31]. Especially, Haruta reported that the stronger contact between Au and TiO$_2$ from high temperature calcination leads to much higher catalytic activity[3], even though the average Au particle size increased to ~10nm. Thus, further progress in study of supported nanoparticles requires an extended focus that goes beyond characterization of nanoparticle structures to interfaces, identification of interfacial atoms and bonding for their specific, functional, roles.

Au interaction with TiO$_2$ is studied here. Au/ TiO$_2$ catalysts are typically prepared by Au precipitation on titania support, followed by calcination in air or reduction under H$_2$ at elevated temperatures[3, 26]. Au supported on the surfaces of single crystal of rutile (TiO$_2$) has been used previously as the model system for studying Au and TiO$_2$ interactions[18, 24, 32]. Electron microscopy observations reported by Delannoy et al. show that the Au nanoparticles are mostly flattened by interacting with the support with the particle shapes varying from hemispherical to faceted truncated cubo-octahedra [33]. Suggestions have also been made in the literature regarding the mechanism of CO oxidation catalyzed by interfacial Au atoms or Au-assisted interfacial sites[26, 30, 34]. While a number of reports have been made on the observation of perimeter Au atoms[6, 29, 31], up to now, no evidence of interfacial Au atoms has been reported.

Recent advances in aberration correction enable the use of a larger condenser aperture than the conventional STEM. The large aperture provides a reduced depth of focus
and the improved depth sensitivity [35-38]. Together with the small electron probe (1 Å or less), this technique allows depth sectioning at high lateral resolution following the same principle as optical sectioning. Using an annular dark field (ADF) detector for Z-contrast imaging, several research groups have demonstrated 3D imaging of the shape of nanoparticles or detection of single atom with a depth resolution of several nanometers[35-40]. Here, we have extended this technique using quantitative intensity analysis and applied it to the study of atomic scale structure at the Au/TiO$_2$ interface.

4.2. Experimental

The experiment started with forming epitaxial Au nanocrystals on single crystal rutile (110) surfaces to meet the requirements of cross-sectional STEM observations and preserve the nanocrystals’ structure and its interface. We follow previously reported procedures of Au deposition and annealing to promote epitaxial nanocrystal formation [25, 28, 41, 42] (see appendix for more details). After the Au nanocrystals were formed, no further TEM sample preparation procedures were needed. The epitaxial relationship observed here can be described as $Au(1 \overline{1} 1) || TiO_2(110)$ and $Au[1 \overline{1} 0] || TiO_2[001] [43]$. For imaging, we used the JEOL 2200FS installed at the Center for Microscopy and Microanalysis, Frederick Seitz Materials Research Laboratory, at 200kV. This microscope is equipped with the CEOS probe aberration-corrector for STEM. It is capable of resolving atoms separated by 1 Å [28]. The sizes of the Au nanocrystals ranged from 3.5 to 12 nm in width depending on the annealing conditions.
4.3. Results

4.3.1. Depth Sectioning STEM Image of Au/TiO$_2$(110) Interface

Figure 4.1(a) and (c) show two Z-contrast images using a high angle ADF detector (inner cutoff angle at 100 mrad) along TiO$_2$ [001] (Au [110]). The Z-contrast images show that the Ti atomic columns form a square lattice in the TiO$_2$ [001] projection, while the O atomic columns are too weak to be detected. For the Au nanocrystal, the atomic columns are individually resolved at the spacing of 2.49 Å along [112] in the (11-1) planes parallel to the TiO$_2$ surface. A distinct interfacial layer is observed in both images (as marked by arrows in Figure 4.1(a) and (c), where a few columns of bright intensity located amongst much darker columns within a single atomic layer). The interfacial layer’s contrast differs markedly from that of TiO$_2$ and Au.
Figure 4.1. (a) and (c) are two Z-contrast images recorded along TiO$_2$ [001] direction. Au atoms are brighter than Ti atoms due to its larger Z. An atomic model of Au nanocrystal on TiO$_2$ [110] surface is shown in the inset of (c), with Ti atoms in grey, O atoms in red and Au in yellow (color online). Figure (b) shows the same image as (a) with the contrast adjusted to show the TiO$_2$ lattice, and reduced the effect of the strong Au intensity in (a) on the other side of the TiO$_2$ crystal. In all images, a distinct interfacial layer is observed and indicated by the arrows.

To further examine the Au/TiO$_2$ interfacial structure, we recorded the Z-contrast images in a focal series for depth sectioning. The principle of depth-sectioning using the STEM Z-contrast imaging is illustrated in Figure 4.2(a). The electron probe was formed by converging the electron beam onto the specimen; the probe intensity peaks where the
probe is smallest. With aberration correction, the smallest probe diameter decreases as the numerical aperture increases, up to a limit. As we move away from the peak probe intensity along the optical axis, the intensity of the probe falls off and the depth of focus (DoF) is defined as $dz=1.77\lambda/\alpha^2$. For the 26 mrad aperture and 200 kV electrons that we used here, $dz=6.5$ nm. Because of this, for a very thin sample, a point object will appear elongated as a rod in the focus direction with the intensity peaked at the point object. By changing the defocus of the electron beam, a series of images can be recorded with the peak electron intensity being located at different depths along the focus direction. Upon interacting with a real solid, the electron probe gets modified by electron scattering. Simulations are therefore required in the interpretation of depth-sectioning data. Using this principle described above, an atom can be located in 3D depending on how well the intensity distribution can be resolved and interpreted.
Figure 4.2. (a) An illustration of the principle of depth sectioning using STEM Z-contrast imaging. The electron probe is formed by converging the electron beam onto the specimen; the probe intensity peaks where the probe is smallest. (b) The focal series of Z-contrast images recorded from the Au nanocrystal near the interfacial region shown in Figure 1(c). The images were aligned using the cross-correlation method. These intensity profiles were then used to form the depth-sectioning images shown in (c) for the Au, TiO and interfacial layers respectively. The intensity bands were marked using the color boxes to identify the column as a Au-column, Ti-column or an interfacial-column. For more detailed interpretation, see text.
Figure 4.2(b) shows a series of the Z-contrast images from the interfacial region of the Au nanocrystal shown in Figure 1(c), recorded at 9 different probe focuses. The images were aligned using the cross-correlation method. After the alignment, at each focus setting, three intensity profiles were taken along a) the interfacial layer, b) the Au layer immediately adjacent to the interfacial layer and c) the TiO layer next to the interface, respectively (the positions of these layers of are marked by red lines in Figure 2(b)). These intensity profiles were then used to form the depth-sectioning images shown in Figure 2(c) for the Au, TiO and interfacial layers. In both Au and TiO layers, atomic columns give rise to vertical intensity bands along the focus axis in the depth-sectioning images. Each band corresponds to an atomic column, which is resolved horizontally along the scanning direction. Within the atomic column, the atoms are not resolved in the depth direction because of the limited depth resolution.

Notably, at the interface, the depth-sectioning image shows intermediate intensities between these of Ti- and Au-columns. Furthermore, there are intensity variations along the focus direction in the interfacial layer. For example, the column marked as A in Figure 4.2(c) resembles the intensity of Au columns observed in the Au layer, while the columns marked as T have similar intensities as that of Ti columns in the Ti layer. Regions marked as I show distinct intensity peaks that are very different from either the TiO or Au layers.

Intensity modulations are also seen along the atomic columns of Au on the TiO$_2$ layer adjacent to the interface. Modulation is stronger in some of TiO$_2$ columns than Au columns. These modulations indicate atoms deviating from their standard lattice positions. The presence of interfacial Au atoms has a large impact on the interfacial atomic positions, which can be seen from the 3D plot of the located atomic column positions (Figure S4.4).
They indicate a rumpled interfacial layer, which shifts upward or downward by 92±40 pm. These atomic shifts are expected to influence the positions of neighboring Au, Ti and O atoms. For TiO$_2$, the presence of interfacial Au atoms promotes the TiO$_2$ surface reduction and creating surface oxygen vacancies[34].

4.3.2. Simulation of STEM Depth Sectioning Images and Estimation of Au Atoms Embedded on TiO$_2$ Surface

To further our analysis, the STEM depth-sectioning images were simulated using the multi-slice method[44-46]. Atomic models consisting of the Ti columns, the Au columns and the mixed Ti/Au columns were constructed (details are in appendix). In each case, the focal series images were simulated using focuses from -7 nm to 12.5 nm at a 0.5 nm step. The simulated images were then processed following the same procedure used for the experimental images (Figure S4.2). Figure 4.3(a) shows the calculated depth-sectioning images for the Ti column and hypothetical cases of Ti atomic columns substituted by 1 to 3 Au atoms. When Au atoms substitute Ti atoms in a Ti atomic column, the peak intensity depends on the number of Au atoms as well as their positions, which is plotted in Figure 4.3(b) (and also see Figure S4.3). Overall, the peak intensity increases with number of Au atoms. In case of a single Au atom embedded in the Ti atomic columns, the highest peak intensity is observed with the Au placed at 1.08 nm above the center (0 focus) (Figure S4.3). The width of peak along the focus direction in the depth-sectioning image also increases with the number of Au atoms, which is not significantly affected by the position of the Au atoms in our simulations.
Figure 4.3. (a) Simulated depth-sectioning images for a Ti column and those with Ti atoms replaced by 1 to 3 Au atoms in the center. (b) Plots of peak intensities for Ti column, Ti with one Au atoms located at four different positions, and with two and three Au atoms in the center. The intensity profiles along scanning direction in 0 defocus are plotted in the inset of (b) for all cases in (a).

The above simulation results suggest that the number of Au atoms at the intermixed interface can be estimated by their peak intensities in the focal series. To identify columns with interfacial Au atoms and their location, we carried out a peak intensity analysis of the depth-sectioning images. Figure 4.4 plots the histogram of the peak intensities for Au, Ti and interfacial atoms in the series STEM images. The intensity of the Ti atomic columns has a narrow distribution characterized by the mean value of $3.5 \times 10^4$ in digital counts and
a deviation of $1.4 \times 10^4$, while the intensity of the Au atomic columns in the nanocrystal has a broad distribution with intensity ranging from $2.3 \times 10^4$ to $3.6 \times 10^6$ for the Au nanocrystal of 9 nm in diameter. This difference in the intensity distribution between the Ti and Au can be explained by variations in thickness in these two cases; the thickness of TiO$_2$ is relatively uniform which leads to a narrow intensity distribution, while the thickness of Au nanocrystal varies from 1 atom at the corner to 15 atoms at the middle of the 9 nm diameter nanocrystal. Using the Ti and Au intensity histograms as references, the peak intensities of the interfacial layer can be separated into these belonging to Ti (labeled as IS) and these belonging to Au (Labeled as IL). Next, by comparing the experimental and the simulated depth-sectioning intensity profile for Ti, Au and intermixed atoms, we can estimate the number of embedded Au atoms in each column at the interface using the intensity values (details provided in appendix). At the interface, as labeled in Figure 4.5 (a) and (b), column 1 has 3-5 Au atoms, column 2 has 4-6 Au atoms, while columns of 3, 4, 5, 6, 9 and 10 have 1-3 atoms. Columns 7 and 8 have most Au atoms estimated as 6-8 atoms or more. All other columns are determined to be consisting of only Ti Atoms.

The above analysis also shows that most interfacial Au atoms are located near the top, bottom and two edges of the depth-sectioning intensity image. This indicates that they locate at or near the perimeter of the interface in 3D. Since surface Ti and O atoms close to the interfacial perimeter are freer to move than interior ones, the formation of interfacial Au atoms appears to be diffusion limited.
Figure 4.4. The histograms of the peak intensities for Ti in (a), weak interfacial peak intensity in (b), strong interfacial peak intensity in (c), and Au atoms in (d).

The interfacial structural model we propose to explain our experimental data is the added-row model of the reconstructed 1×2 TiO$_2$ (110) surface [47, 48], where one row of Ti atoms with its sub-bridging O row per 1×2 cell are missing on top of a fully reduced surface with no bridging O atoms. For the Au/TiO$_2$ interface, the reduced surface allows the Au atoms to approach the surface without obstruction of the bridging O atoms. The missing Ti atoms in the added-row model of reconstructed 1×2 rutile (110) surface provide
sites for interfacial Au atoms. In the previous proposed theoretical model, it was assumed that the entire row of Ti atoms is replaced by Au atoms at the interface. Our experimental results show that most columns have only a few Au atoms (for example columns 1-6, 9, and 10 in Figure 4.5) while a few columns have more Au atoms (column 7 and 8 in Figure 4.5).

Figure 4.5. Intensity analysis of the STEM depth-sectioning images for the interface and Ti layer (a) (taken from Figure 4.2 (c)). The columns with different features from Ti intensity are labelled by box 1-10 at the interface. Integrated intensity profiles along the scanning direction for both layers are plotted in (b) with peaks 1-10 corresponding to the labelled boxes.
Further support for the above interfacial structure model comes from the observation of the interfacial distances, which is influenced by the interaction in the Au/TiO$_2$ interface [34]. The interfacial spacing can be measured directly from the atomic resolution images. The interface with embedded Au atoms on average gives an interfacial distance between the Au layer and interfacial layer at 2.35±0.16 Å, compared to the calculated value of 2.44±0.01 Å [34]. The same calculation predicted a 3.4 Å interfacial distance between Au and the interfacial layer if the TiO$_2$ surface was terminated O atoms [34].

4.4. Discussion

4.4.1. Image of the Interface along TiO$_2$[110] (Au[112]) Direction

Figure 4.6 shows the Z-contrast images of Au nanocrystals (NCs) of three different sizes recorded along the TiO$_2$ [-110] and Au [112] zone axis direction. An interfacial layer marked by the arrow forming between the Au NCs and TiO$_2$ support is seen in all three NCs. The interface shows a distinctive contrast with greater intensity variations when compared with that of TiO$_2$ or Au atomic columns. The Au NCs are epitaxially oriented on TiO$_2$; because of this, both Au and Ti atoms are resolved at atomic resolution. The epitaxial relationship here can be described as $Au(11\bar{1})\|TiO_2(110)$ and $Au[1\bar{1}0]\|TiO_2[001][43]$. In the Au [112] zone axis orientation, the Au atoms are arranged in a rectangular lattice defined by the basis lattice vectors of $Au[11\bar{1}]$ and $Au[1\bar{1}0]$. The $Au[11\bar{1}]$ close packed planes are seen parallel to the interface; the atomic columns in each layer are separated by a distance of 1.44 Å. On the rutile support, two types of atomic columns are seen along TiO$_2$ [-110] zone axis – ‘Ti-only’ columns and ‘Ti-O’ columns, which have the same
number of Ti atoms as the Ti-only columns and two extra oxygen atoms for every Ti atom. Ti-O columns have a stronger HAADF signal than Ti only columns[27] due to higher mass. The two types of Ti columns are marked as A and B in the structure illustration shown in the inset. Overall, the brightness of TiO₂ is low compared to Au due to the lower electron charge of Ti. Oxygen atoms are not observed in the image. At the interface, atomic columns with bright contrast are observed among neighboring dark atomic columns; the bright columns are separated by distances very distinct from that of TiO₂ or Au.

![Image](image.png)

**Figure 4.6.** (a-c) shows the Z-contrast images of Au NCs of three different sizes recorded along the TiO₂ [-110] and Au [112] zone axis direction. An interfacial layer marked by the arrow forming between the Au NCs and TiO₂ support is seen in all three NCs. The epitaxial relationship here can be described as Au [112] || TiO₂ [-110] and Au [1-10] || TiO₂ [001].

### 4.4.2. Details of STEM Simulation

The atomic model and STEM simulation results are summarized in Figure 4.7. A TiO₂ slab with Au NC on top is used to simulate the STEM focal series images. The TiO₂
support is made of the Ti columns with 23 atoms with the total thickness of 6.57 nm. A single, or multiple, Ti atom(s) at the interface was replaced by Au to model the interfacial atomic columns with the intermixed Ti and Au atoms. The effect of Au atom positions were tested for a single Au atom located at 2.96, 2.07 and 1.18 nm above the center of the model. A single, two and three Au atoms were placed in the middle of the sample to simulate the effect of the number of Au atoms on the ADF-STEM intensity. An Au column with 9 atoms was employed to simulate the Au ADF-STEM intensity.

A 2D intensity profile similar to that of Ti profile in Figure 4.2(c) is seen for Ti column in the first row in Figure 4.7 with the intensity peak locating in the center. The intensity peak increases for columns with one, two and three Au atoms in the center, so as the image in 0 focus. With more Au atoms, the stronger intensity becomes elongated more as well, similar to the profiles from interfacial layer in Figure 4.2(c). For Ti columns with single Au atom, an upper shift of intensity peak is seen in depth direction along with Au atom at 0, 1.18, 2.07 and 2.96 nm above the center. For each Au atom at near 1 nm above the previous one, the peak shift with 1 pixel in depth, corresponding to 0.5 nm defocus, with their width at the same value, as in Figure 4.8. The strongest and most elongated intensity profile comes from Au column, because it has most Au atoms and thus strongest scattering.
Figure 4.7. The atomic model and STEM simulation results. The TiO$_2$ support is made of Ti columns with 23 atoms with the thickness of 6.57 nm. A single and multiple Ti atoms in the interface columns were replaced by Au atoms and stand for columns with intermixed Ti and Au atoms. The single Au atoms were located at 2.96, 2.07 and 1.18 nm above the center. A single, two and three Au atoms were also put in the center. An Au column with 9 atoms was employed to simulate Au intensity. The models are demonstrated in the second row. The simulated 2D intensity profiles are plotted in the third row. The fourth row shows simulated atomic images at 0 defocus.

4.4.3. Sensitivity of Depth Sectioning along Defocus Direction

In Figure 4.8, we test the sensitivity of depth sectioning along the defocus direction. With individual gold atoms inserted at four different positions from the center to the top of the Ti column. Four STEM focal series of images are simulated. The strongest intensity
peak comes from the column with Au atom at 1.18nm above the center. It is seen, that from center to top, with each single gold atom moving 1nm above the other one, the intensity peak shift upwards by 1 pixel, corresponding to 0.5 nm in defocus. Thus in simulation condition, the change of atom position along defocus direction could be detected. In experiments, however, the S/N ratio and accuracy of defocus steps can hardly compare with ideal simulations. Thus location information with accuracy better than 3 nm along defocus direction is not expected with current STEM experiments, while intensity peaks that are seen with large differentiation are reliable to represent relative atom positions in defocus direction.

**Figure 4.8.** The sensitivity of depth sectioning along defocus direction. (a) shows simulated depth sectioning images with one Au atom located at 2.96 nm, 2.07 nm, 1.18 nm above the center and one located right at the center of the Ti column. The intensity profiles along depth direction of the four images are plotted in (b).
4.4.4. Peak Intensity Analysis

In the peak intensity analysis, we first performed a peak search using the template matching technique [25, 49]. This is then followed by peak intensity measurement using the average of top 10% peak following the published example [50]. For each defocus, the average peak intensity, and its position (x and y) are measured. The intensity peak positions are then plotted in 3D in Figure 4.9 with x, y values in each scanning plane and z values as the defocus value. The yellow spheres resemble Au intensity, grey spheres resemble Ti intensity, and the small grey and large pink ones resemble IS (interfacial Ti) and IL (interfacial Au) intensity, respectively. Because an individual atom could lead to atomic images at different focuses, these plotted spheres are not individual atoms. The positions of the spheres in 3D, however, illustrate the relative position of atomic intensity peaks of different elements. Partial Au intensity located in a row of Ti intensity is seen, similar as that shown in the depth sectioning intensity profile. The position of these peaks indicates a rumpled interfacial layer, which shift upward or downward by 92.4±40 pm. These localized atomic shifts likely reflect the influence of local interactions among Au, Ti and O atoms.
Figure 4.9. 3D plot of intensity peak positions. The yellow spheres resemble Au intensity, grey spheres resemble Ti intensity, and the small grey and large pink ones resemble IS (interfacial Ti) and IL (interfacial Au) intensity, respectively.

4.4.5. Estimation of the Number of Au Atoms in Interfacial Atomic Column

To estimate the number of gold atoms in a column at the interface, we combined the information obtained from experiment with the simulated depth sectioning images. In the inset of Figure 4.3, we plotted the intensity profiles from STEM images of Ti columns with 0, 1, 2, 3 Au atoms in the center. Increment of the peak intensity is seen with more Au atoms embedded in the Ti column. The increase is also monotonously linear up to with 3 Au atoms, as seen in Figure 4.3. After normalizing the Ti column intensity with experimental image, we applied the result to estimate the number of Au atoms in each column at the interface using the interface depth sectioning image. As shown in Figure 4.5, the intensity profile from TiO₂ top layer shows the peaks at near 15000. There are peaks from the interface layer showing similar intensity values and overlaps with the peaks from TiO₂ layer. This indicates those interfacial peaks are from TiO₂ layers without embedded
Au atoms. There are other interfacial intensity peaks label as column 1 at the value 57000, column 2 at 67000, column 3 at 37000, column 4 at 33000, column 5 at 32000, column 6 at 31000, column 7 at 85000, column 8 at 340000, column 9 at 48000 and column 10 at 31000. These therefore represents Ti columns with 3-5, 4-6, 1-3, 1-3, 1-3, 1-3, 6-8, >10, 2-4, 1-3 Au atoms, respectively. Among them, column 8 with 340000 peak intensity has strong signals for the entire focal series images, hence can represent the case that an entire column of Ti is replaced by Au atoms.

4.5. Conclusions

In conclusion, using depth-sectioning STEM, we have identified interfacial Au atoms at the Au nanocrystal and TiO$_2$ interface. They are embedded inside a single atomic layer. The mechanism for the interfacial layer formation is suggested based on the reduction of TiO$_2$ surface in the form of the added-row 1x2 reconstruction. This is supported by the evidence of interfacial Au atoms as well as the measured interfacial spacing. Furthermore, experimental results show that reconstruction is not homogenous, where certain rows having more Ti atoms and embedded Au atoms than others. Thus, our results show while the surface of TiO$_2$ support determines the initial Au-TiO$_2$ interface, the presence of an Au nanocrystal can lead to the formation of a special interfacial layer embedded with interfacial Au atoms.

We expect two major impacts of interfacial Au atoms on Au catalysis. The first is a strong Au-TiO$_2$ interaction as evidenced by a reduction of surface TiO$_2$, the reduced Au-TiO$_2$ interfacial spacing and flattening of Au nanocrystal. This strong interaction between Au and support correlates with the enhanced catalytic activity previously demonstrated in Au nanoparticles prepared by high temperature calcination according to Widmann[30],
Akita[31] and Haruta[3]. Secondly, the interfacial Au atoms are primarily formed near the perimeter of the Au-TiO$_2$ interface. Previous theoretical study has shown that the interfacial Au atoms are stabilized by the formation of oxygen vacancies[34]. Since the perimeter sites are the most accessible sites at the interface and the catalyst activity scales with the length of interface perimeter[30], our observation thus provides a possible mechanism for the promotion of the oxygenation – reduction cycles at the interface.
4.6. References


CHAPTER 5

OXYGEN STATE CHANGE IN THE INTERFACE OF GOLD NANOCRYSTAL
SUPPORTED ON RUTILE SURFACE

5.1. Introduction

Au, which is inert as bulk material, becomes increasingly active when they are nanoparticles with sizes approaching 5nm in diameter for selective oxidation of CO or LT-WGS (low-temperature water gas-shift) reactions [1-4]. Extensive results from experiments and calculations demonstrate three major factors affecting the catalytic activity and selectivity; the selection of metal oxide supports[2, 5-8], the sizes of the Au nanoparticles[2, 9], and the structure in Au-support contact[10-12]. All three factors are related to the catalyst preparation method[13]. Several proposed mechanisms focused on the structure of Au nanoparticles or the interfacial interaction, in order to explain the dramatic size-dependent chemical activities of gold. The role of low-coordination surface Au atoms[14-17] or quantum size effect[18-20] can be directly related to the structure of Au nanoparticles, while interfacial charge transfer[6, 17, 21], strong support interaction[12, 22-24], strain[25] and interfacial atoms[26] are the major proposed mechanisms involving the interface.

Direct evidences of support effect in the catalytic reactions come from several experiments, which have shown that reducible interfaces have demonstrated advantages over non-reducible ones for Au catalysts [2, 3, 27, 28]. Widmann proposed that the reducible interfaces could provide moving oxygen and oxygen vacancies that are necessary to enhance the reaction rate and stabilize the Au NCs [27]. The other interfacial effect is its large impact on the nanoparticle’s morphology and strain[22, 24, 25, 29, 30], as well as
the atoms near perimeter of the nanoparticles[12, 31]. Suggestions have been made in the literature regarding the mechanism of CO oxidation catalyzed by interfacial Au/oxygen atoms or Au-assisted interfacial sites [26, 27, 32]. While interfacial Au atoms have been observed recently (Chapter 4), no directly interpretable images of interfacial oxygen atoms between Au and the supports have been reported.

The major obstacle for imaging oxygen is its small electron scattering cross section. Recently, several groups have demonstrated the technique of Annular Bright Field (ABF) STEM imaging for detecting light atoms in the aberration corrected STEM [33, 34]. The ABF detector uses smaller cut-off angles for the collection of scattered electrons than the annular dark field (ADF) detector. At the cutoff angles of 11-22 mrad, the ABF detector could efficiently collect electrons scattered by light atoms, such as oxygen. The other approach to detect light atoms is to use phase contrast imaging [35, 36]. In a chromatic aberration (Cc) corrected TEM, information transfer and image resolution are significantly improved; the flexibility of adjusting individual aberration coefficients with the Cc corrector also allows a precise control of the contrast transfer function which can be used to improve the contrast between heavy and light atoms, and thus helps to enhance the sensitivity to light elements in thin samples using phase contrast. Both ABF and the Cc-corrected TEM techniques thus provide possibility to image oxygen atoms at atomic resolution, even in instances where the oxygen atoms are situated a short distance away from strong scatters of heavy atoms like gold and titanium.

Here, we report an atomic scale study of interfacial oxygen at the Au/TiO₂ interface using ABF-STEM and Cc-corrected TEM imaging. The influence on interfacial oxygen by
heat treatments is investigated by imaging the same type of interface before and after the heat treatment.

5.2. Experimental

To prepare the cross sectional sample for electron microscopy, we started with a single crystal rutile (TiO$_2$) substrate. The single crystal TiO$_2$ (110) surface is selected for study. The (1x1) surface of TiO$_2$ (110) is terminated by oxygen atoms that are two-fold coordinated to titanium atoms [37] and it is the most thermodynamically stable surface of TiO$_2$. To prepare electron transparent samples, we use mechanical pre-thinning and ion milling. Afterward, oxygen atoms can be removed and the surface restructures into several possible reconstructions [37]. The reduced surfaces can be re-oxygenated by annealing in O$_2$ or in air at high temperatures [37]. The specimens we prepared were annealed in air at 1000 º C, then e-beam evaporation deposition of gold was performed at room temperature, which was followed by annealing in air at 500ºC to form epitaxial Au NCs (The same annealing procedure used for activation of Au catalyst [3, 26, 38, 39]).

The ABF STEM imaging was performed using a JEOL ARM200 S/TEM equipped with ABF detector and the probe corrector (installed in Brookhaven National Laboratory). C-corrected HRTEM was done on ACAT (Argonne Chromatic Aberration-corrected TEM) at Electron Microscopy Center in Argonne National Laboratory.

5.3. Results

Figure 5.1(a)-(c) show three STEM images of the Au NCs viewed along the TiO$_2$ (001) zone axis direction. At this orientation, the projected tetragonal rutile structure appears as a square lattice. Figure 5.1(a) is a Z-contrast image showing Au NCs deposited on TiO$_2$
surfaces with a size distribution from 3.3 nm to 5.7 nm in the nanocrystal width as measured parallel to the support surface. An atomic resolution HAADF image and the corresponding ABF image are shown in Figure 5.1(b) and (c). In Figure 5.1(b), both atomic columns of Au with bright contrast in the NC and Ti in TiO$_2$ with less bright contrast are resolved, showing a sharp interface in between. Oxygen is hard to see in the HAADF images, due to its low atomic number. The Au NC has a shape that could be fitted with truncated Wulff construction [25, 40-42]. The Ti columns are in a square lattice fitting with the 2D projection of TiO$_2$ atomic structure from (100) zone axis. In the ABF image in Figure 5.1(c), the background contrast from vacuum is bright, atomic columns are dark. Atoms in the Au NC are thus in invert contrast from the HAADF image. The TiO$_2$ support is seen as a lattice of horizontal and vertical dark contrast triplets. In each triplet, the center is Ti column with the adjacent intensity from oxygen as the 2D TiO$_2$ unit cell in the inset of Figure 5.1(c), where Ti atoms are in grey and oxygen in red.

**Figure 5.1.** Aberration corrected STEM images of Au/TiO$_2$. A low magnification image of Au NCs deposited on TiO$_2$ surface is shown in (a). (b) is an magnified HAADF image with atomic resolution. The ABF image of the same area as (b) is shown in (c). The inset shows 2D projection of a TiO$_2$ unit cell, with Ti atoms in grey and oxygen in red.
5.3.1. Interfacial States of TiO$_2$

The interface is examined using in ABF STEM. For ABF images, the atoms are in dark and vacuum in bright. In Figure 5.2, we inverted the contrast. In Figure 5.2(a), the Au NC is 4.5nm in width with clear facets. Oxygen contrast is seen at the interface between the Au NC and the top Ti layer. The Au atom next to the bridging oxygen shifts downwards along the Au bottom layer, indicated by the black triangle in the zoomed in image in Figure 5.2(b). The spacing between the bottom of Au NC and the top Ti layer is measured to be 3.11 Å, consistent with the spacing predicted by DFT calculation [32]. In Figure 5.3, the Au NC is near 5nm in width with facets as well. The interface is different from Figure 5.2. No bridging oxygen is observed. The interfacial spacing is 2.46 Å, close to the model in DFT calculation [32].

![Figure 5.2](image.png)

**Figure 5.2.** An ABF image of Au on TiO$_2$ surface with bridging oxygen viewed from TiO$_2$ (001) zone axis, with the contrast inverted and shown in color in (a). (b) shows the zoom-in image of the interfacial area, with the inset showing 2D projection of a TiO$_2$ unit cell, Ti atoms being in grey and oxygen in red. The black triangle indicates the downward shift of an Au atom next to the bridging oxygen. Atomic displacements measured from the atomic resolution image are shown in (c). The atom positions in an undistorted lattice are marked by circles, while the colored image is from experimental image.
Figure 5.3. An ABF image of Au on reduced TiO$_2$ surface viewed from TiO$_2$ (001) zone axis, with the contrast inverted and shown in color in (a). (b) shows the zoom-in image of the interfacial area, with the inset showing 2D projection of a reduced TiO$_2$ unit cell on the surface, Ti atoms being in grey and oxygen in red. The black triangle indicates the downward shift of an Au atom next to the bridging oxygen. Atomic displacements measured from the atomic resolution image are shown in (c). The atom positions in an undistorted lattice are marked by circles, while the colored image is from experimental image.

Oxide support with different surface structures would influence the atomic structure of the epitaxy Au NCs. To measure the displacement of the Au atoms, we first applied TeMA to the as recorded STEM images, the positions of each atom columns are located; an average lattice is then generated using the positions. Scanning distortion is corrected using TiO$_2$ lattice as reference. For Figure 5.2, where the interface is oxidized, before the correction, the TiO$_2$ lattice is measured as $a=3.25$ Å, $b=3.15$ Å, alpha= 90.21°, and Au lattice as $a=2.49$ Å, $b=2.42$ Å, alpha=110.55°, for the Au NC; after the correction, Au lattice is $a=2.49$ Å, $b=2.48$ Å, alpha=109.07°, comparing to the standard lattice of $a=2.50$ Å, $b=2.50$ Å, alpha=109.5°. The averaged lattice from calculation is superposition on the corresponding HAADF image with a different color code in Figure 5.2(c). In Figure 5.2(b),
a zoomed in image in the interface of Figure 5.2(a), displacement of Au atoms near the interface is seen that the entire bottom of Au is elevated by the oxygen interface while some Au atoms residing between bridging oxygen atoms shift downward, as indicated by the black triangle. The atoms are thus modulated by the surface of TiO$_2$ and could also move horizontally. The downward shift of Au atom between the bridging oxygen is around 0.6 Å. The atomic shift is propagating through the whole NC and relaxed after 4 layers as shown in the image. The image showing the atomic position deviation of Au NC on reduced surface is shown in Figure 5.3(c). In this case the Au lattice is a=2.48 Å, b=2.47 Å, alpha=108.492° after correction. At the reduced interface, no obvious vertical shift of Au atoms is seen, since the TiO$_2$ surface is flat without bridging oxygen, while horizontal shift and larger deformation of Au lattice indicates a stronger interaction between Au and reduced TiO$_2$ surface.

The different oxygen contrast between the interfaces reveals the change of the interfacial oxidation state. Starting with an oxidized surface, the Au NC is deposited on the substrate. During the annealing, the structure of Au NC is influenced by the substrate, and so is the TiO$_2$ surface by the NC. A layer of oxygen atoms could repulse the entire Au NC upwards, while some Au atoms shift back to close to Ti atoms between bridging oxygen atoms; on the other hand, Au atoms could promote the reduction of the interface. The former process results in the modulation of Au atoms, and the latter could results in a reduced interface without terminating oxygen.
5.3.2. Interfacial Spacing

In DFT calculations used to refine the structure of the Au/TiO$_2$ interface, different models were compared from their adhesion energies and interfacial spacing [32]. According to the models in DFT calculation, the interfacial spacing between Au bottom and Ti top layers can be largely influenced by the oxidation state and the localized reduction. From the models, a fully oxidized interface between Au and Ti has a spacing of 3.6 Å, and a fully reduced interface of 2.45 Å. The spacing of a reconstructed interface with embedded Au atoms is even smaller. We measured the interfacial spacing from 32 selected Au NCs on TiO$_2$ (110) surfaces, as shown in Figure 5.4. The measurement of our experimental result shows a distance transition from 2.14 Å to 3.35 Å in Figure 5.5. No obvious abrupt change is seen, instead, the transition is smooth. In the histogram of interfacial spacing in the inset of Figure 5.5, only a few Au NCs show very small interfacial space, which indicates potentially significant reduction, all other Au NCs show an approximately uniform distribution of spacing between 2.4 Å and 3.4 Å. On the TiO$_2$ surface in the DFT model, the bridging oxygen atoms are either all kept or all gone, which are ideal cases. The measured data in experiment, on the other hand, indicates partial local oxidation and reduction. Taking the partial reduction of oxygen sites in consideration, the spacing between gold bottom layer and the interfacial layer could have a range from 2.44 Å to 3.5 Å, which is a good explanation for the experimental result.
Figure 5.4. A schematic illustration of the shape of an Au NC (labeled by the red frame) on TiO$_2$ surfaces based on an aberration corrected HREM image. Parameters used to describe the truncated Wulff construction are labeled as $h$, for the height from center to top, $H$, total height of the NC. The interfacial spacing is measured from the two adjacent Au and Ti layers at the interface.

Figure 5.5. The interfacial spacing of 32 Au NCs supported on TiO$_2$ (110) surface. The histogram of the spacing is shown in the inset.
5.3.3. Interfacial Energy

Oxidation states in the interface influences the interaction. The interfacial interaction between Au and TiO$_2$ (110) surface is related to the interfacial energy, which could be revealed by the geometry parameters of the Au NC [41, 43]. Our previous study shows that the equilibrium shape of an Au NC could be fitted with the truncated Wulff construction or Winterbottom construction [41, 43]. In this model, the relationship among the surface energy of Au ($r_{Au}$), the surface energy of TiO$_2$ ($r_{TiO2}$) and the interfacial energy ($r_{Int}$) could be quantified by the equation:

$$\frac{h-H}{h} = \frac{r_{TiO2}-r_{Int}}{r_{Au}}$$  \hspace{1cm} (5.1)

where $h$ and $H$ are the center-to-top distance and total height of the NC respectively.

The interfacial energy, which is the quantification of interaction, could then be estimated from Eqn. 5.1, as $r_{Int} = r_{TiO2} + \left(\frac{H}{h} - 1\right)r_{Au}$. In the experiment, TiO$_2$ (110) and Au (111) surfaces are selected, so the interfacial energy is dependent only on the factor of $\frac{H}{h}$.

In Figure 5.2, the NC on oxidized interface has a value of 1.71 for $\frac{H}{h}$, in the reduced interface case of Figure 5.3, the value is 1.49. Larger value of $\frac{H}{h}$ indicates higher interfacial energy and less stable interface. According to the equation: $r_{int} = r_{TiO2} + r_{Au} - r_{bonding}$, where $r_{bonding}$ is the bonding energy between the two surface, larger interfacial energy also indicates weaker interaction. A distribution of H/h value for all the Au NCs is plotted in Figure 5.6(a). Two small but obvious peaks appear between 1.5-1.6 and 1.8-1.9. Higher H/h value corresponds to large amount of truncation of Wulff construction, like Figure 5.6(b), lower value indicates small truncation like Figure 5.6(c).
Figure 5.6. (a) The histogram of $H/h$ for the 32 selected Au NCs supported on TiO$_2$ (110) surface. (b) shows a NC with large truncation of Wulff construction. (c) shows a NC with small amount of truncation.
To correlate the interaction with oxidation states, we further plot H/h vs. interfacial spacing in Figure 5.5. A major trend is seen that the H/h value increases along with interfacial spacing. Within the lower interfacial spacing region in the blue box, H/h value is distributed in a range from 1.3 to 1.7, with the majority around 1.5. For Au NCs showing a larger interfacial spacing as shown in the region of red box, the H/h value has a range from 1.45 to 1.95, with most of the points above 1.75. Large interfacial space is a strong indication of oxidized interface, where Au NCs are locating on oxygen terminated surface. The larger interfacial energy should result from weak bonding between Au and oxygen. In contrast, a strong interaction between Au and Ti leads to a stable interface with lower energy. This further concludes that the stable Au/TiO$_2$ system is in favor of interfacial reduction. From the two HREM images in Figure 5.6, Figure 5.6(b) shows a truncated Au NC on an reduced TiO$_2$ surface, and the Figure 5.6(c) a less truncated NC on a oxidized interface.

5.4. Conclusions

The experimental observations of both surface and interface, measurement of the interfacial spacing lead to the following conclusions: a) Au NCs deposited on rutile TiO$_2$ (110) surfaces are modulated in the interface by the TiO$_2$ support; b) the bridging oxygen at the interface repels the Au NC upwards with Au atoms between bridging oxygen atoms shifting downwards; c) Au NCs could also facilitate the reduction of the TiO$_2$ surface and formation of a stable interface during heat treatment; and d) the interfacial spacing distribution reveals partial reduction at the interface instead of a complete one.
5.5. References


CHAPTER 6

SCIENTIFIC OPPORTUNITIES IN ENVIRONMENTAL ELECTRON MICROSCOPY USING FAST ELECTRON DIRECT DETECTION CAMERA

Significant progress has been made in spatial resolution using environmental transmission electron microscopes (ETEM), which now enables atomic resolution visualization of structural transformation under variable temperature and gas environments close to materials’ real operational conditions (for a review, see ref [1]). Structural transformations have been observed by recording images or diffraction patterns at various time intervals using a video camera or by taking snap shots using electron pulses [2]. While time resolution at 15 ns has been reported using pulsed electron beams [2], the time interval that can be recorded by this technique is currently very limited. For longer recording, however, time resolution using ETEM has been limited by electron cameras to ~1/30 seconds for a long time. Using the recently developed direct electron detection technology [3], we have significantly improved the time resolution of ETEM to 2.5 ms (milliseconds) for full frame or 0.625 ms for ¼ frames.

Here two systems are employed to study the nanoscale catalyst behaviors at the improved time resolution and spatial resolution, including Au NPs on Si nanowires (NW) and Pt icosahedral NPs. Experiments were carried out using Hitachi H-9500 ETEM with a LaB₆ emitter, operated at 300 kV. The instrument provides direct gas injection into sample chamber as well as gas injection through a specially designed sample holder. In imaging mode, the instrument is capable of resolving features in thin crystalline samples at 0.18 nm point to point. The samples are heated using a W filament by passing current [4]. The direct electron detection camera (model K2-IS) made by Gatan (Pleasanton, CA) is used for video
recording, which has 3838x3710 pixels of 5 μm in size.

6.1. Au Nanoparticle Kinking and Au Atomic Diffusion on Si Nanowire

Figure 6.1 shows four image frames at 2.5 ms apart from a 300 seconds video recorded in bright field. The images focused on the tip of a silicon NW, where the Au catalyst after heating at 400 °C tilted from the tip to the side of the NW. When this occurred, Au was seen diffuse away along the NW surface. At 0 ms (10 min after the start of heating), Au diffusion was observed on the side of the NW as indicated by the arrow. At 2.5 ms, we saw further surface diffusion followed by a significant change in the wetting angle of Au nanoparticle at 5 ms, as well as image contrast change indicating significant amount of atomic movements. Image contrast associated with Au diffusion was observed over a distance of tens of nm along the NW within 7.5 ms. Further analysis shows a diffusion coefficient of approximately 10^{-8} cm²/s.
Figure 6.1. Bright field TEM images of the tip of SiNW taken at different time. The diffusion of Au atoms is indicated by the propagation of dark contrast starting from the tip along the NW surface vertically and horizontally. A schematic illustration of the Au diffusion process is provided beneath the images.

6.2. Transformation of Pt Icosahedral Nanoparticles into FCC Single Crystal

Icosahedral nanoparticles have 12 fivefold axes and 20 triangular \{111\} faces, which belong to the icosahedral symmetry group [5-8]. They are in a special class of nanostructures, called multiple twinned particles (MTP) [5-7, 9]. The structure of MTPs in general can be formed by face joining FCC tetrahedral subunits together. However, space-filling of those subunits is not complete, leaving a large angular misfit. Thus, MTPs are formed with strain from internal distortion or modification to the crystal structure. MTPs have attracted special interest in nanoscience and technology because of their unusual atomic packing and noncrystallographic symmetry [10, 11]. Large MTPs can be grown
from small seeds under controlled conditions [11, 12]. However, they are predicted to be unstable compared to the bulk FCC structure at large sizes [5-7].

Recently, uniformly large IC nanoparticles of 20 to 36 nm have been successfully synthesized through careful control of growth kinetics [11, 12]. They demonstrate outstanding chemical activities for fuel cell catalysis. TEM results have shown they are also stable under the electron beam [13], due to the large energy barrier built-up by the strain preventing their transformation[6, 7]. However, experimental evidences suggest that those IC structure is unstable when exposed to oxygen at elevated temperatures [11]. To investigate this and to address the critical question of transformation between the metastable MTPs and stable FCC structure, we carried out an in-situ study using an environmental TEM with fast electron imaging capability.

Upon heating in air at elevated temperatures, we observed the transformation of Pt icosahedral particles in contact with each other to FCC crystals. Figure 6.2 shows a cluster of Pt icosahedral nanoparticles before and after phase transformation. In Figure 6.2(a), which was recorded at the beginning of the experiment, all nanoparticles were faceted showing their characteristic hexagonal shape as viewed along the icosahedral 2/3 fold axis. The icosahedral structure is evidenced by the diffraction pattern in Figure 6.2(e) obtained from the particle in Figure 6.2(d). After transformation, the particles showed rounded shapes as well as evidences of particle coalescence. The diffraction pattern recorded from the particles show that they are FCC crystal of the same orientation.

Previous HREM studies of small MTPs using video recording revealed fast phase changes between a numbers of structures, including FCC single crystal, single twinned cuboctahedron, fivefold twinned decahedron, and icosahedron[14]. The small MTPs do not
transform into the same structure, as there is only a small energy difference among different configurations, and the observed structural changes were suggested to reflect the statistical fluctuations of particle configurations [15]. Unlike these previous reports, we observed that the transformation started from a single or few grains succeeded in turning hundreds or more of equally sized and strained FCC grains of different orientations in the IC NPs into a single FCC crystal.

Figure 6.2. Transformation of a group of Pt IC NPs to FCC crystal as demonstrated by electron images recorded (a) before and (b) after the transformation. The IC NPs were oriented approximately as illustrated in (c). The IC structure is evidenced by electron diffraction (e) recorded from (d). (f) is an electron diffraction pattern recorded from the transformed NPs using a probe indicated by the circle in b).
In summary, we have achieved significant improvement in time resolution for in-situ environmental TEM. Preliminary results presented here demonstrate the capture of atomic diffusion process of Au on Si NW surface at 2.5 ms intervals. The time resolution is sufficient in revealing two processes, involving an initial wetting of Si NW surface by Au atoms followed by a change in Au nanoparticle morphology [6]. For the Pt icosahedral NPs, the transformation was triggered by exposure to air and facilitated by grain boundary migration. These results provide insights for understanding the mechanisms in both systems.
6.3. References


CHAPTER 7

CONCLUSIONS AND FUTURE PERSPECTIVES

7.1. Conclusions

This thesis has outlined a systematic study of the interfacial structure of Au/TiO$_2$ and interfacial interactions, and a first study of time-resolved imaging of reaction dynamics for Pt icosahedral nanoparticles enabled by the use of fast electron direct detection camera.

Using a combination of advanced TEM and the model Au/TiO$_2$ interfaces prepared by e-beam evaporation deposition and high temperature air annealing, we have demonstrated the following:

1) The interaction of Au NCs with stepped rutile (TiO$_2$) (110) surfaces is elucidated by examining the rotation of Au NCs, modification of interfacial energy, triple line energy and atomic strain. From the atomic resolution Z-contrast images provided by AD-STEM, we discovered that the approximated epitaxial orientation relationship between Au and TiO$_2$ remains in the case of Au on vicinal TiO$_2$ (110) surfaces. The surface steps induce a small rotation in the NCs in an amount less than the surface miscut angle, the high miscut surface does not necessarily lead to higher rotation angle. Significant strain builds up near the surface steps inside Au NCs and relaxes into the body of the NCs. The shapes of Au NCs on low miscut surfaces demonstrate certain similarity in a large height/width ratio. Based on the modified Wulff construction, the calculated interfacial energy is lower compared to Au NCs on flat surfaces, indicating a more stable interface, while the triple line energy is increased.
2) From the study on the shape and structure of Au NCs, the support effect by the interface is seen to be significant. It is thus necessary to investigate the 3D interfacial structure in details. Using the improved resolution along beam direction by depth-sectioning brought by AC-STEM, we identified interfacial Au atoms embedded inside a single atomic layer at the Au/TiO$_2$ (110) interface. The mechanism for the formation of interfacial layer is suggested based on the reduction of TiO$_2$ surface in the form of the added-row 1x2 reconstruction. This is further supported by the measured interfacial spacing. Quantitative estimation on the number of Au atoms along each projection column shows that there are certain rows having more Ti atoms or more embedded Au atoms than others, the interfacial reconstruction is therefore not homogenous.

3) To achieve a complete picture of the interfacial structure requires interpretable images of oxygen atoms. The use of ABF STEM imaging and chromatic AC-HREM enables the observation of oxygen in TiO$_2$ lattice. At the Au/TiO$_2$ interface, both terminated oxygen atoms and reduced oxygen vacancies are observed, indicating the promotion of oxygen reduction by Au NCs. Deformation is seen at the bottom of Au NCs near the oxygen terminated interface, where the entire Au NCs are elevated and Au atoms between two bridging oxygen atoms shift downwards. On reduced interface, the Au NC forms a smooth bottom layer. The stability of interface can be revealed by measurement of the interfacial spacing and energy. It is found that with smaller interfacial spacing at the reduced interface, the Au NCs share a larger H/h ratio, further indicating stronger interaction and more stable structure. Therefore the
stability resulted from high temperature annealing is brought by partial reduction at the interface thanks to Au NCs.

Thus, our results in the study of Au/TiO$_2$ catalyst show while the surface of TiO$_2$ support determines the initial Au/TiO$_2$ interface, the presence of an Au nanocrystal can promote the formation of interface with different oxidation states and a special interfacial layer embedded with interfacial Au atoms. We expect two major impacts of the interfacial reduction and embedded Au atoms on Au catalysis. The first is that a strong Au/TiO$_2$ interaction is observed as evidenced by a reduction of surface TiO$_2$, with reduced Au/TiO$_2$ interfacial spacing and Au nanocrystal flattening. This strong interaction between Au and oxide support is directly related to the enhanced catalytic activity previously reported in Au nanoparticles prepared by high temperature calcination according to Widmann[1], Akita[2] and Haruta[3, 4]. Secondly, the interfacial Au atoms are primarily observed near the perimeter of the Au/TiO$_2$ interface. In theoretical study, it is shown that the interfacial Au atoms are stabilized by the formation of oxygen vacancies [1, 5]. Since the perimeter sites are the most accessible sites at the interface and the catalyst activity scales with the length of interface perimeter [1, 4], our study using electron microscopy thus provides a possible mechanism for the promotion of the oxygenation – reduction cycles at the interface.

In studying the nanoparticle dynamics using a fast environmental TEM, we captured the atomic diffusion process of Au on Si NW surface at 2.5 ms intervals. The time resolution is sufficient in revealing two processes, involving an initial wetting of Si NW surface by Au atoms followed by a change in Au nanoparticle morphology. We also captured the staged transformation of Pt icosahedral nanoparticles to FCC single crystal.
The structure prior and post the phase transformation is confirmed by both in situ HREM and electron diffraction. Our experiments show that the transformation is activated by chemical reaction and assisted by grain boundary diffusion and grain growth. This shed light on the mechanism into the instability and evolution of nanoparticle catalyst during reaction. In situ environmental TEM therefore provides informative results on revealing the reaction dynamics, especially at high spatial and time resolution exceeding other available techniques.

7.2. Future Perspectives

Strain evolution of catalyst surface/body during reaction

In our study, it is shown that the catalyst structure could change during reaction; in the extreme case the structure evolution is not reversible. As catalytic behaviors take places mostly on the surface. The reaction rate and selectivity largely depends on the availability of active sites. Therefore surface structure change and modification is one hypothesis in mechanisms of nanoparticle catalysis. Our preliminary study on Pt icosahedral nanoparticles with different sizes indicated that the surface strain that changes the surface atomic spacing could be one major factor that influences the activity in ORR reaction. In TEM, it is difficult to image only one surface plane in a nanoparticle, however, the change of surface strain will introduce corresponding changes in inner planes as well. Observing the strain evolution of the nanoparticle could thus provide critical insights in revealing the surface effect on catalysis, taken advantages of the high resolution and possible image processing provided by the fast electron camera.
In situ liquid phase study with enhanced resolution provided by fast electron detection camera

In imaging nanoparticle growth, corrosion and reaction in liquid cell in TEM, one major factor that influences the image quality is the random motion of nanoparticles. This is unavoidable due to the nature of Brownian motion for all particles in low dimension. The fast electron camera could achieve interpretable images at the speed of 400 fps up to 1600 fps, while normally a high quality electron camera only takes up to 30 images per second, resulting in blur image due to average signal acquisition in down to 33 ms. With the fast electron camera, the image is taken in 2.5 ms up to 0.625 ms, which could largely reduce the average effect during imaging. Single images could be aligned by cross correlation shift and then averaged to enhance the signal/noise ratio. Thus the use of fast camera brings promising opportunity in improving image quality and resolution, thus unprecedentedly informative details and progress in liquid cell electron microscopy.

Low dose high resolution electron imaging using electron direction detection camera

Chemical reactions in principle are all about electron transfer. The high energy electrons in TEM for image formation will interact with the imaged atoms, liquids and affect the reaction rate or even change the reaction behavior during observation. Extensive effort has been made to reduce the electron beam effect in imaging chemical reactions, reducing electron dose being the most promising way. However reduced electron dose also lowers the contrast and signal noise ratio, resulting in worse image quality. The enhanced sensitivity of electron direct detection camera will improve the image quality even in low dose imaging condition. In combination with post-acquisition image processing, the informative details could be achieved with better image quality as well as better time
resolution.

**Imaging of electric field of shape controlled nanoparticles in electrochemical reaction**

Imaging catalyst structure and structure changes during reaction is an indirect way to acquire information about active sites for reaction. A more direct way is to derive the electric field of catalyst during reaction. A site with large changes in electric field could possibly be active for catalysis. In electron microscopy, the image formation is based on electron interaction with objects. Electric field could be imaged in TEM and therefore bring better understanding on catalyst activity.
7.3. References


