Crystal phase effect and site confinement effect of metals in heterogeneous catalysis

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**CRYSTAL PHASE EFFECT AND SITE CONFINEMENT
EFFECT OF METALS IN HETEROGENEOUS CATALYSIS**

ZHONG LIXIANG

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2020

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EFFECT OF METALS IN HETEROGENEOUS CATALYSIS**

ZHONG LIXIANG

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

A thesis submitted to the Nanyang Technological University
in partial fulfilment of the requirement for the degree of
Doctor of Philosophy

2020

Statement of Originality

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Zhong Lixiang

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Assoc. Prof. Li Shuzhou

Authorship Attribution Statement

This thesis contains material from 2 papers published in the following peer-reviewed journals in which I am listed as an author.

Chapter 4 is published as L. Zhong and S. Li, Crystal phase effect upon O₂ activation on gold surfaces through intrinsic strain. *Nanoscale* **11**, 14587-14591 (2019). DOI: 10.1039/c9nr04510d

The contributions of the co-authors are as follows:

- I performed the simulations and drafted the manuscript.
- A/Prof Li Shuzhou supervised the whole project.

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Abstract

The rapid development of nanotechnology facilitates the design and synthesis of unusual nanomaterials with well-controlled atomic structures, such as metal nanostructures with unconventional crystal phases and confined single metal atoms. An important application of these novel materials is heterogeneous catalysis. The aim of this thesis is to study the catalytic performance of them by using density functional calculations. Specifically, this thesis mainly focuses on oxygen activation and reduction, which is important in both thermal catalysis and electrocatalysis, such as selective oxidation reactions and oxygen reduction reactions (ORR). Gold nanostructures are well-known catalysts for selective oxidation reactions and the crystal phase effect is studied in this thesis. Atomically dispersed Me/N/C (Me = Fe, Co, etc.) are promising nonprecious catalysts for electrochemical ORR, and the reaction mechanism on these single-atom sites is also studied here.

Crystal phase engineering is a promising strategy to tune the catalytic performance of metal nanomaterials. Generally, the crystal phase effect on catalysis is ascribed to distinct surface atomic arrangements of catalysts with different crystal phases. This thesis shows that even for similar surfaces, such as the close-packed surfaces, different crystal phases have considerably different surface reactivity due to their distinct intrinsic surface strains. From first-principles calculations, it is found that the close-packed surfaces of hexagonal close-packed (HCP) and double HCP (4H) gold have significantly smaller intrinsic strains ($\sim 1.3\%$) than that of face-centered cubic (FCC) gold ($\sim 2.3\%$). These distinct intrinsic surface strains result in various oxygen adsorption energies and O_2 dissociation barriers on these close-packed gold surfaces, and the dissociation of O_2 on different crystal phases and surfaces follows the Brønsted-Evans-Polanyi principle.

The electrochemical oxygen reduction reaction (ORR) mechanism was generally considered to be $O_2 \rightarrow OOH^* \rightarrow O^* \rightarrow OH^* \rightarrow H_2O$ (O^* mechanism). This O^* mechanism predicted reasonable ORR half-wave potential ($E_{1/2}$) of Co/N/C but abnormally underestimated the one of Fe/N/C. This thesis highlights an unconventional $2OH^*$ ORR

mechanism ($\text{O}_2 \rightarrow \text{OOH}^* \rightarrow 2\text{OH}^* \rightarrow \text{OH}^* \rightarrow \text{H}_2\text{O}$), which was often ignored because the free energies (ΔG) of 2OH^* and O^* are equal according to the famous scaling relation: $2\Delta G(\text{OH}^*) = \Delta G(\text{O}^*)$. This scaling relation is true for traditional catalysts with near-continuous active sites. This thesis shows a different scaling relation: $\Delta G(2\text{OH}^*) = \Delta G(\text{O}^*) + 1.5 \text{ eV}$ on single-atom catalysts (Me/N/C , $\text{Me} = \text{Fe}, \text{Co}$, etc.) because of the confinement of two OH^* on the same active site, and suggests that the 2OH^* mechanism should not be overlooked. In consideration of both O^* and 2OH^* mechanisms, the ORR $E_{1/2}$ of Co/N/C and Fe/N/C are in good agreement with experimental results. This thesis reveals the site confinement effect on ORR reaction mechanisms and scaling relations in single-atom catalysis, and it is also heuristic for other reactions such as O_2 evolution and N_2 reduction on single-atom catalysts.

Lay Summary

Metal based materials are important catalysts, which could accelerate specific chemical reactions. The crystal phase and size of metals are important parameters that determine the catalytic performance. The rapid development of nanotechnology has spawned many novel nanomaterials with well-designed atomic structures, such as metal nanostructures with unconventional crystal phases and single metal atoms supported on inert substrates. The aim of this thesis is to study the catalytic performance of crystal phase-controlled metal nanostructures and single metal atoms. Specifically, this thesis mainly focuses on the catalysis of oxygen activation and reduction, which is important in selective production of chemicals and the cathode of fuel cells. Gold nanostructures are well-known catalysts for selective oxidation reactions and the crystal phase effect is studied in this thesis. Single metal atoms supported on nitrogen doped carbon materials are promising nonprecious catalysts for oxygen reduction in fuel cells, and the reaction route on these single-atom catalysts is also studied here.

On the one hand, the crystal phase effect on catalysis is usually ascribed to distinct surface atomic arrangements of metal particles with different crystal phases. This thesis shows that even for similar close-packed surfaces, different crystal phases have considerably different surface reactivity due to their distinct surface strains, which affect the interaction between the catalyst surface and reactants. From simulations and calculations, it is found that the close-packed surfaces of unconventional hexagonal close-packed gold have significantly smaller surface strains ($\sim 1.3\%$) than that of normal gold ($\sim 2.3\%$). These distinct intrinsic surface strains result in various oxygen adsorption strengths and O_2 dissociation rates on these close-packed gold surfaces. This thesis further proposes that the surface strain can be controlled through the size of gold. The results indicate the important role of intrinsic strain and studied the crystal phase and size effect on it, which are heuristic for design better metal catalysts.

On the other hand, a smaller size of metal particles generally means better catalytic activity and the ultimate size is single atoms, which means atomically dispersed active sites for

catalysis. For the single-atom catalysts, the reactants and reaction intermediates are confined to a single site, which is different from the near-continuous active sites on traditional catalyst surfaces. This thesis finds that this confinement effect is important in the stability of reaction intermediates and could affect reaction pathways. For example, the O_2 reduction process was generally considered to be $O_2 \rightarrow OOH^* \rightarrow O^* \rightarrow OH^* \rightarrow H_2O$ (O^* mechanism). This O^* mechanism predicted reasonable O_2 reduction activity of cobalt-nitrogen-carbon but abnormally underestimated the one of iron-nitrogen-carbon. This thesis highlights an unconventional $2OH^*$ mechanism ($O_2 \rightarrow OOH^* \rightarrow 2OH^* \rightarrow OH^* \rightarrow H_2O$), which was often ignored because the stabilities (ΔG) of $2OH^*$ and O^* are equal according to a well-known scaling relation: $2\Delta G(OH^*) = \Delta G(O^*)$. This scaling relation is true for traditional catalysts with near-continuous sites. This thesis shows a new scaling relation: $\Delta G(2OH^*) = \Delta G(O^*) + 1.5 \text{ eV}$ on single-atom catalysts and suggests that the $2OH^*$ mechanism should not be overlooked. In consideration of both O^* and $2OH^*$ mechanisms, the O_2 reduction activities of cobalt-nitrogen-carbon and iron-nitrogen-carbon are in good agreement with experimental results. This thesis reveals the site confinement effect upon O_2 reduction process on single-atom catalysts, and it is also heuristic for similar reactions such as O_2 evolution and N_2 reduction on single-atom catalysts. The unconventional oxygen reduction mechanism and novel scaling relation provide new opportunities in catalyst design.

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Abbreviations

AAO	Anodized Aluminum Oxide
BCT	Body-Centered Tetragonal
BEP	Brønsted-Evans-Polanyi
CHE	Computational Hydrogen Electrode
DFT	Density Functional Theory
FCC	Face-Centered Cubic
FCT	Face-Centered Tetragonal
FTS	Fischer-Tropsch Synthesis
GGA	Generalized Gradient Approximation
HAADF	High-Angle Annular Dark-Field
HCP	Hexagonal Close Packed
HER	Hydrogen Evolution Reaction
HOMO	Highest Occupied Molecular Orbital
LDA	Local Density Approximation
LUMO	Lowest Unoccupied Molecular Orbital
MEP	Minimum Energy Path
NEB	Nudged Elastic Band
ORR	Oxygen Reduction Reaction
PANI	Polyaniline
PBE	Perdew-Burke-Ernzerhof
PEM	Proton Exchange Membrane
RHE	Reversible Hydrogen Electrode
SEM	Scanning Electron Microscopy
SERS	Surface-Enhanced Raman Scattering
SHE	Standard Hydrogen Electrode
STEM	Scanning Transmission Electron Microscopy
TEM	Transmission Electron Microscopy
TMD	Transition Metal Dichalcogenide
VASP	Vienna Ab-initio Simulation Package

XRD	X-ray Diffraction
ZPE	Zero-Point Energy

Chapter 1

Introduction

This chapter provides a rationale for the research and outlines the goals and scope. The rapid development of nanotechnology has spawned many unusual nanomaterials with well-designed atomic structures, such as metal nanostructures with unconventional crystal phases and confined single atoms. An important application of these novel materials is heterogeneous catalysis. How these novel structures affect catalytic mechanisms and performances? The general objective of this thesis is to study the catalytic performance of unconventional catalysts by using density functional calculations. Specifically, this thesis mainly focuses on oxygen activation and reduction, which is very important in both thermal catalysis and electrocatalysis, such as selective oxidation reactions and oxygen reduction reactions. Gold nanostructures are well-known catalysts for selective oxidation reactions and the crystal phase effect will be studied. Atomically dispersed Me/N/C (Me = Fe, Co, etc.) are promising nonprecious catalysts for electrochemical oxygen reduction reactions, and the reaction mechanism on these single-atom sites will be studied.

1.1 Background

The controlled activation and reduction of molecular oxygen (O_2) on catalysts is very important in thermal catalysis and electrocatalysis. Understanding the oxygen adsorption and reduction mechanism is critical to improve the selectivity and activity in selective oxidation reactions and oxygen reduction reactions (ORR). With the rapid development of nanotechnology, novel nanomaterials with unconventional structures have been reported in recent years, such as crystal phase engineering and single-atom catalysts,^{1,2} which raises the question: How these novel structures affect catalytic mechanisms and performances? The purpose of this thesis is trying to shed some light on this question by taking O_2 activation and reduction as an example. Gold with different crystal phases are chosen to study the crystal phase effect, and Me/N/C (Me = Fe, Co, etc.) single-atom catalysts are adopted for ORR.

1.2 Hypothesis

In this thesis, two hypotheses were tested:

“When the crystal phase of gold changes from FCC to HCP or 4H in nanostructures, the catalytic performance of gold should be different, such as the O_2 activation and dissociation on gold surfaces, which is important in selective oxidation reactions.”

and

“The ORR mechanism on single-atom catalysts may be different from the one ($O_2 \rightarrow OOH^ \rightarrow O^* \rightarrow OH^* \rightarrow H_2O$) on traditional catalysts with near-continuous active sites, because of the site confinement effect on the adsorption of reaction intermediates.”*

Both two hypotheses focus on the O_2 activation and reduction on novel catalysts with

unconventional structures developed in recent years.

1.2.1 Crystal Phase Effect upon O₂ Activation on Gold

Gold catalysis attracted wide research interest in last three decades,³ and crystal phase engineering becomes a novel method to control the properties of metal nanoparticles in the past two decades.^{4, 5} Gold nanostructures have relatively high activity at low temperature, while further improvement of activity impairs the selectivity of desired partial oxidations.^{6, 7} Unconventional hexagonal close-packed (HCP) and double HCP (4H) gold nanostructures have been synthesized in recent years.^{8, 9} As crystal phase effect on catalysis has been confirmed in ruthenium and cobalt nanoparticles,^{10, 11} it is highly desired to study the crystal phase effect on the surface activity of gold.

Gold is the noblest metal because of full electrons filling in *d* bands and large cohesive energy,¹² and therefore it is an inert catalyst with low reactivity toward molecules or atoms on its surfaces. However, the pioneer work of Haruta et al. in 1987 demonstrated that gold nanoparticles could catalyze the oxidation of carbon monoxide (CO) at temperatures as low as -70 °C, which indicates high catalytic activity of gold nanoparticles in this reaction.¹³ This finding attracted tremendous research interests to study the catalytic mechanism of gold in CO oxidation from both experiments and simulations.¹⁴ The particle size of gold is found to be critical in catalytic activity and only nanoscale gold particles or clusters are active.¹⁵ Meanwhile, nanoscale gold was also found to be a good catalyst in many other reactions, such as the water-gas shift,¹⁶ propylene epoxidation,¹⁷ and selective oxidation of glycerol to glyceric acid.¹⁸ Gold is particularly promising in selectively catalytic oxidation under mild and green conditions, because of its high activity using oxygen as clean oxidant at low temperature that inhibits side reactions.¹⁹ It is also economic to use gold instead of some other more precious metal catalysts such as platinum and rhodium.

However, for catalytic reactions, there is usually a trade-off between selectivity and activity. High activity generally results in insufficient selectivity, while high selectivity

often means low activity and poor conversion rate of reactants. For example, reaction temperature is very important in catalysis, especially in selective oxidation reactions. High temperature can promote the activity and reaction rate of catalysis, but it facilitates the complete oxidation of reactants and reduce the selectivity of desired partial oxidation products. This phenomenon is also quite common in gold catalysis. Wittstock et al. reported selective oxidative coupling of methanol using gold catalyst, and demonstrated that the selectivity of methyl formate decreases from ~100% at 20 °C to 75% at 75 °C.⁶

Aside from extrinsic reaction conditions such as temperature, the intrinsic property of the catalyst is even more important to decide the catalytic performance. As mentioned above, particle size is very important in gold catalysis and only nanosized gold structures are active. The catalytic performance of gold nanoparticles can be adjusted simply by modifying the particle size. The particle size is easy to control by using different preparation method and reaction time or changing the concentration of reducing agent and gold precursor. Nikolaos et al. investigated the selective oxidation of glycerol to glyceric acid in liquid phase using gold nanoparticles as catalyst and presented the effect of particle size on the activity and selectivity in this reaction.⁷ When the particle size of gold decreases from 16 nm to 3 nm, the turnover frequency increases from 10 h⁻¹ to 830 h⁻¹, which indicates the activity increases with decreasing size of gold nanoparticles. However, the selectivity of glyceric acid decreases from 80% to less than 60% as particle size of gold decreases from 16 nm to 3 nm. Like temperature effect, there is still a dilemma between activity and selectivity when tuning the particle size to optimize the performance in gold heterogeneous catalysis. Therefore, it is highly desired to study how to increase the activity of gold nanostructures while maintain a high level of selectivity.

For heterogeneous catalysis, catalytic reaction usually occurs on the surface of catalysts. The surface of a gold nanoparticle is generally composed of different crystal facets of face-centered cubic (FCC) gold. It is obvious that different crystal facets have different catalytic performance because of different arrangements of surface atoms, which interact with the reactants in catalytic reactions. For oxidation reactions using molecular oxygen (O₂) as oxidant, the activation of O₂ on the surface of catalyst is very important because of strong

bond in O_2 and then the direct reaction between O_2 and reactants is difficult. This is also the significance of catalyst in partial oxidation reactions at relative low temperature. Otherwise, high temperature is needed to break the strong bond in O_2 and then lower the selectivity of partial oxidation as mentioned above. The activation of O_2 on gold surface is quite difficult because of weak interaction between oxygen and gold, and it is well-known that gold does not reaction with O_2 .²⁰ Liu et al. studied the dissociation of O_2 on different gold surfaces and found that the dissociation barrier of O_2 is as high as 2.23 eV on Au(111), which is the most stable surface of FCC gold. Even the lowest dissociation barrier of O_2 is 0.93 eV on Au(211), indicating no dissociation of O_2 on gold at low temperature. However, it can be seen that the facet effect on the dissociation of O_2 is significant, which decreases the dissociation barrier from 2.23 eV on Au(111) to 0.93 eV on Au(211).²¹

Another important intrinsic aspect that affect the catalytic performance of gold is strain effect.^{22, 23} Strain is widespread in various metal nanostructures, such as core-shell structures and supported nanoparticles. Strain modifies the bond length between metal atoms, and changes the electronic structures of metal surfaces, which is closely related to the interaction between molecules and the surface. The catalytic performance can be modified by applying strain to the surface of catalysts, and it has been widely studied in platinum catalysis with core-shell structure.^{24, 25} The strain effect on gold catalysis also attracted a lot of research interests in recent years. Ye et al. investigated the strain effect on adsorption and dissociation of O_2 in gold catalysis and found that tensile strain applied in gold surface can promote the adsorption and reduce the dissociation energy of O_2 .²²

Currently, the studies of all the effects discussed above are based on FCC gold, which is the stable crystallographic structure of bulk gold. In recent years, crystal phase engineering was found to be important in catalysts. For example, the application of cobalt catalysts in Fischer-Tropsch synthesis (FTS) generally involves two crystal phases of cobalt, namely, HCP and FCC. Liu et al. studied the crystal phase effect of cobalt on carbon monoxide activation, which is an important step in FTS, and found that HCP cobalt is significantly more active than FCC cobalt.¹¹ Different crystal phases have different atom arrangements in the bulk and on the surface, which affect the interaction between catalysts and reactants.

Crystal phase engineering opens a new door to optimize the performance of catalysts.

Gold is famous for its physical and chemical stability. The crystallographic structure of gold, namely, FCC is also highly stable in a wide range of temperature and pressure. Dubrovinsky et al. reported that it needs pressures above 240 GPa to change the crystal phase of gold from FCC to HCP.²⁶ Obviously, such an extreme pressure cannot be applied in gold catalysis. Although the crystal phase of metal is generally stable under different temperatures and pressures, the crystal phase may change when the size of metal particles shrinks down to nanoscale.^{4,5} The size effect on crystal phase is due to high specific surface area of nanoparticles, which makes the surface energy dominating in total energy. It is worth noting that HCP and 4H gold nanostructures have been reported in recent years.^{8,9} As discussed above, crystal phase effect is very important in modifying the performance of catalysts. It is highly desired and urgent to study the crystal phase effect on gold catalysis.

This thesis tests the hypothesis that when the crystal phase of gold changes from FCC to HCP or 4H in nanostructures, the catalytic performance of gold should be different, such as the O₂ activation and dissociation on gold surfaces, which is important in selective oxidation reactions.

1.2.2 ORR Mechanism on Single-Atom Catalysts

Single-atom catalysis is a new frontier in heterogeneous catalysis,² and ORR is a critical reaction in energy conversion and storage devices (e.g. fuel cell and metal-air battery).^{27,28} Pt and Pt-based materials are good ORR catalysts but too expensive for large scale applications. Single-atom catalysis can maximize the atom utilization, and some single-atom catalysts such as Fe/N/C and Co/N/C are promising nonprecious ORR catalysts.²⁹ Understanding the active sites and ORR mechanism in single-atom catalysis is important to further improve the stability and activity for practical devices. The scaling relations between the adsorption free energies of ORR intermediates result in intrinsic ORR overpotential, which limits the ORR activity.³⁰ The ORR mechanism and scaling relations

on single-atom catalysts may be different from traditional catalysts with near-continuous active sites due to the site confinement in single-atom catalysis.

The particle size of catalysts is important in heterogeneous. A smaller size could increase specific surface area and the ratio of exposed active atoms, which decreases the loading of costly metals. Meanwhile, smaller particles usually have higher catalytic activities because of more undercoordinated surface sites, such as step, kink, edge, and corner. Therefore, reducing particle size could achieve better catalytic performance and lower cost simultaneously. What is the smallest size of a particle? Ideally, it is a single atom. In 2005, Thomas et al. proposed the concept of heterogeneous single-site catalyst,³¹ which means isolated active sites atomically dispersed on a continuous solid support. They summarized four categories of single-site catalysts as follow:

- 1) isolated ions, atoms, molecular complexes, or bimetallic clusters immobilized on substrates (e.g. silica) with high surface area.
- 2) Asymmetric organometallic species anchored to high area mesoporous supports with pore diameters in the range of 15 to 500 Å.
- 3) “Ship-in-bottle” structures: isolated active molecules or organometallic complexes entrapped in the cage of zeolites which should be permeable to specific reactants and products.
- 4) Open-structure microporous materials, such as molecular sieves, with pore diameters in the range of 3.5 to ~10 Å. The isolated active sites are located at or adjacent to doped ions in the parent structure.

In 2011, Zhang et al. reported a single-atom catalyst (Pt_1/FeO_x) which consists of isolated Pt atoms supported on iron oxide nanocrystals, and found that it has high activity selectivity, and stability for CO oxidation even in H_2 .³² Importantly, the Pt single atoms were clearly identified in the atomic resolution high-angle annular dark-field (HAADF) images from aberration-corrected scanning transmission electron microscopy (STEM). By using different beam focus settings, the observed Pt single atoms were confirmed to be on the surface of FeO_x . Their density functional theory (DFT) simulations confirmed that the

most stable adsorption sites for Pt single atoms were the three-fold hollow sites on the O-terminated FeO_x surface, which was consistent with the HAADF-STEM image. Since then, single-atom catalysts received great attention in heterogeneous catalysis in recent years.^{2,}

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For traditional catalysts, various active sites may exist for a specific reaction. The catalytic performance is the overall behaviors of actives with different configurations, which impede the understanding of the relations between structure and activity. The isolated and uniform active sites on single-atom catalysts provide a perfect platform to study the structure-activity relations and reaction mechanisms in heterogeneous catalysis, which facilitates the design of better catalysts. ORR is very important in sustainable energy storage and conversion devices such as metal-air batteries and fuel cells,^{27, 28} where the oxidant i.e. dioxygen (O₂) is electrochemically reduced to water (H₂O). The reaction equation is $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ in acid condition or $O_2 + 4H_2O + 4e^- \rightarrow 2H_2O + 4OH^-$ in alkaline (or neutral) condition, and the thermodynamic equilibrium potential of ORR is 1.23 V vs. RHE (reversible hydrogen electrode). While even the optimum Pt/C electrode only has a half-wave potential around 0.85 V, and the corresponding overpotential is as high as 0.38 V.³⁴

Based on density functional calculations, Nørskov et al. developed a computational hydrogen electrode (CHE) model to figure out the stability of reaction intermediates in electrocatalysis.³⁵ They found that the adsorbed oxygen (O*, * denotes the adsorption site) and hydroxyl (OH*) on Pt surfaces are too stable at potentials close to equilibrium, which is origin of overpotential for ORR. Further studies found that the underlying reason of the intrinsic ORR overpotential is the correlations between the adsorption free energies of reaction intermediates.³⁰ The reaction pathway of ORR was generally considered to be $O_2 \rightarrow OOH^* \rightarrow O^* \rightarrow OH^* \rightarrow H_2O$. All the intermediates (OH*, O*, and OOH*) bond to the catalysts through the O atom. They have similar trend in bonding strength when modifying or changing the adsorption site, and the correlations between them are found to be scaling relations.³⁶ The widely accepted scaling relations are $\Delta G(OOH^*) = \Delta G(OH^*) + 3.2 \text{ eV}$ and $\Delta G(O^*) = 2\Delta G(OH^*)$,³⁰ where ΔG is the adsorption free energy defined in the CHE model. Within the CHE model, the free energies of H₂O and H₂ are set to zero, and the one of O₂

is determined to be 4.92 eV according the known reaction energy of four-electron ORR ($2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$). The ideal free energies of OOH^* , O^* , and OH^* are 3.69, 2.46, and 1.23 eV, respectively, and the corresponding equilibrium potential is 1.23 V (no overpotential). However, according to the scaling relations, the optimum free energy of OH^* is 0.86 eV, and they are 1.72 eV and 4.06 eV for O^* and OOH^* , respectively, which results in a thermodynamic limiting potential of 0.86 V and the corresponding overpotential is 0.37 V.

Due to the universality of scaling relations between $\Delta\text{G}(\text{OH}^*)$, $\Delta\text{G}(\text{O}^*)$, and $\Delta\text{G}(\text{OOH}^*)$,^{37, 38} the intrinsic ORR overpotential cannot be overcome if the reaction mechanism ($\text{O}_2 \rightarrow \text{OOH}^* \rightarrow \text{O}^* \rightarrow \text{OH}^* \rightarrow \text{H}_2\text{O}$, noted as O^* mechanism here) remain unchanged. Note that the reduction of OOH^* may also produce two OH^* , another ORR mechanism (i.e. $\text{O}_2 \rightarrow \text{OOH}^* \rightarrow 2\text{OH}^* \rightarrow \text{OH}^* \rightarrow \text{H}_2\text{O}$, noted as 2OH^* mechanism here) has also been proposed.^{39, 40} This 2OH^* mechanism replaces the O^* intermediate in the O^* pathway by two OH^* , and keeps other intermediates unchanged. According to the scaling relation between OH^* and O^* : $\Delta\text{G}(\text{O}^*) = 2\Delta\text{G}(\text{OH}^*)$, these two mechanisms are thermodynamically equivalent as $\Delta\text{G}(2\text{OH}^*)$ equals $2\Delta\text{G}(\text{OH}^*)$. This is true for traditional catalysts with near-continuous active sites, as two OH^* can bound to different active sites during the reduction of OOH^* . Therefore, usually only the O^* mechanism was studied in previous reports.³⁰ How about single-atom catalysts? The situation should be different because two OH^* need to connect to the same atomic site, and $\Delta\text{G}(2\text{OH}^*)$ no longer equals $2\Delta\text{G}(\text{OH}^*)$ due to the confinement and coordinate effect.

This thesis further tests the hypothesis that the ORR mechanism on single-atom catalysts may be different from the one ($\text{O}_2 \rightarrow \text{OOH}^* \rightarrow \text{O}^* \rightarrow \text{OH}^* \rightarrow \text{H}_2\text{O}$) on traditional catalysts with near-continuous active sites, because of the site confinement effect on the adsorption of reaction intermediates. The understanding of reaction mechanisms could facilitate the design of better ORR catalysts.

1.3 Objectives and Scope

The rapid development of nanotechnology has spawned many unusual nanomaterials with well-designed atomic structures, such as metal nanostructures with unconventional crystal phases and confined single atoms. An important application of these novel materials is heterogeneous catalysis. The general objective of this thesis is to study the catalytic performance of these novel nanomaterials by using DFT calculations. Specifically, this thesis mainly focuses on oxygen activation and reduction, which is very important in both thermal catalysis and electrocatalysis, such as selective oxidation reactions and ORR. Gold nanostructures are well-known catalysts for selective oxidation reactions and the crystal phase effect will be studied. Atomically dispersed Me/N/C (Me = Fe, Co, etc.) are promising nonprecious catalysts for electrochemical ORR, and the reaction mechanism on these single-atom sites will be studied.

The approach adopted here is DFT simulation, which is an effective method to study materials and reactions in atomic scale. The study of catalytic mechanism in experiments is very difficult, while simulations can provide the full details of the reactions, such as the configurations, stabilities and evolution of intermediates. In addition, the synthesis of those novel structures is still not easy in experiments. Therefore, the DFT simulations is important and desired in this new frontier.

1.4 Dissertation Overview

The thesis consists of six chapters and addresses the crystal phase effect and site confinement effect on oxygen activation and reduction.

Chapter 1 provides a rationale for the research and outlines the goals and scope.

Chapter 2 reviews the developments of gold catalysis, crystal phase engineering, oxygen reduction reaction, and single-atom catalysis. Outstanding questions are also highlighted.

Chapter 3 elucidates the computational methodology.

Chapter 4 elaborates the first major set of results: crystal phase effect on surface activity of gold.

Chapter 5 elaborates the second major set of results: oxygen reduction on single-atom catalysts.

Chapter 6 is the summary and outlook. The hypotheses are discussed.

1.5 Findings and Outcomes/Originality

This research led to several novel outcomes by:

1. Demonstrating that crystal phases have significant effects on surface reactivity even for close-packed surfaces due to their distinct intrinsic strains. Proposing that the close-packed surfaces of hexagonal HCP and 4H gold have significantly smaller intrinsic strains ($\sim 1.3\%$) than those of FCC gold ($\sim 2.3\%$).
2. Correlating the intrinsic surface strains with oxygen adsorption energies and O_2 dissociation barriers on various gold surfaces. Showing that the dissociation barriers and reaction energies of O_2 on different crystal phases and surfaces follow the Brønsted–Evans–Polanyi principle.
3. Unraveling the effect of the thickness on the surface strains of gold nanosheets: In-plane bond lengths of gold nanosheets increase rapidly when the layer number is less than 20 (< 5 nm in thickness) and then tend to be stable at distinct intrinsic strains for different crystal phases.
4. Proposing that the unconventional $2OH^*$ ORR mechanism for ORR ($O_2 \rightarrow OOH^* \rightarrow 2OH^* \rightarrow OH^* \rightarrow H_2O$) is important on single-atom catalysts such as Fe/N/C, where two OH^* are confined to the same active site and the rate-determining step in the O^* ORR mechanism involves the formation or consumption of O^* .

5. Identifying a new free-energy scaling relation for 2OH* ORR mechanism on single-atom catalysts: $\Delta G(2OH^*) = 2\Delta G(OH^*) + 1.5 \text{ eV}$, in contrast to $\Delta G(O^*) = 2\Delta G(OH^*)$ in the traditional O* ORR mechanism, because of the site confinement effect in single-atom catalysis.
6. Emphasizing that the two ORR mechanisms compete with each other and different single-atom catalysts may prefer different mechanisms. Indicating that Fe/N/C prefers the 2OH* mechanism and Co/N/C still follows the O* mechanism.

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Chapter 2

Literature Review

The content of this chapter includes two parts, i.e. crystal phase effect on gold catalysis and oxygen reduction on single-atom catalysts. Firstly, gold nanostructures have relatively high activity at low temperature, while further improvement of activity impairs the selectivity of desired partial oxidations. The crystal phase of metal nanostructures could be different from their bulk counterparts because of size effect, and unconventional HCP and 4H gold have been reported. As crystal phase has an important effect on catalysis, it is reasonable to expect that crystal phase engineering may improve the performance of gold catalysts. Secondly, ORR is a critical reaction in energy conversion and storage devices. Pt and Pt-based materials are good ORR catalysts but expensive for large scale applications. Single-atom catalysis can maximize the atom utilization, and some single-atom catalysts such Fe/N/C and Co/N/C are promising nonprecious ORR catalysts. Understanding the site confinement effect on ORR mechanism in single-atom catalysis is important to further improve the stability and activity for practical devices. The scaling relations between the adsorption free energies of ORR intermediates result in intrinsic ORR overpotential, which limits the ORR activity. The ORR mechanism and scaling relations on single-atom catalysts may be different from traditional catalysts with near-continuous active sites.

2.1 Gold Catalysis and Crystal Phase Engineering

2.1.1 Heterogeneous Gold Catalysis

Heterogeneous gold catalysis attracted wide research interests since the pioneer work of Haruta et al. in 1987 that reported the oxidation of CO catalyzed by supported gold nanoparticles at temperature as low as $-70\text{ }^{\circ}\text{C}$, which indicates high activity of gold in this reaction.¹ Then gold was also found to have good catalytic performance in many other reactions such the water-gas shift,² partial oxidation of alcohols or sugars,^{3, 4} and epoxidation of propylene.⁵ Gold catalysis is particularly promising in selective oxidations because of its high selectivity and reasonable activity under mild reaction conditions.⁶ For example, Comotti and co-workers evaluated the selective oxidation of glucose to gluconic acid catalyzed by gold nanoparticles supported on activated carbon.⁴ The reaction was performed at only $50\text{ }^{\circ}\text{C}$ and atmospheric pressure. They reported high selectivity up to 99% for gluconic acid and the turnover frequency is higher than 12500 h^{-1} . In selective catalysis, both selectivity and activity are very important for practical applications. It is highly desired to enhance the activity in gold catalysis while maintain its high selectivity.

Figure 2.1 The selectivity of methyl formate versus reaction temperature in the catalytic gas-phase oxidation of methanol on nanoporous gold.⁷

Temperature is a simple way to modify the activity or turnover frequency in metal catalysis. High temperature can significantly enhance the turnover frequency. However, in partial oxidation reactions, high temperature facilitates the further or complete oxidation of reactants, which reduces the selectivity of desired partial oxidation products. Figure 2.1 shows the relationship between selectivity and reaction temperature in oxidative coupling

of methanol catalyzed by nanoporous gold. When the temperature is lower than 40 °C, the selectivity of methyl formate is near 99%. Further increasing the temperature from 40 to 75 °C, the selectivity of methyl formate gradually decrease to 73% because of the competition of combustion to carbon dioxide.⁷

It is well known that size effect is very important in heterogeneous gold catalysis.⁸ Bulk gold is regarded as poor catalyst and only gold nanostructures are active in catalysis reactions. The most common studied gold nanostructure in catalysis is nanoparticles, and the activity usually increases with decreasing size of gold particles. This is because smaller particles have higher fraction of low coordinated gold atoms such as edges and corners. Nørskov et al. proposed that these under-coordinated atoms on metal surfaces are more active in catalysis because of their high lying d-electron states.⁹ In addition, the electronic states of a surface atom are not only affected by the nearest atoms but also significantly related to the second-nearest atoms and even third-nearest atoms. The generalized coordination number proposed by Federico et al. includes the contribution of second-nearest atoms and becomes more accurate than the traditional coordination number, which only counts the nearest neighbors.¹⁰ The surface atoms of nanoparticles or clusters have smaller generalized coordination number than the one on extended surface even with the same Miller indices, because of partial loss of second-nearest atoms in nanoparticles. The generalized coordination number is also affected by particle size that smaller nanoparticles or clusters have smaller generalized coordination numbers. Therefore, the catalytic activity of gold nanoparticles increases with decreasing particle size.

Dimitratos et al. studied the effect of particle size on the catalytic performance of gold nanoparticles on the selective oxidation of glycerol to glyceric acid.¹¹ Their results shown that the activity of gold nanoparticles strong related to the particle size in the range of 4 to 16 nm. As shown in Figure 2.2, the turnover frequency increases from ~100 to ~1000 h⁻¹ when the particle size decreases from 16 to 2 nm. This phenomenon is in accordance with the particle size effect discussed above. It is worth noting that the selectivity in Figure 2.2 has an opposite trend in compared with activity, namely, high activity is accompanied by low selectivity. Like the temperature effect, there is usually a counterbalance between

activity and selectivity in selective catalysis.

Figure 2.2 Selective oxidation of glycerol catalyzed by gold nanoparticles supported on carbon. The selectivity of glyceric acid and turnover frequency versus the gold particle size.¹¹

Therefore, although heterogeneous gold catalysis shows great promise in selective catalysis, it is still limited by the counterbalance between activity and selectivity. Simply changing the reaction conditions or morphology of gold is not enough to get desirable performance in selective gold catalysis. Further study and improvement are still needed for realizing its industrial applications in selective catalysis.

2.1.2 Crystal Phase Engineering

Gold nanomaterials attracted great research interests because of their wide applications in physics, chemistry, biology, and materials.¹² Nanosized metal particles provide good models to study the quantum effects on physical properties, such as magnetic and electronic properties. Gold nanoparticles are also famous for high surface-enhanced Raman scattering (SERS) effect and can be used in ultrasensitive and selective detection of specific molecules.^{13, 14} The surface plasmon resonance absorption of gold nanoparticle is also promising in laser photothermal therapy and drug release trigger.^{15, 16} In addition, gold nanostructures have wide applications in catalysis as reviewed in the last section.

The properties of metal nanomaterials are usually tuned by size, shape, and architecture.

The size of metal nanoparticles could be controlled by seeding growth, which separates the nucleation and growth in different processes. Brust et al. first reported the synthesis of 1-3 nm gold nanoparticles through the reduction of gold salt by borohydride.¹⁷ The strong reducibility of borohydride and the addition of thiol as capping agent are critical in controlling the particle size in 1-3 nm. These small particles can be used as seeds and further growth into larger nanoparticles in a gentle reducing environment with gold salt, which inhibits secondary nucleation. Jana et al. synthesized gold nanoparticles in the size from 5 to 40 nm with standard deviation lower than 15% by seeding growth method.¹⁸ The size was well controlled by changing the ration of seed to metal salt.

The size control of gold nanoparticles reviewed above is mainly nanospheres because of relatively large growth rate and isotropic growth of seeds. The shape of gold nanoparticles can be controlled by different additives such as capping agent, silver nitrite, and pH regulator, which modify the growth rate of different crystal faces and result in anisotropic growth of gold nanoparticles.¹⁹ On the other hand, twin planes in the nanocrystals play an important role in determining the growth direction and shape of nanoparticles. For example, a single twin plane generally results in a triangular prism with limited size, while two parallel twin planes allow six sides to grow fast and form a hexagonal platelet without limit of size.²⁰ Now a range of shapes can be synthesized in gold nanoparticles, including polyhedrons, nanorods, nanoplates, branched nanostructures, etc.¹⁹ The studies on size and shape control of metal nanoparticles are important in both basic research and practical applications.

When the size drops to nanoscale, the properties of metal particles are quite different from bulk states. For example, phase transition temperatures are significantly lower for metal nanoparticles because of high specific surface area and the surface energy becomes important or even dominate in the total energy of nanoparticles. Consequently, the melting point usually declines with decreasing size.²¹ More importantly, the crystal phase of metal nanostructures may be different from their bulk counterparts, and solid-solution alloy of traditional immiscible systems become possible in nanoparticles.^{22, 23} Liu et al. reported the coexistence of double HCP (4H) and FCC phases in silver nanowires prepared by

electrochemical deposition with porous anodized aluminum oxide (AAO) templates.²⁴

Figure 2.3 Coexistence of 4H and FCC phases in silver nanowires: a) XRD spectra of silver nanowires in AAO templates with different pore sizes, b) Ratio of 4H to FCC crystal phases versus diameters of silver nanowires according to TEM characterizations.²⁴

X-ray diffraction (XRD) spectra of silver nanowires in AAO templates with different pore sizes are shown in Figure 2.3(a). The peak around $2\theta = 36^\circ$ that marked as Peak I can be assigned to $\{0004\}$ or $\{10\bar{1}0\}$ crystal planes of 4H silver. Peak I exists in all the five silver nanowire samples except the empty template that contains no silver nanowires, indicating the existence of 4H phase in all these silver nanowires. In addition, transmission electron microscopy (TEM) characterizations on released individual silver nanowires confirmed the existence of 4H nanowires. Figure 2.3(b) presents the ration of 4H to FCC phases as a function of diameters based on TEM studies on about 130 silver nanowires. Both XRD spectra and TEM characterizations demonstrated the coexistence of 4H and FCC phases in silver nanowires and the size effect on crystal structure.²⁴

In addition to 4H phase of silver introduced above, body-centered tetragonal (BCT) silver nanowires and nanoparticles have also been reported.²⁵ The BCT phase of silver is stabilized in fivefold twinning nanoparticles and anisotropic growth into nanowires. The strains in fivefold twinning structure distort crystal lattice and sometimes induce crystal phase transition. This phenomenon is not restricted in silver. Kusada et al reported the synthesis of FCC ruthenium nanoparticles, which are also fivefold twinning structure.²⁶ FCC structure is not in the phase diagram of bulk ruthenium, whose thermodynamic stable

phase is HCP in solid state. On the other hand, Huang et al. reported HCP nanoparticles of rhodium, which is FCC structure in bulk state.²⁷

Gold plays a special role in human history as coin metal and it is famous for its stability to chemical reactions. In the phase diagram of gold, FCC is the crystal phase for solid state under normal conditions. The FCC structure of gold is very stable even under extremely high pressure up to 180 GPa. Dubrovinsky et al. reported that a crystal phase transition from FCC to HCP only occurs when the pressure reaches 240 GPa.²⁸ Crystal phase transition of metal under high pressure is quite common, while the novel crystal phase obtained under high pressure is not useful in practical applications such as catalysis that cannot bear such a harsh condition. Fortunately, the crystal phase of metal nanostructures under ambient conditions may be different from their bulk counterparts as reviewed above. Zhang and coworkers developed several wet chemical methods in the synthesis of gold nanostructures, and successfully obtained HCP gold square nanosheets and 4H gold nanoribbons.^{29, 30}

Figure 2.4 Characterizations of HCP gold square sheets: a) TEM image of gold square sheets supported on graphene oxide (scale bar, 500 nm), and the insert is crystal model of a gold square sheet, b) High-resolution TEM image of a small section of a gold square sheet along the $[110]_h$ direction (scale bar, 2 nm), and the insert is selected area electron diffraction pattern of it.²⁹

Huang et al. reported the first synthesis of HCP gold square nanosheets in 2011.²⁹ In their experiments, chloroauric acid was reduced by oleylamine in the mixed solvent of hexane and ethanol at 55 °C. Importantly, graphene oxide was added as template. After 16 hours

of reaction, gold square nanosheets were synthesized on graphene oxide sheets. Although control experiments without graphene oxide could also produce gold square nanosheets, the yield and quality are significantly lower than the ones added graphene oxide as template. Figure 2.4(a) shows the TEM image and schematic diagram of gold nanosheets supported on graphene oxide. The size of obtained gold nanosheets is between 200 and 500 nm with the thickness around 2.4 nm. High-resolution TEM image and electron diffraction pattern indicate that the gold nanosheet has an unusual HCP crystal phase as shown in Figure 2.4(b). Further experiments indicate that if the reaction time increases from 16 to 28 hours, the thickness of gold nanosheets would increase from 2.4 to 6 nm. As the thickness increases, FCC phase begins to appear and forms a kind of FCC/HCP mixed structure, which demonstrates size effect on crystal phase.

Figure 2.5 Characterizations and crystal model of 4H gold nanoribbons: a) TEM image of 4H gold nanoribbons (scale bar, 100 nm), b) Aberration-corrected high-resolution TEM image of a small section of a gold nanoribbon along the $[110]_h$ direction (scale bar, 1 nm), c-d) Crystal model of 4H gold nanoribbon.³⁰

In a similar way, Fan et al. synthesized 4H gold nanoribbons, which is thermodynamically

more stable than HCP gold and can be used as templates for epitaxial growth of other metals with novel 4H phase.³⁰ The typical experimental procedure is that chloroauric acid reduced by oleylamine in the mixed solvent of hexane and 1,2-dichloropropane at 58 °C for 16 hours. Gold nanoribbons formed in the experiment as shown in Figure 2.5(a) are typically 0.5 to 6 μm in length, 15 to 60 nm in width, and 2.0 to 6.0 nm in thickness. High-resolution TEM image confirmed the 4H structure of the nanoribbons as shown in Figure 2.5(b). The existence of 1,2-dichloropropane in the solution is important in producing 4H phase and facilitating the anisotropic growth of gold. Normal FCC gold will be obtained without 1,2-dichloropropane. Time-dependent experiments showed that HCP gold nanowires about 2 nm in diameter were formed in the beginning, and then gradually grow into 4H nanoribbons as shown in Figure 2.5(a). This phase transition from HCP to 4H among growth also indicates strong size effect on crystal phase. Figure 2.5(c) shows a unit cell of 4H gold and Figure 2.5(d) is the crystal model of a typical 4H gold nanoribbon.

In short, crystal phase engineering becomes an important field in the study of metal nanostructures in recent years. The properties of metal nanoparticles can be affected by the crystal phase, which will provide more potential in the applications of metal nanomaterials. Therefore, the study of crystal phase effect on different properties of metal nanostructures is highly desired.

2.1.3 Crystal Phase Effect on Catalysis

Platinum (Pt) is one of most important catalysts in various fields. Because Pt is scarce and expensive, Pt-based alloy catalysts are widely studied to reduce the use of Pt and improve the mass specific catalytic activity of Pt.³¹ The catalytic performance of Pt-based alloy is usually investigated by size, shape, and composition.³² In recent years, the crystal phases of Pt-based alloy catalysts are found to have significant effect on their catalytic activity. Sun et al. reported the synthesis of monodisperse iron-platinum (FePt) alloy nanoparticles with a chemically disordered FCC phase.³³ The size and composition of FePt nanoparticles are easily controlled, and more importantly, the crystal phase can also be controlled upon thermal annealing. After annealing at 560 °C for 30 min, the as prepared chemically

disordered FCC nanoparticles converted into ordered face-centered tetragonal (FCT) phase. Sun et al. further reported that FCT phase FePt nanoparticles are chemically more stable than the FCC ones in dilute H_2SO_4 solutions, and the oxygen reduction reaction (ORR) activity of FCT FePt is 1.75 times of the FCC one in terms of current densities at the half-wave potential.³⁴ The fully ordered FCT FePt nanoparticles also have superior catalytic performance in hydrogen evolution reaction (HER). The HER activity of FCT FePt nanoparticles is higher than Pt, which is the benchmark of HER, and it is highly durable without potential shift after 10 000 potential cycling.³⁵

Cobalt-platinum (Co-Pt) alloy also attracted wide research interests in ORR because of relatively high activity and stability.^{36, 37} Like FePt nanoparticles mentioned above, there are also different crystal phases of Co-Pt nanoparticles, including disordered FCC phase, ordered FCT phase CoPt, and ordered primitive cubic phase CoPt_3 .³⁶ The crystal phase of Co-Pt nanoparticles could be controlled by composition and annealing temperature. Wang et al. synthesized chemically disordered FCC CoPt_3 nanoparticles and ordered primitive cubic CoPt_3 nanoparticles coated by 2-3 layers of Pt atoms and found that the ordered core-shell $\text{CoPt}_3@\text{Pt}$ structure presented significantly higher ORR activity and durability than disordered CoPt_3 nanoparticles.³⁷ The good performance of ordered nanoparticles comes from the strained Pt shell and the stable FCT CoPt_3 core.

The crystal phase of pure metal catalyst is also closely related to its catalytic performance, which is reasonable because of different morphologies and surface atomic arrangements for different phases.³⁸ For example, cobalt is HCP phase under the standard conditions, and would transform into FCC phase at 400 °C.³⁹ These two phases have distinct crystallographic symmetries and exposed surfaces with different catalytic performance. Although the temperature in a specific catalytic reaction is usually fixed, the coexistence of different crystal phases is still possible due to size effect and the control of crystal phase becomes important. As catalyst is usually in forms of nanostructures, which have high specific area and catalytic activity, the crystal phase of catalyst may be different from bulk state as introduced in the last section. Kitakami et al. studied the size effect on cobalt nanoparticles. They found that a mix of HCP and FCC phases exists in cobalt nanoparticles

around 30 nm in diameter and pure FCC cobalt emerges when the particle size is smaller than 20 nm.⁴⁰

Figure 2.6 Crystal effect of cobalt on the FTS activity: a) Wulff construction of HCP and FCC cobalt based on DFT calculations, b) Calculated dissociation rate of CO on different surfaces of HCP and FCC cobalt.⁴¹

Cobalt nanoparticles are widely used as catalysts in the FTS that produces liquid oil from CO and H₂, which comes from coal, biomass, or natural gas.⁴² The FTS reaction temperature is typically lower than the crystal phase transition temperature of cobalt, but the crystal phase effect is still important as the particle size of cobalt is in nanoscale. Moreover, other factors such as supports, promoters, and pretreatment of cobalt catalysts can also affect the crystal phase of cobalt.⁴³⁻⁴⁵ The crystal effect of cobalt on FTS has been studied by many groups in experiments, and HCP cobalt is reported to have higher activity than FCC cobalt in the FTS. For example, Gnanamani et al. reported that HCP cobalt has presented higher CO conversion rate and lower methane selectivity than FCC cobalt in the FTS.⁴⁶ On the other hand, Li and coworkers studied the crystal phase effect of cobalt on

the FTS activity from first-principles calculations.⁴¹ They found that the substantial open surfaces of HCP cobalt nanoparticles could facilitate the activation and direct dissociation of CO, while FCC particles are dominated by close-packed surface and even the open surfaces of FCC particles are less active than the HCP ones. Figure 2.6(a) shows the equilibrium morphology of HCP and FCC cobalt based on Wulff construction, which is derived from surface energies calculated from first-principles calculations. The equilibrium morphology of HCP cobalt contains five different crystal surfaces, including close-packed (0001) surface and open surfaces such as (1010), (1011), and (1012). Close-packed (0001) facets only cover 18% of the total surface area, which is even smaller than that of (1010) or (1011) open surface. The situation on FCC cobalt is totally different from HCP cobalt. Close-packed (111) surface covers as high as 70% of the total surface area. Open surfaces are significantly more active than close-packed surfaces in the dissociation of CO, and Figure 2.6(b) shows the calculated dissociation rate of CO on open surfaces of HCP and FCC cobalt. The dissociation rates on open surfaces except (1010) of HCP cobalt are significantly larger than the ones of FCC cobalt. In combination of larger coverage of open surfaces for HCP cobalt, it can be concluded that HCP cobalt is more active than FCC cobalt in the dissociation of CO, which is a critical step in the FTS.⁴¹

Ruthenium is another promising catalyst for the FTS because of its high activity under relatively low temperature in compared with cobalt.⁴⁷ The crystal phase of ruthenium can also be modified by size effect. Somorjai and coworkers reported the coexistence of FCC and HCP phases in ruthenium nanoparticles from 2 to 6 nm, and Kitagawa et al. reported the synthesis of pure FCC ruthenium nanoparticles with controlled diameters of 2-5.5 nm.^{26, 48} They also reported the crystal phase effect of ruthenium on CO oxidation. The CO oxidation activity of HCP ruthenium increases with decreasing size, while the trend is reversed for FCC ruthenium and the activity of FCC phase is higher than HCP phase when the size is larger than 3 nm. Recently, Li et al. reported the crystal phase effect of ruthenium on the FTS activity.⁴⁷ They found that there are several open surfaces of FCC ruthenium with relatively low dissociation barriers for CO, while the barriers on HCP ruthenium are generally higher. FCC ruthenium nanoparticles with large coverage of open surfaces are synthesized and presented unprecedented mass-specific FTS activity.

2.1.4 Outstanding Questions

Gold catalysis is especially promising in selective oxidation reactions because of its relatively high activity at low temperature. However, further improvements in terms of activity are still needed for practical applications. Trying to improve the activity through conventional methods such as increasing temperature or decreasing the size of catalyst generally impairs the selectivity of desired partial oxidations at the same time. Crystal phase engineering emerged as a novel method to modify the properties of metal nanostructures in recent years. It has been reported that crystal phase has significant effect on the catalytic performance for various catalysts such as cobalt and ruthenium. On the other hand, unconventional HCP and 4H gold nanostructures have been synthesized in recent years. The crystal phase effect on gold catalysis is still unclear in experiments. First-principles calculation is an effective approach to study the reaction mechanism of catalysis. Therefore, the study on crystal phase engineering of gold catalysis from first-principles calculation is highly desired in guiding experiments and facilitating its industrial applications

2.2 Oxygen Reduction and Single-Atom Catalysts

2.2.1 Oxygen Reduction Reaction

The oxygen reduction reaction (ORR) is very important in sustainable energy conversion and storage devices such as metal-air batteries and fuel cells,^{49, 50} where the oxidant i.e. dioxygen (O_2) is electrochemically reduced to water (H_2O). The reaction equation is $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ in acid condition or $O_2 + 4H_2O + 4e^- \rightarrow 2H_2O + 4OH^-$ in alkaline (or neutral) condition, and the thermodynamic equilibrium potential of ORR is 1.23 V vs. RHE (reversible hydrogen electrode). While even the optimized Pt/C electrode only has a half-wave potential around 0.85 V, and the corresponding overpotential is as high as 0.38 V.⁵¹ Catalysts with high ORR activity under low overpotential are highly desired to achieve high conversion efficiency from chemical energy to electric energy for example in the

proton exchange membrane (PEM) fuel cell, which is promising in vehicles and portable electronics because of its high power density and low working temperature.⁵² Currently, the PEM fuel cell still requires high Pt loading to achieve an acceptable overall performance, especially on the cathode where ORR occurs. Because Pt is a scarce and costly metal, minimizing Pt loading by alloy or nanotechnology and exploring nonprecious ORR catalysts attracted great research interest in recent years.⁵³

Figure 2.7 a) Size effect on specific activity (blue) and mass activity (red) of Pt/C for oxygen reduction reaction at 0.93 V,⁵⁴ b) Specific activities of Pt-early transition metal alloys as compared to pure Pt at 0.9 V.⁵¹

The catalytic activity in heterogeneous catalysis depends on the interaction between reactants and the surface of catalysts. The ORR performances on different Pt surfaces have been widely studied. For low index surfaces, it was found that Pt(111) and (110) facets have much higher ORR activity than the Pt(100) facet.⁵⁵ In addition, the (111) terrace edge on high index Pt surfaces was believed to have higher ORR activity than the (100) terrace.⁵⁶ In practical applications, Pt nanoparticles were used to maximize the utilization rate of Pt atoms because of their large specific surface area. Shao et al. studied ORR on Pt nanoparticles with different sizes in the range of 1–5 nm and reported significant size effect on the ORR performance in terms of mass activity or specific activity, and they found that the optimum mass activity located around 2.2 nm as shown in Figure 2.7a.⁵⁴ As for specific activity, they found that it increased with the particle size, especially from 1 to 3 nm. On the other hand, it is worth to note that size effect on the specific activity of Pt is still under debate. Nesselberger et al. reported similar specific ORR activity for Pt nanoparticles

between 1 and 5 nm,⁵⁷ and they further proposed that the specific activity depends on the distance between Pt nanoparticles instead.⁵⁸

Alloying Pt with other metals could reduce the use of Pt for economic purposes, and some Pt alloys achieved better ORR activity than pure Pt (Figure 2.7b). For example, Stamenkovic et al. studied the ORR performance of several as-prepared Pt-bimetallic alloys Pt_3M ($\text{M}=\text{Ni}, \text{Co}, \text{Fe}, \text{Ti}, \text{and V}$), and the activities followed the sequence of $\text{Pt} < \text{Pt}_3\text{Ti} < \text{Pt}_3\text{V} < \text{Pt}_3\text{Ni} < \text{Pt}_3\text{Fe} \approx \text{Pt}_3\text{Co}$.⁵⁹ The ORR stability of Pt alloy relates to dissolution of the non-Pt elements under the working potential. Further studies found that heat treatment of Pt_3M could improve the ORR stability because of the surface segregation of Pt, which forms Pt-skin and protects the alloying elements from dissolution. Such annealed Pt_3M have a slightly different ORR activity sequence of $\text{Pt} < \text{Pt}_3\text{Ti} < \text{Pt}_3\text{V} < \text{Pt}_3\text{Fe} < \text{Pt}_3\text{Ni} < \text{Pt}_3\text{Co}$, where the activity of Pt_3Co is significantly improved when compared to the nonannealed one. The high ORR activity may come from the surface strain of the Pt skin and the interaction between Pt skin and the sublayer alloy.^{60, 61} Some Pt-early transition metal alloys (e.g. Pt–Gd, Pt–Y, Pt–La) were also found to have better or comparable ORR activities than Pt-late transition metal alloys (e.g. Pt–Co, Pt–Ni, Pt–Fe). For example, Hwang et al. reported an ORR activity sequence of $\text{Pt}_3\text{Ti} < \text{Pt} < \text{Pt}_3\text{Zr} < \text{Pt}_3\text{Co} < \text{Pt}_3\text{Ni} < \text{Pt}_3\text{Y}$, where Pt_3Y was found to be highly ORR active.⁶² On the other hand, several Pt–lanthanide metal alloys, such as Pt_5Gd , Pt_5Ce , and Pt_5La , also presented superior ORR activities.^{63, 64} Similarly, during the ORR experiments, the surface lanthanide atoms of Pt_5M were dissolved into the electrolyte and a Pt skin was formed, which prevents further corrosion and provides a high ORR stability. In addition, some ternary, quaternary, and even quinary Pt alloys have also been reported in recent years.^{65, 66}

Aside from Pt and its alloys, nonprecious metal (e.g. the first-row transition metals) based ORR catalysts have also been widely studied.⁵³ ORR is a common reaction in living organisms such as human body. Animals and many micro-organisms consume O_2 and organics all the time to provide energy for life activities, and the oxygen reduction is catalyzed by enzymes, which are highly efficient catalysts with negligible overpotentials in cells. However, enzymes are highly sensitive to environments and generally cannot work

on the electrode of fuel cells. The density of active sites is also limited by the large volume of enzymes, which leads to low current density if applied in fuel cells.⁶⁷ Meanwhile, metal-porphyrins/phthalocyanines based catalysts with kind of enzyme-like active sites have been tested for ORR in fuel cells since more than 50 years ago.⁶⁸ More generalized Me-N-C (Me = Fe, Co etc.), N-doped carbon, and pure carbon materials have also been studied for ORR in recent years and some of them have promising performance.⁶⁹

Figure 2.8 Synthesis summary for typical nonprecious metal-based ORR catalysts.⁵³

Pure carbon or N-doped carbon generally has much better ORR onset and half-wave potentials in alkaline conditions than in acidic conditions. Meanwhile, for Fe- or Co-based catalysts, the difference is relatively less significant, which suggests the ORR active sites may be metal-free sites in base and metal-based sites in acid.⁵³ Figure 2.8 summarized the typical procedures for the synthesis of nonprecious metal-based ORR catalysts. To improve the ORR activity and stability, acid washing and second pyrolysis were introduced after the initial pyrolysis of precursors. Due to the structure complexity of Me-N-C system, the active site and source of ORR activity is complicated, which may be carbon, N-doped carbon, Me-N_x, crystalline Me species, and the synergistic effect between them. For example, Jiang et al. used carbon nanotubes, glucose, Fe(NO₃)₃·9H₂O, and melamine as precursors to synthesize Fe-N-C catalysts.⁷⁰ They reported that FeN_x sites or Fe/Fe₃C nanocrystals did not show good ORR activity without each other, and only the samples with both FeN_x sites and Fe/Fe₃C nanocrystals exhibited good ORR activity (comparable to Pt/C in alkaline solution). In addition, a higher content of exposed FeN_x sites delivered a higher ORR activity with the existence of Fe/Fe₃C nanocrystals. Therefore, the Fe/Fe₃C was suggested to promote the ORR activity of FeN_x sites in the carbon substate. On the other hand, Kramm et al. argued that the removal of metallic iron in the Fe-N-C system

could lead to a tremendous increase in ORR activity.⁷¹ They performed a second heat treatment of the as-prepared Fe-N-C catalysts in N₂/H₂ following by an acid-washing step to fully remove the inorganic iron species. Meanwhile, the density of FeN₄ sites remained nearly unchanged.

Figure 2.9 a) ORR polarization plots (bottom) and the yields of hydrogen peroxide (top) obtained in acid using different catalysts: 1, carbon black; 2, heat-treated carbon black; 3, heat-treated PANI-C; 4, PANI-Co-C; 5&6, PANI-FeCo-C with different ratios between Fe and Co; 7, PANI-Fe-C; 8, Pt/C. b) ORR polarization plots (bottom) and the yields of hydrogen peroxide (top) obtained from the PANI-Fe-C catalysts with different heat treatment temperatures: 1, 400°C; 2, 600°C; 3, 850°C; 4, 900°C; 5, 950°C; 6, 1000°C.⁶⁹

Fe/N/C and Co/N/C have been widely studied as ORR catalysts in recent years because of their promising activity and low cost.⁷² For example, Wu et al. used polyaniline (PANI), carbon black, and Fe (or Co) salt as precursors and obtained a series of Fe(Co)/N/C with different compositions and pyrolysis temperatures.⁶⁹ Figure 2.9a shows the ORR activity and selectivity of their studied catalysts with different compositions, including different PANI-derived catalysts and reference materials. Samples 1-3 are metal-free materials as references, sample 4 is Co/N/C, samples 5-6 are CoFe/N/C, sample 7 is Fe/N/C, and sample

8 is Pt/C as a benchmark. The metal-free samples 1-3 were found to have poor ORR performance (high H₂O₂ selectivity and low active potential). Meanwhile, Fe(or Co)/N/C was found to have relatively good ORR performance, and Fe/N/C was better than Co/N/C in terms of both selectivity and activity. Figure 2.9b shows the effect of heat treatment temperature (400-1000 °C) on the ORR performance of Fe/N/C, and the results indicated that the optimum temperature was ~900 °C. Overall, their optimized Fe/N/C catalyst achieved a half-wave ORR potential higher than 0.8V (vs. RHE) and the four-electron (H₂O) selectivity was higher than 99%.

2.2.2 Single-Atom Catalysts

Metal nanomaterials play an important role in heterogeneous catalysis because of their high specific surface area and activity. Generally, a smaller particle size corresponds to a larger specific surface area and higher ratio of undercoordinated sites, such as terrace, step, kink, edge, and corner sites, which are usually the active sites in catalysis. Although the nanosized particles are easy to aggregate due to their high surface energy, proper substrates can be used to anchor the nanoparticles and improve the durability. Therefore, by using nanomaterials instead of micro particles or bulk metals, better performance in catalysis and less cost in noble metal usage can be achieved simultaneously. What is the smallest size of catalysts? The ultimate answer is the single-atom catalyst. In 2005, Thomas et al. raised the concept of single-site heterogeneous catalysts based on immobilized organometallic compounds, and a single-site may contain one or more metal atoms and ligands.⁷³ In 2011, Thomas et al. further discussed the possibility of a single atom serving as the active site in heterogeneous catalysis,⁷⁴ based on some pioneer reports.⁷⁵⁻⁷⁷ Importantly, in the same year, Zhang et al. synthesized and observed a single-atom catalyst (Pt₁/FeO_x), which consists of isolated Pt atoms supported on iron oxide nanocrystals, and found it had high activity and stability for CO oxidation.⁷⁸ Since then, single-atom catalysts received great attention in heterogeneous catalysis in recent years.^{79, 80} Aside from high specific activity, single-atom catalysts could also achieve high selectivity thanks to their uniform active sites, making them promising in selective oxidation or hydrogenation reactions.

Like nanoparticles, single-atom catalysts should be anchored on substrates, such as metal oxide and graphene, for heterogeneous catalysis. The coordination environments and electronic structures of these single atoms are much different from their counterparts in clusters, nanoparticles, or extended metal surface. Therefore, the catalytic performance of single-atom sites can be totally different from traditional catalysts. In 2005, Zhang et al. studied the catalytic performance of Au/ZrO₂ in the selective hydrogenation of 1,3-butadiene to butenes, and found that the specific activity dramatically increased with decreased particle sizes and became a constant value when the loading were low enough to let all the Au atoms isolated from each other, which suggested that isolated Au atoms were the most active sites in the Au/ZrO₂ system (Figure 2.10).⁸¹ Their work actually demonstrated the significantly different catalytic performances between single-atom catalysts and nanoparticles, although the concept of single-atom catalyst was not widely accepted at that time.

Figure 2.10 The effect of metal loadings/sizes on the specific activity in selective hydrogenation of 1,3-butadiene over supported gold catalysts.⁸²

The single-atom Pt₁/FeO_x catalyst reported by Zhang et al. was prepared by a co-precipitation method. Very low loading of Pt atoms (0.17 wt%) were dispersed on FeO_x nanocrystals with high surface area (~290 m²·g⁻¹).⁷⁸ Aberration-corrected scanning transmission electron microscopy (STEM) with subangstrom resolution was adopted to characterize the atomic structure of Pt₁/FeO_x, and the heavy Pt atoms were clearly identified in the high-angle annular dark-field (HAADF) image as indicated by white circles in Figure 2.11a, where the Pt single atoms located exactly at the Fe sites. By using

different beam focus settings, the observed Pt single atoms were confirmed to be on the surface of FeO_x . In addition, the observed density of Pt single atoms (0.07 nm^{-2}) was very close to the designed Pt loading (0.09 nm^{-2}). Their DFT simulations confirmed that the most stable adsorption sites for Pt single atoms were the three-fold hollow sites on the O-terminated FeO_x surface as shown in Figure 2.11b. Each Pt single atom was coordinated to three O atoms and can be regarded as occupied the Fe sites on the Fe-terminated FeO_x surface, which was consistent with the HAADF-STEM image as shown in Figure 2.11a. This Pt_1/FeO_x catalyst was highly active and stable for CO oxidation and selective CO oxidation in H_2 , which was attributed to the partly vacant 5d states of the Pt atom coordinated by three surface O atoms.

Figure 2.11 a) Atomic resolution high-angle annular dark-field (HAADF) -STEM image and b) density functional modeling of Pt_1/FeO_x .⁷⁸

Figure 2.12 Illustration of the unique electronic structures derived from the combination of two-dimensional materials and single metal atoms.⁸⁰

The distinct catalytic performance of single-atom catalyst comes from its unique electronic structures, which determine the interaction between catalysts and reactions. The electronic structures of metal nanoparticles consist of near-continuous energy band, while it becomes molecular orbitals for clusters and atomic orbitals for single atoms (Figure 2.12, right). In addition, the work function, the position of the lowest unoccupied molecular orbital (LUMO), and the bandgap between LUMO and HOMO (the highest occupied molecular orbital) are also varied from single atoms to clusters and nanoparticles.⁸³ Therefore, the optical properties of single atoms, clusters, and nanoparticles are also much different from each other, and this would also affect their catalytic performances in photocatalysis. In the case of supported single atoms, the interaction between single atoms and the substrate should be taken into consideration. Two-dimensional (2D) materials such as graphene, graphitic carbon nitride (g-C₃N₄) and transition metal dichalcogenide (TMD) are popular supports for single atoms, taking the advantage of their large specific surface areas. As the most famous 2D material, graphene is an ideal support with high mechanical strength, high conductivity, and unique electronic structures (Figure 2.12, left).⁸⁰ There are three categories of graphene supported single-atom catalyst: nonmetal atoms (e.g. N, B, etc.),⁸⁴ pure metal atoms (Me),⁸⁵⁻⁸⁷ and N-coordinated metal atoms (MeN_x).⁸⁸ Among them, graphene (or other carbon nanomaterials) supported MeN_x (Me-N-C) have promising ORR performance as mentioned in last section.

2.2.3 Scaling Relations and Volcano Plot

Catalysts work through their interactions with reactants, intermediates, and products. A typical reaction pathway consists of n sequential elementary steps involves $n-1$ intermediates, tuning the relatively stabilities of which on the catalysts is essential to improve the overall reaction rate. However, the adsorption energies of different intermediates cannot be modified arbitrarily and independently, because the intermediates in the same reaction usually consists of similar atoms and moieties. In other words, the adsorption energies of these intermediates relate to each other, and if one of them changed, the others would also be changed accordingly. For example, OH*, O*, and OOH* (* denotes the adsorption site) are important intermediates in ORR, and all of them bond to

the catalysts through the O atom. They have similar trend in adsorption energy when modifying or changing the adsorption site, and the correlations between them are found to be scaling relations.⁸⁹ In this case, one and only one of them (e.g. OH*) can be chosen as a variable (or descriptor) to characterize the interaction between the catalysts and ORR intermediates, and the ORR activity can be expressed as a function of OH* adsorption free energy $\Delta G(\text{OH}^*)$. Based on the classical Sabatier principle, the adsorption of intermediates on the optimized catalyst should be moderate, and either too strong or weak impairs the activity. Therefore, the activity trend along the $\Delta G(\text{OH}^*)$ has a volcano shape, which is the so-called volcano plot.⁹⁰ Volcano plots provide the direction in searching and designing catalysts with better performance.

By using DFT calculations, Abild-Pedersen et al. studied the adsorption of CH_x ($x = 0, 1, 2, 3$), NH_x ($x = 0, 1, 2$), OH_x ($x = 0, 1$), and SH_x ($x = 0, 1$) on various metal surfaces, and found that the adsorption energy (E_{ads}) of any AH_x ($A = \text{C, N, O, S}$) approximately scales with the adsorption energy of the central atom $E_{\text{ads}}(A)$:

$$E_{\text{ads}}(\text{AH}_x) = \gamma E_{\text{ads}}(A) + \zeta$$

as shown in Figure 2.13.⁹¹ The scaling constant (γ) can be determined by the actual number (x) and the saturate number (x_{max}) of H atoms bonding to the A atom as follow:

$$\gamma = (x_{\text{max}} - x) / x_{\text{max}}$$

where the value of x_{max} is 4 for $A = \text{C}$, 3 for $A = \text{N}$, 2 for $A = \text{O}$ and S . For example, the values of γ are 0.25, 0.50, and 0.75 for CH_3 , CH_2 , and CH , respectively, which is in good agreement with the fitting slopes as indicated in Figure 2.13 (top-left panel). For other AH_x , the experimental slopes also agree well with γ predicted by ' $(x_{\text{max}} - x) / x_{\text{max}}$ ' (Figure 2.13). A straightforward bond-counting theory can be used to explain these scaling relations. Taking OH and O as an example, OH bonds to the metal surface through a single bond, meanwhile O need two single bonds or one double bond to be saturated. Therefore, the change in bonding energy of OH should be a half of O when the substrate varies among different metals, which indicates the scaling constant γ is 1/2. The authors also rationalized the scaling relations from d -band model and effective medium theory. Aside from the scaling relations between the atom (A) and its hydrogenated specie (AH_x), Calle-Vallejo et al. further demonstrated that the scalability between the adsorption of different atoms with

similar electronic structures, such as elements in a same column of the periodic table (e.g. C and Si, N and P, O and S, etc.), and they found that the scaling relations originate from the valence configurations of the adsorbates and substrates.⁹²

Figure 2.13 Adsorption energies of CH_x (crosses: $x=1$; circles: $x=2$; triangles: $x=3$), NH_x (circles: $x=1$; triangles: $x=2$), OH, and SH intermediates versus adsorption energies of C, N, O, and S, respectively, on close-packed (black) and stepped (red) metal surfaces. For OH, (100) surfaces (blue) of FCC metals have also been plotted.⁹¹

Figure 2.14 Free-energy profiles of a) the ideal catalyst and b) a practical catalyst (Fe-phthalocyanine) for the ORR at zero potential ($U = 0$ V vs RHE), ideal ORR potential ($U = 1.23$ V vs RHE) and at the potential that makes all the steps exothermal.⁹³

The reaction pathway of ORR was usually considered to be $O_2 \rightarrow OOH^* \rightarrow O^* \rightarrow OH^* \rightarrow H_2O$.⁹⁴ The adsorption energies of O^* and OH^* are linearly correlated to each other according to scaling relations as shown in Figure 2.13 (lower-left panel). On the other hand, Rossmeisl et al. reported a linear relation between the adsorption energies of O^* and OOH^* ($\Delta E_{OOH^*} = 0.53\Delta E_{O^*} + 3.18$), which is similar to the one of O^* and OH^* ($\Delta E_{OH^*} = 0.50\Delta E_{O^*} + 0.05$).⁸⁹ Note that constant term in the expression of ΔE_{OH^*} here is different from the one in Figure 2.13 because of a different definition of ΔE , which is from the computational hydrogen electrode (CHE) developed by Nørskov et al.⁹⁵ Based on the CHE model, the free energies of H_2O and H_2 are set to zero, and the one of O_2 is determined to be 4.92 eV according the known reaction energy of four-electron ORR ($2H_2 + O_2 \rightarrow 2H_2O$). The ideal free energies of OOH^* , O^* , and OH^* are 3.69, 2.46, and 1.23 eV, respectively, and the corresponding equilibrium potential is 1.23 V (no overpotential) as shown Figure 2.14a. It means that each elementary step releases the same amount of energy (1.23 eV) and becomes thermodynamic equilibrium at 1.23 V. However, according to the scaling relations, if the free energy of O^* is 2.46 eV, the one of OOH^* should be ca. 4.4 eV, which results in a small free-energy decrease (ca. 0.5 eV) from O_2 to OOH^* and a large overpotential ($1.23 - 0.5 = 0.73$ V). Figure 2.14b presents the free-energies of ORR intermediates on Fe-phthalocyanine, which is a typical nonprecious ORR catalyst.⁹³ The scaling relations still hold, and the maximum potential is only 0.67 V to ensure all steps

are downhill in free energy.

Figure 2.15 a) Scaling relations for $\Delta G(\text{OOH}^*)$ and $\Delta G(\text{O}^*)$ on the (111) surfaces of different metals using $\Delta G(\text{OH}^*)$ as a descriptor. The solid lines represent $\Delta G(\text{OOH}^*) = \Delta G(\text{OH}^*) + 3.2$ and $\Delta G(\text{O}^*) = 2\Delta G(\text{OH}^*)$. b) Volcano plots for ORR on different metal surfaces, indicating the strong (solid blue line) and weak (solid green line) bonding regions.⁹⁴

The scaling relations between OOH^* , O^* , and OH^* indicate that only one independent variable is needed to depict the adsorption free energy (ΔG) of all these ORR intermediates. Although the pioneer researches generally used $\Delta G(\text{O}^*)$ as the descriptor,^{89, 95} currently $\Delta G(\text{OH}^*)$ is more common, because the rate determining step of ORR usually involves OH^* or OOH^* , and the linear fitting between $\Delta G(\text{OH}^*)$ and $\Delta G(\text{OOH}^*)$ is better. The widely accepted scaling relations are $\Delta G(\text{OOH}^*) = \Delta G(\text{OH}^*) + 3.2$ and $\Delta G(\text{O}^*) = 2\Delta G(\text{OH}^*)$ as shown in Figure 2.15a. The overall thermodynamic limiting potential (U_L) of ORR is determined by the smallest one of its elementary steps. As the reaction energy and U_L of each ORR step can be expressed as the function of $\Delta G(\text{OH}^*)$, the overall U_L of ORR becomes a function of $\Delta G(\text{OH}^*)$ as shown in Figure 2.15b, which turns out to be a volcano type plot. A larger $\Delta G(\text{OH}^*)$ indicates less stable and weak adsorption of ORR intermediates on the catalysts. For metals with large $\Delta G(\text{OH}^*)$ such as Au, their $\Delta G(\text{O}^*)$ and $\Delta G(\text{OOH}^*)$ are also large according to the scaling relation. They are less effective to stabilize ORR intermediates and the rate-determining step is the activation of O_2 to OOH^* , as indicated by the solid green line in Figure 2.15b. While for metals with small $\Delta G(\text{OH}^*)$ such as Rh, O_2 is easy to be activated, but the adsorbed ORR intermediates are too stable,

and the reduction of OH^* to H_2O becomes the rate-determining step (Figure 2.15b, solid blue line). Pt(111) surface was found to have moderate $\Delta G(\text{OH}^*)$ near the top of the volcano plot, which is in agreement with the good ORR activity of Pt in experiments. However, for other Pt surfaces such as (211), the adsorption of OH^* is too strong and the ORR activity is predicted to be relatively low, which may be the reason of decreased ORR activity on smaller Pt particles with more stepped sites.⁹⁶ The $\Delta G(\text{OH}^*)$ on Pt(111) is slightly smaller than the optimal value indicated by the volcano plot, which means the adsorption of OH^* is a little too strong. Inducing compress strain or using proper Pt alloy could increase $\Delta G(\text{OH}^*)$ to achieve better ORR activity.⁹⁷ In addition, it is worth noting that even for the optimal catalyst indicated in the ORR volcano plot, there is still a considerable overpotential (ca. 0.37 V).

2.2.4 Outstanding Questions

ORR is a critical reaction in energy storage and conversion devices. Currently, the most stable and active ORR catalysts are Pt and Pt-based materials. High loading of Pt is required to achieve applicable current and power, while it is economically prevented by the scarcity and high price of Pt. Therefore, it is important to increase the specific activity per Pt atom to reduce the use of Pt, and another way is to develop nonprecious ORR catalysts. Using single-atom catalysts can achieve the maximum utilization of Pt atoms, and some nonprecious single-atom catalysts also shown promising ORR performance such as Fe/N/C and Co/N/C. While the stability and activity of single-atom ORR catalysts are still inferior to Pt nanoparticles. Understanding the active site and reaction mechanism of ORR is important to further improve the performance of single-atom catalysts. Because of the atomically dispersed active sites and site confinement effect in single-atom catalyst, the ORR reaction mechanism can be different from the traditional catalysts with near-continuous active sites. There are some discrepancies between simulations and experiments about the ORR activity of single-atom catalysts such as Fe/N/C and Co/N/C, by using the traditional ORR mechanism. Therefore, the re-examination of ORR mechanism on single-atom catalysts is highly desired.

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Chapter 3

Computational Methodology

First-principles calculations are directly derived from basic physical principles without any assumptions. The Schrödinger equations of many-body systems cannot be accurately solved because of the complex interactions between particles. Generalized first-principles calculations are referred to all the theoretical calculations based on quantum mechanics. Density functional theory (DFT) proposed by Hohenberg, Kohn, and Sham use the electron density as the basic variations instead of electronic wave functions, which significantly lowers the computation in solving Schrödinger equations and makes it possible to study the electronic structures of complex systems. The whole edifice of DFT is based on two Hohenberg-Kohn theorems and the Kohn-Sham equation. The exchange-correlation functional must be defined to solve the Kohn-Sham equation and many approximate forms of it have been developed. Importantly, the rate of chemical processes can be calculated by DFT using transition state theory. The critical step in transition state theory is to calculate the activation energy of chemical processes, which directly determines the reaction rate.

3.1 Rationale for Selection of Methods

First-principles calculations in this report are based on density functional theory (DFT) and performed in Vienna ab-initio simulation package (VASP).^{1, 2} First principle is a term derived from philosophy and logic that refers to the most fundamental proposition. In materials physics and other fields, theoretic studies that directly derived from basic physical principles without any assumptions are called as first-principles or ab initio studies. Strictly speaking, first-principles calculations do not need any empirical model or fitting parameter and only relies on several basic physical constants such as speed of light and Plank constant. For example, the electronic energy levels of a hydrogen atom can be obtained by solving its Schrödinger equation in quantum mechanics. However, the Schrödinger equation of many-particle system cannot be solved accurately because of the complex interactions between microscopic particles. Some approximate methods are needed to get the solution and sometimes the adoption of some empirical parameters can significantly speed up the calculations. The generalized first-principles calculations can refer to all the theoretical calculations based on quantum mechanics.

Quantum mechanics is a basic theory in physics that describes the motion and interactions of microscopic particles including electrons, atoms, and molecules. Thanks to the rapid development of computer in recent decades, several computing subjects such as computational physics, quantum chemistry, and computational materials science are developed based on quantum mechanics. These emerging computing subjects significantly facilitate the developments and applications of physics, chemistry, and materials science, making it possible to predict, design, and analyze new materials from simulations. First-principles calculation is the most accurate and feasible method in materials simulations, which can provide accurate information on the atomic level that is difficult and even impossible to detect in current experimental facilities. The complex system in a practical application is generally simplified to a unit cell with hundreds of electrons and nucleus in first-principles calculations. The Schrödinger equation of the many-body unit cell can be solved by supercomputers. The eigenvalues and eigenfunctions of the Schrödinger equation are the energies and electronic wave functions of the system, respectively. Other

properties such as electronic structures, optical properties of the system can be derived from the energies and electronic wave functions.

3.2 Density Functional Theory

Density functional theory (DFT) was proposed by Hohenberg, Kohn, Sham et al. in the 1960s.^{3, 4} Electron density is used as basic variable in DFT instead of electronic wave functions in previous methods such as Hartree-Fock method. DFT significantly lowers the computation in solving Schrödinger equations and makes it possible to study the electronic structures of complex systems. The whole edifice of DFT is based on two theorems proved by Hohenberg and Kohn and a set of equations derived by Kohn and Sham.^{3, 4} The first Hohenberg-Kohn theorem states that ‘the ground state of any interacting many particle system with a given fixed inter-particle interaction is a unique functional of the electron density $n(\mathbf{r})$ ’, which indicates that there is a one to one mapping between ground-state electronic wave functions and ground-state electron density. Therefore, the ground-state energy E can be expressed as $E[n(\mathbf{r})]$, where $n(\mathbf{r})$ is electron density. This is the origin of the name of density functional theory.

The first Hohenberg-Kohn theorem can be interpreted as that the ground-state electron density of a system determines all its properties including ground-state energy and wave functions. It is significant that the Schrödinger equation can be solved by electron density in three dimensions instead of electronic wave functions in $3N$ dimensions, where N is the number of electrons in the system. Although the first Hohenberg-Kohn theorem demonstrates the existence of such an electron density functional that can be used to solve the Schrödinger equation, the specifics of this functional are still unknown. The second Hohenberg-Kohn theorem states that ‘the electron density that minimizes the energy of the overall functional is the true electron density corresponding to the full solutions of the Schrödinger equation’, which defines an important property of this functional that the electron density minimized the energy functional $E[n(\mathbf{r})]$ is the solution of the Schrödinger equation. Therefore, if the functional form is known, the electron density and ground-state energy of the system can be obtained through variational approach.

If focused on a single electron, by using the mean-field approximation of Hartree method, the interactions with nucleus and other electrons can be treated as an effective potential V_{eff} . In this way, the interactions between electrons are integrated in the V_{eff} and then the total electronic wave function can be expressed as the product of every single-electron wave function $\phi_i[n(r)]$. Using single-electron wave function ϕ_i , the energy functional in Hohenberg-Kohn theorems can be expressed as follows,

$$E[\phi_i[n(r)]] = E_{\text{known}}[\phi_i[n(r)]] + E_{\text{XC}}[\phi_i[n(r)]], \quad (3.1)$$

where $E_{\text{known}}[\phi_i[n(r)]]$ is the items with known expressions, including the kinetic energy of electrons and all kinds of Coulomb potentials. All the other energies are included in exchange-correlation functional $E_{\text{XC}}[\phi_i[n(r)]]$. What is the expression of this $E_{\text{XC}}[\phi_i]$ and how to get the minimum of this functional? This problem is solved by Kohn and Sham, and they demonstrated that the electron density can be obtained by solving a series of single-electron Schrödinger equations as follows,

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V_{\text{C}}(r) + V_{\text{H}}(r) + V_{\text{XC}}(r) \right] \phi_i(r) = \varepsilon_i \phi_i(r) \quad (3.2)$$

This equation is the famous Kohn-Sham equation, whose solution is single-electron wave function in three dimensions. In this equation, V_{C} is Coulomb potential, V_{H} is Hartree potential, and the exchange-correlation potential V_{XC} is given by,

$$V_{\text{XC}}(r) = \frac{\delta E_{\text{XC}}[n(r)]}{\delta n(r)} \quad (3.3)$$

Note that the potentials in the Kohn-Sham equation is based on electron density and the electron density should be derived from single-electron wave function, which comes from the solution of the Kohn-Sham equation. Therefore, the Kohn-Sham equation should be solved by iteration. Firstly, a tentative electron density is given to solve the Kohn-Sham equation. Secondly, a new electron density is obtained from the single-electron wave function, which is the solution of the Kohn-Sham equation in the first step. This process iterates until convergence is reached.

3.3 Exchange-Correlation Functional

The exchange-correlation functional $E_{XC}[\{\phi_i\}]$ must be defined to solve the Kohn-Sham equation, while the real expression of $E_{XC}[\{\phi_i\}]$ is unknown. Fortunately, the exchange-correlation functional of homogeneous electron gas can be accurately derived, which has a constant electron density. Although the electron density of practical system is generally not constant, the homogeneous electron gas model provides an ideal system to apply the Kohn-Sham equation. In this case, the exchange-correlation potential V_{XC} is only related to the constant electron density $n(r)$. In practice, a simple approximation is using the local electron density to define the exchange-correlation potential like it in homogeneous electron gas model, which is called local density approximation (LDA). The LDA enables full definition and expression of the Kohn-Sham equation and works well in most cases, though the solution of this equation is not the exact solution of the ideal Schrödinger equation because of the adoption of an approximated exchange-correlation functional.

Aside from the LDA, other exchange-correlation functionals are also proposed and the development of exchange-correlation functionals is one of the most important fields in DFT calculations. If anyone proposed the accurate expression of exchange-correlation functional and it worked well in many-body system, it is possible to win a Nobel Prize. The generalized gradient approximation (GGA) includes the local electron density and gradient in the functional, which is the most famous one after the LDA. Although the GGA includes more information than the LDA, the GGA is not always more accurate than the LDA. Generally, the LDA is very accurate in systems with relatively smooth density variations.

For the GGA, there are different methods to integrate the gradient into the functional, therefore different forms of the GGA are available now. The Perdew-Wang (PW91) and Perdew-Burke-Ernzerhof (PBE) are two most popular GGA functionals in solid state physics.^{5, 6} It is worth noting that the exchange-correlation functional is not only related to the local electron density and gradient. More information can be taken into consideration to construct more complex exchange-correlation functionals. For a certain system, different

exchange-correlation functionals may have different results. Therefore, the selection of exchange-correlation functionals should be tested or based on previous simulations and experiments.

3.4 Transition State Theory

This section will introduce how to calculate the rate of a chemical process from DFT calculations. The process here includes both chemical reactions and physical migrations. The total energy of a system can be defined by the coordinates of all the atoms in the system. Generally, there are many local minimums in the total energy, and a basic process is the transition between two neighboring minimums without passing through any other minimums. The rate of this basic process can be accurately calculated in DFT.

A simple example is the diffusion of adsorbed atoms on a close-packed metal surface. Suppose the surface lies in the x-y surface, the adsorption energy of an atom in any coordinates of this surface can be calculated. Fixing the x and y coordinates of the adsorbed atom, the adsorption energy can be calculated by relaxing the metal surface and the z coordinate of the adsorbed atom. The adsorption energy on any position can be determined and then a two-dimensional potential surface is obtained in this way. Local maximums, local minimums, and saddle points are three kinds of important positions on the potential surface. Hollow sites are the local maximums on the close-packed metal surface. Top sites and bridge sites are local minimums and saddle points, respectively.

Most of the adsorbed atoms are in the hollow sites according to thermodynamics because of minimum potential energies. The diffusion of an adsorbed atom is determined by its motion between neighboring hollow sites. There are numerous routes between two minimums on the potential surface, and the critical route is the one with the lowest energy barrier, which is referred as minimum energy path (MEP). The energy maximum point along a MEP is the transition state of this process and the point is also a saddle point on the potential surface. Therefore, the diffusion rate k between two local minimums can be expressed as follows,

$$k = \frac{1}{2} v_T p^* \quad (3.4)$$

where v_T is the average thermal velocity of the jumping atom, p^* is the probability of the transition state, and the factor of $1/2$ is because the transition state can jump into both minimums with equal probability. The probability of a state x is proportional to $\exp[-E(x)/k_B T]$ in the thermodynamic equilibrium. The average thermal velocity is equal to $(2k_B T/\pi m)^{1/2}$ according to the Maxwell-Boltzmann distribution. Therefore, the diffusion rate k can be further expressed as follows,

$$k = \frac{1}{2} \left(\frac{2}{\beta \pi m} \right)^{\frac{1}{2}} \frac{e^{-\beta E^*}}{\int e^{\beta E(x)} dx}, \quad (3.5)$$

where β equals $1/k_B T$, and E^* is energy of the transition state. Using the second order approximation of Taylor expansion in $e^{\beta E(x)}$, the diffusion rate k can be simplified as follows,

$$k = v e^{-\beta(E^* - E_0)}, \quad (3.6)$$

where v is the vibration frequency of the system in the local minimums. This result is called harmonic transition state theory because of the second order Taylor expansion used as approximation. In this theory, the rate k is only related to two parameters, i.e. v and $E^* - E_0$, both of which can be easily obtained from the potential surface. The latter one is the energy difference between the transition state and the initial state and is usually referred as ΔE , which is also the activation energy of the process.

3.5 Computational Hydrogen Electrode Model

Nørskov et al. proposed a computational hydrogen electrode (CHE) model to calculate the stability of reaction intermediates in electrocatalysis from DFT simulations.⁷ The relative stabilities of reaction intermediates on the catalysts are characterized by adsorption free energy and a free-energy profiles of the electrochemical reaction can be calculated. The voltage effect, pH effect, and solvation effect on the adsorption free energies of reaction intermediates can be simply included in the CHE model. The procedure for the calculation of adsorption free energy is shown as follows:

1. By taking the standard hydrogen electrode (SHE) as the reference potential, the free energy of $H^+ + e^-$ (pH = 0, $U = 0$) equals a half of H_2 (1 bar) at 298 K according to the equilibrium of the reversible reaction: $H^+ + e^- \rightarrow \frac{1}{2} H_2$ in the standard hydrogen electrode. The energy of H_2 can be obtained from DFT calculations. In this way, the reaction energy (ΔE) of proton-coupled electron transfer process ($A + H^+ + e^- \rightarrow AH$, A refers to reactants or reaction intermediates) in electrocatalysis can be calculated from $A + \frac{1}{2} H_2 \rightarrow AH$, which associates the relative stability of different reaction intermediates.
2. The solvation effect on free energy can be included by an implicit model such as the Poisson-Boltzmann continuum-solvation model.⁸ Alternatively, water molecules can also be added in the DFT calculations as an explicit model, which requires more computing resources.
3. The bias effect can be included by modifying the energy of $H^+ + e^-$ by $-eU$, where U is the electrode potential versus SHE.
4. The pH effect can be included by modifying the energy of $H^+ + e^-$ by $kT \cdot \ln[H^+]$, where k is the Boltzmann constant, T is the temperature, and $[H^+]$ is related to the pH.
5. The interaction between the adsorbates and electric field in the electrochemical double layer can be estimated by calculating the coupling between the dipole moment of the adsorbate and average field near the electrode surface.
6. The reaction energy ΔE can be further corrected to reaction free energy ΔG by: $\Delta G = \Delta E + \Delta(ZPE - TS)$, where ZPE is the zero-point energy and TS is the entropy effect. The ZPE and TS can be calculated by DFT calculations or taken from handbooks.

By using this CHE model, Nørskov et al. successfully explained the origin of intrinsic overpotential for oxygen reduction reaction.⁷ The adsorbed oxygen and hydroxyl were found to be too stable on the optimum Pt surface at potentials near the thermodynamic equilibrium state.

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Chapter 4*

Crystal Phase Effect on Surface Activity of Gold

Crystal phase engineering is a promising strategy to tune the catalytic performance of metal nanomaterials. Generally, the crystal phase effect on catalysis is ascribed to distinct surface atomic arrangements of catalysts with different crystal phases. Here we show that even for similar surfaces, such as the close-packed surfaces, different crystal phases have considerably different surface reactivity due to their distinct intrinsic surface strains. Using first-principles calculations, we find that the close-packed surfaces of hexagonal close-packed (HCP) and double HCP (4H) gold have significantly smaller intrinsic strains ($\sim 1.3\%$) than that of face-centered cubic (FCC) gold ($\sim 2.3\%$). These distinct intrinsic surface strains result in various oxygen adsorption energies and O_2 dissociation barriers on these close-packed gold surfaces, and the dissociation of O_2 on different crystal phases and surfaces follows the Brønsted-Evans-Polanyi principle.

*This section published substantially as “Crystal phase effect upon O_2 activation on gold surfaces through intrinsic strain” in *Nanoscale* (DOI: 10.1039/c9nr04510d).¹ Reproduced by permission of The Royal Society of Chemistry.

4.1 Introduction

Crystal phase engineering has emerged as an effective method to modify the catalytic performance of metal catalysts in recent years.²⁻⁵ Traditionally crystal phases are controlled by temperature and pressure.^{6, 7} However, catalytic conditions are usually far away from the phase transition boundaries, which generally require high temperatures and/or high pressures for metals. In recent years, various metal nanostructures with unconventional crystal phases have been synthesized under mild conditions,⁸⁻¹² which are stabilized via high specific surface areas⁸⁻¹⁰ or inner strain induced by five-fold twin boundaries^{11, 12}. In addition, nanostructures with high specific surface areas are also highly desired in catalysis. Therefore, the application of crystal phase engineering in nanosized catalysts is promising and attracts great research interest.² It has been reported that catalytic performances of cobalt^{13, 14} and ruthenium^{11, 15-17} nanoparticles are closely related to their crystal phases.

Nørskov et al. have predicted the effect of strain on the reactivity of metal surfaces with conventional crystal phases using density functional theory (DFT) calculations.^{18, 19} Recently, Wang et al. reported the fine-tuning of intrinsic strain in palladium nanosheets through atomic-level control of thickness and achieved high catalytic activity in oxygen reduction and hydrogen evolution reactions,²⁰ which confirmed the effect of intrinsic strain on catalysis. Note that Yao et al. reported the selective growth of hexagonal close-packed (HCP) and face-centered cubic (FCC) ruthenium on the surface of palladium-copper alloy via varying lattice mismatch and surface strain,¹⁵ which implies potential connection between crystal phase and intrinsic surface strain. Therefore, understanding the relationship between crystal phase, intrinsic strain, and surface reactivity is critical for both catalyst design and crystal phase engineering. While it is very difficult to study it in experiments,²¹ first-principles calculations provide the possibility to figure out catalytic mechanism for different crystal phases at the atomic level. For example, Liu et al. proposed that HCP cobalt particles has more active sites and favorable reaction route for Fischer-Tropsch synthesis than the FCC ones through DFT calculations.¹⁴ However, previous studies mainly focused on the comparison between different exposed metal surfaces of different crystal phases, which have distinct arrangements of surface atoms.^{14, 16} Close-

packed surfaces have low surface energy and generally take up a large proportion of the surface of metal particles according to the Wulff construction,^{17, 22} and they have exactly the same atomic arrangement for at least top two atom layers. So far, the crystal phase effect on close-packed surface properties remains elusive.

Herein, we investigate crystal phase effect on the intrinsic strain and reactivity of gold close-packed surfaces via DFT calculations. Gold is taken as an example because of the good performance of gold catalysts in various reactions²³⁻²⁵ and the successful synthesis of unconventional HCP and double HCP (4H) gold in recent years.^{8, 9, 26} We analyze the structural parameters of bulk gold surfaces and free-standing gold nanosheets with different crystal phases, including HCP, FCC, and 4H, and find significantly different intrinsic surface strains even for their close-packed surfaces. Free-standing gold nanosheets composed of several (<10) close-packed atom layers have similar in-plane Au-Au lengths regardless of the stacking sequence, while remarkably different intrinsic surface strains appeared for thicker (>5 nm) nanosheets and bulk surfaces among different crystal phases. We further show that distinct intrinsic surface strains result in various surface reactivities for such as oxygen adsorption and O₂ dissociation, which are very important in gold catalysis for selective oxidation and oxygen electroreduction reactions.^{25, 27, 28} The adsorption energy of oxygen is found to have linear relationship with the intrinsic surface strain, and the dissociation barriers of O₂ on different crystal phases and surfaces follow the Brønsted-Evans-Polanyi principle.²⁹ Although the precisely controlling of exposed surfaces and the number of atom layers remains a challenge, free-standing gold nanosheets with various thicknesses have been reported.^{8, 30-33} The understanding of the relationship between crystal phase, size (thickness), and intrinsic surface strain indicates new opportunities for crystal phase engineering and its application in catalysis.

4.2 Computational Methods

Spin-unrestricted calculations were performed using density functional theory as implemented in the Vienna *ab initio* simulation package (VASP).^{34, 35} The ion-electron interactions are treated with the projected augmented wave pseudopotentials,³⁶ and the

plane-wave basis set was cut off at 400 eV. Generalized gradient approximation with the Perdew-Burke-Ernzerhof functional was used to determine the exchange-correlation energy.³⁷ The slab model was adopted to mimic the metal surfaces and the separation between two slabs was larger than 15 Å to eliminate spurious interactions. There are two kinds of slab models adopted in our calculations. The first one is fully relaxed slab models to simulate free-standing gold nanosheets. Another one with fixed in-plane Au-Au bond length is used to simulate bulk surfaces or strained nanosheets, and the fixed values come from the corresponding lattices of bulk gold or strains. A six-layer slab with 3×3 surface unit cell was adopted when simulating the oxygen adsorption and O₂ dissociation on the Au(111) surface with different crystal phases, and a 7×7×1 *k*-point mesh was sampled by the Monkhorst-Pack scheme.³⁸ The 1×1 (111) unit cell was used when studying the layer number effect, and the corresponding *k*-point mesh was increased to 21×21×1. All structures were optimized by the conjugate gradient method until the residual force on each unfixed atom was less than 0.01 eV/Å, and only the lower half of the slab was fixed. The climbing image nudged elastic band method was used to find the transition states and calculate the corresponding energy barriers.³⁹ The DFT-D3 method with Becke-Jonson damping was adopted to include van der Waals interactions and was only applied in the simulations of O₂ dissociations,^{40, 41} which involve the adsorption of O₂ on gold surfaces. In addition, the structure models were visualized in the VESTA software.⁴²

4.3 Results and Discussion

All of HCP, FCC, and 4H are close-packed structures, which are composed of a series of close-packed atom layers. There are three distinguishable close-packed atom layers (labeled as A, B, and C in Figure 4.1) with separate relative displacements. The stacking sequences and periods of HCP, FCC, and 4H phases are ‘AB’, ‘ABC’, and ‘ABCB’, respectively. Traditionally we only focus on the aspect of stacking sequence, but it cannot fully explain the difference in surface properties between HCP, FCC, and 4H closed-pack surfaces, which have the same structures for at least two surface atom layers. It is still unclear how deep structures affect surface properties. Here we use two structural parameters (interplanar spacing and in-plane bond length), in addition with the well-known

stacking sequence, to fully characterize the atomic structures of close-packed phases (as shown in Figure 4.1). The plane in these two terms refers to close-packed surfaces, i.e., HCP(001), FCC(111), and 4H(001).

Figure 4.1 Structural parameters, including stacking sequence, interplanar spacing, and in-plane bond length, used to characterize close-packed structures comprehensively.

Figure 4.2 (a) Potential energy per atom of gold with different crystal phases under isotropic strain as a function of in-plane Au-Au length. (b) Nearly linear relationship between interplanar spacing and in-plane Au-Au length under isotropic strain.

Table 4.1 The structural parameters of HCP, FCC, and 4H bulk gold.

	HCP	FCC	4H
Stacking sequence	... AB ...	... ABC ...	... ABCB ...
Interplanar spacing (Å)	2.451 2.451 ^{ref 43}	2.399 2.409 ^{ref 43}	2.440

In-plane Au-Au length (Å)	2.909 2.927 ^{ref 43}	2.938 2.951 ^{ref 43}	2.915
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Using first-principles calculations, firstly we obtain the equilibrium structures of HCP, FCC and 4H bulk gold and observe considerably different interplanar spacings and in-plane Au-Au lengths between them. The results are shown in Figure 4.2 and Table 4.1, which are in good agreement with previous studies.^{43, 44} The interplanar spacing of FCC gold is only 2.399 Å, while they are 2.451 and 2.440 Å for HCP and 4H gold, respectively. The difference in interplanar spacing between FCC and HCP is more than 2%, and it is around 1.7% between FCC and 4H. On the other hand, the in-plane Au-Au length of FCC gold (2.938 Å) is about 1% larger than HCP (2.909 Å) and 4H gold (2.915 Å), which complements its smaller interplanar spacing. These results reveal intrinsic difference in structural parameters between HCP, FCC, and 4H phases aside from the well-known stacking sequence. Larger in-plane Au-Au length indicates weaker in-plane bond strength and results in lower in-plane electron density.⁴⁵ Consequently, the interaction between close-packed layers becomes stronger to compensate and the interplanar spacing is smaller accordingly. The difference in in-plane bond lengths and interplanar spacings of HCP (4H) and FCC gold is due to their different symmetries. More specifically, the ratio of a/c in hexagonal crystal systems may have slight deviation from the perfect close-packed values ($\sqrt{3/8}$ for HCP and $\sqrt{3/32}$ for 4H) without breaking the symmetry, which leads to different in-plane bond lengths and interplanar spacings. While for FCC phase, the ratio should equal to the perfect close-packed value for FCC ($\sqrt{1/6}$) because of its high O_h symmetry.

Table 4.2 The structural parameters of HCP, FCC, and 4H free-standing 6-layer gold nanosheets.

	HCP	FCC	4H
Stacking sequence	... AB ...	... ABC ...	... ABCB ...
Interplanar spacing (Å)	2.536	2.521	2.520
In-plane Au-Au length (Å)	2.871	2.873	2.874

Currently, non-FCC phases of gold can only be stabilized in nanostructures with high specific area.^{8,9} We further consider free-standing gold nanosheets composed of a few atom layers. Surprisingly, the in-plane Au-Au length is almost the same for HCP, FCC, and 4H, and it is about 2.87 Å for 6-atom layer sheets (Table 4.2). This in-plane Au-Au length is much smaller than the values (2.91 – 2.94 Å) of bulk gold (Table 4.1) due to compressive in-plane strain.²⁰ Meanwhile, the surface interplanar spacing of these gold nanosheets is also similar to each other (2.536, 2.521, and 2.520 Å) and significantly ($\sim 3\%$) larger than those of bulk gold. The small in-plane Au-Au length and large interplanar spacing of nanosheets originate from their broken symmetry, which results in strong in-plane interactions and relatively weak interactions perpendicular to the surface and minimizes the effect of stacking sequence on in-plane bond length and interplanar spacing.

Figure 4.3 (a) Energy per atom as the function of in-plane Au-Au lengths for free-standing 6-layer gold nanosheets. (b) Inverse correlation between interplanar spacing and in-plane Au-Au length under surface strain. The dashed lines represent the equilibrium positions of free-standing 6-layer nanosheets ($\epsilon = 0$), and the solid lines represent the positions of bulk surfaces.

Strain is an important factor and easy to be induced in metal nanosheets and interfaces,^{20, 46} and it has been used to modulate the crystal phase of ruthenium synthesized through epitaxial growth.¹⁵ Figure 4.3a shows the relationship between energetic stability and strain (in-plane Au-Au length) of HCP, FCC, and 4H gold nanosheets with 6 atom-layers, which

is the smallest layer number to show the distinct stacking sequences of these crystal phases. The equilibrium in-plane Au-Au lengths of HCP, FCC, and 4H are nearly same (dashed line in Figure 4.3a). In order to unify and compare the strains among different crystal phases, the zero point of intrinsic strain (ϵ) is set at this common equilibrium in-plane Au-Au length (2.87 Å) of free-standing 6-layer nanosheets. In addition, it is worth noting that in Figure 4.3a the energies of different crystal phases are slightly different from each other when the in-plane Au-Au length is larger than the equilibrium value (2.87 Å), while no difference is observed when the in-plane Au-Au length is smaller. This is due to different interplanar spacings upon different in-plane Au-Au lengths. Figure 4.3b presents the relationship between in-plane Au-Au length and interplanar spacing for gold nanosheets with different crystal phases. Under two-dimensional strain in the plane of close-packed surfaces, interplanar spacing decreases with the rise of in-plane Au-Au length due to the Poisson effect.⁴⁷ Large in-plane Au-Au lengths correspond to small interplanar spacings, therefore, the interactions between adjacent atom layers are relatively strong and the effect of stacking sequence on energy becomes remarkable (Figure 4.3a). In contrary, small in-plane Au-Au lengths correspond to large interplanar spacings and weak interplanar interactions, which make the stacking sequence less important and diminish the difference in energy between HCP, FCC, and 4H (Figure 4.3a).

The in-plane Au-Au lengths of bulk gold phases are noted in Figure 4.3b by solid vertical lines, which are significantly larger than the free-standing 6-layer nanosheets indicated by the dashed vertical line. As in-plane Au-Au length on a bulk surface is epitaxial determined by inner bulk gold phases, the near-surface atom layers experience intrinsic in-plane strains compared to free-standing 6-layer nanosheets. The deviations of in-plane Au-Au length of 6-layer nanosheets from bulk gold are ~ 2.3% for bulk FCC and ~ 1.3% for bulk HCP and 4H, which indicates the near-surface atom layers of FCC(111) experiences larger intrinsic strain than HCP(001) and 4H(001). It has been reported that strain has remarkable effect on surface properties and catalytic activities.^{18, 19, 48} Therefore, it is reasonable to propose that FCC(111) has distinct surface properties with HCP(001) and 4H(001) even they have similar surface atomic arrangements.

Figure 4.4 (a) Oxygen adsorption energy as the function of in-plane Au-Au length on different close-packed surfaces. The dashed lines represent the positions of free-standing 6-layer nanosheets, and the solid lines represent the positions of bulk surfaces. (b) Brønsted-Evans-Polanyi relationship for O_2 dissociation on different gold crystal phases and surfaces.

We further study the effect of intrinsic strain (in-plane Au-Au length) from crystal phases on the adsorption of oxygen atom and the dissociation of O_2 , which is very important in heterogeneous catalysis.^{49, 50} Figure 4.4a presents that the adsorption energy of an oxygen atom on the close-packed gold surfaces is strongly related to the in-plane Au-Au length, which is consistent with previous report about oxygen adsorption on strained metal surfaces.^{18, 48} The adsorption energy is defined as:

$$E_{\text{ads}} = E(\text{ads/metal}) - E(\text{ads}) - E(\text{metal})$$

where $E(\text{ads/metal})$ and $E(\text{metal})$ are the energies of metal surfaces with and without adsorbates, respectively, and $E(\text{ads})$ is the energy of adsorbates in a vacuum, which is generally calculated from a single O atom in this case.^{51, 52} According to this definition, lower E_{ads} means stronger adsorption, and vice versa. Longer in-plane Au-Au length indicates weaker Au-Au bond strength and results in stronger Au-O interaction (lower adsorption energy). The adsorption of oxygen on gold FCC(111) is 0.36 eV stronger than on free-standing 6-layer nanosheets because of 2.3% intrinsic strain as shown in Figure 4.4a, and it is about 0.20 eV stronger for HCP(001) and 4H(001). It is worth noting that the data in Figure 4.4a can be divided into two parts (negative and positive strains), and the negative part has a greater slope between adsorption energy and in-plane Au-Au length.

This could be due to strong in-plane interactions between gold atoms under negative strain, consistent with the rapid increase of energy under negative strain in Figure 4.3a.

Figure 4.5 Dissociation processes of O_2 on close-packed and (110) gold surfaces with different crystal phases.

We next consider the dissociation of O_2 on different gold surfaces and crystal phases. The dissociation processes of O_2 on different Au surfaces are shown in Figure 4.5, and the corresponding reaction energies and reaction barriers are shown in Figure 4.4b. The dissociation of O_2 on gold is closely related to the oxygen adsorption energy, which reflects the interaction strength between oxygen and gold. Therefore, lower oxygen adsorption energy means stronger Au-O interaction and implies lower dissociation barrier of O_2 on gold. From Figure 4.4a we know that for close-packed surfaces, the sequence of oxygen adsorption energy is $FCC(111) < 4H(001) < HCP(001)$, which should be the same as the sequence of O_2 dissociation barrier. The calculated O_2 dissociation barriers are shown in Figure 4.4b, and the relative values are consistent with our analysis. Figure 4.4b also shows that the dissociation barrier of O_2 is proportional to the reaction energy (Brønsted-Evans-Polanyi principle).²⁹ Aside from close-packed surfaces, the results on (110) open surfaces are also shown in Figure 4.4b and similar linear relationship is identified.

Figure 4.6 The effect of layer numbers on (a) in-plane Au-Au length and (b) average interplanar spacing of gold nanosheets. Lines are provided to guide the eye.

Figure 4.7 Distribution of interplanar spacing in 6-layer and 60-layer gold nanosheets with different crystal phases.

The previous results are based on bulk gold (surfaces) and 6-atom layer nanosheets (~ 1.5 nm in thickness). In practical applications such as heterogeneous catalysis, the sizes of gold catalysts are usually between these two.²³ Then we further study the layer number (i.e. thickness) effect on the structural parameters of gold nanosheets with different crystal phases. Figure 4.6a shows that the in-plane Au-Au length increases with the number of

atom layers for all of HCP, FCC, and 4H gold nanosheets. Before 10 layers (~ 2.5 nm), in-plane Au-Au length increases quickly with the layer number and different crystal phases have similar in-plane Au-Au lengths. Whereas remarkably separation of in-plane Au-Au lengths between different crystal phases appears when the layer number is larger than 20 (>5 nm in thickness) and results in distinct intrinsic strains accordingly. All the in-plane Au-Au lengths approach their bulk-state values upon further increasing the number of layers. Besides, the effect of layer number on interplanar spacing is also studied. In free-standing nanosheets, the interplanar spacing varies at different positions of the slab, especially for atom layers close to the surface (Figure 4.7). The average interplanar spacing of the middle region is calculated for each nanosheet and the results are shown in Figure 4.6b. Larger numbers of layers have smaller interplanar spacings, which tends to be stable after 20 layers as well. Figure 4.6a and 4.6b reveal opposite trends of in-plane Au-Au length and interplanar spacing upon the rise of layer number, and larger in-plane Au-Au length is accompanied by smaller interplanar spacing, which is consistent with the inverse correlation between them in Figure 4.3b. Counter-intuitively, thinner gold nanosheets are expected to have weaker oxygen adsorption because of their smaller in-plane Au-Au lengths (Figure 4.6a) according to Figure 4.4a. This result indicates that the high activity of nanoscale gold catalysts in oxidation reactions may be due to other under-coordinated active sites other than the close-packed surfaces.

It has been reported in experiments that the HCP gold nanosheet is unstable on exposure to an electron beam during transmission electron microscopy analysis.⁸ We further studied the phase transition of close-packed gold surfaces between HCP and FCC phases. The effect of oxygen atom adsorption on this kind of phase transition is also studied. For HCP(001) surface, transition of stacking sequence from ABABAB to CBABAB has been simulated and the transition barrier is determined to be 0.016 eV per surface Au atom. The energy descent of this process is 0.007 eV per surface Au atom. Interestingly, when a monolayer of oxygen atoms was adsorbed on the HCP(001) surface, the energy descent becomes only 0.002 eV per surface Au atom and the transition barrier disappears. This may be because the O-Au interaction impairs the interplanar Au-Au interaction, which facilitates the slide of surface Au atom layer and eliminates the effect of stacking sequence.

Therefore, oxygen atom adsorption can facilitate the phase transition according to our DFT calculations.

4.4 Conclusions

In summary, we demonstrate crystal phases have significant effects on surface reactivity even for close-packed surfaces due to their distinct intrinsic strains. HCP and 4H phases of bulk gold have remarkably smaller in-plane Au-Au lengths than FCC gold, while they have similar in-plane bond lengths in free-standing few-layer nanosheets. As in-plane Au-Au length on a bulk surface is epitaxial determined by inner bulk gold phases, the near-surface atom layers of different crystal phases experience distinct intrinsic in-plane strains compared to free-standing nanosheets and have different surface reactivities. The dissociation barriers of O₂ on various crystal phases and surfaces are calculated and conform to the Brønsted-Evans-Polanyi relationship. Effect of thickness on the structural parameters of gold nanosheets is also investigated. In-plane bond lengths of gold nanosheets increase rapidly when the layer number is less than 20 (< 5 nm in thickness), and then tend to be stable at distinct intrinsic strains for different crystal phases. The understanding between crystal phase, nanosheet thickness, intrinsic strain, and surface reactivity provides new opportunities in phase-controlled synthesis of metal nanostructures and their applications in catalysis.

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Chapter 5*

Oxygen Reduction on Single-Atom Catalysts

The electrochemical oxygen reduction reaction (ORR) mechanism was generally considered to be $O_2 \rightarrow OOH^ \rightarrow O^* \rightarrow OH^* \rightarrow H_2O$ (O^* mechanism). This O^* mechanism predicted reasonable ORR half-wave potential ($E_{1/2}$) of Co/N/C but abnormally underestimated the one of Fe/N/C. Herein we highlight an unconventional $2OH^*$ ORR mechanism ($O_2 \rightarrow OOH^* \rightarrow 2OH^* \rightarrow OH^* \rightarrow H_2O$), which was often ignored because the free energies (ΔG) of $2OH^*$ and O^* are equal according to the famous scaling relation: $2\Delta G(OH^*) = \Delta G(O^*)$. This scaling relation is true for traditional catalysts with near-continuous active sites. We find a different scaling relation: $\Delta G(2OH^*) = \Delta G(O^*) + 1.5 \text{ eV}$ on single-atom catalysts (Me/N/C, Me = Fe, Co, etc.) and suggest that the $2OH^*$ mechanism should not be overlooked. In consideration of both O^* and $2OH^*$ mechanisms, the ORR $E_{1/2}$ of Co/N/C and Fe/N/C are in good agreement with experimental results. This work reveals the structure dependence of ORR reaction mechanisms and scaling relations in single-atom catalysis, and it is also heuristic for other reactions such as O_2 evolution and N_2 reduction on single-atom catalysts.*

*This section published substantially as “Unconventional oxygen reduction reaction mechanism and scaling relation on single-atom catalysts” in *ACS Catalysis* (DOI: 10.1021/acscatal.0c00815).¹ Reprinted with permission. Copyright (2020) American Chemical Society.

5.1 Introduction

In the previous Chapter, the oxygen adsorption and O₂ activation on gold surfaces with different crystal phases have been investigated, which is important in heterogeneous gold catalysis for selective oxidation reactions. The activation and reduction of O₂ is also critical in the oxygen reduction reaction (ORR). For example, electrochemical ORR plays an important role in sustainable energy conversion and storage devices such as fuel cells and metal-air batteries.²⁻⁶ ORR is an inherently sluggish four-electron transfer process with a large intrinsic overpotential that originates from the free-energy scaling relations between the ORR intermediates adsorbed on electrocatalysts.⁷⁻⁹ Platinum-based nanomaterials are effective and durable ORR catalysts but too costly for large-scale applications.¹⁰⁻¹⁴ Non-precious metal catalysts with metal-nitrogen coordination sites, such as Fe/N/C and Co/N/C composites, have attracted broad research interest in recent years because of their relatively high ORR activity and low cost.^{4, 15-18}

Further improving the ORR performance such as activity and durability of Me/N/C (Me = Fe, Co, etc.) requires proper understanding of the catalytic active sites and corresponding ORR mechanisms. Fe/N/C was found to have significantly better ORR activity than Co/N/C in various experiments,¹⁹⁻²⁶ and carbon-hosted MeN₄ moieties are identified as the active sites for ORR in heat-treated Me/N/C catalysts.^{27, 28} Previous density functional theory (DFT) studies²⁹⁻³¹ have adopted O* ORR mechanism (O₂ → OOH* → O* → OH* → H₂O) and indicated that the adsorption free energies of *O, *OH, and *OOH on the MeN₄ moieties still follow the scaling relations that are similar to the case of metal surfaces.^{7, 32} Those theoretical simulations predicted reasonable half-wave potentials (E_{1/2}) for ORR of Co/N/C, while abnormally underestimated the E_{1/2} for ORR of Fe/N/C, which was predicted to be even inferior to Co/N/C. This contradiction between experiments and simulations is still a puzzle.

Herein, we further consider an unconventional 2OH* ORR mechanism (O₂ → OOH* → 2OH* → OH* → H₂O) for single-atom catalysts, which involves two confined OH* bonded to a single active site. The computational hydrogen electrode model is adopted to

study the ORR mechanism.⁷ Several previous reports have noted the probably existence of 2OH* on various catalysts,^{26, 33-35} and Wang et al. have studied the 2OH* pathway of ORR on Me/N/C (Me = Fe, Co, or Ni) and predicted the single site 4e⁻ mechanism using DFT calculations.^{26, 35-37} However, the 2OH* mechanism was often overlooked because the free energies of 2OH* and O* are equal on traditional catalysts with near-continuous active sites according to the free-energy scaling relation: $\Delta G(O^*) = 2\Delta G(OH^*) = \Delta G(2OH^*)$.^{8, 34} Here a new scaling relation is identified: $\Delta G(2OH^*) = \Delta G(O^*) + 1.5 \text{ eV}$ on single Me/N/C active sites, thus the 2OH* mechanism cannot be ignored. This unconventional 2OH* mechanism predicts better and reasonable $E_{1/2}$ for ORR of Fe/N/C, and ORR on Co/N/C is found to still follow the O* mechanism. Overall, the simulated $E_{1/2}$ is in good agreement with the superior ORR activity of Fe/N/C compared to Co/N/C as reported in experiments.

5.2 Computational Methods

Spin-unrestricted calculations were performed using density functional theory as implemented in the Vienna *ab initio* simulation package (VASP).^{38, 39} The ion-electron interactions were treated with the projected augmented wave pseudopotentials,⁴⁰ and the plane-wave basis set was cut off at 400 eV. Generalized gradient approximation with the revised Perdew-Burke-Ernzerhof functional was used to determine the exchange-correlation energy.^{41, 42} MeN₄C₂₀ (Me = Cr, Mn, Fe, Co) porphyrin structures terminated by hydrogen atoms were adopted to simulate the Me/N/C catalysts according to previous reports.^{28, 29} The porphyrin structures or other molecules such as H₂ and H₂O were put in boxes larger than 20 Å in each direction, and the gamma k-point was used in the calculations. All structures with and without adsorbates were fully relaxed by the conjugate gradient method until the residual force on each atom was less than 0.01 eV/Å. In addition, the structure models were visualized in the VESTA software.⁴³

The adsorption energies (E_{ads}) of ORR intermediates (OH*, O*, 2OH*, and OOH*) were calculated as follows:

$$E_{\text{ads}} = E(\text{ads/substrate}) - E(\text{ads}) - E(\text{substrate}),$$

where $E(\text{ads/substrate})$ and $E(\text{substrate})$ are the energies of substrates with and without adsorbates, respectively, and $E(\text{ads})$ is the energy of adsorbates in a vacuum, which is calculated from H_2 and H_2O based on the computational hydrogen electrode (CHE) model developed by Nørskov et al.⁷ using the following relations:

where the energy of $(\text{H}^+ + \text{e}^-)$ is calculated by $\frac{1}{2} \text{H}_2$ according to the CHE model.

The adsorption free energies (ΔG) were calculated as follows:

$$\Delta G = E_{\text{ads}} + \Delta(ZPE - TS + E_{\text{solv}}),$$

where ZPE is the zero-point energy, TS refers to entropy, and E_{solv} represents the solvation effects that were simulated by using the Poisson-Boltzmann continuum-solvation model in the VASPsol code.⁴⁴ The temperature (T) was set at 298.15 K.

The volcano plots are constructed based on the reaction mechanisms and scaling relations. For example, the 2OH^* mechanism ($\text{O}_2 \rightarrow \text{OOH}^* \rightarrow 2\text{OH}^* \rightarrow \text{OH}^* \rightarrow \text{H}_2\text{O}$) is composed of four steps:

The standard equilibrium potentials for these reactions are, respectively:

$$eE_1 = \Delta G(\text{O}_2) - \Delta G(\text{OOH}^*) = 4.92 \text{ eV} - [\Delta G(\text{OH}^*) + 3.2 \text{ eV}] = 1.72 \text{ eV} - \Delta G(\text{OH}^*)$$

$$eE_2 = \Delta G(\text{OOH}^*) - \Delta G(2\text{OH}^*) = [\Delta G(\text{OH}^*) + 3.2 \text{ eV}] - [2\Delta G(\text{OH}^*) + 1.5 \text{ eV}] = 1.7 \text{ eV} - \Delta G(\text{OH}^*)$$

$$eE_3 = \Delta G(2\text{OH}^*) - \Delta G(\text{OH}^*) - \Delta G(\text{H}_2\text{O}) = [2\Delta G(\text{OH}^*) + 1.5 \text{ eV}] - \Delta G(\text{OH}^*) - 0 \text{ eV} = 1.5 \text{ eV} + \Delta G(\text{OH}^*)$$

$$eE_4 = \Delta G(\text{OH}^*) - \Delta G(\text{H}_2\text{O}) = \Delta G(\text{OH}^*) - 0 \text{ eV} = \Delta G(\text{OH}^*)$$

All E_1 , E_2 , E_3 , and E_4 are linear functions of $\Delta G(\text{OH}^*)$, and the volcano plot is constructed from these linear functions. As for the O^* mechanism, the procedures for the construction of volcano plot are similar and more details can be found in the previous reports.^{7, 45}

5.3 Results and Discussion

Figure 5.1a shows the half-wave potentials ($E_{1/2}$) for ORR of Fe/N/C and Co/N/C obtained from various experiments (cyan) and simulations (orange and red). The data are retrieved from previous reports and this work as shown in Table 5.1.^{19-26, 29-31} Each data point includes the half-wave potentials of both Co/N/C and Fe/N/C tested or calculated under the same conditions. Note that only the O^* ORR mechanism was adopted in those previous simulations.^{8, 29-31} Obviously, there is a remarkable discrepancy between the experimental (blue) and previous theoretical (orange) results as shown in Figure 5.1a. Fe/N/C has larger $E_{1/2}$ for ORR than Co/N/C in experiments, while it is opposite in previous simulations. The simulations with O^* mechanism significantly underestimate the $E_{1/2}$ for ORR of Fe/N/C (~ 0.6 V), which are larger than 0.7 V in experiments, and lead to even lower ORR activity than Co/N/C. However, the $E_{1/2}$ for Co/N/C are consistent between simulations and experiments, both of which are around 0.7 - 0.9 V. Therefore, the O^* ORR mechanism may be applicable for Co/N/C but unreasonable for Fe/N/C.

Figure 5.1 (a) Comparison between half-wave potentials ($E_{1/2}$) for ORR of Co/N/C and Fe/N/C obtained from various experiments (cyan) and simulations with the O* mechanisms (orange). The ‘red star’ symbol represents the $E_{1/2}$ of 2OH* mechanism for Fe/N/C and the $E_{1/2}$ of O* mechanism for Co/N/C. (b) Calculated free energy profiles of conventional O* mechanism for ORR on Co/N/C and Fe/N/C porphyrins.

Table 5.1 Half-wave potentials ($E_{1/2}$) for ORR of Co/N/C and Fe/N/C obtained from various simulations and experiments.^{19-26, 29-31}

$E_{1/2}$ (V vs RHE)	Co/N/C	Fe/N/C	References
Simulations	0.80	0.65	Phys Chem Chem Phys, 13, 15639, 2011
	0.846	0.585	Chem Sci, 8, 124, 2017
	0.87	0.66	J Am Chem Soc, 136, 1320, 2014
	0.736	0.590	This work (O* mechanism)
	0.736	0.771	This work (O* and 2OH* mechanisms)
Experiments	0.770	0.825	Nat Catal, 1, 935, 2018
	0.751	0.806	Science, 332, 443, 2011
	0.811	0.881	J Phys Chem C, 113, 20689, 2009
	0.692	0.715	ChemSusChem, 10, 3019, 2017
	0.849	0.866	ChemSusChem, 10, 3019, 2017
	0.768	0.899	Chem Commun, 54, 4274, 2018
	0.825	0.871	Carbon, 78, 49, 2014
	0.740	0.778	Carbon, 78, 49, 2014
	0.800	0.844	Sci Rep, 4, 4386, 2014
	0.72	0.76	ACS Catal, 4, 3797, 2014

To identify the potential problems in the O* ORR mechanism, simulated free energy profiles for Fe/N/C and Co/N/C porphyrins are shown in Figure 5.1b. ORR is a four-

electron transfer reaction and the $E_{1/2}$ is limited by the step with the smallest free-energy drop, which is also the rate-determining step of ORR.⁸ A smaller free-energy drop in the rate-determining step indicates a lower $E_{1/2}$ for ORR. The rate-determining steps are highlighted by dashed boxes in Figure 5.1b, and the corresponding values are 0.74 and 0.59 eV for Co/N/C and Fe/N/C, respectively. The rate-determining step of ORR on Co/N/C is identified to be $O_2 \rightarrow OOH^*$, which can be reasonable as its energy descent is in good agreement with the half-wave potentials for ORR obtained in various experiments as shown in Figure 5.1a. While for Fe/N/C, the free energy declines only 0.59 eV from O^* to OH^* and the $E_{1/2}$ for ORR should be around 0.59 V accordingly, which is abnormal and smaller than the one of Co/N/C and the experimental observations for Fe/N/C ($> \text{Co/N/C}$ and $> 0.7 \text{ V}$ as shown in Figure 5.1a). Therefore, the step $O^* \rightarrow OH^*$ might be circumvented during ORR on Fe/N/C.

Figure 5.2 The $2OH^*$ and O^* ORR mechanisms on (a) near-continuous and (b) single site catalysts. These two ORR mechanisms are thermodynamically equivalent on catalysts with near-continuous active sites, while they are different on single-atom catalysts.

Currently, the widely accepted associative ORR mechanism is $O_2 \rightarrow OOH^* \rightarrow O^* \rightarrow OH^* \rightarrow H_2O$ (O^* mechanism).⁸ In fact, there is another possible route: $O_2 \rightarrow OOH^* \rightarrow 2OH^* \rightarrow OH^* \rightarrow H_2O$ ($2OH^*$ mechanism), where the intermediate O^* in the O^* mechanism is replaced by $2OH^*$.^{34, 35} These two routes are thermodynamically equivalent for catalysts with near-continuous active sites as shown in Figure 5.2a, because two OH^* can bond to

different active sites and the free energy of 2OH^* approximately equals it of O^* according to the well-known scaling relation $\Delta G(\text{O}^*) = 2 \Delta G(\text{OH}^*)$.^{8, 34, 45} Generally, people only considered the O^* route, which is reasonable and equivalent to the 2OH^* route for traditional catalysts. In recent years, single-atom catalyst with isolated active sites has emerged as a new promising field in heterogeneous catalysis.^{46, 47} Reaction mechanism may change on the single-atom catalyst because of its unique atomically dispersed active sites. Fe/N/C and Co/N/C can be regarded as single-atom ORR catalysts because their active sites are separated single metal atoms.^{27, 28} Here we highlight that the ORR mechanism can be different on single-atom catalysts as the appearance of O^* can be bypassed through the formation of 2OH^* . For single-atom catalysis, the two OH^* are confined and connected to the same atom as shown in Figure 5.2b. For example, the adsorption of OH^* on the N atom of the Me/N/C site is highly unstable (Figure 5.3) and both two OH^* prefer to adsorb on the central metal atom. Consequently, these two OH^* have significant “ligand” effect to each other and the total free energy of them is generally larger than two single $\Delta G(\text{OH}^*)$ or one $\Delta G(\text{O}^*)$. In this case, the 2OH^* mechanism is no longer thermodynamically equivalent to the O^* mechanism and should not be overlooked.

Figure 5.3 The structural configurations of 2OH^* on Me/N/C porphyrins with one of the OH^* adsorbed on the N atom. These N-adsorbed 2OH^* are 1.754, 1.722, 1.181, 0.519 eV less stable than the ones that both of the two OH^* are adsorbed on the central metal atom for Cr/N/C, Mn/N/C, Fe/N/C and Co/N/C, respectively. Therefore, both two OH^* prefer to adsorb on the central metal atom of the Me/N/C active sites.

Both O^* and $2OH^*$ mechanisms of ORR have three surface intermediates, two of which (OOH^* and OH^*) are the same in different mechanisms as shown in Figure 5.2b and the atomic structural models of intermediates adsorbed on Fe/N/C porphyrin are presented in Figure 5.4a. As can be seen from the $2OH^*$ model in Figure 5.4a, the two OH^* are bonded to the same Fe atom, which is slightly lifted away from the substrate to afford two OH^* simultaneously. For ORR on Co/N/C porphyrin, the free energy of $2OH^*$ (4.107 eV) is very close to OOH^* (4.184 eV), which indicates the step $OOH^* \rightarrow 2OH^*$ in ORR requires potential close to the reversible hydrogen electrode (RHE) for the $2OH^*$ pathway. Therefore, the O^* mechanism (0.74 V vs. RHE) is preferable for ORR on Co/N/C. However, the ORR performance of Fe/N/C is limited by small free energy decrease of $O^* \rightarrow OH^*$ ($\Delta G = -0.59$ eV) in the O^* pathway, which contradicts the superior ORR activity of Fe/N/C in experiments (Figure 5.1a). The free energy profiles of O^* and $2OH^*$ mechanisms on Fe/N/C are shown in Figure 5.4b. Importantly, the unconventional $2OH^*$ pathway circumvents the step from O^* to OH^* and predicts an alternative rate-determining step $OOH^* \rightarrow 2OH^*$ ($\Delta G = -0.77$ eV), which is better than the O^* or $2OH^*$ mechanism on Co/N/C and in good agreement with experimental reports.

Figure 5.4 (a) Structural models of ORR intermediates. (b) Comparison between O^* and $2OH^*$ pathways of ORR on Fe/N/C porphyrin.

Table 5.2 ZPE and TS corrections for H_2O and H_2 .^{7, 29}

	<i>ZPE</i> (eV)	<i>TS</i> (eV)
H₂O	0.56	0.67
H₂	0.27	0.41

Table 5.3 E_{ads} in eV for the ORR intermediates on Me/N/C porphyrins in this study.

	OH*	O*	2OH*	OOH*
Cr/N/C	0.239	1.066	1.921	3.411
Mn/N/C	0.432	1.436	1.850	3.612
Fe/N/C	0.665	1.569	2.615	3.707
Co/N/C	1.164	2.647	3.626	3.972

Table 5.4 *ZPE* in eV for the Me/N/C porphyrins (with and without adsorbates) in this study.

	clean	OH*	O*	2OH*	OOH*
Cr/N/C	7.273	7.630	7.375	8.000	7.721
Mn/N/C	7.264	7.598	7.358	8.009	7.703
Fe/N/C	7.288	7.614	7.372	7.964	7.722
Co/N/C	7.298	7.632	7.303	7.953	7.744

Table 5.5 E_{solv} in eV for the Me/N/C porphyrins (with and without adsorbates) in this study.

	clean	OH*	O*	2OH*	OOH*
Cr/N/C	-0.186	-0.442	-0.335	-0.450	-0.494
Mn/N/C	-0.213	-0.493	-0.544	-0.470	-0.531
Fe/N/C	-0.198	-0.445	-0.447	-0.436	-0.444
Co/N/C	-0.212	-0.417	-0.392	-0.466	-0.455

Table 5.6 ΔG in eV for the ORR intermediates on Me/N/C porphyrins in this study.

	OH*	O*	2OH*	OOH*
Cr/N/C	0.380	0.989	2.464	3.561
Mn/N/C	0.526	1.168	2.418	3.742
Fe/N/C	0.784	1.374	3.133	3.904
Co/N/C	1.332	2.442	4.107	4.184

Table 5.7 Ground-state spin configurations (i.e. the difference between the number of spin-up and spin-down electrons) of different porphyrins with different adsorbates. Different spin states were tested and only the most stable ones were adopted.

	clean	OH*	O*	2OH*	OOH*
Cr/N/C	4	3	0	2	3
Mn/N/C	3	4	3	3	4
Fe/N/C	2	3	2	4	1
Co/N/C	1	2	3	3	0

Figure 5.5 (a) Scaling relations between the free energies of OH*, O*, 2OH*, and OOH* on

Me/N/C (Me = Cr, Mn, Fe, Co) single porphyrin sites. (b) Volcano plot of the equilibrium ORR potentials of O^* and $2OH^*$ mechanisms as a function of the free energy of OH^* .

Figure 5.6 The models of different porphyrins (Me/N/C, Me = Cr, Mn, Fe, Co) with and without ORR intermediates, including OH^* , O^* , $2OH^*$, OOH^* .

The free energies of OOH^* , O^* , $2OH^*$, and OH^* on various Me/N/C (Me = Cr, Mn, Fe, Co) single porphyrin sites are calculated and plotted in Figure 5.5a (the DFT adsorption energies, zero-point energies, entropy and solvation corrections needed to calculate free energies are available in Tables 5.2-5.7, and the structure configurations are shown in Figure 5.6). The scaling relations between $\Delta G(OH^*)$, $\Delta G(O^*)$, and $\Delta G(OOH^*)$ are still

applicable in this Me/N/C system, which are in good agreement with previous reports.²⁹⁻³¹ Importantly, here a new scaling relation is identified for 2OH* adsorbed on a single active site: $\Delta G(2OH^*) = 2\Delta G(OH^*) + 1.5 \text{ eV} = \Delta G(O^*) + 1.5 \text{ eV}$. The $\Delta G(OH^*)$ represents the free energy of a single OH* adsorbed on the active site, and the $\Delta G(2OH^*)$ represents the free energy of two OH* adsorbed on a single active site. In other words, the OH* in $\Delta G(OH^*)$ can be regarded as the first OH* in $\Delta G(2OH^*)$. Note that it is $\Delta G(2OH^*) = 2\Delta G(OH^*) = \Delta G(O^*)$ on traditional catalysts with near-continuous active sites, as two OH* can bond to different active sites and have relatively little effect on the free energy of each other.^{34, 45} This 2OH* mechanism with new scaling relations has similar volcano plot and intrinsic ORR overpotential with the previous O* mechanism (Figure 5.5b). However, the adsorption free energies of ORR intermediates do not strictly follow the scaling relations and have considerable deviations in some cases such as O* on Fe/N/C and OOH* on Co/N/C (Figure 5.5a).^{8, 48} The unconventional 2OH* mechanism may still affect the ORR performance compared to the O* mechanism. For example, the free energy of O* on Fe/N/C is negatively deviated from the its scaling relation (Figure 5.5a), which impairs the $E_{1/2}$ as shown in Figures 5.4b and 5.5b. While the free energy of 2OH* follows the scaling relation well (Figure 5.5a). By replacing O* with 2OH*, the simulated $E_{1/2}$ of Fe/N/C agrees well with experiments results.

Figure 5.7 (a) Atomistic structures of different Me/N/C sites (Me = Cr, Mn, Fe, Co), including Me-porphyrin, MeN₄-zzG, MeN₄-acG and MeN₄-G. (b) Scaling relations between the free energies

of OH*, O*, 2OH*, and OOH* on Me-porphyrin, MeN₄-zzG, MeN₄-acG, and MeN₄-G. The dash lines represent $\Delta G(\text{OOH}^*) = \Delta G(\text{OH}^*) + 3.2 \text{ eV}$, $\Delta G(2\text{OH}^*) = 2\Delta G(\text{OH}^*) + 1.5 \text{ eV}$, $\Delta G(\text{O}^*) = 2\Delta G(\text{OH}^*)$, and $\Delta G(\text{OH}^*) = \Delta G(\text{OH}^*)$, respectively.

Table 5.8 ΔG in eV for the ORR intermediates on MeN₄-G, MeN₄-acG, and MeN₄-zzG.

	OH*	O*	2OH*	OOH*
CrN₄-G	-0.033	0.169	1.248	3.184
MnN₄-G	0.457	1.070	1.738	3.693
FeN₄-G	0.659	1.171	2.399	3.626
CoN₄-G	1.027	2.344	3.580	4.025
CrN₄-acG	0.067	0.159	1.540	3.260
MnN₄-acG	0.615	1.138	2.139	3.794
FeN₄-acG	0.750	1.231	2.777	3.703
CoN₄-acG	1.060	2.322	3.615	4.055
CrN₄-zzG	0.388	0.991	2.626	3.600
MnN₄-zzG	0.735	1.449	2.792	3.982
FeN₄-zzG	0.876	1.530	3.076	3.928
CoN₄-zzG	1.333	2.329	3.766	4.307

Only the porphyrin-like Me/N/C structures (Figure 5.4a) were studied so far, while the local carbon structure surrounding MeN₄ sites can be complicated in real catalysts and different models have been proposed in previous experiments and simulations.^{36, 49-51} We further studied three more models (MeN₄-zzG: MeN₄ between graphene zigzag edges, MeN₄-acG: MeN₄ between graphene armchair edges, and MeN₄-G: MeN₄ embedded in graphene) as shown in Figure 5.7a. The free energies of OH*, O*, 2OH*, and OOH* on these models are shown in Table 5.8 and Figure 5.7b. Although there are some fluctuations as shown in Figure 5.7b, the free energies of OH*, O*, 2OH*, and OOH* on all the studied models still follow the scaling relations which we previously obtained from metal-

porphyrin (Figure 5.5a). Moreover, the rate-determining step for ORR through the O^* mechanism on all FeN_4 structures is $O^* \rightarrow OH^*$ as shown in Table 5.8, and the corresponding free-energy drops ($\Delta G(O^*) - \Delta G(OH^*)$) are $(1.171 - 0.659 =) 0.512$ eV for FeN_4 -G, $(1.231 - 0.750 =) 0.481$ eV for FeN_4 -acG, and $(1.530 - 0.876 =) 0.654$ eV for FeN_4 -zzG, respectively. These relatively small free-energy drops require low ORR potentials and large overpotentials, which is inconsistent with the good ORR performance of Fe/N/C catalysts in experiments. While for the $2OH^*$ ORR mechanism, this $O^* \rightarrow OH^*$ step is bypassed, and the theoretical ORR half-wave potentials agree better with experiments. As for Co/N/C structures, the $2OH^*$ ORR mechanism is always unfavorable because of small free-energy drop from OOH^* to $2OH^*$, which are $(4.025 - 3.580 =) 0.445$ eV for CoN_4 -G, $(4.055 - 3.615 =) 0.440$ eV for CoN_4 -acG, and $(4.307 - 3.766 =) 0.541$ eV for CoN_4 -zzG, respectively. Therefore, for all the MeN_4 models considered, Fe/N/C catalysts prefer the novel $2OH^*$ ORR mechanism and the corresponding results agree better with experiments. Co/N/C catalysts prefer the traditional O^* ORR mechanism. Importantly, the free energies of OH^* and $2OH^*$ on all these models still follow the new scaling relation $\Delta G(2OH^*) = 2\Delta G(OH^*) + 1.5$ eV.

Table 5.9 The dissociation barriers of O-O for different ORR mechanisms on Fe-porphyrin.

Reaction equations for O-O break	Activation barriers
a) O_2 dissociation: $O_2^* \rightarrow O^* + O^*$	1.163 eV
b) Direct OOH^* dissociation: $OOH^* \rightarrow O^* + OH^*$	0.934 eV
c) H-assisted OOH^* dissociation into O^* : $OOH^* + H^* \rightarrow O^* + H_2O$	0.001 eV
d) H-assisted OOH^* dissociation into $2OH^*$: $OOH^* + H^* \rightarrow 2OH^*$	0.056 eV

Figure 5.8 Atomic structures of the initial states, transition states, and final states for breaking the O-O bond in different ORR mechanisms on the Fe/N/C active site.

Aside from the O^* mechanism and $2OH^*$ mechanism, other ORR mechanisms such as direct OOH^* dissociation mechanism and O_2 dissociation mechanism have been widely studied in previous reports.⁵²⁻⁵⁵ The difference between these ORR mechanisms lies in how the O-O bond breaks, which may be

- a) O_2 dissociation mechanism: $O_2^* \rightarrow O^* + O^*$
- b) Direct OOH^* dissociation mechanism: $OOH^* \rightarrow O^* + OH^*$
- c) H-assisted OOH^* dissociation into O^* (O^* mechanism): $OOH^* + H^* \rightarrow O^* + H_2O$
- d) H-assisted OOH^* dissociation into $2OH^*$ ($2OH^*$ mechanism): $OOH^* + H^* \rightarrow 2OH^*$

The a), b), and c) have been widely studied for example by Goddard III et al. and Wang et al.,⁵²⁻⁵⁵ and d) is the new one proposed in this work. We calculated the activation barriers of all these four reactions using the climbing image nudged elastic band method.⁵⁶ The activation barriers are shown in Table 5.9, and the corresponding atomic structures of initial

states, transition states, and final states on the Fe/N/C active site are shown in Figure 5.8. As shown in Table 5.9, the O₂ dissociation and direct OOH* dissociation reactions have high activation barriers (~ 1 eV), and these barriers cannot be lowered by applied potentials as the equations ($O_2^* \rightarrow O^* + O^*$; $OOH^* \rightarrow O^* + OH^*$) do not involve external electrons. Therefore, the O₂ dissociation or direct OOH* dissociation is kinetically sluggish. While the H-assisted OOH* dissociation is much easier with smaller activation barriers (0.001 eV for O* mechanism “ $OOH^* + H^* \rightarrow O^* + H_2O$ ”, and 0.056 eV for 2OH* mechanism “ $OOH^* + H^* \rightarrow 2OH^*$ ”, respectively), which can be overcome under room temperature. Therefore, the break of O-O bond in both the O* mechanism and 2OH* mechanism is kinetically viable.

The Nernst potential for H₂O₂ production is 0.7 V vs. RHE,⁵⁷ and the free energy of H₂O₂ is 3.52 eV, which is much higher than the $\Delta G(2OH^*)$ on Fe/N/C (3.133 eV), Mn/N/C (2.418 eV), and Cr/N/C (2.464 eV) that may follow the 2OH* mechanism as shown in Table 5.6. In addition, it has been reported that the O-O bond in H₂O₂ was broken in the lowest-energy adsorption configuration on the Fe/N/C and Co/N/C,^{35, 36} which is also in agreement with the experimental findings of 4e⁻ ORR on Me/N/C catalysts.⁴ Therefore, the 2OH* mechanism is expected to prevail over the formation of H₂O₂ on Fe/N/C, Mn/N/C, and Cr/N/C. Importantly, oxygen evolution reaction (OER) is the reverse reaction of ORR. The 2OH* mechanism is also applicable to OER on single-atom catalysts, and the corresponding 2OH* pathway is $H_2O \rightarrow OH^* \rightarrow 2OH^* \rightarrow OOH^* \rightarrow O_2$, and it is $H_2O \rightarrow OH^* \rightarrow O^* \rightarrow OOH^* \rightarrow O_2$ for the traditional O* OER mechanism. Future studies of OER on single-atom catalysts should take the 2OH* mechanism into consideration. As for nitrogen reduction reaction (NRR), Nørskov et al. reported scaling relations between NRR intermediates and constructed the NRR volcano plot on traditional metal surfaces.⁵⁸ We expect that new scaling relations, new reaction mechanism, and new volcano plot could be found for NRR on single-atom catalysts because of the dispersed single active sites for the adsorption of intermediates.

5.4 Conclusions

In summary, the unconventional 2OH* mechanism for ORR is found to be important on single-atom catalysts such as Fe/N/C, where two OH* are bonded to the same active site. A new free-energy scaling relation is identified: $\Delta G(2OH^*) = 2\Delta G(OH^*) + 1.5 \text{ eV}$ in contrast to $\Delta G(O^*) = 2\Delta G(OH^*)$ in the traditional O* ORR mechanism. These two ORR mechanisms are competition and different single-atom catalysts may prefer different mechanisms. The 2OH* mechanism can remarkably affect the ORR activity when the rate-determining step in O* mechanism involves the formation or consumption of O* by avoiding the appearance of O*. The conventional O* mechanism significantly underestimates the half-wave potential for ORR of Fe/N/C due to abnormally small free-energy decrease from O* to OH*, and the 2OH* mechanism circumvents this rate-determining step and predicts higher and reasonable half-wave potential for ORR that is in good agreement with experimental results of Fe/N/C. While Co/N/C still prefers the conventional O* mechanism to 2OH* mechanism for ORR because of no O* involved in the rate-determining step of O* mechanism and too high $\Delta G(2OH^*)$ in the 2OH* mechanism. This work suggests that both O* and 2OH* mechanisms should be taken into consideration in future theoretical simulations and experimental designs of single-atom catalysts for ORR. Our understanding about the structure effect of single-atom catalysts on reaction mechanism not only provides new insights in ORR, but also can be informative for similar reactions such as oxygen evolution and nitrogen reduction on single-atom catalysts.

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Chapter 6

Summary and Outlook

1) Crystal phases have significant effects on surface reactivity even for close-packed surfaces due to their distinct intrinsic strains. 2) The unconventional 2OH^ mechanism for ORR is found to be important on single-atom catalysts such as Fe/N/C, where two OH^* are confined to the same active site and the rate-determining step in the O^* mechanism involves the formation or consumption of O^* . 3) There are various molecules, reactions, and materials for future work.*

6.1 Summary

This thesis provides fundamental understandings about the recently developed crystal phase engineering, single-atom catalysts, and their unique performances in heterogeneous catalysis. Oxygen activation and reduction on phase-controlled gold and Me/N/C (Me = Fe, Co, etc.) single-atom catalysts have been studied. The two hypotheses proposed in Chapter 1 are well addressed.

Hypothesis 1: *When the crystal phase of gold changes from FCC to HCP or 4H in nanostructures, the catalytic performance of gold should be different, such as the O_2 activation and dissociation on gold surfaces, which is important in selective oxidation reactions.*

Figure 6.1 Crystal phase effect on catalysis through intrinsic strain.

All of FCC, HCP, and 4H are close-packed structures, which consist of a series of close-packed atom layers. The stacking sequences and periods are ‘ABC’, ‘AB’, and ‘ABCB’ for FCC, HCP, and 4H, respectively. For close-packed surfaces, i.e., FCC(111), HCP(001), and 4H(001), the top two atom layers are the same in stacking sequence for all these phases. To fully characterize the structural difference between different close-packed phases, two additional parameters (interplanar spacing and in-plane bond length) are introduced. For bulk gold, interplanar spacing and in-plane bond length negatively correlated with each other due to the Poisson effect. For gold surfaces, the in-plane bond length is important as

it directly relates to the surface strain, and surface strain closely relates to surface reactivity.^{1, 2} Using first-principles calculations, the equilibrium structures of HCP, FCC and 4H bulk gold were obtained. The in-plane Au–Au length of FCC gold (2.938 Å) is about 1% larger than HCP (2.909 Å) and 4H gold (2.915 Å). These results reveal the intrinsic difference in structural parameters between HCP, FCC, and 4H phases aside from the well-known stacking sequence.

Currently, non-FCC phases of gold can only be stabilized in nanostructures with a high specific surface area.^{3, 4} Free-standing gold nanosheets composed of a few atom layers were further studied. Surprisingly, the in-plane Au–Au length is almost the same for HCP, FCC, and 4H, and it is about 2.87 Å for 6-atom layer sheets, which is much smaller than the values (2.91–2.94 Å) of bulk gold. Strain is an important factor and easy to be induced in metal nanosheets and interfaces. In order to unify and compare the strains among different crystal phases, the zero point of intrinsic strain is set at this common equilibrium in-plane Au–Au length (2.87 Å) of free-standing 6-layer nanosheets. The deviations of the in-plane Au–Au length of 6-layer nanosheets from bulk gold are ~2.3% for bulk FCC and ~1.3% for bulk HCP and 4H, which indicates that the near-surface atom layers of FCC(111) experience larger intrinsic strain than HCP(001) and 4H(001).

This thesis further studied the effect of intrinsic strain (in-plane Au–Au length) from crystal phases on the adsorption of the oxygen atom and the dissociation of O₂, which is very important in heterogeneous catalysis. The adsorption of oxygen on gold FCC(111) is 0.36 eV stronger than that on free-standing 6-layer nanosheets because of 2.3% intrinsic strain, and it is about 0.20 eV stronger for HCP(001) and 4H(001). Stronger oxygen adsorption means stronger Au–O interaction and implies the lower dissociation barrier of O₂ on gold, and the dissociation barrier of O₂ is proportional to the reaction energy (Brønsted–Evans–Polanyi principle). In addition, the layer number (i.e. thickness) effect on the structural parameters of gold nanosheets with different crystal phases has been studied. The in-plane Au–Au length increases with the number of atom layers for all of HCP, FCC, and 4H gold nanosheets, which indicates that the surface strain could be controlled by the size of gold nanostructures.

In summary, this work demonstrated that crystal phases have significant effects on surface reactivity even for close-packed surfaces due to their distinct intrinsic strains (Figure 6.1).

Hypothesis 2: The ORR mechanism on single-atom catalysts may be different from the one ($O_2 \rightarrow OOH^* \rightarrow O^* \rightarrow OH^* \rightarrow H_2O$) on traditional catalysts with near-continuous active sites, because of the site confinement effect on the adsorption of reaction intermediates.

Figure 6.2 Different oxygen reduction reaction mechanisms on single-atom catalysts.

Nonprecious-metal catalysts with metal–nitrogen coordination sites, such as Fe/N/C and Co/N/C composites, have attracted broad research interest in recent years, because of their relatively high ORR activity and low cost.⁵ Fe/N/C was found to have significantly better ORR activity than Co/N/C in various experiments. The electrochemical oxygen reduction reaction (ORR) mechanism was generally considered to be $O_2 \rightarrow OOH^* \rightarrow O^* \rightarrow OH^* \rightarrow H_2O$ (noted as O^* mechanism here). Previous DFT studies adopted this O^* mechanism and predicted reasonable half-wave potentials ($E_{1/2}$) for ORR of Co/N/C, while abnormally underestimated the $E_{1/2}$ value for ORR of Fe/N/C, which was predicted to be even inferior to that of Co/N/C.^{6, 7}

The ORR mechanism can be different on single-atom catalysts as the appearance of O^* can be bypassed through the formation of $2OH^*$ ($O_2 \rightarrow OOH^* \rightarrow 2OH^* \rightarrow OH^* \rightarrow H_2O$, noted as $2OH^*$ mechanism here). For traditional catalysts with near-continuous active sites, two OH^* can bond to different active sites and the free energy of $2OH^*$ is approximately equal to that of O^* , according to the well-known scaling relation $\Delta G(O^*) = 2\Delta G(OH^*)$.⁸

Generally, people only considered the O^* route, which is reasonable and thermodynamically equivalent to the $2OH^*$ route for traditional catalysts. However, for single-atom catalysis, the two OH^* are confined and connected to the same atom. These two OH^* have a significant “ligand” effect to each other and the total free energy of them is generally larger than two single $\Delta G(OH^*)$ or one $\Delta G(O^*)$. In this case, the $2OH^*$ mechanism is no longer thermodynamically equivalent to the O^* mechanism and should not be overlooked. A new scaling relation is identified for $2OH^*$ adsorbed on a single active site:

$$\Delta G(2OH^*) = 2\Delta G(OH^*) + 1.5 \text{ eV} = \Delta G(O^*) + 1.5 \text{ eV},$$

in contrast to $2\Delta G(OH^*) = \Delta G(O^*)$ in the traditional O^* ORR mechanism. The $2OH^*$ mechanism can remarkably affect the ORR activity when the rate-determining step in the O^* mechanism involves the formation or consumption of O^* by avoiding the appearance of O^* . The conventional O^* mechanism significantly underestimates the half-wave potential for ORR of Fe/N/C, because of the abnormally small free-energy decrease from O^* to OH^* , and the $2OH^*$ mechanism circumvents this rate-determining step and predicts a higher and reasonable half-wave potential for ORR that is in good agreement with experimental results. Meanwhile, Co/N/C still prefers the conventional O^* mechanism to the $2OH^*$ mechanism for ORR (Figure 6.2), because of no O^* being involved in the rate-determining step of the O^* mechanism and too high $\Delta G(2OH^*)$ in the $2OH^*$ mechanism.

In summary, the unconventional $2OH^*$ mechanism for ORR is found to be important on single-atom catalysts such as Fe/N/C, where two OH^* are confined to the same active site and the rate-determining step in the O^* mechanism involves the formation or consumption of O^* .

6.2 Outlook

This thesis mainly focuses on the O_2 activation and reduction on gold and Me/N/C (Me = Fe, Co, etc.) single-atom catalysts. Crystal phase effect on intrinsic strain and unconventional $2OH^*$ ORR mechanism have been highlighted. Based on the results of this thesis, there are lots of opportunities for future work:

1. For crystal phase effect on catalysis: the crystal phases of other metals (such Co, Ag, Ru, Rh, etc.),⁹⁻¹² the activation and dissociation of other molecules (such as H₂, CO, etc.), the intrinsic strain of non-close-packed surfaces.
2. For confinement effect in single-atom catalysis: other single-atom catalysts (such as single atoms or ions supported on metal oxides),^{13, 14} other reactions (such as oxygen evolution, nitrogen reduction, and CO₂ reduction),^{15, 16} kinetic analysis, solvation effect.

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