

**FIRST-PRINCIPLES SIMULATIONS OF ELECTROCATALYTIC
ENVIRONMENTS**

by

Stephen Arlow Giles

A dissertation submitted to the Faculty of the University of Delaware in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemical Engineering

Summer 2018

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ACKNOWLEDGMENTS

First and foremost, I would like to express my gratitude to my thesis advisors, Professors Dion Vlachos and Yushan Yan. Their patience, wit, and personal guidance have helped me achieve more than I ever thought I could. Their understanding and encouragement throughout the past four and a half years has been unrelenting. It is thanks to them that if given the chance to do everything all over again, I would join their group in a heartbeat.

Though not an official “advisor”, Dr. Glen Jenness deserves special acknowledgment for his scientific guidance and friendship. Glen was a postdoc in Dion’s group, and we shared an office together for the first three years I was at Delaware. As someone with zero prior experience in molecular simulations, I was faced with a steep learning curve to begin my Ph.D. research. He essentially functioned as my intellectual lifeline throughout the first couple of years of my research. I cannot repay him, but only say “thank you”.

I would like to extend my gratitude to my thesis committee: Prof. Antony Beris, Dr. Stavros Caratzoulas, and Prof. Feng Jiao. Their willingness to meet to discuss and further hone my work is a tribute to their selflessness and intellect.

I would also like to extend my gratitude to all Vlachos and Yan group members, past and present, who I have worked with during my time here. These include experimental collaborators, namely Zhongbin Zhuang, Weiqing Zheng, Jie Zheng, Yan Wang, Jared Nash, and Mingchuan Luo, who greatly helped to enrich the quality of my work. I would also like to thank Andrew Tibbits, Ed Schreiner, and

Pierre Desir who, although they did not contribute directly to my work, offered an unparalleled sense of friendship that my work undoubtedly benefited from. Long live Trivia Night at Rooney's, and Rest in Peace Kildare's. I hope we will be friends for life.

This section would be wholly incomplete without me thanking my parents. I would almost certainly not be obtaining a Ph.D. in Chemical Engineering from the University of Delaware if it were not for my parents making the sacrifice of homeschooling me some twenty years ago. It would have been far easier for them to ship me to public school, and it would have spared Mom from having to deal with my sometimes frequent outbursts. They have continued to make sacrifices and help me in every way they can throughout my undergraduate and graduate career. Those sacrifices are far too many to list here.

And finally, to my longtime lover Kate Stanford, here's to living a bit closer to each other for a change. "Beside you in time". I love you.

"Solve the problem on paper before approaching the machine." – Bob Ashurst

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ABSTRACT

Within the overarching goal of increasing energy sustainability and decreasing emissions, the hydrogen fuel cell holds a key place. The proton exchange membrane fuel cell (PEMFC) has been commercialized in the Toyota Mirai. The PEMFC, however, uses a Pt catalyst and is economically unaffordable by many consumers.

Hydroxide exchange membrane fuel cells (HEMFC) enable the use of a broad variety of non-precious metal catalysts. However, a drawback to commercialization of HEMFC technology is the decreased rate of hydrogen oxidation reaction (HOR) in base. Herein, computational studies are performed to predict active catalysts for basic environments, as well as to elucidate the cause of the decreased rate of HOR.

Molecular simulations are performed for a variety of nanoparticles supported on graphene and graphene doped with nitrogen or boron. The presence of either nitrogen or boron leads to a greater nanoparticle-support interaction, and influences nanoparticle properties. The development of a predictive adsorption model, size effects, and the impact on HOR activity are discussed.

To explain the dependence of the HOR kinetics on pH, a new thermodynamic descriptor for HOR, the apparent Gibbs free energy of hydrogen adsorption, is introduced. This descriptor, which accounts for pH-dependent water adsorption, is computed and shown to be consistent with measured HOR kinetics.

Future directions include direct computation of HOR free energy barriers, as well as the dynamic simulation of the electrode interface. Experimentally, controlling nanoparticle size and tuning water adsorption should be points of emphasis.

Chapter 1

INTRODUCTION

1.1 Motivation

1.1.1 Fuel cells in the renewable energy landscape

Recently, the atmospheric level of carbon dioxide (CO_2) has risen above 400 parts per million for the first time in human history and is continuing to rise^{1,2}. The sudden rise of atmospheric CO_2 in the past 100+ years is directly related to the rapid growth of industrial processes which produce CO_2 as a byproduct³. These CO_2 -producing processes include everyday commodities such as automobiles, of which there were estimated to be nearly 1.3 billion on earth as of 2015⁴. New, sustainable technologies must be engineered to mitigate environmental harm.

One such emergent technology is the hydrogen fuel cell. A hydrogen fuel cell produces electricity via the oxidation of hydrogen at the anode and the reduction of oxygen at the cathode. In contrast to combustion of carbon-containing fuels, the only byproduct of the hydrogen fuel cell is water. The hydrogen fuel cell technology has recently been commercialized in the Toyota Mirai. Although currently ~95% of the world's hydrogen is produced from fossil fuels such as natural gas and oil^{5,6}, advances in solar electrolyzer technology, which split water into hydrogen and oxygen, could make the hydrogen fuel cell a truly renewable process.

1.1.2 Comparison of proton and hydroxide exchange membrane fuel cells

The most mature hydrogen fuel cell technology is the proton exchange membrane fuel cell (PEMFC), which uses a platinum catalyst in an acidic electrolyte to oxidize hydrogen at the anode while reducing oxygen at the cathode. Kinetic losses in the PEMFC originate almost entirely from the cathode due to the sluggishness of the oxygen reduction reaction (ORR)^{7,8}. As a result, most studies on PEMFC kinetics

have focused on improving the rate of ORR while placing little importance on HOR. However, a fundamental limitation to PEMFC technology is that very few non-precious metal catalysts are both stable and active under acidic conditions⁹. Platinum is universally accepted to be the best single metal catalyst in acid (both for HOR and ORR), with the catalyst layers ultimately contributing 21% of the final cost of an assembled PEMFC¹⁰.

Clearly, being able to circumvent the use of platinum in a fuel cell would be advantageous. The hydroxide exchange membrane fuel cell (HEMFC) offers an opportunity to achieve this goal. A schematic comparing the PEMFC to the HEMFC is shown in Figure 1.1. The PEMFC and HEMFC share much in common: both oxidize hydrogen at the anode and reduce oxygen at the cathode, producing water in the process. Both produce electricity which can be used to power an external load, *e.g.*, an electric vehicle. However, the PEMFC produces protons at the anode which are transported through a proton exchange membrane (PEM) to the cathode. The HEMFC produces hydroxide ions at the cathode which are then transported through a hydroxide exchange membrane (HEM) to the anode.

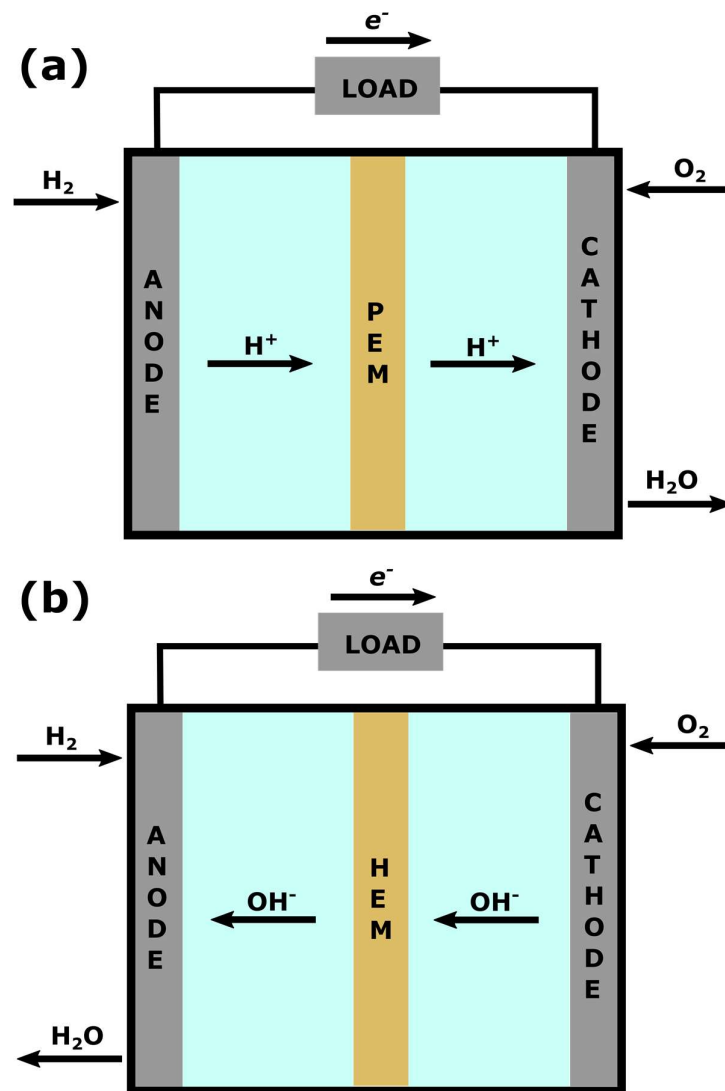


Figure 1.1. (a) Schematic of a PEMFC. (b) Schematic of a HEMFC.

A primary advantage to operating under basic conditions with the HEMFC is that a much broader variety of metal catalysts are thermodynamically stable than under acidic conditions with the PEMFC^{11–14}. Figure 1.2 shows the electrode potential on a reversible hydrogen electrode (RHE) scale at which the initial oxidized species forms at pH 0 and pH 14 for Ni and Co.

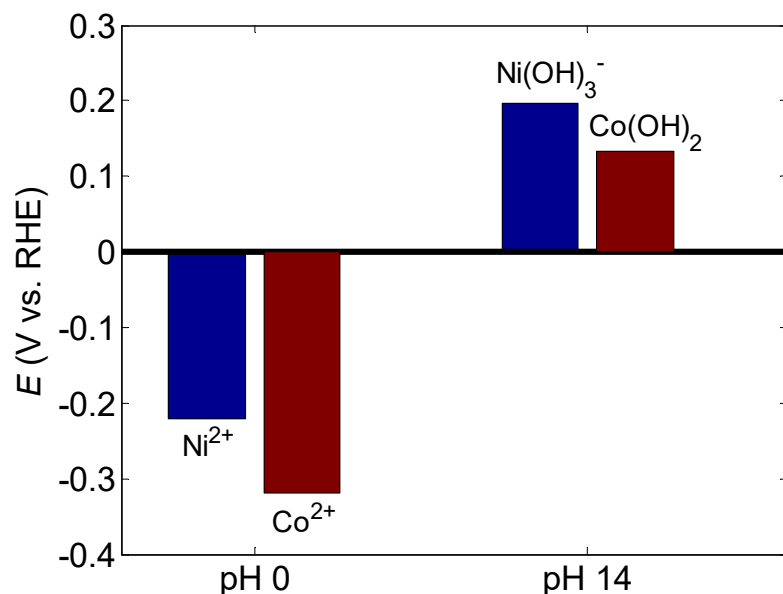


Figure 1.2. RHE potentials at which the first oxidized species (indicated with label) of Ni and Co appears for pH 0 and pH 14. The bold black line represents the equilibrium potential for HOR/HER. Data taken from references^{15,16}.

For both Ni and Co, oxidation of the metal occurs at a more positive potential at pH 14 than at pH 0. Because of the greater oxidative potential required, dissolution of the catalyst is generally less problematic in base than in acid. Therefore, the HEMFC is the clear choice for greatly expanding the design space of fuel cell catalysts.

Despite the HEMFC's clear superiority of catalyst stability, it suffers from a key drawback that has hindered the commercialization of HEMFC technology in comparison to PEMFC technology. The rate of HOR, which proceeds with minimal overpotential in acid, decreases by around two orders of magnitude in base¹⁷⁻¹⁹. While ORR remains the largest source of overpotential losses in the HEMFC¹⁰, the rate of ORR is approximately the same in acid and base^{20,21}. Therefore, to make the HEMFC competitive with PEMFCs on a performance basis, tuning of HOR catalyst properties and identification of the origin of HOR's pH dependence are a necessary and impactful goal.

1.2 Fundamentals of Modeling Electrochemical Hydrogen Oxidation

1.2.1 Transition state theory approach of reaction kinetics

In predicting rate constants and reaction rates in general, one important approach that has been developed is transition state theory. Transition state theory is an extension of the Arrhenius equation^{22,23}, an empirical relationship which relates the frequency factor and activation energy to the rate constant,

$$k = Ae^{-\frac{E_a}{RT}} \quad (1.2)$$

where A is the Arrhenius frequency factor and E_a is the activation energy. However, both A and E_a can vary widely depending on the reaction of interest. Transition state theory typically recasts the energetic quantity E_a in terms of a Gibbs free energy, and statistical mechanics are used to predict the values of the frequency factor. The most common form of the rate constant expression in transition state theory is²⁴,

$$k = \kappa \frac{k_B T}{h} e^{-\frac{\Delta G^\ddagger}{RT}} \quad (1.3)$$

where κ is the transmission coefficient (often taken to be unity), k_B is Boltzmann's constant, h is Planck's constant, and $\Delta G^\ddagger$ is the Gibbs free energy of activation.

1.2.2 Butler-Volmer model of electrode kinetics

Transition state theory has been adapted for electrochemical reactions to incorporate the effect of the electrode potential on reaction barriers. The most common adaption is the Butler-Volmer model of electrode kinetics^{25,26}. In the realm of chemical reactions, one can influence the thermodynamics and kinetics of a reaction through the manipulation of state variables, such as temperature, pressure, and chemical composition (e.g., concentration). In an *electrochemical* reaction, a new independent variable is introduced which has a direct influence on the thermodynamics and kinetics of the electrochemical reaction. This variable is the *electrode potential*. By definition, an electrochemical reaction involves the explicit transfer of electrons to (from) a species during a reduction (oxidation) process. The electrode potential is directly related to the chemical potential of the electron: a

negative potential will tend to increase the rate of reduction processes, whereas a positive potential will tend to increase the rate of oxidation processes.

The simplest formulation of the Butler-Volmer model begins by considering a one-step, one-electron process:



where O, e , and R are the oxidant species, an electron, and the reductant species, respectively. Figure 1.3 provides an example of the free energy surface of the elementary electron process indicated by Equation 1.3. As aforementioned, a change in the electrode potential portends a change in the chemical potential of the electron. As a result, the free energy profile of a state involving an electron (the reactant in the case of Figure 1.3) will shift proportionately with a change of the electrode potential. In the case of the reduction process shown in Figure 1.3, the reaction step is made more endergonic when the electrode potential is shifted positively.

In addition to impacting the relative energies of the initial and final state, a change in electrode potential leads to a change of the activation free energy of the forward and backward reactions. If the free energy profiles of the initial and final states are approximately linear near the transition state, the potential-induced change in the reaction barriers can be shown to be linearly dependent on α , the charge transfer coefficient, as shown in the lower panel of Figure 1.3. Thus, the *potential-dependent* anodic and cathodic activation free energies can be expressed as,

$$\Delta G_a^\ddagger = \Delta G_{0a}^\ddagger - (1 - \alpha)F(E - E^{0'}) \quad (1.4)$$

$$\Delta G_c^\ddagger = \Delta G_{0c}^\ddagger + \alpha F(E - E^{0'}) \quad (1.5)$$

where $\Delta G_{0a}^\ddagger$ and $\Delta G_{0c}^\ddagger$ are the anodic and cathodic activation free energies at the reference potential, respectively, F is Faraday's constant, E is the electrode potential, and $E^{0'}$ is the reference potential.

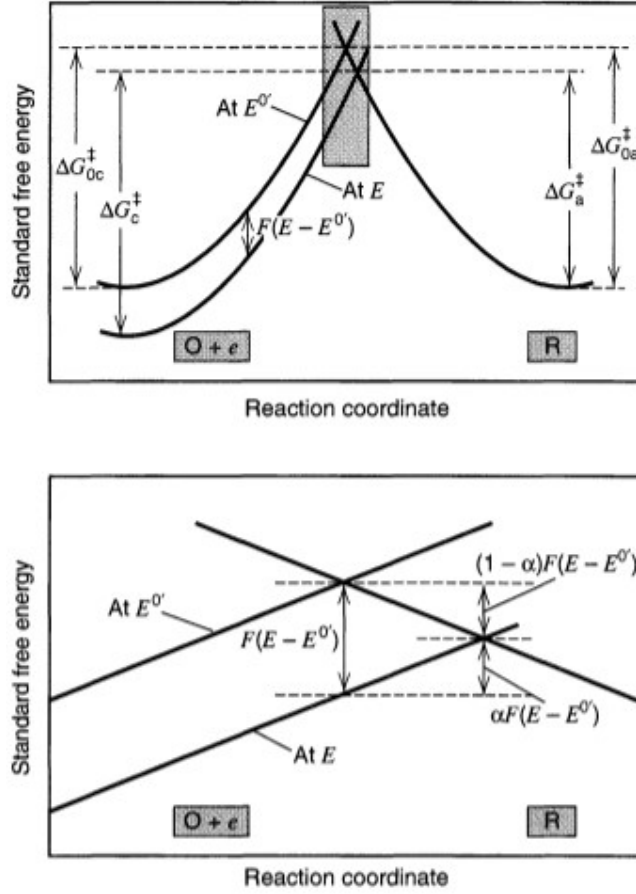


Figure 1.3. Effects of a potential change on the standard free energies of activation for oxidation and reduction. The lower frame is a magnified picture of the boxed area in the upper frame²⁷.

Equations 1.4 and 1.5 are incorporated into rate constant expressions to yield the forward and backward rate constants, respectively,

$$k_f = k^0 \exp \left[\frac{-\alpha F(E - E^0)}{RT} \right] \quad (1.6)$$

$$k_b = k^0 \exp \left[\frac{(1 - \alpha) F(E - E^0)}{RT} \right] \quad (1.7)$$

where k^0 is the standard rate constant. Employing the potential-dependent rate constant into a rate expression, the net current can be related to the potential as,

$$i = F A k^0 \left[C_O(0, t) e^{\frac{-\alpha F(E - E^0)}{RT}} - C_R(0, t) e^{\frac{(1 - \alpha) F(E - E^0)}{RT}} \right] \quad (1.8)$$

where A is the electrode area, and $C_O(0, t)$ and $C_R(0, t)$ are the time-dependent surface concentrations of the oxidant and reductant, respectively. In the Butler-Volmer formalism, where steady state and no mass transport effects are assumed, Equation 1.8 can be simplified into the frequently seen expression,

$$i = i_0 \left[e^{\frac{-\alpha}{RT}} - e^{\frac{(1-\alpha)F\eta}{RT}} \right] \quad (1.9)$$

where i_0 is the exchange current (i.e., the current of either the forward or reverse reactions at equilibrium), and η is the overpotential, defined as $E - E_{eq}$, where E_{eq} is the electrode potential at equilibrium. Consequently, the exchange current i_0 is a measure of the intrinsic rate of the reaction; its value, however, is dependent on the energy barrier of Equation 1.3, as well as the oxidant and reductant concentrations. As will be discussed in the next section, however, the choice of the reference electrode can, in special cases, remove the inherent dependence of the exchange current on the oxidant and reductant concentrations.

Since the introduction of the Butler-Volmer model of electrode kinetics, more detailed, and precise, theories of electrode kinetics have been formulated. A notable example tailored specifically for electron transfer reactions is Marcus theory²⁸. Marcus theory accounts for the reorganization of the solvent which facilitates the occurrence of an electron transfer reaction^{29–32}. Marcus theory was first developed for “outer-sphere” reactions (i.e., an electrochemical reaction which occurs in the solution phase and not on the electrode surface). Marcus theory has since been adapted to model reaction kinetics occurring on electrode surfaces, or “inner-sphere” reactions; however, due to the complexity of modeling a dynamic solvent phase, the use of Marcus theory in first-principles simulations is only in its infancy³³.

1.2.3 Standard and reversible hydrogen electrodes: a choice of reference

In this thesis, two reference electrodes will be mentioned extensively. The first is the standard hydrogen electrode (SHE). The SHE is defined by the equilibrium potential of the following reaction:



At standard conditions (298 K, a hydrogen pressure of 1 atm, and 1 M concentration of H^+), the equilibrium potential of Equation 1.10 is defined as 0 V. According to the Nernst equation, the equilibrium potential of Equation 1.10 depends on the proton concentration as,

$$E_{\text{eq}} = E^{0'} + \frac{RT}{F} \ln \frac{a_{\text{H}^+}/a_{\text{H}^+}^0}{\sqrt{p_{\text{H}_2}/p_{\text{H}_2}^0}} \quad (1.11)$$

where $E^{0'}$ is the reference potential (0 V vs. SHE), F is Faraday's constant, a_{H^+} is the proton activity, $a_{\text{H}^+}^0$ is the reference proton activity, p_{H_2} is the hydrogen pressure, and $p_{\text{H}_2}^0$ is the reference hydrogen pressure. The proton activity terms are related to the pH as,

$$\text{pH} = -\log_{10} \left(\frac{a_{\text{H}^+}}{a_{\text{H}^+}^0} \right) \quad (1.12)$$

A central theme of this work, however, is to directly compare electrochemical kinetics performed across a *range* of pH. Consequently, the SHE potential, whose equilibrium potential is intrinsically dependent on the pH, is not the most suitable choice of reference. Instead, the reversible hydrogen electrode (RHE) is frequently employed. On an RHE scale, the reference proton activity is no longer unity, but is defined as equal to the proton activity of the bulk solution. Thus, Equation 1.11 becomes simply,

$$E_{\text{eq}} = E^{0'} \quad (1.13)$$

where the $a_{\text{H}^+}/a_{\text{H}^+}^0$ term is always equal to unity by definition, and the influence of hydrogen pressure has been ignored for simplicity. Consequently, when using the RHE as the reference electrode, no proton activity terms appear in the kinetic rate expression, and electrochemical rates at different pH can be directly compared.

1.3 Current Research

1.3.1 Hydrogen oxidation reaction: state of the field and outlook

As HEMFCs have recently garnered increased attention, the scientific community has launched many efforts attempting to explain why the kinetics of HOR, as well as its reverse reaction, the hydrogen evolution reaction (HER), are dependent on pH. However, no consensus has been reached on what the unifying mechanism of the pH-dependence of HOR is, or if a single unifying mechanism exists at all. An overview of each of the most prevalent theories to date is given below.

HOR has been proposed to proceed through the Tafel-Heyrovsky-Volmer mechanism wherein adsorbed hydrogen, H^* , is formed on the electrode surface and is desorbed to produce a proton-electron pair.



Consequently, the binding energy of H^* on the electrode surface has been demonstrated to be a key descriptor of the electrochemical activity of a given electrode. Due to H^* being the sole intermediate species in Equations 1.4 – 1.6 (aside from the vacant catalyst site), a “volcano” relationship has been observed between the HOR/HER activity and the energy of the metal-hydrogen bond³⁴. In recent years, with the widespread use of density functional theory (DFT) calculations, correlating DFT-computed hydrogen binding energies to experimentally measured exchange current densities has been shown to also result in a volcano relationship for a given pH^{18,35,36}.

However, the simple picture of HOR described in Equations 1.4 – 1.6 cannot explain why the rate of HOR is dependent on the pH. While the chemical potential of both the proton and the electron are dependent on the pH when referenced to the *SHE* scale, the HOR kinetics are widely observed to become slower with increasing pH on an *RHE* scale. Moreover, the negligible dipole present in the metal-hydrogen bond implies that the changing electric field with increasing pH should not have an impact

on the energy of the metal-hydrogen bond³⁷. Despite the negligible change in the energy of the metal-hydrogen bond with pH, the experimentally determined underpotential-deposited hydrogen (H_{upd}) desorption peak shifts by as much as 0.2 V vs. RHE from acid to base; this shift in the “apparent” hydrogen binding energy has been correlated to the decrease in the HOR/HER activity for the platinum group metals (PGMs)³⁸. Thus, while Equations 1.4 – 1.6 have been implemented to explain the relative activities of metals at a specific pH, a unified theory which explains the pH dependence of HOR/HER has remained elusive.

One proposed explanation of the decreased HOR activity at high pH is the blocking of active surface sites by adsorbed hydroxyl. There are two primary routes through which hydroxyl can form on the electrode surface:



where $*$ represents a vacant site on the catalyst, OH^* is an adsorbed hydroxyl species, and OH^- is a hydroxide ion in solution. Within this theory, however, OH^* is assumed to have a *negative* impact on HOR/HER by blocking metal sites from forming H^* , either from H_2 (HOR) or from H^+ (HER). Recent studies have shown that the formation of the OH^* species can, in fact, lead to higher activity^{19,39,40}.

Janik *et al.* have used DFT calculations to argue that cation adsorption (e.g., K^+) in base weakens the formation of OH^* on the electrode surface⁴¹. Within their proposed mechanism, OH^* displaces adsorbed hydrogen on the catalyst surface. Experimental evidence does suggest that adsorption of K^+ and other cation species can occur in base, although this is not a universal phenomenon for all catalytic surfaces. This phenomenon is a consequence of the electrode operating at a more negative potential on an *SHE scale* in base, thereby facilitating the adsorption of cation species. Adsorption of K^+ onto (110) and (100) step sites of Pt was found to weaken OH^* formation by 0.15 eV and 0.09 eV, which in turn shifts the H_{upd} peak positively by 0.15 V and 0.09 V vs. RHE, respectively. While these results compare well to

experimental data, the hypothesis that OH* formation weakens with increasing pH contradicts CO stripping experiments performed for similar systems with suggests that OH* formation becomes *more* favorable with increasing pH³⁸.

Thus far, a hypothesis which has perhaps come the closest to explaining the *universal* pH dependence of HOR/HER is the recent work by Schwarz *et al.* In their framework, adsorption of water is argued to be a ubiquitous phenomenon occurring at the electrode/electrolyte interface⁴². Furthermore, water is argued to be a suitable candidate for the desorption of H* from the catalyst surface due to its ability to act as a proton shuttle. Though the partial oxidation of water can explain the pH dependence of both the H_{upd} peak *and* the HOR/HER activity, this theory is limited to explaining the pH dependent nature of the platinum group metals (Pt, Ir, Pd, and Rh). The PGMs lie on the strong adsorption branch of the HOR/HER volcano curve. Therefore, as the pH increases, the adsorption of partially oxidized water weakens and a greater overpotential is required to desorb H* from the catalytic surface, leading to lower activity.

To date, there is no theory that exists which has been able to explain, for *all* catalyst surfaces, the origin of the decrease in HOR activity with increasing pH. An additional challenge is that the H_{upd} peak as measured by *in situ* cyclic voltammetry (CV) experiments can only be observed for PGMs. Therefore, experiments alone are currently unable to determine whether the *in situ* hydrogen adsorption energy is a universal thermodynamic descriptor for HOR/HER, or whether other factors, such as cation adsorption or hydroxyl formation drive the pH dependence.

1.4 Dissertation Scope and Overview

This thesis uses molecular simulations, in conjunction with complementary experimental data, to better understand the progression of electrochemical reactions at interfaces.

Chapter 2 discusses the use of Ni nanoparticles supported on nitrogen-doped carbon nanotubes as an effective catalyst for the hydrogen oxidation reaction. Experiments characterized the synthesized Ni-based catalysts through a combination of microscopy, spectroscopy, and electrochemical performance measurements. DFT calculations were performed to understand the interaction of the nanoparticle with graphene and N-graphene supports through calculations of the hydrogen binding energy and electronic properties of the nanoparticle.

Chapter 3 discusses the tuning of Ni, Cu, and Ag nanoparticles through substitutional doping by either nitrogen or boron into graphene supports. Electronic effects of substitutional doping, support effects on hydrogen adsorption energy and HOR activity, heterogeneity of nanoparticle site properties, a principal component analysis driven adsorption model, and a size-dependent activity model are discussed.

Chapter 4 examines site and size effects on Fe_3O_4 nanoparticles for the oxygen evolution reaction occurring at the anode of the electrolyzer. FeO_x and NiFeO_x are synthesized, characterized, and tested for their electrochemical performance. Potential-determining steps of the oxygen evolution pathway on Fe_3O_4 nanoparticles are determined through DFT.

Chapters 5 and 6 introduce a new thermodynamic descriptor for HOR, the apparent Gibbs free energy of hydrogen adsorption, and demonstrate its ability to universally explain the observed pH-dependent HOR kinetics for a variety of electrocatalysts. Direct comparisons to both experimentally measured hydrogen adsorption energy and experimentally measured activity are made.

Finally, Chapter 7 summarizes the overarching conclusions of this work and suggests future research directions.

Chapter 2

NICKEL SUPPORTED ON NITROGEN-DOPED CARBON NANOTUBES AS HYDROGEN OXIDATION REACTION CATALYST IN ALKALINE ELECTROLYTE

2.1 Introduction

The hydrogen economy provides an efficient and environmentally friendly pathway to store and consume energy^{43,44}. Fuel cells, especially the recently developed polymer electrolyte membrane fuel cells, are considered as the most promising device to convert the chemical energy of hydrogen to electricity⁴⁵. The hydrogen fuel cells are based on two half-cell reactions: hydrogen oxidation reaction (HOR) at the anode and oxygen reduction reaction (ORR) at the cathode. To date, Pt is the most active catalyst for both HOR and ORR⁴⁶. However, the commercialization of fuel cells is hindered by the high price of Pt ($\sim \$50 \text{ g}^{-1}$). Although the total content of platinum-group metals (PGMs) in the state-of-the-art proton exchange membrane fuel cell (PEMFC) stacks has decreased significantly in the past decades, more than $0.137 \text{ g}_{\text{Pt}} \text{ kW}^{-1}$ is still needed⁴⁷. One promising approach to reduce the cost of fuel cells is to switch the operating environment from an acidic to a basic one (that is, a hydroxide exchange membrane fuel cell, HEMFC), thus opening up the possibility of using PGM-free catalysts and other cheaper components⁴⁸. For the cathode of the HEMFC, some PGM-free and metal-free ORR catalysts have been developed that show comparable activity to Pt in alkaline media^{49–52}. However, for the anode side, only a few PGMs (for example, Pt, Ir and Pd) show adequate activity^{19,53}. The HOR catalyzed by Pt is very fast in acidic conditions so that a very low loading of the Pt catalyst could be used relative to the cathode side in PEMFCs. However, the HOR activities of PGMs are ~ 100 times slower in alkaline solutions^{17,53}. As a result, a much

higher loading of the HOR catalyst is required ($0.4 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$ in a HEMFC compared with $0.03 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$ in a PEMFC) to achieve similar performance^{47,54}. Thus, it is highly desirable to develop PGM-free anode catalysts for the HOR in alkaline electrolyte. Unlike its reverse reaction (hydrogen evolution reaction, HER)^{55–57}, only a few PGM-free HOR catalysts have been reported. One possibility is to use Raney Ni as the HOR catalyst in liquid alkaline fuel cells^{58–60}. However, it is functional only under very high alkalinity (6 M KOH) while the activity remains low. It is not catalytically active for a HEMFC, which can be mimicked as 0.1–1 M KOH¹². Efforts have been made to improve the HOR activity of the Ni-based catalyst in the last decade. Ni alloys, such as NiMo and NiTi, have been shown to enhance the HOR activity⁵⁸. Our recent work has also shown that electrochemically deposited NiCoMo on an Au substrate has a high HOR activity⁹. Zhuang and co-workers decorated Ni particles with CrO_x to weaken the Ni–O bond and stabilize the Ni catalysts. A HEMFC incorporating this PGM-free catalyst has been fabricated, and it exhibits a peak power density of 50 mW cm^{-2} .¹² Although the power density is still low (compared with the peak power density of more than $1,000 \text{ mW cm}^{-2}$ for PEMFCs), it demonstrates the possibility to fabricate low-cost PGM-free fuel cells. However, their activities are still incomparable with PGM-based catalysts. In the current study, we synthesize Ni nanoparticles supported on N-doped carbon nanotubes (Ni/N-CNT) by a wet chemical method, and the Ni/N-CNT shows a high HOR catalytic activity in 0.1 M KOH solution. N-CNTs are not only the support for the Ni nanoparticles, but also a promoter for the catalytic activity. Owing to its special electronic properties, the N-doped carbon structure has been employed to enhance the catalytic activity of the methanol oxidation reaction and the ORR⁶¹. We use N-CNT as a support for the HOR catalyst and demonstrate that, relative to Ni nanoparticles, the mass activity and exchange current density of Ni/N-CNT increases by a factor of 33 and 21, respectively. To understand the interaction between the Ni nanoparticle and the N-CNT support, density functional theory (DFT) calculations are undertaken. The DFT calculations indicate that, when nitrogen dopants are present at the edge of the

nanoparticle, the Ni nanoparticle is stabilized on the support and locally activated for the HOR because of modulation of the Ni *d*-orbitals. Using the volcano relationship between the HOR activity and the hydrogen adsorption energy, predicted first-principles exchange current densities of the model systems are in good agreement with the measured exchange current densities of the experimental catalysts. Owing to its high activity and low cost, Ni/N-CNT has great potential to be used as the anode in HEMFCs, thereby finally bringing to fruition a high-performance and low-cost PGM-free HEMFC.

2.2 Methods

2.2.1 Experiment

Experiments characterized the synthesized Ni-based catalysts through a combination of microscopy, spectroscopy, and electrochemical performance measurements.

2.2.1.1 Synthesis of nickel-based composite catalyst

In a typical synthesis of Ni/N-CNT, mildly oxidized MWCNTs (25 mg, 10–20 nm in diameter, Shenzhen Nanotech Port Co. Ltd., mildly oxidized through the modified Hummers method⁶²) were dispersed in deionized water (10 mL) assisted by sonication for 30 min. After that, NiSO₄ • 6H₂O (0.262 g, 1 mmol) was added to the MWCNT suspension and sonicated for another 30 min. The suspension was transferred to a flask placed in an ice-water bath. Then ice-cold NaBH₄ aqueous solution (1 wt %, 10 mL, ~ 2.5 mmol) was added dropwise. After reaction at 0 °C for 2 h, the suspension was transferred to a 45 mL Teflon-lined stainless steel autoclave. Ammonium hydroxide solution (28–30% NH₃ basis, 5 mL) and hydrazine hydrate solution (78–82%, 2 mL) were added, and then the autoclave was sealed and subjected to a hydrothermal treatment at 150 °C for 4 h. The final product was collected by centrifugation at 8,000 r.p.m. for 10 min, washed with water and then re-dispersed in water (10 mL). Ni and Ni/CNT were synthesized by similar procedures.

Ni was synthesized without adding oxidized MWCNT and the pH was adjusted to 12 by ammonium hydroxide before the hydrothermal treatment. Ni/CNT was synthesized without adding ammonium hydroxide and hydrazine.

2.2.1.2 Physical characterization

The SEM was performed on a JEOL JSM-7400F SEM working at an acceleration voltage of 3 kV. The TEM, HRTEM and EDS were performed on a JEOL JEM-3010 TEM operating at 300 kV equipped with EDS system. The X-ray diffraction patterns were collected on a Bruker D8 Discovery diffractometer with Cu K α radiation ($\lambda = 0.15418$ nm) operating at 40 kV and 40 mA. The TGA was performed on a Mettler Toledo TGA/DSA 1 STARe System under air flow (60 mL min⁻¹) with a heating rate of 5 °C min⁻¹. The XPS spectra were recorded on Thermo Fisher ESCALAB 250Xi XPS system with a monochromatic Al K α X-ray source. The survey scans were conducted at a pass energy of 100 eV using a step size of 1 eV, and the high-resolution scans were conducted at a pass energy of 50 eV using a step size of 0.05 eV.

2.2.1.3 Electrochemical tests

The electrodes were prepared by casting catalyst inks on glassy carbon electrodes (5 mm in diameter, Pine Instruments, polished to a mirror-finishing with 0.05 mm alumina). The catalyst inks were prepared by dispersing catalyst in water with 0.05 wt.% Nafion at a concentration of 2.5 mg_{Ni} mL⁻¹. The catalyst ink (20 mL) was deposited on a glassy carbon electrode and dried in vacuum at room temperature, resulted in a metal loading of 0.25 mg_{Ni} cm⁻². Electrochemical studies were carried out in a standard three-electrode system controlled with a multichannel potentiostat (Princeton Applied Research). As-prepared thin film electrode, which served as the working electrode, was mounted on a rotator and was immersed into 0.1 M KOH solution. An Ag/AgCl electrode with double junctions was used as the reference electrode. A Pt wire was used as the counterelectrode, which has an outer glass tube

with a ceramic fritz to prevent the contamination of Pt. All potentials reported in this paper are referenced to the reversible hydrogen electrode potential. All the polarization curves were corrected for solution resistance, which was measured using AC-impedance spectroscopy from 200 kHz to 100 mHz and a voltage perturbation of 10 mV.

2.2.2 Theoretical

DFT calculations were performed to understand the interaction of the nanoparticle with graphene and N-graphene supports through calculations of the hydrogen binding energy of the nanoparticle and the electronic properties of the nanoparticle.

2.2.2.1 Computational methodology

Periodic DFT calculations were performed using the Vienna *ab initio* simulation package (VASP, version 5.3.2)⁶³. The optPBE-vdW exchange-correlation functional⁶⁴ was selected because of its qualitatively accurate representation of the potential energy surface of a Ni monolayer and graphene system⁶⁵. The core electrons were represented with the projector-augmented wavefunction (PAW) method^{66,67}, and a plane-wave cutoff of 400eV was used for the valence electrons. The Methfessel–Paxton method of electron smearing was used with a smearing width of 0.1 eV⁶⁸. All geometry optimizations were performed using the conjugate gradient algorithm⁶⁹ as implemented in VASP. The forces and energies were converged to 0.05 eV Å⁻¹ and 10⁻⁴ eV, respectively. All calculations were spin-polarized because of the magnetic moment of Ni. For the Ni nanocluster systems, all calculations were performed at the Γ -point. A 5 × 5 graphene unit cell was used as the support. In the *z* direction, a vacuum layer of 15 Å was included. This unit cell was chosen to minimize interaction of the Ni₁₃ nanocluster with its periodic image while still being computationally tractable. For the single metal surfaces used to establish the hybrid activity model, a 4

$\times 4$ unit cell was used with a $3 \times 3 \times 1$ Monkhorst–Pack k -point sampling of the Brillouin zone⁷⁰.

2.3 Results

2.3.1 Catalyst synthesis and characterization

A two-step approach was developed to synthesize the Ni/N-CNT hybrid catalysts. First, Ni was selectively grown on mildly oxidized multiwalled CNTs by reducing nickel salt in an aqueous solution. Second, ammonia and hydrazine were added and then subjected to a hydrothermal treatment at 150 °C. This step led to better crystallization of the Ni nanoparticles, partial reduction of the oxidized CNTs and, more importantly, doping of nitrogen into the CNTs. The scanning electron microscopy (SEM, Figure 2.1a) and transmission electron microscopy (TEM, Figure 2.1b) images clearly show that the nanoparticles with an average size of 20 nm are selectively grown on the surface of the CNT. The diffraction rings in the selected area electron diffraction (inset of Figure 2.1b) pattern can be either indexed to Ni or CNT. The energy-dispersive X-ray spectroscopy (EDS, Figure A.1) also indicated the presence of the Ni component. The enlarged TEM image (Figure 2.1c) shows that all the nanoparticles are directly supported on the CNT. Moreover, the high-resolution TEM (HRTEM, Figure 2.1d) image clearly indicates the layered structure of the CNT wall, with an interplanar spacing of 0.35 nm, which is similar to the (002) plane of graphite. The lattice fringe of the nanoparticle has an interplanar spacing of 0.21 nm and is ascribed to the (111) plane of Ni. The X-ray diffraction pattern (Figure 2.2a) further confirms the mixed Ni and CNT composition of the catalyst. The loading of Ni on carbon was calculated as ~70 wt.% by thermogravimetric analysis (TGA, method shown in Fig. A.2). The N doping was examined with X-ray photoelectron spectroscopy (XPS, Figure 2.2b). A peak at ca. 400 eV clearly exists in the high-resolution N 1s XPS spectrum (inset of Figure 2.2b), confirming the N doping. It can be deconvoluted into two peaks, 399.0 and 400.3 eV, corresponding to pyridinic N

and pyrrolic N in doped CNT, respectively^{71,72}. The N-doping amount to carbon was calculated from the XPS spectrum as 2.4 at.%.

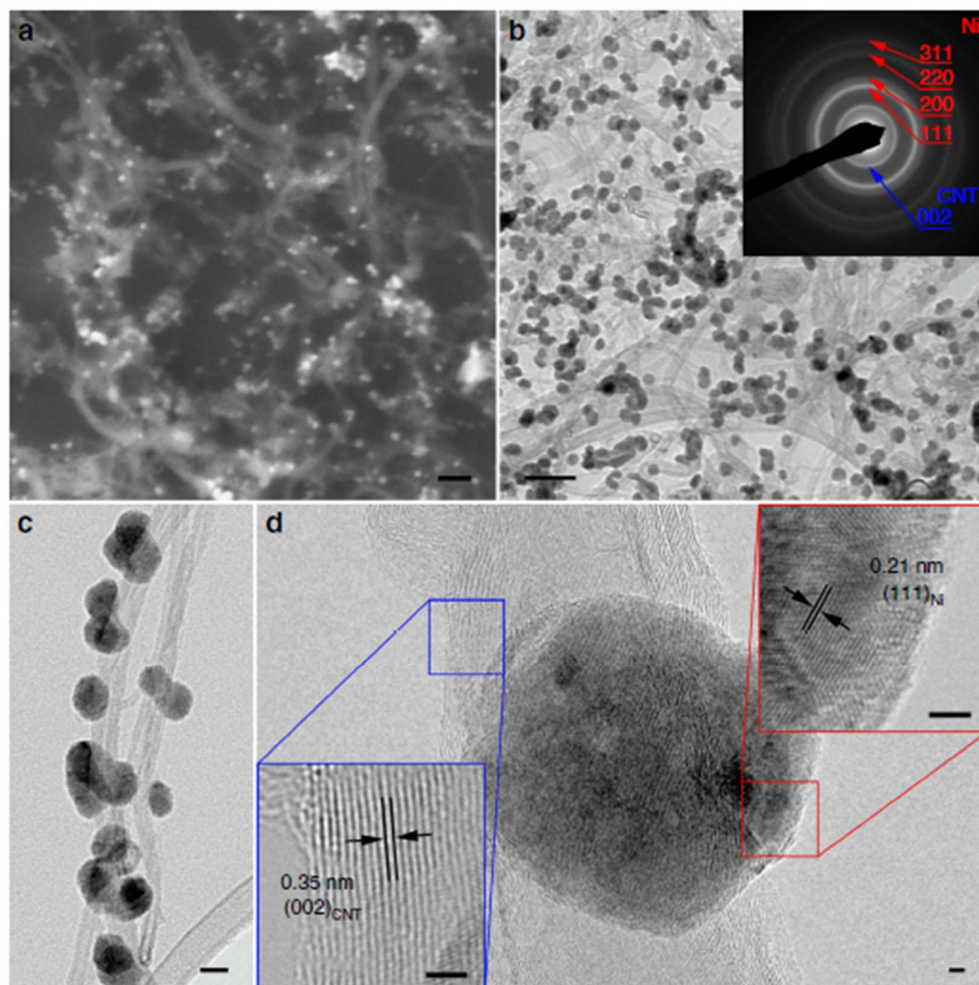


Figure 2.1. Electron microscopy of the Ni/N-CNT. (a) SEM image. Scale bar, 100 nm. (b) TEM image. Scale bar, 100 nm. Inset is selected area electron diffraction pattern. (c) A magnified TEM image. Scale bar, 20 nm. (d) HRTEM images of nickel particle and CNT, respectively. Scale bars, 2 nm.

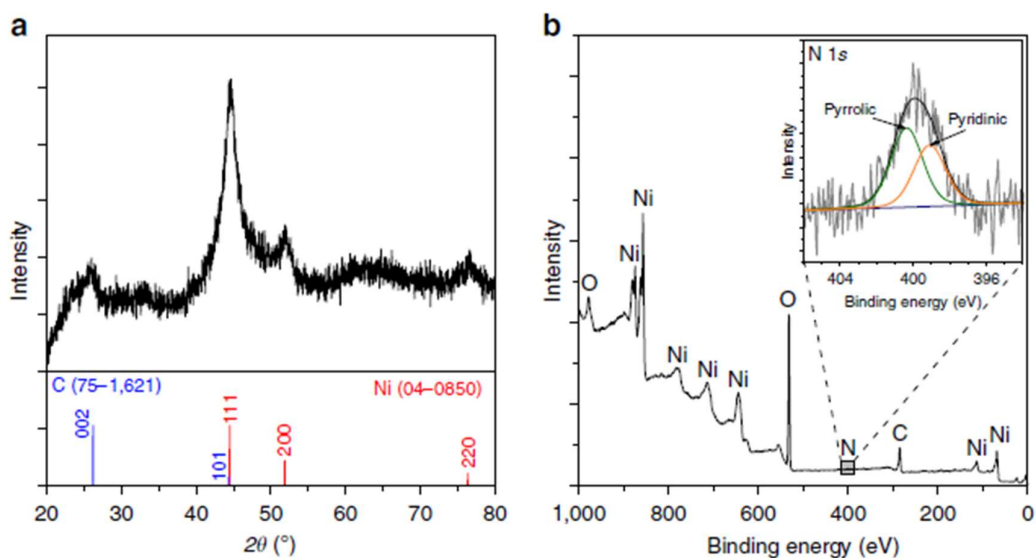


Figure 2.2. X-ray diffraction pattern and XPS spectra of the Ni/N-CNT. (a) X-ray diffraction pattern. The standard pattern of Ni (JCPDS card No. 04-0850) and graphite (JCPDS card No. 75-1621) are shown beneath the plot. (b) XPS spectrum. The inset is the high-resolution N 1s XPS spectrum.

2.3.2 Electrochemical HOR performance

The electrocatalytic activity for the HOR was investigated by rotating disk electrode measurements using a standard three-electrode system in 0.1 M KOH. The catalyst was uniformly cast on a 5-mm glassy carbon electrode with a Ni loading of $0.25 \text{ mg}_{\text{Ni}} \text{ cm}^{-2}$. Undoped CNT supported Ni nanoparticles (represented as Ni/CNT) and unsupported Ni nanoparticles (represented as Ni) catalysts (corresponding TEM images and X-ray diffraction patterns are shown in Figs A.3 and A.4, respectively) with the same loading were also studied for comparison. Figure 2.3a shows the polarization curve of the catalysts in H_2 -saturated electrolyte. The anodic current above 0 V (versus the reversible hydrogen electrode, same hereafter) is assigned to the oxidation of H_2 . The catalytic activity for HOR on the three Ni-based catalysts follows the sequence of $\text{Ni/N-CNT} > \text{Ni/CNT} > \text{Ni}$. The current density of Ni/N-CNT is much higher than either Ni/CNT or Ni and shows an onset potential as low as 0 V. The bare N-CNT shows almost no catalytic activity for HOR, indicating that the enhanced catalytic activity for Ni/N-CNT comes from the synergetic effect of the combined

structure. The Ni/N-CNT catalyst was also tested in an Ar-saturated electrolyte (Figure A.5) and showed no anodic current, confirming the catalytic reaction of HOR. The polarization curves at different rotating speeds have also been studied (Figure 2.3b). The current density increases with increasing rotating speed owing to improved mass transport. The overall current density is under mixed kinetic-diffusion control. The diffusion-limited current density (j_d) for a rotating disk electrode is described by the Levich equation as a function of rotating speed (ω):

$$j_d = Bc_0\omega^{1/2} \quad (2.1)$$

where B is the Levich constant, c_0 is the solubility of H_2 in 0.1 M KOH⁷³. The Levich constant is a function of the diffusivity of H_2 (D), number of the electrons (n) transferred in the HOR and kinematic viscosity of the electrolyte (η). The overall current density (j) can be deconvoluted into kinetic (j_k) and diffusional (j_d) components following the Koutecky–Levich equation:

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_d} = \frac{1}{j_k} + \frac{1}{Bc_0\omega^{1/2}} \quad (2.2)$$

A linear relationship between the inverse of j at 50 mV and $\omega^{1/2}$ is observed in the Koutecky–Levich plots (inset of Figure 2.3b). The calculated slope is $5.21 \text{ cm}^2 \text{ mA}^{-1} \text{ s}^{-1/2}$, which is reasonably close to the theoretical number ($4.87 \text{ cm}^2 \text{ mA}^{-1} \text{ s}^{-1/2}$, for the two-electron transfer of HOR)¹⁷. The intercept of the extrapolated line corresponds to the inverse of the purely kinetic current density, and the j_k for Ni/N-CNT is $2.33 \text{ mA cm}_{\text{disk}}^{-2}$ at 50 mV overpotential. Normalizing by the metal loading of the catalyst, the mass activity of the Ni/N- CNT is $9.3 \text{ mA mg}_{\text{Ni}}^{-1}$ at 50 mV overpotential, shown in Figure 2.3d and Table A.1 along with that of Ni/CNT and Ni. The mass activity of our synthesized unsupported Ni nanoparticles ($0.28 \text{ mA mg}_{\text{Ni}}^{-1}$) is comparable to the activities of Raney Ni reported in the literature^{74–79}. By contrast, the mass activity of the Ni/N-CNT is 33 times as high as the pure Ni nanoparticle, making Ni/N-CNT one of the most active PGM-free catalysts for HOR (Table A.2 lists the HOR mass activity of the PGM-free catalyst reported in the literature). To understand the intrinsic activity of the Ni/N-CNT catalyst, we normalized the current by the

electrochemical surface area (ECSA). The ECSAs of each Ni-based catalyst were measured in Ar-saturated 0.1 M KOH using a cyclic voltammetry method and were calculated from the OH desorption region of Ni subtracted by HER current using a charge density of 514 $\mu\text{C cm}_{\text{Ni}}^{-2}$ for one monolayer of OH adsorption on Ni (Figure A.6)^{80,81}. Figure 2.3c shows the ECSA-normalized kinetic currents as a function of the overpotential. The HOR kinetic current was obtained from the Koutecky–Levich equation (Equation 2.2). The exchange current density (j_0 , shown in Figure 2.3d and Table A.1) was obtained by fitting the ECSA-normalized HOR/ HER kinetic current density to the Butler–Volmer equation:

$$j_k = j_0 \left(e^{\frac{\alpha F}{RT} \eta} - e^{\frac{(1-\alpha)F}{RT} \eta} \right) \quad (2.3)$$

Here α is the charge transfer coefficient, F is Faraday’s constant, R is the universal gas constant, T is the temperature, and η is the overpotential¹⁷. All the curves can be fitted with a value of α in the range of 0.4-0.5, indicating a good symmetry for the HOR and HER branches. The j_0 values obtained from linear fitting of micropolarization regions (-10–10 mV, see Fig. A.7 and Table A.1) are consistent with the values of j_0 obtained from Butler–Volmer fitting. The Ni/N-CNT has an exchange current density of 0.028 $\text{mA cm}_{\text{Ni}}^{-2}$, which is three times higher than Ni/CNT and 21 times higher than Ni. The exchange current density for Ni/N-CNT is among the best PGM-free HOR catalysts and is comparable to some PGM catalysts, such as Pd (Table A.3)^{53,82}. Although the HOR activity of the Ni/N-CNT is still over one order of magnitude less than the state-of-the-art Pt catalyst, the ultralow price of Ni makes it promising for commercial applications.

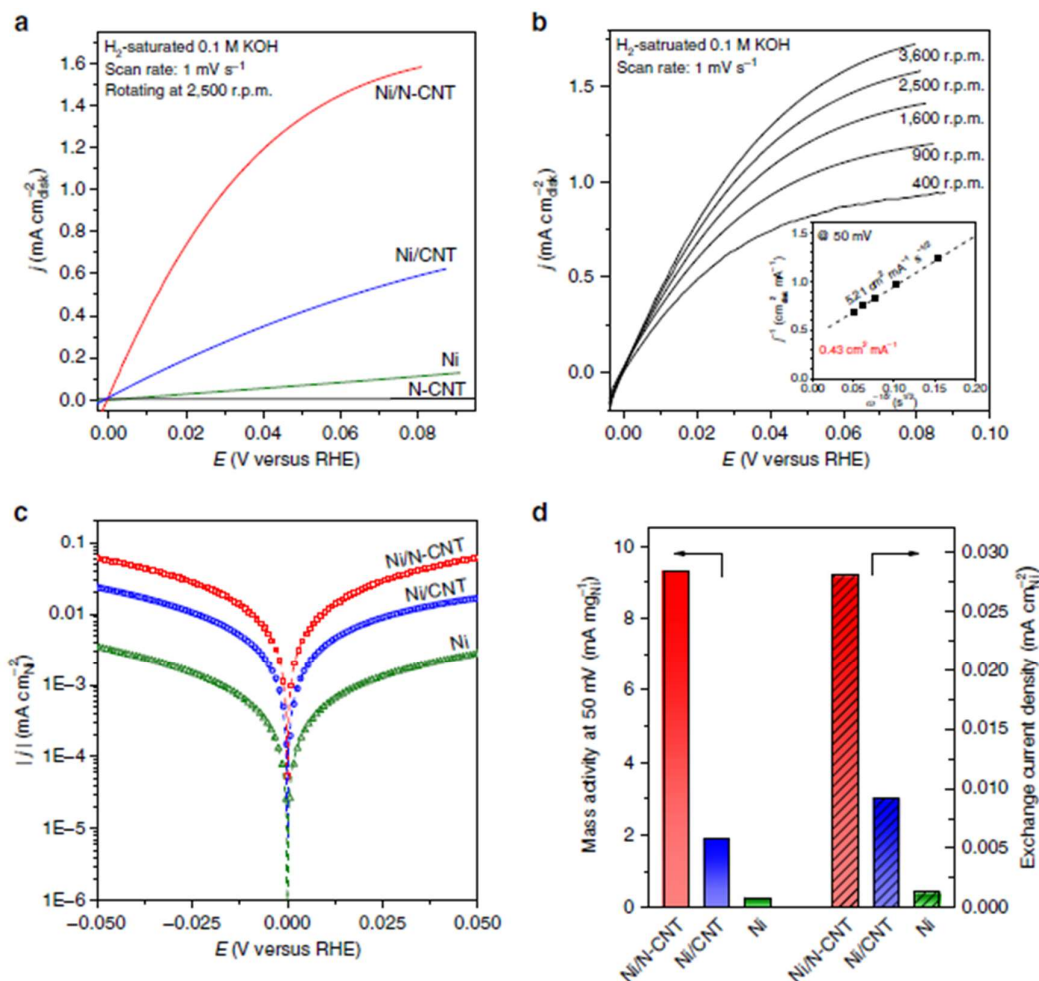
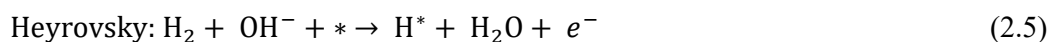


Figure 2.3. HOR performances. (a) Polarization curves of Ni/N-CNT, Ni/CNT, Ni (all of the three catalysts with a loading of 0.25 mg_{Ni} cm⁻²) and N-CNT (0.1 mg_C cm⁻²) catalysts in H₂-saturated 0.1 M KOH at a scan rate of 1 mV s⁻¹ and rotating speed of 2,500 r.p.m. (b) Polarization curves of Ni/N-CNT in H₂-saturated 0.1 M KOH at a scan rate of 1 mV s⁻¹ and various rotating speeds. Inset is the Koutecky–Levich plot at an overpotential of 50 mV. (c) HOR/HER Tafel plots of the specific current density on Ni/N-CNT, Ni/CNT and Ni in H₂-saturated 0.1 M KOH. The dashed lines indicate the Butler–Volmer fitting. (d) Mass activity at 50 mV (unpatterned) and exchange current density (patterned) of the Ni/N-CNT, Ni/CNT and Ni, respectively.

2.3.3 Theoretical Investigation

On the basis of a Wulff construction, *fcc* metals, such as Ni, are known to prefer a cuboctahedral geometry, exposing the (111) and (100) facets⁸³. To model the nanoparticle, a 13-atom Ni nanocluster (Ni₁₃) was chosen, as this was the smallest of the cuboctahedral ‘magic numbers’ (a larger nanoparticle, Ni₃₇, was also studied and is discussed below)⁸⁴. Because of the relatively large size of both the Ni nanoparticles

and carbon nanotubes used experimentally, previous studies suggest that the curvature of the CNT support has a minimal effect⁸⁵; as such, the CNT support is approximated with a graphene sheet to reduce the complexity of the model. This results in a Ni₁₃ nanoparticle being deposited on both graphene (Ni/graphene) and nitrogen-doped graphene (Ni/N-graphene), with both the Ni₁₃ nanoparticle and the support being allowed to relax. We have investigated the effect of the location of the nitrogen dopant relative to the nanoparticle by considering nitrogen at the center (N_c) and nitrogen at the edge (N_e), as shown in Figure A.8. In alkaline solutions, the HOR follows either the Tafel–Volmer or the Heyrovsky–Volmer mechanism. The possible elementary steps comprising the HOR are shown in Equations 2.4–2.6.



The key intermediate is the adsorbed hydrogen (H*) on the catalyst surface, which leads to the existence of a Sabatier volcano relationship with the hydrogen-binding energy of the catalyst as the descriptor³⁴. Although mechanistically the H* written in the elementary steps above is likely the overpotential-deposited hydrogen (H_{OPD}), the HOR/HER activity seems to correlate well to the electrochemical adsorption energy of the underpotential-deposited hydrogen (H_{UPD}), which is shown to be similar to the chemical adsorption energy of hydrogen^{86–88}. In this study we calculate chemical adsorption energy of hydrogen on Ni₁₃ nanoclusters.

The volcano relationship involving adsorbed hydrogen has been well established in acidic solutions³⁵. While some debate remains on the adequacy of using the hydrogen-binding energy as a descriptor in alkaline media, there is significant evidence that the hydrogen-binding energy remains the key descriptor of activity^{18,19,89}. This allows for the implementation of a hybrid data-driven/first-principles model to evaluate the efficacy of different catalysts and to estimate activity compared with single metals. This hybrid approach was employed successfully in

propane total oxidation⁹⁰. Details of the construction of the hybrid activity model are given in the Appendix A. The heterogeneity of the hydrogen-binding sites in the supported Ni nanocluster model system results in a distribution of binding energies shown in Figure 2.4a. Here we see a large amount of variability among the metal-support systems at high binding energies, with an unsupported Ni₁₃ nanocluster and Ni/graphene having a large number of sites that adsorb hydrogen too strongly to be active for HOR. On the other hand, Figure 2.4a shows that a Ni nanoparticle supported on N_c-graphene does not possess large binding energies as in the unsupported Ni and the Ni/graphene systems.

The differences in the binding energies between the unsupported Ni₁₃ nanocluster and the supported Ni₁₃ arise from either an electronic (that is, charge transfer) or a geometric (that is, relaxation) origin⁹¹. For the strong binding sites, the nanocluster undergoes reconstruction as shown in Figure A.9. The relative contributions of the electronic and the geometric support effects are decoupled by considering a nanocluster which is treated as rigid during hydrogen binding. For a rigid nanocluster, any differences in the binding energies result from the differences in the electronic structure of the Ni₁₃ nanocluster because of the support. We define a relaxation energy, E_{relax} , as

$$E_{\text{relax}} = \Delta E_{\text{H}}^{\text{rig}} - \Delta E_{\text{H}}^{\text{rel}} \quad (2.7)$$

where $\Delta E_{\text{H}}^{\text{rig}}$ is the hydrogen-binding energy on the rigid nanocluster, and $\Delta E_{\text{H}}^{\text{rel}}$ is the hydrogen-binding energy on the relaxed nanocluster. Here a larger E_{relax} implies a larger degree of Ni reconstruction. Figure 2.4b shows E_{relax} for all Ni-binding sites for the systems considered. The unsupported nanocluster is the least stable during hydrogen binding. With the exception of a fraction of binding sites, the nitrogen-doped supports exhibit better stabilization of the Ni nanocluster. In agreement with its lack of strongly binding sites (*cf.* Figure 2.4a), Ni/N_c-graphene exhibits local relaxation with minimal reconstruction. In addition, when considering the rigid nanocluster, the difference in the average hydrogen-binding energy of Ni/N_c-graphene

and Ni/N_e-graphene is less than 0.01 eV (versus 0.09 eV difference for the relaxed nanocluster). Thus, we observe that the rigid nanocluster's binding characteristics are not greatly affected by the support (N_e-graphene or N_e-graphene).

Next, we examine what fundamental electronic properties of the Ni₁₃ nanocluster are being affected by the support. A commonly employed electronic descriptor for the binding energies on metal surfaces is the energy of the *d*-band center, ϵ_d , relative to the Fermi level, ϵ_F ⁹². The *d*-band center describes the relative filling of the hybridized (*d-s*) and antibonding (*d-s*)* states of the Ni-H system. For an adsorbate, such as atomic hydrogen with a low-lying electronic state, the stabilization of the bonding states between the metal *d*-states and the hydrogen *s*-states decreases when the *d*-band of the metal is shifted up in energy ($\epsilon_d - \epsilon_F$ is more positive) because of the energy mismatch between the metal *d*-band and the hydrogen *s*-state. As a result, the resulting antibonding part of the band is pushed up just above the Fermi level, which leads to stronger binding between the metal atoms and the adsorbate. In Figure 2.4c, we see an upshift in the *d*-band center of adjacent Ni-binding sites when an edge nitrogen atom is present. Owing to these sites originally lying in the weak binding region of Figure 2.4a, the upshift in the *d*-band center consequently activates these sites adjacent to N_e for the HOR by strengthening the binding energy by 0.1 eV. XPS valence band spectra, which are related to the *d*-band centers, were also studied (Figure A.10)⁹³. Thus, while the geometric effect of the support is responsible for the decrease in strong binding sites, edge nitrogen further tunes local binding sites by modulating the electronic properties of Ni.

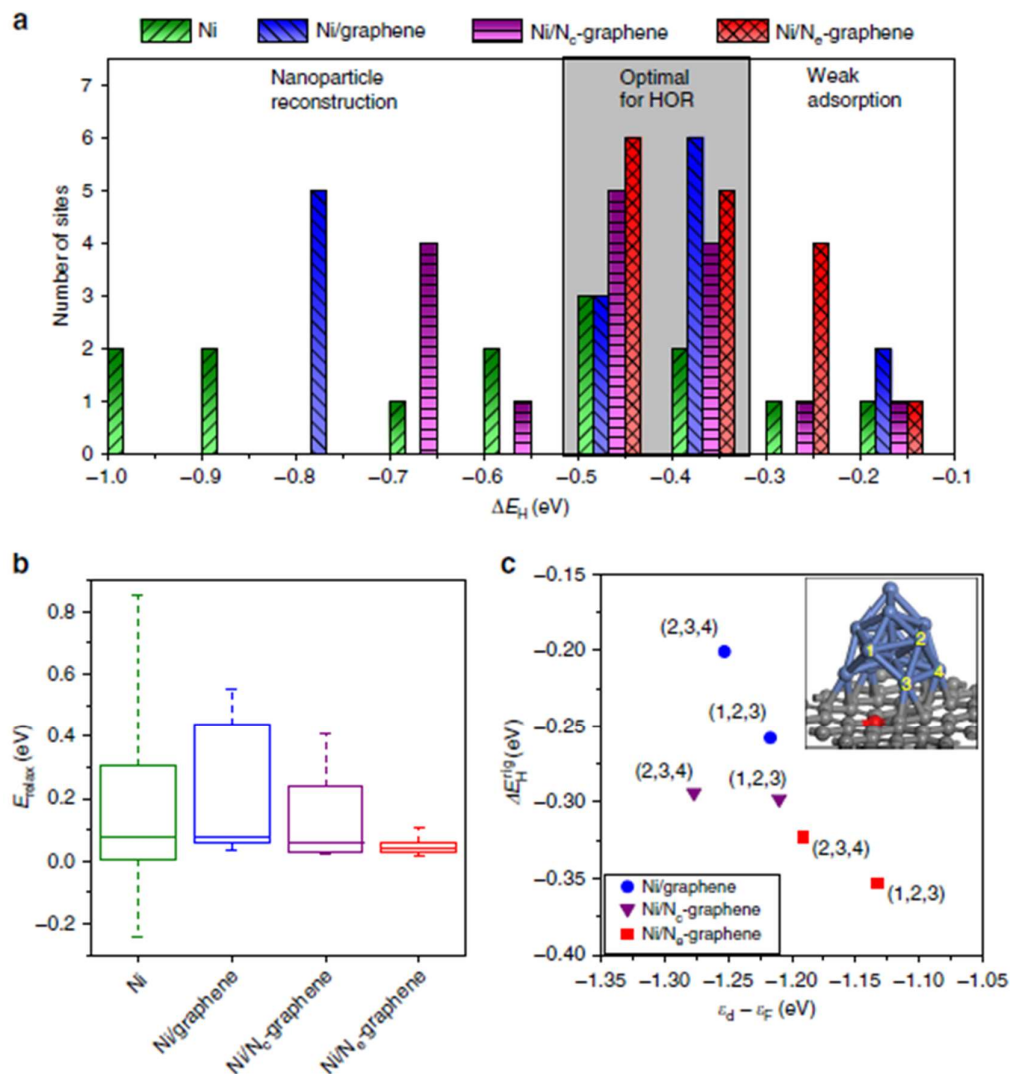


Figure 2.4. (a) Distribution of site-dependent hydrogen-binding energies for each model system. (b) Distribution of relaxation energies for each model system on hydrogen-binding to each site. The ends of the dashed line represent the minimum and maximum values of E_{relax} for each model structure. These ranges collectively represent the distribution of E_{relax} values for each hydrogen adsorption site on the Ni₁₃ cluster. The bottom of the box represents the first quartile (that is, splits the lowest 25% of relaxation energies from the highest 75%) and the top of the box represents the third quartile (that is, splits the highest 25% of relaxation energies from the lowest 75%). Bold horizontal band is the median value. (c) Shifts in the d -band center with respect to the Fermi level and binding energy at adjacent Ni sites (1,2,3) and (2,3,4) for Ni/graphene, Ni/N_c-graphene and Ni/N_c-graphene. Inset is graphical depiction of the sites (Ni/N_c-graphene as an example). The (1,2,3) site represents the hollow site in coordination with the #1, #2 and #3 Ni atoms. The (2,3,4) site represents the hollow site in coordination with the #2, #3 and #4 Ni atoms. Blue, grey and red spheres represent Ni, C and N atoms, respectively.

Using the hybrid activity model for the HOR, we can now predict the intrinsic exchange current density of each of the model systems that were investigated (Figure A.11 and Appendix A: Note 1). In agreement with experimental measurements, Figure 2.5 shows that an order of magnitude increase in the exchange current density is predicted for a graphene- supported nanocluster compared with an unsupported Ni catalyst. Additional improvement occurs when doping the graphene support with nitrogen, where having nitrogen at the edge of nanocluster (that is, directly interacting with surface Ni atoms) appears to be more effective than having nitrogen at the center of the nanoparticle. Relating this discovery to the current experimental procedure, it is expected that edge nitrogen is predominant in the experimental material. This is because nitrogen doping is performed after the Ni nanoparticle was grown from the CNT surface. Thus, it is expected that only sites at the edge of the nanoparticle are available for nitrogen doping, and that lattice diffusion is the only mechanism by which nitrogen could be transported to the center of the nanoparticle.

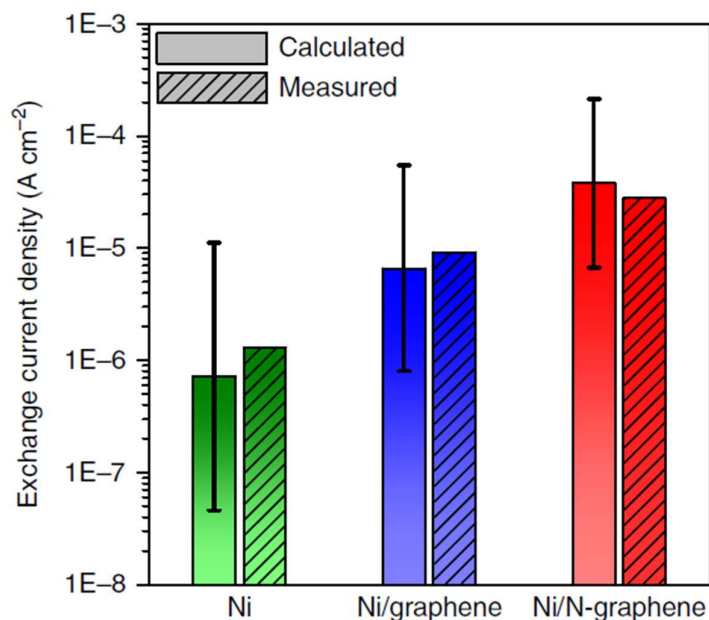


Figure 2.5. Comparison of calculated exchange current densities to measured values. Unpatterned bars are the calculated exchange current densities and patterned bars are the measured values. The calculated exchange current density of Ni/N_e-graphene is shown for Ni/N-graphene. Error bars are 75% confidence intervals resulting from the regression of the volcano relationship in Equation A.2.

To confirm that the Ni₁₃ is sufficiently large to capture the metal-support interaction of the experimental system, we performed calculations on a larger Ni₃₇ nanoparticle (Appendix A: Note 2). The *d*-orbitals of the Ni₁₃ cluster correspond well to the larger Ni₃₇ model (Figure A.12). The difference in the calculated *d*-band center is only 0.01 eV for the two nanoparticles, which indicates that the Ni₁₃ is a good approximation for larger nanoparticles both in terms of its adsorption and electronic properties. The electronic effect of the N-dopant was found localized to the adsorption sites of the nearby Ni atoms (Figure A.13 and Table A.4). Our findings suggest that even higher HOR activity could be obtained by making smaller Ni nanoparticles because of a larger fraction of adsorption sites that could be affected electronically by the N-dopant.

2.4 Conclusions

In summary, Ni/N-CNT as a highly active PGM-free HOR catalyst in alkaline condition was reported in this paper. The promoted HOR activity is attributed to the synergetic effect of the edge N atom in the CNT and Ni. The theoretical investigation indicated that the Ni nanoparticle has more sites with an optimal hydrogen-binding energy because of both a geometric and electronic interaction with the edge N atoms. Relative to Ni nanoparticles, the mass activity and exchange current density of Ni/N-CNT increases by a factor of 33 and 21, respectively. These results show that Ni/N-CNT is promising to be applied as the anode catalyst for HEMFCs.

2.5 Acknowledgements

This material has been adapted with permission from Zhuang, Z., Giles, S. A., Zheng, J., Jenness, G. R., Caratzoulas, S., Vlachos, Dionisios G., and Yan, Y. Nickel supported on nitrogen-doped carbon nanotubes as hydrogen oxidation reaction catalyst in alkaline electrolyte. *Nature Communications* **2016**, 7, 10141, Copyright 2016 Nature Publishing Group. I would like to thank the co-authors of this work, Prof. Zhongbin Zhuang, Dr. Jie Zheng, and Prof. Yushan Yan for their contribution of materials therein related to experimental synthesis, characterization, and electrochemical testing. I would like to thank the co-authors of this work, Dr. Glen R. Jenness, Dr. Stavros Caratzoulas, and Prof. Dionisios G. Vlachos, for their contributions and insights related to the theoretical calculations and the writing of the manuscript.

The experimental work was partially supported by the ARPA-E program of the US Department of Energy under the Award Number DE-AR0000009. The computational work was financially supported from the Catalysis Center for Energy Innovation, an Energy Frontier Research Center funded by the US Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number DE-SC0001004. S. A. Giles acknowledges a UDEI fellowship. This research used resources of the National Energy Research Scientific Computing Center, a DOE

Office of Science User Facility supported by the Office of Science of the US
Department of Energy under Contract No. DE-AC02-05CH11231.

Chapter 3

EFFECT OF SUBSTITUTIONALLY DOPED GRAPHENE ON THE ACTIVITY OF NANOPARTICLE METAL CATALYSTS FOR THE HYDROGEN OXIDATION REACTION

3.1 Introduction

Fuel cells represent an integral part of the future energy mix. The two most common types of hydrogen fuel cells are the proton exchange membrane fuel cell (PEMFC) and the hydroxide exchange membrane fuel cell (HEMFC). In most commercial applications, the PEMFC is the fuel cell of choice due to lower overpotential losses at the catalyst and the high conductivity and stability of the Nafion membrane³. The stability of a large number of non-noble metal catalysts at high pH renders HEMFC attractive but the low rate of the hydrogen oxidation reaction (HOR) at the anode – by approximately two orders of magnitude in a basic environment⁵³ – is currently an impediment.

Adsorbed hydrogen is widely accepted to be the key HOR intermediate^{17,53} as further corroborated by the existence of a "volcano" relationship between the surface binding energy of hydrogen and the observed HOR activity. Thus, tuning hydrogen adsorption has been exploited to enhance the HOR activity in the HEMFC environment^{9,54}.

One route to enhancing the activity of non-noble catalysts is the induction of support effects that modulate the adsorption properties of nanocatalysts. Support effects have been demonstrated to result in increased activity of the hydrogen evolution reaction (HER), the reverse of the HOR⁹⁴. In our work, we have

demonstrated that Ni nanoparticles supported on nitrogen-doped carbon nanotubes (N-CNT) are highly active for HOR in alkaline media⁹⁵. Previously, it was also shown that CoO₃ nanoparticles supported on N-doped carbon materials are active for the oxygen evolution reaction (OER)^{96,97}. Prior work demonstrates that N-CNT supports mitigate nanoparticle sintering, presumably due to a stronger nanoparticle-support interaction^{98,99}. Aside from nitrogen, other dopants, such as boron, have recently been studied^{100,101}. Both nitrogen and boron have been observed to induce local changes in the electronic structure of graphene and CNT, which can lead to the creation of active sites for oxygen reduction and evolution reactions^{102–104}. These studies have primarily focused on the use of doped graphene and CNT as metal-free catalysts, not as catalyst *supports*. Thus, a detailed understanding of nanoparticle-support interactions has yet to be achieved.

Doping of the catalyst support introduces local changes in electronic and adsorption properties of the nanoparticle and increases the diversity of adsorption sites, making analysis of reactivity trends more complex^{105–108}. For *unsupported* nanoparticles, Sautet and co-workers have recently introduced the generalized coordination number (GCN) as a descriptor of adsorption energies with respect to the local binding environment^{109,110}. This builds on earlier work on using coordination numbers as descriptors of adsorption energy^{111,112}. In addition, machine learning has been used to relate molecular-based descriptors, such as the *d* band position and shape, to binding energies of adsorbates on flat surfaces^{113,114}. To our knowledge, however, similar descriptor-based methods have not been demonstrated for nanoparticles where support and dopant effects play a role.

In the current study, we examine, using first-principles calculations, Ni, Cu, and Ag nanoparticles supported on graphene and on N- and B-doped graphene to

understand the nanoparticle/support interaction and predict materials with promising HOR activity. Our results shed light onto the effect of substitutional doping on key electronic-level descriptors for catalysis (e.g., *d* band center). We compute the hydrogen binding energy at each adsorption site on supported nanoparticles (diameter of approximately 1.0 nm) and use the volcano relationship to infer the local HOR activity of each supported nanoparticle of interest. Heterogeneity in site adsorption and activity is visualized through heat maps. The importance of inherent properties of each site are quantitatively compared to dopant-induced changes in adsorption and activity. Principal component analysis is performed to identify descriptors and predict the adsorption at any given nanoparticle site. A size-dependent activity model, which considers a nanoparticle size distribution representative of experiments, is shown to be in good quantitative agreement with measured activities of Ni/CNT and Ni/N-CNT catalysts.

3.2 Methods

3.2.1 Model systems of interest

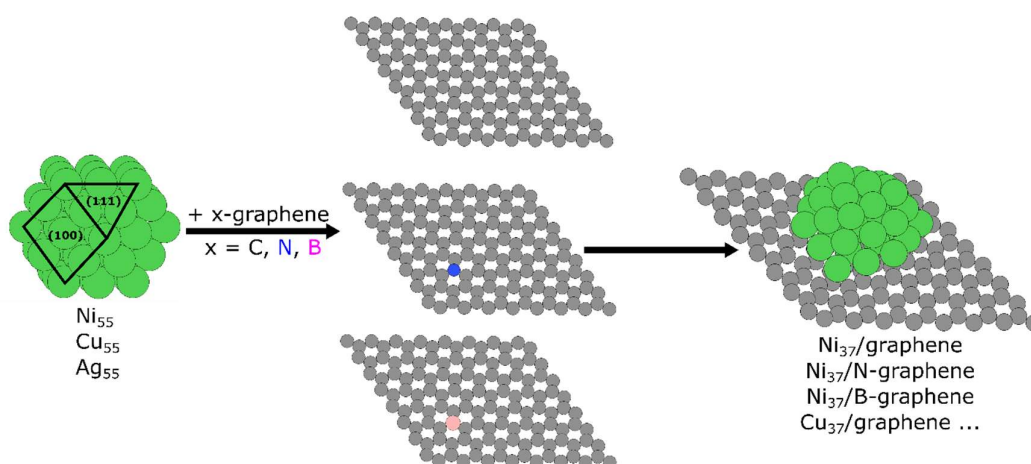


Figure 3.1. Nanoparticle and support systems considered in the current study.

The nanoparticle and support systems of interest are shown in Figure 3.1. Due to the relatively large CNTs used experimentally, we approximate the CNTs as a single graphene layer. Truncation of the 55-atom, gas-phase cuboctahedral nanoparticle results in an approximately hemispherical supported nanoparticle analogous to those synthesized experimentally⁹⁵ and predicted from the Wulff-Kaischew theorem¹¹⁵. Previous theoretical studies have attempted to rationalize the interaction between carbon-based supports and nanoparticles by considering metal clusters of only a few atoms (e.g., $n = 1-4$)¹¹⁶⁻¹¹⁸. Motivated from this work, small metal clusters were also explored to quickly screen supported catalysts (Figure B.1). Our results indicate that the substitutional doping of graphene leads to qualitatively different changes in the electronic properties of metal clusters compared to supported nanoparticles. Therefore, we believe that modeling suitably large nanoparticles is necessary to reliably capture the nanoparticle-support interaction of relevance to experimental catalysts. This leads to complexity arising from the possibly large sizes of experimental nanoparticles and the high computational cost of conducting electronic structure calculations for such sizes. We term this complexity as catalyst size gap.

To model N-graphene and B-graphene, a single nitrogen and boron atom were substitutionally doped into the graphene sheet in their graphitic form, maintaining sp^2 hybridization. Previous studies on nitrogen- and boron-doped CNTs show that graphitic nitrogen and boron are the most prevalent species^{119,120}. Furthermore, a pyridinic N-graphene structure was also computed and found to have similar charge localization properties as graphitic N-graphene (Table B.1). Therefore, in our work, we choose to focus on the interaction of the supported nanoparticles with graphitically

doped graphene. With regard to dopant concentration, literature values range from approximately 1-16 at.%^{119,121–123}. Considering only the support atoms which directly coordinate with the nanoparticle, a dopant concentration of approximately 3 at.% is modeled herein. This dopant concentration is representative of prior work on Ni/N-CNT system⁹⁵. Supports doped with two nitrogen atoms were computed and found to have little additional impact on the adsorption properties of a nanoparticle (Figure B.2), in agreement with the electrical conductivity of N-CNT becoming constant at dopant concentrations larger than ~3 at.%¹¹⁹.

In the current study, we primarily consider the dopant to be located at the edge of the (111) facet of the nanoparticle, as this location was determined to be most favorable thermodynamically (Table B.2). The different dopant locations tested are indicated in Figure B.3. Charge transfer properties of N and B dopants at different locations were also computed and are provided in Figure B.4.

3.2.2 Calculations of hydrogen binding energy and HOR activity

Aside from the dependence of the HOR activity on the hydrogen binding energy estimated experimentally, we have previously also demonstrated that the hydrogen binding energy, calculated using density functional theory (DFT), is a descriptor of the HOR activity⁹⁵. In the current study, we utilize a hybrid experimental data- and DFT-driven approach to understand how the activity of a platinum-group free HOR catalyst changes when interacting with the catalyst support. This hybrid approach was employed successfully in describing propane total oxidation and predicting novel bimetallic catalysts⁹⁰. Specifically, we correlate the DFT-computed hydrogen binding energies of the close-packed plane of metal catalysts, the (111) surface for metals with *fcc* bulk symmetry, with the measured exchange current

densities of polycrystalline catalysts in 0.1 M KOH normalized to the electrochemical surface area (ECSA) taken from Gasteiger and co-workers¹⁸ (Appendix B).

Specifically, the ascending and descending branch of the volcano curve is correlated to the DFT-computed (111) hydrogen binding energy, ΔE_H , via a linear scaling relationship with α and β as fitting parameters.

$$\log j_0 = \alpha \times (\Delta E_H) + \beta \quad (3.1)$$

While there is inherent uncertainty in correlating the DFT-computed hydrogen binding energies on a single surface to experimentally measured exchange current densities of more complex surfaces, qualitative trends should be captured.

Given the site heterogeneity on a single nanoparticle, our adsorption model is site specific. For each adsorption site i , the hydrogen binding energy is calculated according to Equation 3.2

$$\Delta E_{H,i} = E_{i, \text{metal+support+H}} - E_{\text{metal+support}} - \frac{1}{2} E_{H_2} \quad (3.2)$$

where $E_{i, \text{metal+support+H}}$ is the total energy of the nanoparticle and support with a hydrogen atom adsorbed at site i , $E_{\text{metal+support}}$ is the energy of the nanoparticle and support, and E_{H_2} is the energy of a hydrogen molecule in the gas phase. The activity of site i follows then Equation 3.2 with site specific binding energy. The nanoparticle exchange current density $\bar{j}_0$ is computed as an average over all surface binding sites, n , similar to the stochastic method of Gillespie¹²⁴

$$\bar{j}_0 = \frac{1}{n} \sum_i^n j_{0,i} \quad (3.3)$$

To isolate the effect of doping on ΔE_H , $\Delta \Delta E_H$ is defined which represents the dopant-induced change in the hydrogen adsorption energy for a given site i ,

$$\Delta \Delta E_{H,i} = \Delta E_{H,i}(\text{x-graphene}) - \Delta E_{H,i}(\text{graphene}) \quad (3.4)$$

where $\Delta E_{H,i}(\text{x-graphene})$ and $\Delta E_{H,i}(\text{graphene})$ are the hydrogen adsorption energies of hydrogen at site i of the nanoparticle on a N- or B-graphene support (x=N or B) and an undoped graphene support, respectively. Positive values of $\Delta \Delta E_H$

indicate weakened adsorption; conversely, negative values indicate strengthened adsorption.

3.2.3 Principal component analysis of reactivity trends

To identify key descriptors governing reactivity properties of a nanoparticle, principal component analysis (PCA) was performed. The centered and scaled inputs to the PCA included the d band center, d band width, d band skewness, d band kurtosis, the generalized coordination number of a site, and the local charge of the adsorption site. Previous studies have identified these quantities as potentially important^{109,110,114,125}. Upon identifying the number and most important principal components, regression was performed wherein the principal components were used as independent variables to predict the hydrogen adsorption energy at each site of a nanoparticle. The regression model includes up to second-order terms involving each of the principal components, as indicated by

$$\Delta E_H = a_0 + \sum_{i=1}^{np} \sum_{j=1}^{np} a_{ij} x_i x_j \quad (3.5)$$

where a_0 is the intercept, np is the number of principal components included (fewer than the original number of input variables), a_{ij} is the coefficient of the $x_i x_j$ term, and x_i and x_j are the i^{th} and j^{th} principal components. We have used a similar second-order model for predicting CO adsorption energies on Au nanoparticles¹¹².

3.2.4 Size-dependent activity model

Due to the large size of the experimental nanoparticles (~20 nm), accounting for size effects is necessary to quantitatively predict experimental activity. To that end, a geometric model of hemispherical shape, as indicated by high resolution transmission electron microscopy (TEM) images of Ni/CNT and Ni/N-CNT catalysts⁹⁵, was constructed to estimate the number of nanoparticle perimeter sites. A schematic of this model is provided in Figure 3.2a.

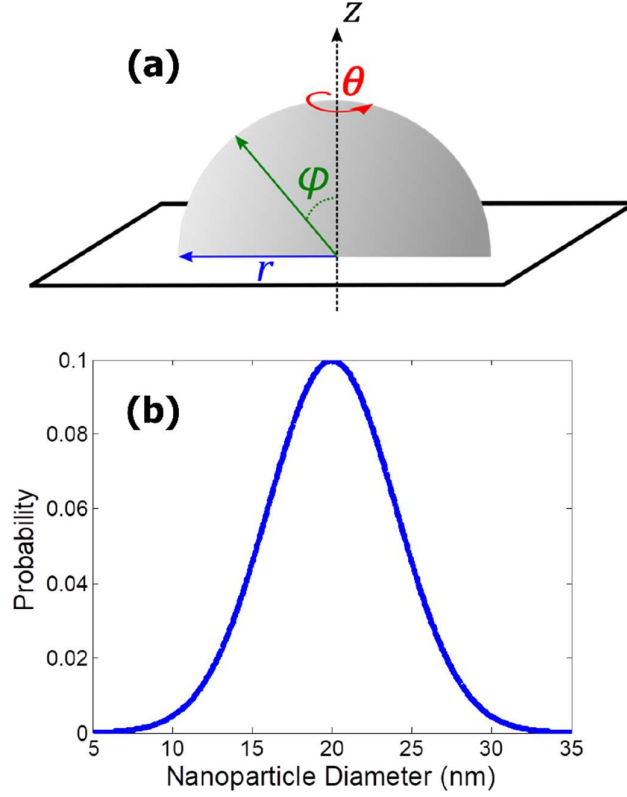


Figure 3.2. (a) Schematic of a supported hemispherical nanoparticle model. (b) Nanoparticle size distribution of previously synthesized Ni/CNT and Ni/N-CNT catalysts⁹⁵.

The surface area of the nanoparticle is determined using a surface integral over the azimuthal angle, θ , and the polar angle, ϕ . The fraction of nanoparticle sites affected by the support (i.e., those captured by the structural models computed with DFT) is estimated for a given diameter d by calculating the value of ϕ corresponding to the outermost layer, as shown in Equation 3.6

$$x_{\text{NP}} = \frac{1}{2\pi} \int_{\frac{\pi}{2} - \frac{2d_{\text{M-M}}N_{\text{layers}}}{d}}^{\frac{\pi}{2}} \sin \phi \, d\phi \int_0^{2\pi} d\theta \quad (3.6)$$

where $d_{\text{M-M}}$ is the bond length between metal atoms, N_{layers} is the number of layers close to the support modeled explicitly with DFT (in this work, three layers are used). The remaining fraction, $1-x_{\text{NP}}$, of a nanoparticle surface is assumed to have adsorption characteristics similar to a bulk metal facet. Ni, Cu, and Ag each have *fcc* bulk symmetry; therefore, the (111) facet is the close packed, lowest surface energy

considered. A derivation of Equation 3.6, along with an example of computing x_{NP} , is provided in the Appendix B and in Figure B.5. Consequently, the exchange current density of a nanoparticle of diameter d is calculated as,

$$j_0(d) = x_{\text{NP}}j_{0,\text{NP}} + (1 - x_{\text{NP}})j_{0,(111)} \quad (3.7)$$

where $j_{0,\text{NP}}$ is the calculated exchange current density of the nanoparticle on graphene or doped graphene (dopant concentration of ~ 3 at.%) computed from DFT (i.e., the result of Equation 3.3), and $j_{0,(111)}$ is the exchange current density of the extended (111) surface of the metal. Equation 3.7 could be refined further with more specific knowledge of the catalyst structure, as the (111) facet may not be the only one which contributes to activity. Equation 3.7 also assumes that the relative fractions of the first, second, and third layer sites are insensitive to nanoparticle diameter. At very small nanoparticle diameters, there will tend to be more first layer (along the perimeter) sites present (Figure B.6); however, the relative ratios of sites between layers are approximately constant. Our approach assumes a geometric similarity in which hemispherical supported nanoparticles of varying diameters are used to model experimental nanoparticles which are outside of the size scale accessible by DFT alone. In turn, for nanoparticles of a given size *distribution*, Equation 3.7 yields the average exchange current density

$$\overline{j_0(d)} = \int_{d_{\min}}^{\infty} P(d)j_0(d) dd \quad (3.8)$$

where $d_{\min}$ is the nanoparticle diameter for which x_{NP} is equal to unity. Nanoparticles smaller than $d_{\min}$ are not considered since this is equal to the nanoparticle size explicitly simulated with DFT. Nanoparticles at the sub-nanometer scale are widely known to have unique and varying catalytic properties; therefore, we assume in Equation 3.8 that nanoparticles smaller than those explicitly simulated with DFT do not exist. $P(d)$ is the normalized probability distribution of nanoparticle diameters. $P(d)$ is assumed to be normally distributed, in accordance with results obtained for Ni/N-CNT⁹⁵ (Figure 3.2b).

3.2.5 Electronic structure calculations

Periodic DFT calculations were performed using the Vienna *ab-initio* simulation package (VASP, version 5.3.2)⁶³. The optPBE-vdW exchange-correlation functional⁶⁴ was selected due to its good representation of the potential energy surface of a Ni monolayer and graphene system⁶⁵. The core electrons were represented with the projector augmented wavefunction (PAW) method⁶⁷ and a plane-wave cutoff of 400 eV was used for the valence electrons. The Methfessel-Paxton method⁶⁸ of electron smearing was used with a smearing width of 0.1 eV. All geometry optimizations were performed using the conjugate gradient algorithm⁶⁹ as implemented in VASP. The forces and energies were converged to 0.05 eV Å⁻¹ and 10⁻⁴ eV, respectively. All calculations were spin-polarized due to the magnetic moment of Ni. An 8 × 8 graphene unit cell was used as the support, leading to a nanoparticle coverage of approximately 0.3 on graphene. In the *z*-direction, a vacuum layer of 15 Å was included. This unit cell was chosen to minimize interaction of the 37-atom metal nanoparticles with its periodic image while still being computationally tractable. The adsorption energy calculations were performed at the Γ -point, and the atom-projected density of states were computed using a 3 × 3 × 3 Monkhorst-Pack *k*-point sampling of the Brillouin zone to ensure high accuracy. For the extended metal surfaces used to establish the hybrid activity model, a 4 × 4 unit cell was used with a 3 × 3 × 1 Monkhorst-Pack *k*-point sampling of the Brillouin-zone⁷⁰.

3.3 Results

3.3.1 Effect of pristine graphene on supported nanoparticles

The support results in truncation of the gas phase nanoparticle and under-coordinated first-layer sites at the interface of the nanoparticle and the support (an example is shown in Figure 3.1). The GCN^{109,110} of the first layer surface sites is between 3.1 and 4.0, whereas all other adsorption sites have a GCN between 4.4 and 5.7. The presence of the support can also lead to modifications in the geometry of the

nanoparticle, wherein the supported nanoparticle tends to expose the (111) facet instead of the (100) (Figure B.7). In addition to changes in local coordination, electron density may be transferred between the graphene support and the nanoparticle. For all systems studied here, the graphene support was found to accept electron density from the nanoparticle, with the total nanoparticle charge for Ni, Cu, and Ag being $+2.68 e^-$, $+0.20 e^-$, and $+0.14 e^-$, respectively.

3.3.2 Effect of doped graphene on supported nanoparticles

Substitutional doping of carbon atoms within the graphene support leads to changes in electronic properties which, in turn, affect the properties of a supported nanoparticle. First we consider the interaction energy between the support and the nanoparticle as a measure of changes in nanoparticle properties⁹¹. The nanoparticle-support interaction energy is defined as

$$IE = E(\text{NP+support}) - E(\text{NP}) - E(\text{support}) \quad (3.9)$$

where $E(\text{NP+support})$ is the energy of the fully relaxed nanoparticle-support system, $E(\text{NP})$ is the energy of the nanoparticle alone in the gas phase, and $E(\text{support})$ is the energy of the support alone in the gas phase. For Ni, Cu, and Ag, Figure 3.3 shows the nanoparticle-support interaction energies for all systems. Significantly, doping (either with N or B) leads to stronger interaction between the nanoparticle and the support compared to the graphene alone and the effect is more pronounced when B is used as dopant. The especially pronounced effect of B-graphene on the interaction energy is rationalized through a stronger electronic interaction as shown by the local Laplacian of the charge density (Figure B.8). The universally stronger interaction between the nanoparticle and the doped supports is consistent with the experimentally observed ability of N-CNT to mitigate nanoparticle sintering^{98,99}.

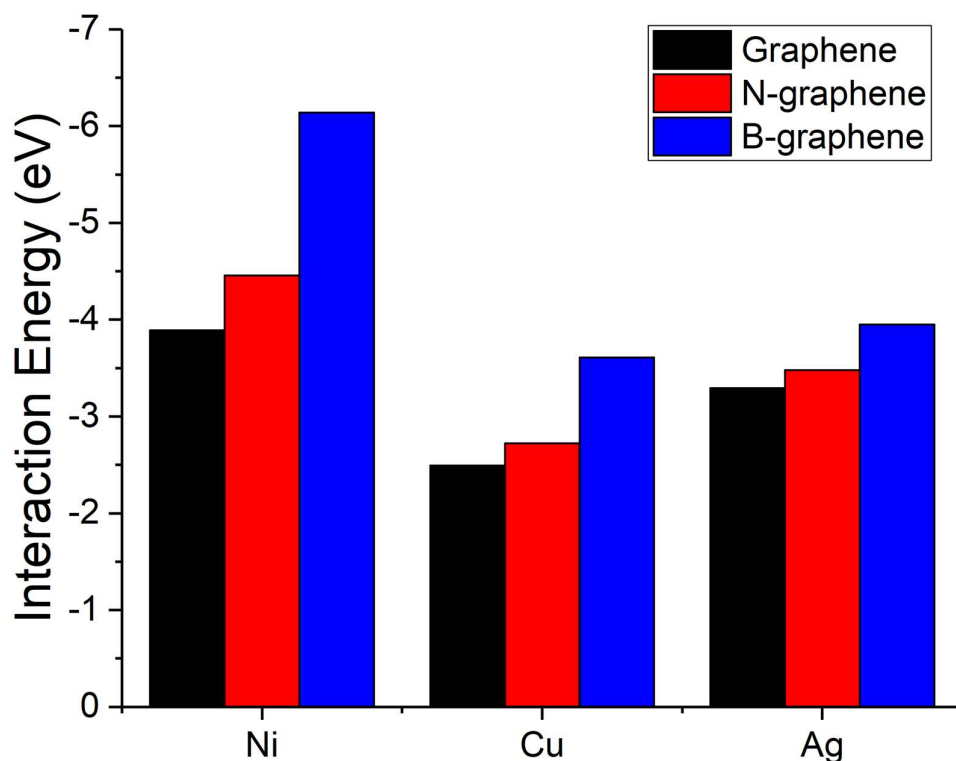


Figure 3.3. Nanoparticle-support interaction energy for various systems. Doping of the graphene support leads to stronger interaction between the support and the nanoparticle.

Figure 3.4 summarizes the variation of the exchange current density for each nanoparticle-support system (panel a), along with the corresponding hydrogen adsorption energy in an HOR/HER volcano plot (panel b). Doping leads to stronger nanoparticle-support interaction and weaker adsorption, reminiscent of bond order conservation, and allows tuning of the activity of catalysts. Doping leads to a benevolent effect on the exchange current density for Ni nanoparticles. Specifically, doping leads to lower activity of metals on the right of the volcano curve, such as Cu and Ag nanoparticles, due to their already residing on the weakly binding branch of the HOR volcano. In contrast, doping leads to higher activity of metals on the left of the volcano, such as Ni, due to decreasing the hydrogen binding energy toward the peak of the volcano.

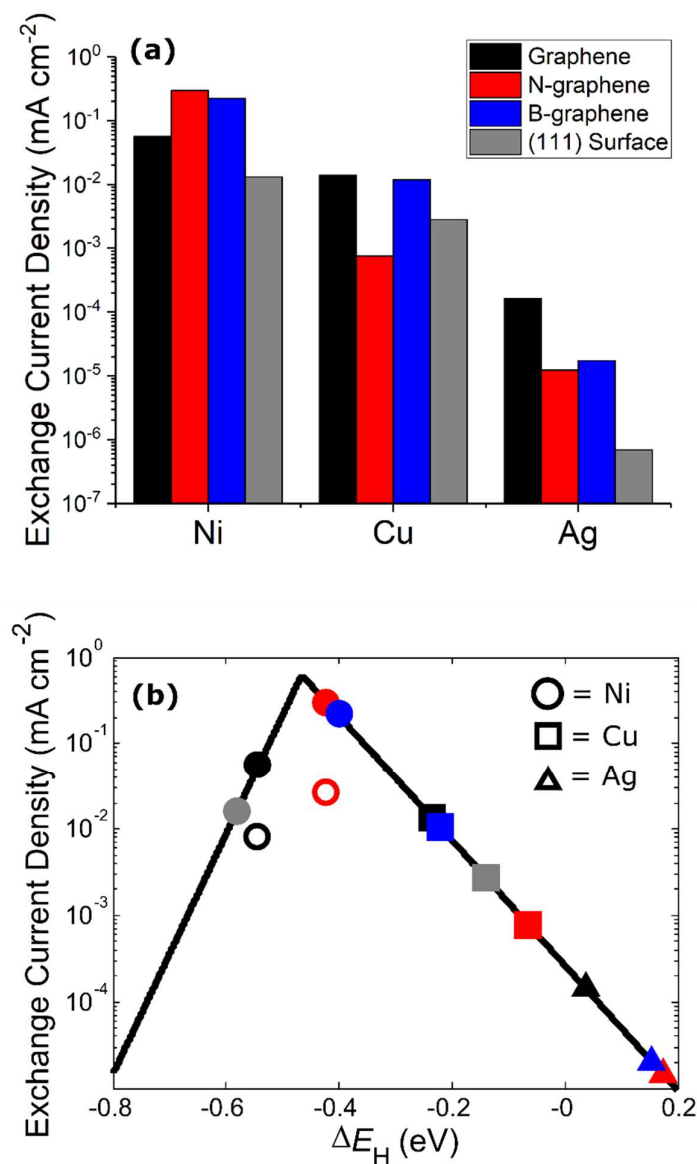


Figure 3.4. (a) Predicted exchange current densities of supported nanoparticle systems, along with the extended (111) surfaces of Ni, Cu, and Ag. (b) Support- and dopant-induced changes in the hydrogen adsorption energy and exchange current density. Black, red, and blue symbols indicate the nanoparticle supported on graphene, N-graphene, and B-graphene, respectively and gray the (111) extended surfaces. Open symbols indicate the experimentally measured exchange current densities of Ni/CNT and Ni/N-CNT⁹⁵ as comparison. The open symbols were not used in the regression relationship between the hydrogen adsorption energy and the exchange current density. See methods for model development.

3.3.3 Site heterogeneity of the hydrogen binding energy and exchange current density

Figure 3.4 clearly shows that the support induces changes in the adsorption properties of a nanoparticle and HOR/HER activity. The predicted activities of the supported nanoparticles shown in Figure 3.4 are averaged over all sites according to Equation 3.3. However, large heterogeneity in both the adsorption and activity exists among individual sites of a supported nanoparticle. An example with respect to site location is provided for supported Ni nanoparticles in Figure 3.5. Corresponding heat maps of the hydrogen adsorption energy for supported Cu and Ag nanoparticles are provided in Figures B.9 and B.10, respectively. A common trait among different nanoparticles is the strongest adsorption sites tend to be located near the nanoparticle-support interface. These sites have quite different adsorption properties from even the sites in only the third layer of the nanoparticle. Doping of the support generally leads to weaker adsorption energies, with the sites nearest the support being the most strongly affected.

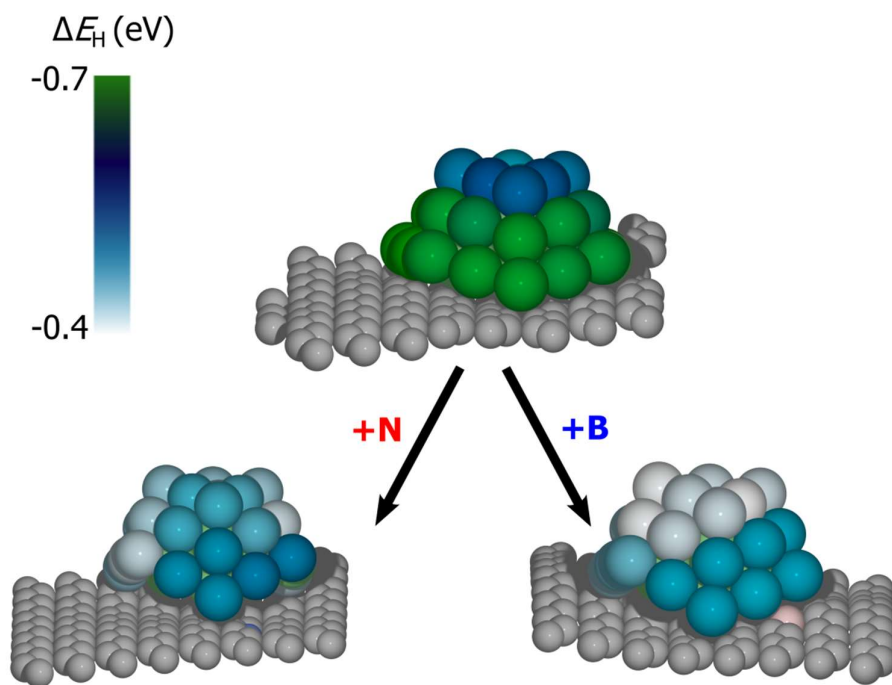


Figure 3.5. Heat map of the local hydrogen adsorption energy for Ni/graphene (top), Ni/N-graphene (bottom left), and Ni/B-graphene (bottom right).

Figure 3.6 shows that the strong adsorption sites on Ni/graphene give only moderate activity. The third layer sites of Ni/graphene with adsorption characteristics similar to Ni (111) possess higher activity, and doping greatly increases the overall activity of the nanoparticle. Analogous activity heat maps for supported Cu and Ag nanoparticles are shown in Figures B.11 and B.12, respectively. For Cu and Ag, which lie on the weak adsorption leg of the HOR/HER volcano, the first and second layer sites give *higher* activity due to being less limited by hydrogen adsorption. Furthermore, doping with nitrogen or boron generally leads to lower activity due to the overall weakening of hydrogen adsorption.

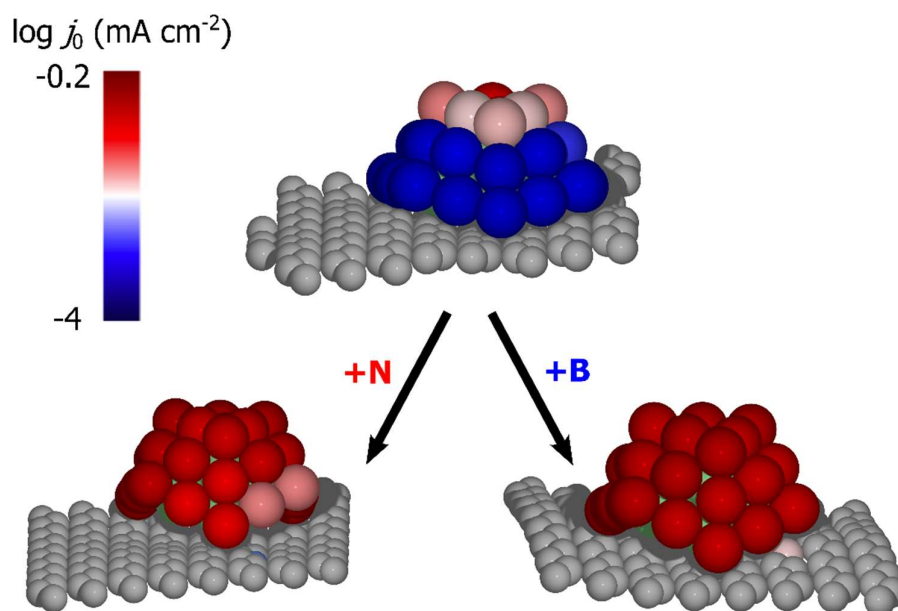


Figure 3.6. Heat map of the local HOR/HER exchange current density for Ni/graphene (top), Ni/N-graphene (bottom left), and Ni/B-graphene (bottom right).

3.3.4 Relative importance of differences in site properties and dopant-induced changes

As can be seen from the heat maps of hydrogen adsorption energy and exchange current density, there is a large degree of site heterogeneity in both the case of doped and undoped supports. Therefore, we desire to quantitatively compare the importance of site effects. The distribution of hydrogen adsorption energies at each

site of the nanoparticle is shown in Figure 3.7 for Ni, Cu, and Ag supported on undoped graphene. Ni, Cu, and Ag nanoparticles supported on graphene have a standard deviation of the hydrogen adsorption energy of ± 0.10 eV, ± 0.13 eV, and ± 0.17 eV, respectively. The relatively broad distribution of hydrogen adsorption energies on Ag/graphene is due to the supported nanoparticle maintaining a cuboctahedral geometry; in this case, there is a larger number of unique adsorption energies due to non-equivalent bridge and hollow sites. Apparent from Figure 3.7 is that the adsorption energies are not normally distributed. In particular, for Ni/graphene and Cu/graphene, the distribution is skewed towards stronger adsorption energies, due to the aforementioned larger number of strong adsorption sites in the first layer at small nanoparticle diameters (Figure B.6). The data set of adsorption energies, however, is small due to the limitation of nanoparticle size which can be simulated with DFT. If one were to compute the hydrogen adsorption energy at each site of a larger nanoparticle, one should expect the relative amount of strong adsorption sites to decay exponentially, with the distribution of adsorption energies resembling more closely the (111) extended surface.

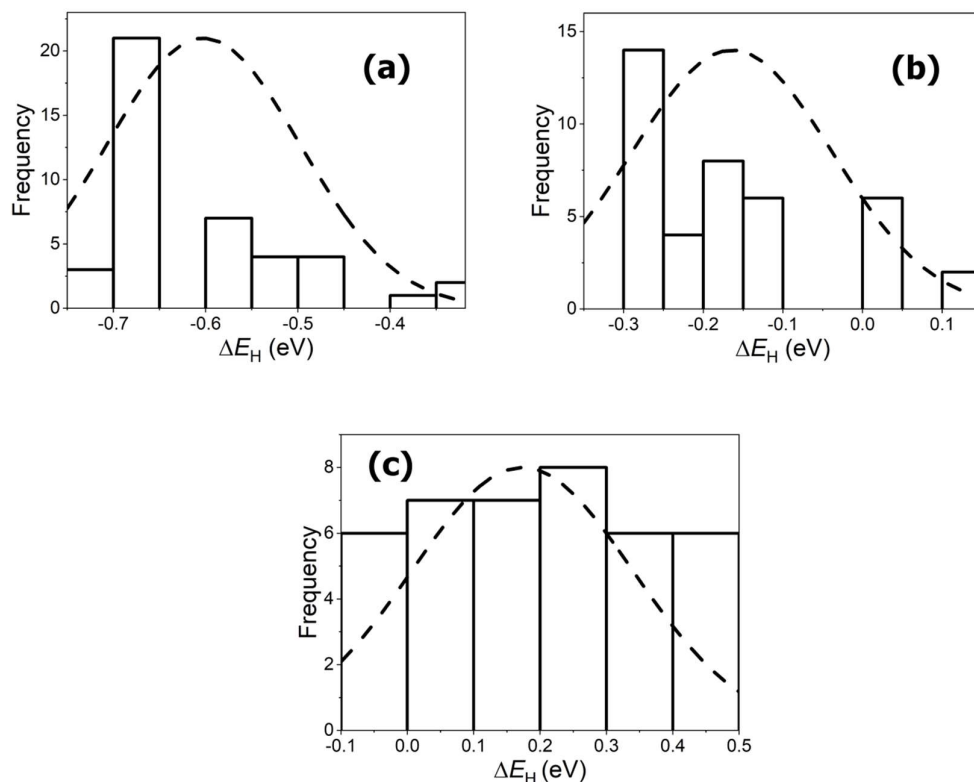


Figure 3.7. Distribution of hydrogen adsorption energies on (a) Ni/graphene, (b) Cu/graphene, and (c) Ag/graphene. The bin widths of the histogram in (a) and (b) are 0.05 eV, and 0.1 eV in (c). The dashed lines in (a)-(c) represent a normal distribution with a mean and standard deviation of -0.60 ± 0.10 eV, -0.16 ± 0.13 eV, and $+0.17 \pm 0.17$ eV.

The distribution of dopant-induced change in the hydrogen adsorption energy $\Delta\Delta E_H$ for Ni, Cu, and Ag nanoparticles supported on N-graphene and B-graphene is shown in Figure 3.8. The doping of nitrogen into graphene is found to universally lead to a weakened adsorption of hydrogen for Ni, Cu, and Ag nanoparticles. For the supported Ni nanoparticles, the doping of boron into graphene leads to a similar change in hydrogen adsorption. The effect of B-graphene on Cu and Ag nanoparticles is less pronounced, potentially due to the aforementioned weaker interaction of the support with Cu and Ag nanoparticles, as well as the induction of strain to the graphene lattice caused by boron substitution¹⁰⁰. Comparing the magnitude of $\Delta\Delta E_H$ to site-specific deviations of ΔE_H for nanoparticles supported on undoped graphene,

the dopant-induced effects on adsorption are deemed to be as important as the inherent differences in the adsorption sites.

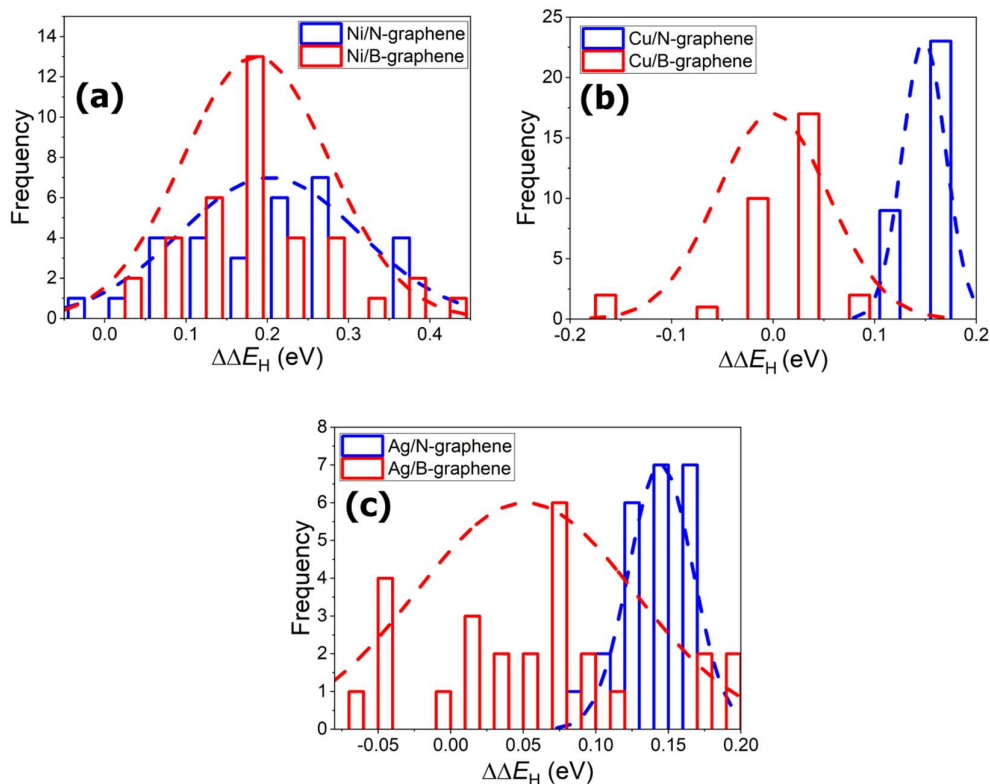


Figure 3.8. Distribution of dopant-induced changes in hydrogen adsorption energies for (a) Ni/x-graphene, (b) Cu/x-graphene, and (c) Ag/x-graphene. The dashed lines in (a)-(c) represent normal distributions. For Ni, Cu, and Ag supported on N-graphene, the means and standard deviations are $+0.20 \pm 0.11$ eV, $+0.15 \pm 0.02$ eV, and $+0.14 \pm 0.02$ eV. For Ni, Cu, and Ag supported on B-graphene, the means and standard deviations are $+0.19 \pm 0.09$ eV, 0.00 ± 0.05 eV, and $+0.05 \pm 0.08$ eV.

3.3.5 Principal component analysis of adsorption properties

The observation that dopant effects can equal or exceed intrinsic differences in site properties motivates the need to understand and predict the computed changes in hydrogen adsorption energies. The hydrogen adsorption energies are predicted through PCA, where molecular-based descriptors are mathematically transformed into orthogonal principal components. The result of this mathematical transformation is

shown in Figure 3.9a, where the first three principal components are expressed in terms of the molecular descriptors which comprise them. The first principal component is mainly composed of the *d* band kurtosis, the second is mainly composed of the *d* band center and width (these two are strongly correlated), and the third is mainly composed of the generalized coordination number. The first principal component explains 85% of the variance in the original descriptors; inclusion of the second and third principal components explains 95% and 99.9% of the variance in the descriptor data, respectively (Figure B.13).

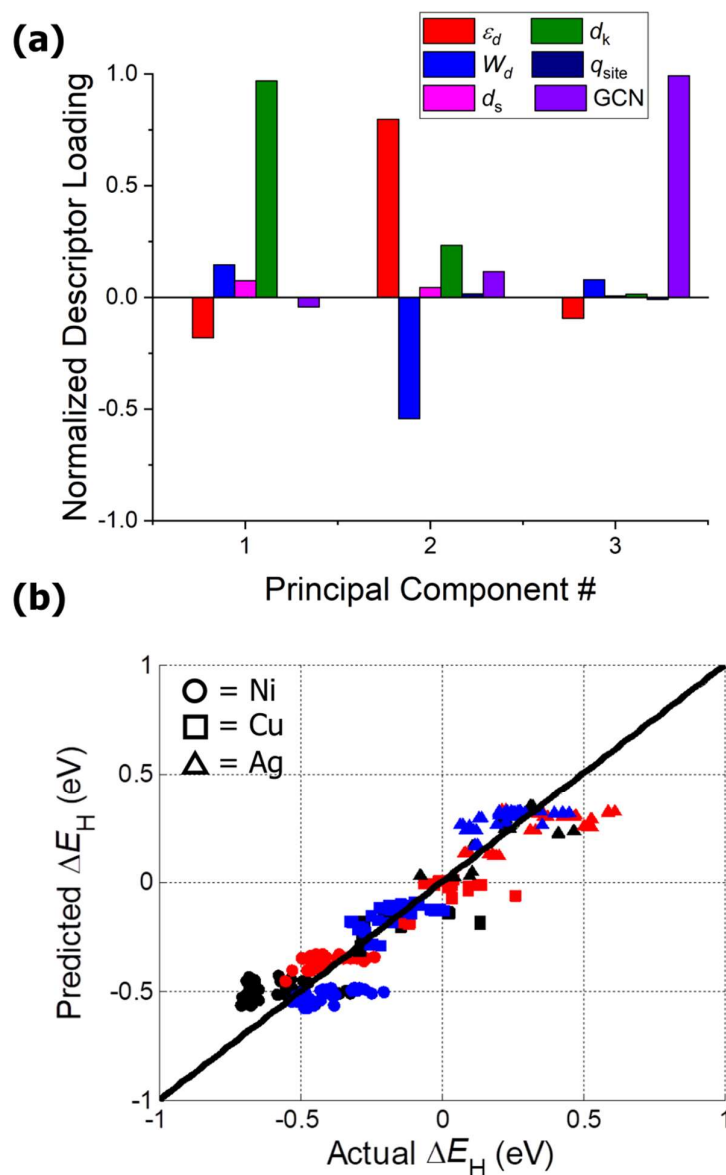


Figure 3.9. (a) Normalized loadings of each descriptor for each of the three primary components included in the regression of hydrogen adsorption energies. ε_d : d band center, W_d : d band width, d_s : skewness of d band, d_k : kurtosis of d band, q_{site} : local charge of the adsorption site, GCN: generalized coordination number. (b) Prediction of adsorption energies of each site for all nanoparticle-supports studied herein. The regression involves a total of 394 data and has a mean absolute error of 0.09 eV. Black, red, and blue data represent graphene, N-graphene, and B-graphene support systems, respectively.

Upon computing the values, or "scores", of each principal component for each adsorption site, the regression model of Equation 3.5 is used to predict the adsorption

energies for each site of the nanoparticle. The full, second-order regression model has ten parameters and is given below:

$$\Delta E_{\text{H}} \text{ (eV)} = -0.058 + 0.014x_1 - 0.315x_2 + 0.088x_3 + 0.004x_1^2 - 0.063x_2^2 - 0.055x_3^2 + 0.003x_1x_2 + 0.008x_1x_3 + 0.002x_2x_3 \quad (3.10)$$

Each principal component, x_i , has a value, or “score”, for each adsorption site which results from the combination of molecular-based descriptors shown in Figure 3.9a.

The standard error of each coefficient was computed according to the method discussed by Faber; all parameters were found to be statistically significant, with the exception for the x_1x_2 and x_2x_3 terms (Figure B.14). Important to note from Equation 3.10 is that the most sensitive term, the linear x_2 term, is the second principal component which primarily captures the d band center and width. This is in accordance with the d band model which usually focuses on the linear contribution of the d band center to surface reactivity⁹². However, from Equation 3.10, the non-linear x_2^2 term, together with both the linear and non-linear x_3 terms (which is primarily composed of the generalized coordination number by Sautet and co-workers) are shown to contribute significantly as well.

As shown in Figure 3.9b, the PCA adsorption model predicts well the adsorption energies on a variety of nanoparticle and support combinations. The mean absolute error is 0.09 eV, which compares well to machine learning adsorption models for CO adsorption where the mean absolute error is approximately 0.2 eV^{113,125}. The main source of error in the PCA model is that its predictions are relatively insensitive to different adsorption sites for the same nanoparticle-support combination, as observed by the horizontal arrangement of data for the same nanoparticle and support in Figure 3.9b. The reason for this shortcoming is twofold. First, the generalized coordination number does not account for the electronic interaction between the nanoparticle and support. The failure of the generalized coordination number model for supported nanoparticles is evident in Figure B.15, where the generalized coordination number is shown to be poorly correlated with the d band center, especially for Ni nanoparticles which were previously shown to interact most strongly

with the support (Figure 3.3). Second, local d band properties are known to differentiate poorly between adsorption sites of similar coordination^{126,127}. In fact, the site-insensitivity of the DFT-computed d band was cited by Sautet and co-workers as a major motivation for the development of the generalized coordination number model¹⁰⁹. Nevertheless, the model does well in predicting the average adsorption properties for each nanoparticle-support combination. Each 37-atom supported nanoparticle has ~ 40 -50 unique adsorption sites; therefore, the PCA model developed herein could potentially enable fast screening of supported nanoparticles by circumventing the need to explicitly compute the adsorption of hydrogen on individual nanoparticle sites.

3.3.6 Size-dependent activity model

Finally, to improve the quantitative accuracy of our HOR/HER activity predictions, we incorporate the nanoparticle size distribution (Equations 3.6-3.8). A normally distributed nanoparticle population with a mean diameter and standard deviation of 20 ± 4 nm is chosen to emulate the published Ni/CNT and Ni/N-CNT systems⁹⁵. Figure 3.10 demonstrates excellent quantitative agreement between the measured and predicted exchange current density for both Ni/CNT and Ni/N-CNT. When size effects are not considered for Ni/N-CNT, the exchange current density is largely overpredicted due to the high density of active sites near the nanoparticle-support interface. For the experimentally synthesized catalysts, however, the fraction of these highly active sites decays exponentially with increasing nanoparticle size. Reducing the size of the Ni nanoparticles supported on N-CNT is predicted to have a highly beneficial impact on the HOR activity (Figure B.16). Based on a recent HEMFC technoeconomic analysis by Yan and co-workers, reducing the nanoparticle size below 5 nm for Ni/N-CNT could allow the power density target of 1 W cm^{-2} to be reached for the HEMFC¹⁰. While our size-dependent activity model is simplistic, it is an important step toward bridging the size gap between computationally tractable DFT models and realistic experimental catalysts. To better assess the general

performance of the size-dependent activity model, experiments with systematic variation of nanoparticle size would be valuable.

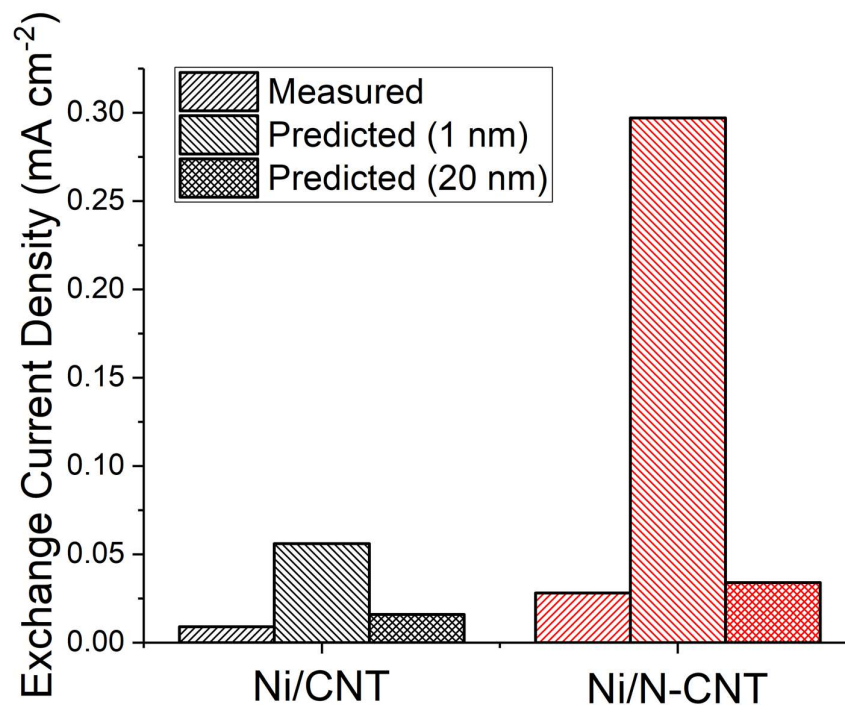


Figure 3.10. Comparison of predicted to measured exchange current densities for the Ni/CNT (Ni/graphene) and Ni/N-CNT (Ni/N-graphene) systems. The "Predicted (1 nm)" exchange current density corresponds to the 37-atom supported nanoparticle computed explicitly herein. The "Predicted (20 nm)" exchange current density is for a nanoparticle size distribution of 20 ± 4 nm (see Figure 3.2b).

3.4 Conclusions

From our studies on nanoparticles of varying compositions supported on graphene and doped graphene, we have found that introduction of either a nitrogen or a boron dopant into graphene leads to a stronger interaction between the nanoparticle and the support. This in turn leads to a weakening of the hydrogen adsorption. For supported Ni nanoparticles, the weakening of hydrogen adsorption leads to higher HOR/HER activity; for the supported Cu and Ag nanoparticles, the weakening of

hydrogen adsorption implies lower HOR/HER activity. Thus, while the effect of dopants on adsorption is qualitatively similar for different metals, the impact of doping on activity depends on the leg of the volcano curve. Heat maps depicting the hydrogen adsorption energy and activity reveal that there is a large degree of site heterogeneity, with sites at the nanoparticle-support interface predicted to have the strongest adsorption in each case. The dopant-induced changes in adsorption energy were shown to be as large as 0.2 eV for supported Ni nanoparticles. We find that the generalized coordination number of Sautet and co-workers is inadequate to describe supported nanoparticles in this size regime. These dopant-induced changes were able to be predicted with a principal component analysis adsorption model, what we believe to be the first use of this method to predict catalytic adsorption properties. Finally, upon accounting for the experimental nanoparticle size distribution, quantitative agreement was obtained between activity predictions and measured values. Given that the interfacial sites of Ni/N-graphene are already most active for HOR, our results suggest that future efforts would benefit from controlling the size of nanoparticles of non-precious catalysts to achieve a greater fraction of sites which are catalytically tuned by the support.

3.5 Acknowledgements

D.G.V., Y.Y., and S.A.G. acknowledge support from the Catalysis Center for Energy Innovation, an Energy Frontier Research Center funded by the U.S. DOE, Office of Science, Office of Basic Energy Sciences under Award No. DE-SC0001004. This research used resources of the National Energy Research Scientific Computing Center, a DOE Office of Science User Facility supported by the Office of Science of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. The authors would like to thank Dr. Stavros Caratzoulas for his assistance in analyzing the Laplacian of the charge density.

Chapter 4

IDENTIFYING ACTIVE SITES OF METAL OXIDES FOR OXYGEN EVOLUTION USING MONODISPERSE NANOPARTICLES

4.1 Introduction

Catalysts for oxygen evolution reaction (OER) are important for water electrolysis, which has been considered a preferable route to the production of renewable hydrogen^{55,128,129}. Identification and manipulation of the active sites are critical to the design and development of high activity OER catalysts. While transition metal oxides (TMOs) have been shown to be a promising OER catalyst, the nature of their active sites remains unclear⁵⁷. The active sites of solid heterogeneous OER catalysts are generally difficult to understand due to the existence of various sites on the solid surface, such as terrace sites, steps, and defects. Thus, model catalysts with controlled site distributions are beneficial for identifying the active sites.

Single crystalline metal electrodes are ideal to identify the facet dependence of the electrochemical activity¹³⁰. For TMOs, however, such an approach has not been adopted because of the difficulty in preparation of single crystalline TMOs electrodes and charge transport limitations arising from the semi-conducting/insulating nature of the oxide¹³¹. The application of TMOs nanoparticles on conductive supports can overcome the charge transport limitations; however, commercially available TMO electrocatalysts have wide size distributions and a variety of nanoparticle morphologies, making the active sites difficult to determine¹³². The monodisperse

nanoparticles developed in the past decades have opened the possibility to precisely control the sites on the surface of the nanoparticles, which can serve as model catalysts for the identification of active sites in the catalytic process^{133–135}. When the size and morphology of each nanoparticle in the supported electrocatalyst is approximately the same, the overall OER performance can be directly correlated to the configuration of a single particle. By adjusting the size and crystallinity of the nanoparticles, the surface sites of the nanoparticles can be manipulated, which allows deeper understanding of the active sites for electrocatalysis and improved design of highly active electrocatalysts. Moreover, the nanoparticle-based model system resembles the practical catalysts more than the single crystal surfaces and thus might provide more relevant insights for catalyst design.

In order to examine the nature of the active sites, we synthesized a series of size- and shape-controlled monodisperse iron oxide nanoparticles as the model electrocatalysts, as iron is found to be an active component for OER in TMOs^{136–138}. The OER activities for the same size nanoparticles with narrow size distributions and varying crystallinity are compared, showing that the amorphous nanoparticles have advantages in OER, a characteristic observed previously but hitherto unexplained in terms of the OER active sites^{139–143}. A systematic study on the nanoparticle size-dependent OER performance for both crystalline and amorphous nanoparticles was conducted. The OER mass activity was found to be linearly correlated to the edge length of the crystalline nanoparticles, and to the volume-normalized surface area of the amorphous nanoparticles. This finding allows for the effect of the edge/defect sites to be identified, and we demonstrate that an increased number of edge/defect sites corresponds to an increased OER activity. Application of density functional theory (DFT) calculations indicates that the increase in activity with decreasing nanoparticle

size is due to the weaker adsorption occurring at the step edge of the nanoparticle. Based on our results on iron oxides, we synthesized amorphous NiFeO_x nanoparticles and demonstrate an order-of-magnitude enhancement of the OER activity compared to the state-of-the-art IrO₂ catalyst. We believe that tuning the crystallinity of the nanoparticle can lead to improved OER performance for a variety of metal oxides, and potentially for a variety of chemistries beyond the OER.

4.2 Methods

4.2.1 Experimental

Experiments synthesized and characterized nanoparticle metal oxide catalysts using a combination of microscopy, x-ray diffraction, and electrochemical tests.

4.2.1.1 Synthesis of carbon supported nanoparticle catalysts

The monodisperse iron oxides nanoparticles were synthesized through slightly modified procedures in literature^{144–146}. The details are described in Appendix C.

For amorphous NiFeO_x nanoparticles (A-NiFeO_x), nickel(II) acetylacetonate (0.25 g, 1.0 mmol), oleylamine (1.60 g, 6.0 mmol) were introduced in a three-neck flask with octadecene (18 mL) at room temperature and magnetically stirred. Then the mixture was flowed with N₂ and heated to 160 °C. A solution made by dissolving Fe(CO)₅ (0.14 mL, 1.0 mmol) and *tert*-butylamine borane (0.26 g, 3.0 mmol) in oleylamine (2 mL) was quickly injected into the solution. The resulting mixture was kept at 160 °C for 20 min and then cooled down to room temperature. Ethanol (50 mL) was added and the precipitate was collected by centrifugation at 8000 rpm for 10 min. The product was washed with ethanol and re-dispersed in hexane.

For loading the nanoparticles on carbon supports, high surface area carbon (Vulcan XC-72, 25 mg) was dispersed in hexane (10 mL) by sonication for 30 min. Then the nanoparticle (10 ~ 20 wt.% to carbon) dispersion in hexane was added, and then sonicated for 1 h. Then the dispersion was transferred to a ceramic boat and

hexane was evaporated naturally in air. The ceramic boat was then placed in a tube furnace under dry air flow (c.a. 100 mL min⁻¹), heated to 185 °C and maintained at this temperature for 5 h before it was cooled down to room temperature. The carbon supported nanoparticle catalysts were collected.

4.2.1.2 Electrochemical measurements

Thin film electrodes of carbon supported metal oxides nanoparticles catalysts were prepared by casting catalyst inks on glassy carbon electrodes (5 mm in diameter, Pine Instruments, polished to a mirror-finishing with 0.05 µm alumina). The catalyst inks were prepared by dispersing 2 mg of carbon supported catalyst in 1 mL of isopropanol with 0.05 wt.% Nafion. The dispersion was sonicated for at least 30 min to form a homogeneous ink. Next, 4 µL of the catalyst ink was deposited on a glassy carbon electrode and dried in air. This procedure was repeated four more times so that a total amount of 20 µL catalyst ink was loaded on electrode, with a total loading (metal oxide and carbon support) of 0.2 mg_(catalyst+C) cm⁻². The metal contents in the catalysts were measured by TGA, which is in range of 10 ~ 20 wt %. Thus, the metal loading of the electrode is in range of 0.02 - 0.04 mg_{metal} cm⁻².

Electrochemical studies were carried out in a standard three electrode system controlled by a potentiostat (Princeton Applied Research). The as-prepared thin film electrode, which served as the working electrode, was mounted onto a rotator. An Ag/AgCl electrode and a Pt wire were used as the reference and counter electrode, respectively. The polarization curves were recorded in O₂-saturated 0.1 M KOH electrolyte with a rotation rate of 2500 rpm. All potentials reported in this paper are referenced to the reversible hydrogen electrode (RHE) potential. The zero volt potential versus RHE was calibrated in the same electrolyte by measuring HOR/HER currents on the Pt disk electrode, whereby the potential at zero current is corresponding to 0 V vs. RHE. All the polarization curves were corrected for solution resistance, which was measured using AC-impedance spectroscopy from 200 kHz to 100 mHz and a voltage perturbation of 10 mV.

4.2.2 Theoretical

DFT calculations were performed to gain an atomistic understanding of the progression of the OER on the Fe₃O₄ nanoparticles with respect to the rate-determining step and the activity of different facets.

4.2.2.1 Computational investigation

DFT+*U* calculations were performed within the Vienna *ab initio* simulation package (VASP, v.5.3.2)⁶³. A 1×1 unit cell with two repeated cells in the *z*-direction was used for each surface, with 15 Å of vacuum included in the *z*-direction to avoid interaction of the surface with its periodic image. Valence electrons of Fe and O were represented with a plane-wave basis set and a 400 eV energy cutoff. Core electrons of Fe and O were represented with the projector augmented wave (PAW) pseudopotential^{66,67}. To represent the electronic exchange and correlation, the RPBE base functional was used due to its improved prediction of adsorption energetics¹⁴⁷. For the 3d electrons of Fe, the Hubbard-type *U* on-site term was implemented according to the rotationally invariant approach introduced by Dudarev *et al*¹⁴⁸. An on-site interaction of $U_{\text{eff}} = U - J = 3.3$ eV was included in accordance with previously used values for Fe^{137,149,150}. Aspherical corrections to the PAW spheres were also included since the use of DFT+*U* frequently results in aspherical charge densities.

The Brillouin zone of each surface was sampled with a $3 \times 3 \times 1$ Monkhorst-Pack *k*-point mesh⁷⁰. A convergence threshold of 10^{-4} eV was used for the electronic optimization. For the geometry optimization, the conjugate gradient method was used, and all ionic forces were converged within 0.05 eV Å⁻¹. The Davidson-block iteration scheme¹⁵¹ was found to provide the best combination of speed and stability for the electronic optimizations.

4.3 Results

4.3.1 Effect of nanoparticle crystallinities

Three types of iron oxide nanoparticles (Figures 4.1a-c) with a narrow size distribution (average size ~ 10 nm, standard deviation less than 10%) and differing crystallinity have been successfully synthesized: crystalline Fe_3O_4 (C- Fe_3O_4), defected crystalline Fe_3O_4 (D- Fe_3O_4), and amorphous iron oxide (A- FeO_x). The degree of crystallinity was controlled by application of the oxidant trimethylamine N-oxide (Me_3NO) and the heating rate during synthesis^{144,145,152}. The selected area electron diffraction (SAED, bottom left in Figures 4.1a-c) and the X-ray diffraction (XRD, Figure C.1) patterns, show that the C- and D- Fe_3O_4 are crystalline, and in the magnetite phase (JCPDS card No. 65-3107). In contrast, only diffuse rings were shown in the pattern for A- FeO_x . To isolate the edge/defect sites of the iron oxide electrocatalyst as the key variable in the current study, it is important that the electronic character of A- FeO_x be similar to C- and D- Fe_3O_4 . In this regard, Wang *et al.* have reported that amorphous FeO_x from air oxidation of Fe has similar electron energy loss spectra (EELS) fine structure features on the O K-edge compared to C- Fe_3O_4 ¹⁵³, which supports the use of C- and D- Fe_3O_4 as appropriate analogs to the A- FeO_x . The high resolution TEM (HRTEM) image in Figure 4.1a shows C- Fe_3O_4 has a cuboctahedral morphology with flat facets and a well-defined lattice fringe. D- Fe_3O_4 shows evidence of a lattice fringe; however, numerous defects are present on the surface (indicated by arrows in Figure 4.1b). A- FeO_x did not show any evidence of a lattice fringe due to the lack of crystallinity (Figure 4.1c). In order to examine their electrochemical activity, the nanoparticles were loaded onto a conductive, high surface area carbon support (VC-72), as indicated by the TEM images (right images in Figures 4.1a-c). After calcination in air, the surfactant on the surface of the nanoparticles was removed while maintaining the crystallinity (XRD in Figure 4.1d, HRTEM and SAED in Figure C.2).

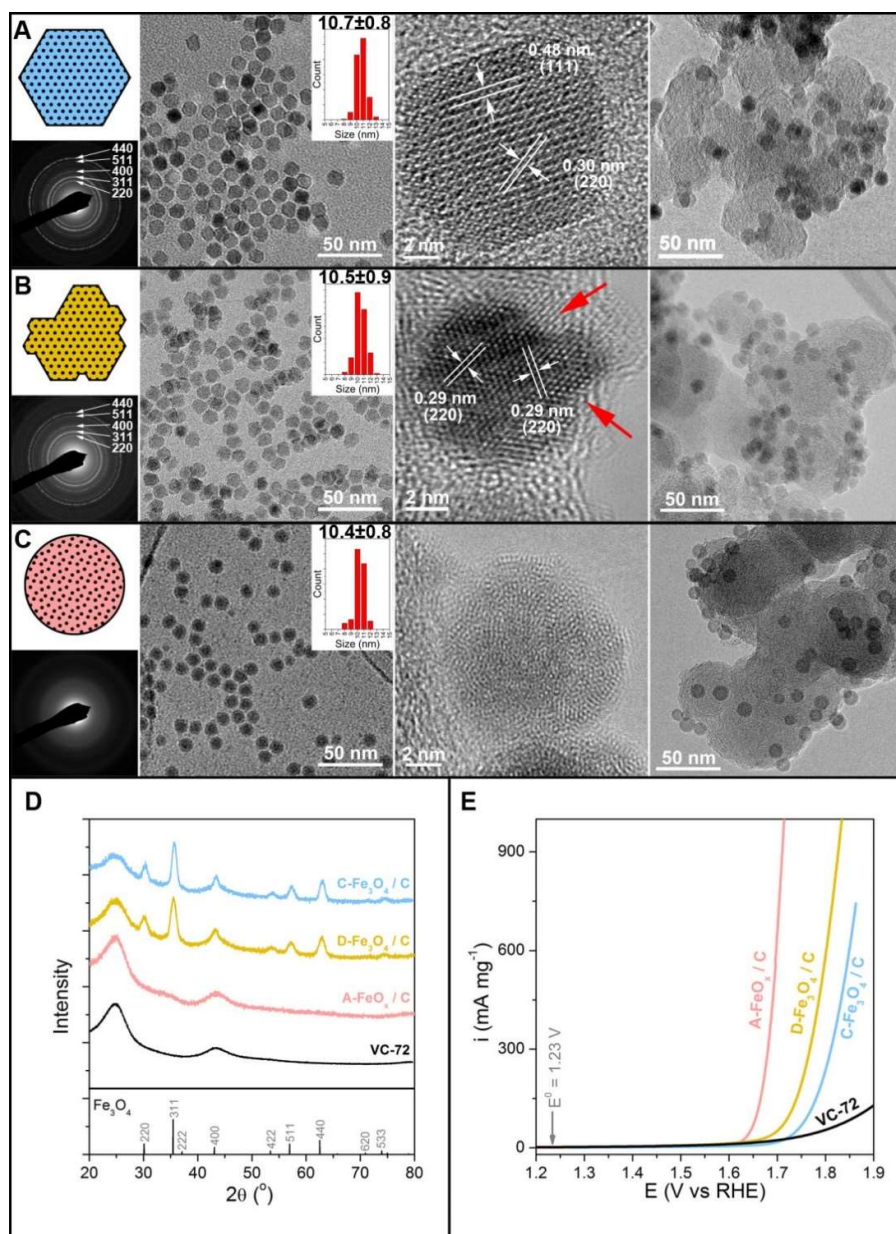


Figure 4.1. Characterizations of C-Fe₃O₄, D-Fe₃O₄ and A-FeO_x nanoparticles and their OER performance. A-C, schematic illustration, SAED pattern, TEM image, size distribution, HRTEM image of the unsupported nanoparticles, and TEM image of the nanoparticles supported on carbon: C-Fe₃O₄ (A); D-Fe₃O₄ (B); A-FeO_x (C). The red arrows in B indicate the defects on the nanoparticle. D, XRD patterns of C-Fe₃O₄/C, D-Fe₃O₄/C and A-FeO_x/C, respectively. The XRD pattern for carbon support (VC-72) is also shown for comparison. The standard pattern of Fe₃O₄ (JCPDS card No. 65-3107) is shown at the bottom of the plot. E, mass normalized polarization curves tested in O₂-saturated 0.1 M KOH at a scan rate of 10 mV s⁻¹. For C-Fe₃O₄/C, D-Fe₃O₄/C and A-FeO_x/C, the curves were normalized to the mass of Fe. For VC-72, the curve was normalized to the mass of 10% of the carbon.

The OER activity was measured through a standard three-electrode system in an O₂-saturated 0.1 M KOH electrolyte. The OER activities were normalized by the metal mass of the nanoparticles (Figure 4.1e) obtained by a thermogravimetric analysis (TGA, shown in Figure C.3). Here, nanoparticles with the same sizes are utilized to exclude size effects and charge transport limitations. The A-FeO_x nanoparticles demonstrate the best performance, followed by D-Fe₃O₄, and C-Fe₃O₄. Furthermore, the oxidation of the VC-72 support is shown to be negligible when testing the OER performances of the iron oxide nanoparticles. The trend in the electrochemical activity was hypothesized to result from the presence of surface defects, since the OER activity of the iron oxide catalysts was found to correlate with the number of edge/defect sites on the catalyst.

4.3.2 Effect on nanoparticle sizes

As the size of the cuboctahedral nanoparticle decreases, a larger fraction of the edge sites become exposed. Based on our hypothesis that the increased OER activity is a result of the edge/defect sites, the electrocatalytic activity should increase with decreasing nanoparticle size. To confirm this hypothesis, a series of the monodisperse crystalline Fe₃O₄ nanoparticles (Figure 4.2a) with different particle sizes were systematically studied. Another series of the monodisperse amorphous FeO_x nanoparticles (Figure 4.2d) was selected for comparison. A detailed characterization of the nanoparticles is shown in Figures C.4-C.6. A full description of the effect of the nanoparticle size on the edge length and surface area is shown in the Table C.1, with the results for our nanoparticles being summarized in Table C.2. The OER activities of the C-Fe₃O₄ with different sizes at an overpotential of 0.55 V were normalized to the surface area and plotted versus the nanoparticle size in Figure C.7a. The smaller nanoparticles demonstrate a higher surface area specific activity, similar to what has been reported previously for Co₃O₄¹⁵⁴. A linear relationship was demonstrated correlated between the OER mass activity with the edge length (Figure 4.2c) rather than the surface area (Figure 4.2b), indicating the active sites are located on the edge

of the crystalline nanoparticles. By contrast, the surface-area-normalized activity of A-FeO_x nanoparticles does not show size effect (Table C.3 and Figure C.7b), while their mass activity shows a linear dependence on the overall surface area of the amorphous nanoparticles (Figures 4.2e-f). This suggests that due to the isotropic nature of the amorphous nanoparticle, the active sites are evenly distributed on the amorphous nanoparticle surface. Note that the current densities for amorphous nanoparticles are obtained at a lower overpotential (0.45 V) than the crystalline nanoparticles (0.55 V) due to the amorphous nanoparticles having a higher OER activity.

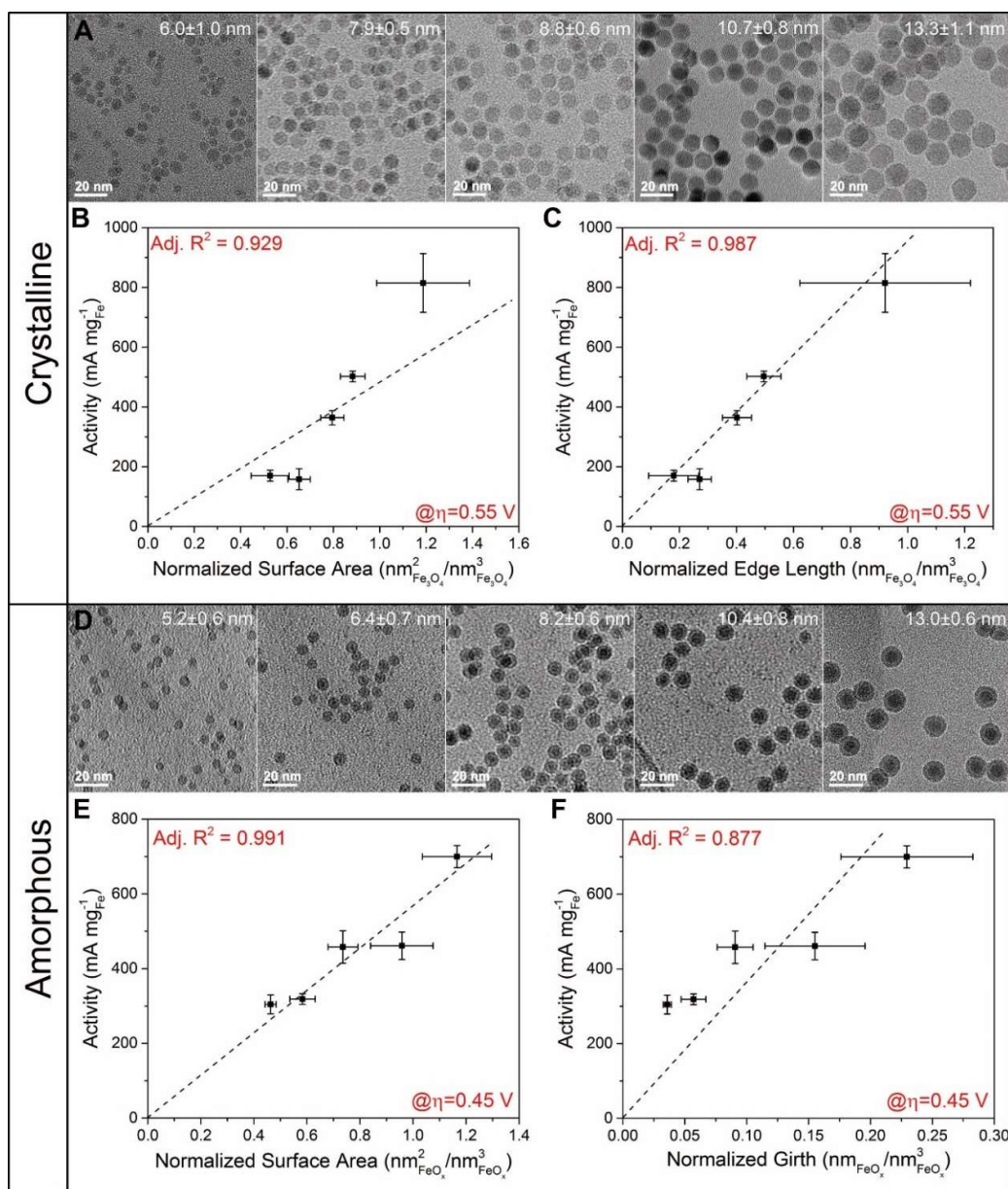


Figure 4.2. Size effects on OER of crystalline and amorphous nanoparticles. A, TEM images of C-Fe₃O₄ nanoparticles with different sizes. B, plot of mass activity at 0.55 V overpotential versus surface area for C-Fe₃O₄ nanoparticles. C, plot of mass activity at 0.55 V overpotential versus edge length of C-Fe₃O₄ nanoparticles. D, TEM images of A-FeO_x nanoparticles. E, plot of mass activity at 0.45 V overpotential versus surface area for A-FeO_x nanoparticles. F, plot of mass activity at 0.45 V overpotential versus girth for A-FeO_x nanoparticles. The error bar of the activity comes from at least three independent tests. Note that the current densities for amorphous nanoparticles are obtained at a lower overpotential (0.45 V) than the crystalline nanoparticles (0.55 V) due to the amorphous nanoparticles having a higher OER activity.

4.3.3 Theoretical Investigation

To gain an atomistic understanding of the origin of the enhanced edge site activity, the thermodynamics for the OER process is examined at the DFT level. OER is assumed to proceed through a four-electron electrochemical oxide pathway,¹⁵⁵ with one electron being transferred per step (see Appendix C for details). Consistent with the TEM images, we consider a cuboctahedral Fe_3O_4 nanoparticle (Figure 4.3), which exposes six (100) and eight (111) facets, resulting in 24 edges located at the boundary of the (100) and (111) facets. Here, the stepped (211) facet shown in Figure C.8 was used to model the edge, a common approximation made in the literature^{91,156}. The lowest energy terminations of the (100), (111), and (211) facets are shown in Figure C.9, and the adsorption of OH^* on each surface is shown in Figure 4.3a.

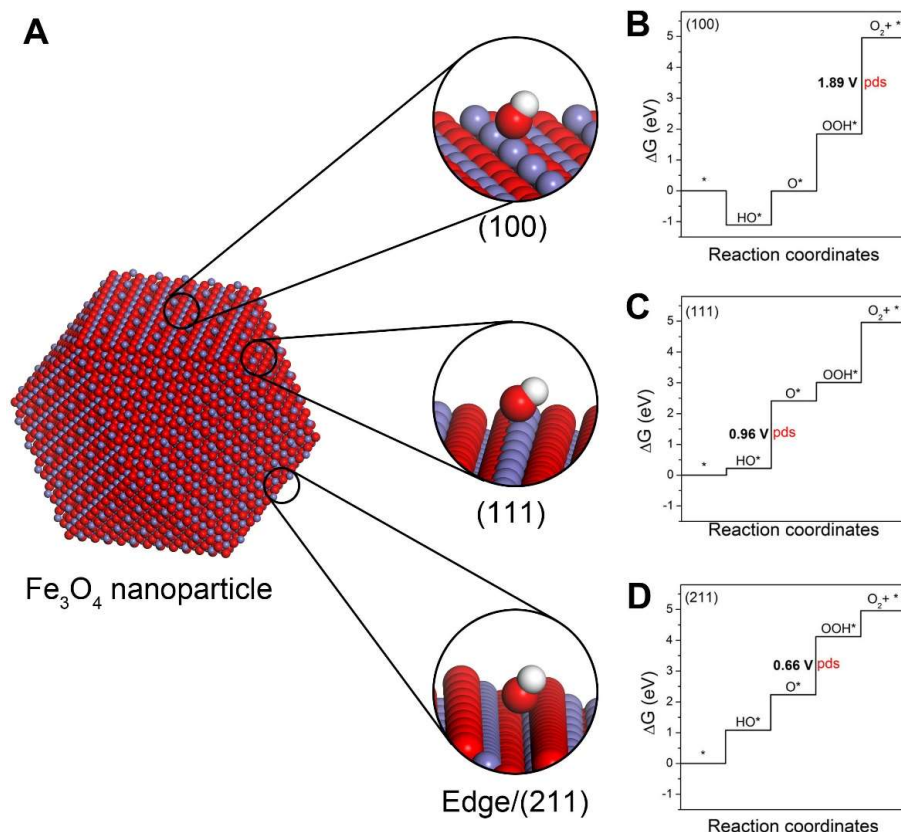


Figure 4.3. Structural model of a cuboctahedral Fe_3O_4 nanoparticle and the standard free energy diagram for the OER calculated with RPBE+ U . A, structural illustration of a cuboctahedral Fe_3O_4 nanoparticle and adsorption sites on (100), (111) surfaces, and edge, respectively. Purple, red, and white spheres represent Fe, O, and H, respectively. B-D, the free energy diagram for the OER on different Fe_3O_4 surfaces with the overpotential of the potentially-determining step (pds) labeled.

The standard free energy diagrams for the OER process on the different active sites are shown in Figures 4.3b-d, with the overpotential given in Table C.4. On the (100) and (111) surfaces, the intermediates are strongly bound to the undercoordinated Fe_{tet} surface atoms. Consequently, the desorption of the OOH^* intermediate is always highly endergonic for these surfaces. The (100) and (111) surfaces require an overpotential of 1.89 V and 0.96 V, respectively. The strong adsorption of intermediates observed at the undercoordinated sites is in agreement with recent work by Sautet *et al.*¹¹⁰ For the (211) surface, the intermediates adopt a bridge configuration, as shown in Figure 4.3a. Adsorption is less favorable and is found to

decrease along the step edge resulting in an overpotential of 0.66 V. In agreement with experiment, the DFT calculations indicate the step edges are the active site, with reaction intermediates adsorbed at the Fe_{tet}-Fe_{oct} bridge location. Moreover, the free energies for the formation of OH* and OOH* are linearly related with a slope of unity, in agreement with the universal scaling relation proposed by Nørskov *et al.*¹⁵⁵. Insertion of the DFT results into the Butler-Volmer model (Figure C.10) demonstrates the specific current density decreases as the nanoparticle size increases (in agreement with experiment). As the step edge density decreases as the nanoparticle size increases, this provides further evidence that only the edge sites are electrochemically active.

It is important to note that the Fe_{oct} termination of the (100) surface (Figure C.11) can become more favorable at high oxygen chemical potential (i.e., oxidative electrode potentials)¹⁵⁷. The Fe_{oct}-terminated (100) surface yields a similar overpotential (within ~0.01 eV) to the (211) edge (Table C.4), indicating an enhanced activity for OER as the potential increases. However, the Fe_{oct}-terminated (100) surface will only be stable over a small potential. Additionally, the as-synthesized Fe₃O₄ nanoparticles can be oxidized to Fe₂O₃ at the pH and electrode potential of relevance to the OER¹⁵⁸. We note, however, that the lowest energy termination of the Fe₂O₃ (100) surface, across a broad range of oxygen chemical potentials, has a similar Fe_{tet} termination to the Fe₃O₄ (100) surface considered in the present work¹⁵⁹. As a result, we believe the qualitative trends predicted from our Fe₃O₄ (100) surface are still applicable even in the presence of surface oxidation. A possible OER proceeding through a Mars-van Krevelen mechanism¹⁶⁰, wherein a defect site is consumed and regenerated, has also been calculated for the (211) surface (Figure C.12 and Table C.5). Overall, we find the OOH decomposition step (which regenerates the vacancy) is determined to be highly endothermic, thus we rule out the occurrence of a Mars-van Krevelen mechanism at the step sites.

Clearly, though, the role of the defects in OER is not limited to the active sites found on the step edges, raising the possibility of terrace defects causing enhanced

electrochemical activity. Furthermore, previous studies have demonstrated that sub-surface defects (such as metal interstitials) can migrate to the surface¹⁶¹, but their effect on the electrochemical activity is unknown. Thus, the role of surface defects on OER will require a deeper understanding of the defect chemistry of TMOs, which is beyond the scope of the current study.

4.3.4 Discussion

The step edge sites are analogous to the low-coordination sites in crystalline nanoparticles. The amorphous nanoparticles, however, do not have long-range ordering and are full of surface defects. Thus, amorphous nanoparticles have high concentrations of low-coordination sites at their surface which appear analogous to the edge sites of crystalline nanoparticles. Prior work has demonstrated a significant decrease in the metal coordination number, a frequently used descriptor for surface reactivity¹¹⁰, when transitioning to the amorphous phase^{162,163}. Due to the high concentration of these sites on the surface of the amorphous nanoparticles, they have higher OER activity than the corresponding crystalline nanoparticles. Furthermore, since the amorphous nanoparticles are isotropic, no size effect is exhibited (they have the same surface area specific activity regardless of their size).

Based on these understandings, we evaluate the benefit of an amorphous nanoparticle structure in NiFeO_x to gain superior OER activity, as NiFe mixed oxides have been shown better OER activity than single oxides^{137,138,142}. Amorphous NiFe nanoparticles were synthesized, then supported on carbon and further oxidized to amorphous NiFeO_x nanoparticles supported on carbon (A-NiFeO_x/C). The morphology of the NiFeO_x nanoparticles was subsequently examined using TEM and HRTEM, and their structure studied through XRD as shown in Figure 4.4a and Figure C.13, confirming the amorphous nature of the NiFeO_x nanoparticles. Energy dispersive spectra (EDS) (Figure C.13h) indicate the mixed composition of Ni and Fe. As expected (Figure 4.4b), the A-NiFeO_x/C displayed higher OER activity than the crystalline NiFe₂O₄ nanoparticles supported on carbon (C-NiFe₂O₄/C, TEM, HRTEM

images, SAED, XRD patterns and EDS spectra are shown in Figure C.14). The A-NiFeO_x/C demonstrated ultra-high OER activity, even higher than the state-of-the-art OER catalyst IrO₂. Comparing the mass activity at 300 mV overpotential, the A-NiFeO_x/C shows over an order-of-magnitude improvement compared to IrO₂ (inset of Figure 4.4b). The A-NiFeO_x also shows a low Tafel slope of 32 mV dec⁻¹ (Figure 4.4c) and outstanding durability (Figure 4.4d). At a loading of 0.1 mg_{Fe+Ni} cm⁻², only 0.28 V of overpotential is needed to achieve a current density of 10 mA cm⁻², which is among the best OER catalysts to date (Table C.6). After a 12 h durability test at a current density of 10 mA cm⁻², the A-NiFeO_x maintained the OER performance with only a few millivolts increase of the overpotential. In contrast, the overpotential for the benchmark IrO₂ catalyst increased throughout the test period, probably due to the dissolution of IrO₄²⁻ formed during the test^{164,165}. After the durability test, the A-NiFeO_x maintained its amorphous structure (Figure C.15).

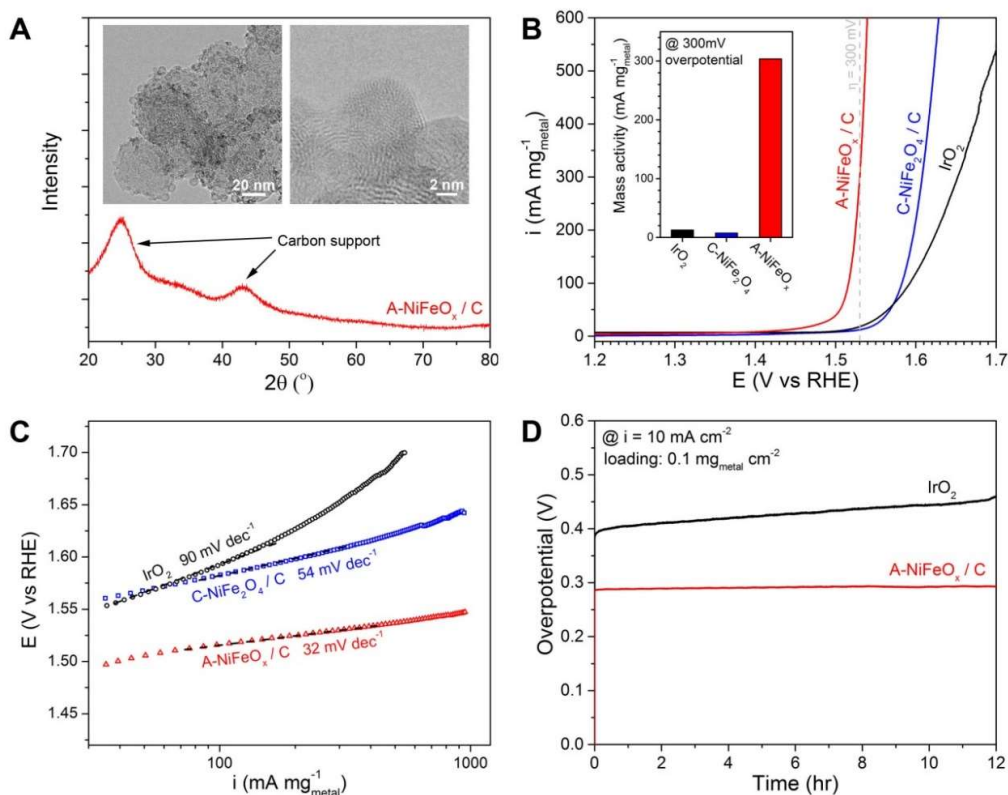


Figure 4.4. Amorphous NiFeO_x nanoparticles supported on carbon and their OER performances. A, XRD of the A-NiFeO_x/C catalysts. Insets are the TEM and HRTEM images of the A-NiFeO_x/C. B, total metal mass normalized polarization curves of the A-NiFeO_x/C, C-NiFe₂O₄/C, and IrO₂ catalysts in O₂-saturated 0.1 M KOH at a scan rate of 10 mV s⁻¹. Inset is the mass activity at 300 mV overpotential. C, Tafel slopes of the A-NiFeO_x/C, C-NiFe₂O₄/C, and IrO₂. D, chronopotentiometry curves of A-NiFeO_x/C and IrO₂ at a current density of 10 mA cm⁻² in O₂-saturated 0.1 M KOH.

4.4 Conclusions

In summary, the active sites for OER were identified as the low-coordination sites (edge, defects or amorphous sites) by using monodisperse nanoparticles as the model catalysts. The correlation of the OER activity with sites distribution of the nanoparticle surface was systematically studied through a series of sizes and crystallinity controlled monodisperse nanoparticles. The amorphous nanoparticles showed the highest OER activity and no size dependent area specific activity, due to the high concentration of defect sites evenly distributed on the surface. Our findings demonstrate that a significantly higher OER activity can be achieved through the use

of amorphous nanoparticles, and that these amorphous nanoparticles exhibit excellent stability for use in electrolyzers.

4.5 Acknowledgements

I would like to thank the co-authors of this work, Prof. Zhongbin Zhuang and Prof. Yushan Yan, for their contribution of materials therein related to experimental synthesis, characterization, and electrochemical testing. I would like to thank the co-authors of this work, Dr. Glen R. Jenness and Prof. Dionisios G. Vlachos, for their contributions and insights related to the computational calculations and the writing of the manuscript.

This work was supported by the Advanced Research Projects Agency – Energy (ARPA-E) under the award No. DE-AR-0000009. The computational work was financially supported from the Catalysis Center for Energy Innovation, an Energy Frontier Research Center funded by the US Department of Energy, Office of Science, Office of Basic Energy Sciences under Award No. DE-SC0001004. S.A.G. acknowledges a UDEI fellowship. This research used resources of the National Energy Research Scientific Computing Center, a DOE Office of Science User Facility supported by the Office of Science of the US Department of Energy under Contract No. DE-AC02-05CH11231.

Chapter 5

A UNIVERSAL DESCRIPTOR FOR HYDROGEN OXIDATION AND EVOLUTION REACTIONS OVER PLATINUM GROUP AND COINAGE METALS

5.1 Introduction

Hydrogen oxidation and evolution reactions (HOR/HER) are the simplest electrochemical reactions and yet some of the most technologically important reactions for fuel cells, electrolyzers, and flow batteries where HER is often an undesirable side reaction. For platinum group metals (PGMs) such as Pt, Ir, Pd, and Rh, the HOR/HER activity decreases by about two orders of magnitude from acid to base^{17,38,53,89}. The Gibbs free energy of hydrogen adsorption (ΔG_H^0), or the associated hydrogen binding energy (HBE), has been recognized as the descriptor for HOR/HER activities: correlating HOR/HER activities and ΔG_H^0 of various metals generates a volcano shaped plot in both acid and base^{18,34,35,166}. The binding energy between hydrogen and a metal surface, however, is relatively constant with respect to the electric field and pH³⁷. Consequently, the adsorption energy of hydrogen alone cannot explain the pH-dependent nature of either the HOR/HER activity or the H_{upd} desorption peak position, as measured in cyclic voltammograms (CVs).

Despite the simultaneous change in both the HOR/HER activity and H_{upd} peak position with pH, most theoretical research thus far has focused on attempting to explain the pH dependence of the H_{upd} peak position. Schwarz *et al.* found that approximately 0.2 electrons (e^-) are transferred from water to Pt (110), and attributed the pH effect on the H_{upd} peak potential to the partial oxidation of water adsorption on step sites of metals⁴². However, Schwarz *et al.* found no evidence for the partial *reduction* of water on coinage metals (Au, Cu, and Ag), and thereby were unable to explain why the HOR/HER activity decreases for these metals as experimentally

observed in this study. Alternatively, Janik *et al.* explained the positively shifted H_{upd} peak via the weakened OH_{ad} adsorption strength induced by the co-adsorption of cations (e.g., K^+ , Li^+ , Na^+ , Cs^+)¹⁶⁷. However, the hypothesis that OH_{ad} formation is weakened at high pH due to cation adsorption contradicts the CO stripping data which indicate that OH_{ad} formation strengthens with increasing pH.³⁸ Moreover, the equilibrium adsorption potential for K^+ on the Pt (110) step had previously been computed to occur at ~ -0.73 V vs. SHE⁴¹. Therefore, for HOR/HER occurring at 0 V vs. the reversible hydrogen electrode (RHE), the K^+ adsorption reaction would not become exergonic until $\sim \text{pH } 12$. In contrast, experimental evidence shows that the H_{upd} peak position and the HOR/HER exchange current density vary across the *entire* pH range.

While all the aforementioned theories on the pH-dependent nature of the H_{upd} adsorption/desorption energies and the HOR/HER rates have aided in providing physical insights, none of them can satisfactorily explain the behavior of different metals across the entire pH range. In a recent Perspective, Zheng *et al.* have suggested that water, which is ubiquitously present at the electrochemical interface, could act to displace, or be displaced by, adsorbed hydrogen during the HOR/HER process³⁶. In this study, we use density functional theory (DFT) simulations to isolate the interaction of water with a variety of electrode surfaces as a function of pH. The Gibbs free energy of water adsorption was found to weaken with increasing pH for the (110) surfaces of PGMs (Pt, Ir, Pd, and Rh). For Au and Cu, however, water adsorption was found to strengthen with increasing pH. Water was found to interact only weakly with Ag, and its adsorption was unaffected by pH. The newly defined apparent Gibbs free energy of hydrogen adsorption, $\Delta G_{\text{H, app}}$, was found to be in good quantitative agreement with the measured H_{upd} peak potentials for Pt, Ir, Pd, and Rh. Combination of the measured HOR/HER exchange current densities of both PGMs and the coinage metals with the simulated $\Delta G_{\text{H, app}}$ values from DFT suggests the existence of a universal HOR/HER volcano plot for all metals and pHs when $\Delta G_{\text{H, app}}$ is employed as the thermodynamic descriptor. The weakened water adsorption with

increasing pH for the PGMs is also shown to lead to earlier formation of OH_{ad}, in qualitative agreement with CO stripping results.

5.2 Methods

Zheng *et al.* have previously suggested that water adsorption (desorption) accompanies hydrogen desorption (adsorption) in the experimental CVs and HOR/HER in general³⁶. Consequently, we define a new thermodynamic descriptor for HOR/HER, the apparent Gibbs free energy of hydrogen adsorption, as follows:

$$\Delta G_{H,app} = \Delta G_{H,vac} - \Delta G_{H_2O} \quad (5.1)$$

where $\Delta G_{H,vac}$ is the Gibbs free energy of hydrogen adsorption in vacuum and ΔG_{H_2O} is the Gibbs free energy of water adsorption. The Gibbs free energy of hydrogen adsorption in vacuum is defined with reference to the gas-phase hydrogen molecule

$$\Delta G_{H,vac} = G_{H^*} - G_* - \frac{1}{2} G_{H_2} \quad (5.2)$$

where G_{H^*} is the Gibbs free energy of the electrode surface with hydrogen adsorbed, G_* is the Gibbs free energy of the clean electrode surface, and G_{H_2} is the Gibbs free energy of the gas-phase hydrogen molecule. In this work, we have applied a constant entropic correction of 0.24 eV as suggested by Nørskov *et al.*³⁵ to the electronic energies obtained from DFT. Therefore, Equation 5.2 is rewritten as

$$\Delta G_{H,vac} = \Delta E_{H,vac} + 0.24 \text{ eV} = E_{H^*} - E_* - \frac{1}{2} E_{H_2} + 0.24 \text{ eV} \quad (5.3)$$

where E_i is the DFT energy for species i .

To compute ΔG_{H_2O} , we use an extended hydrogen-bonded water network consisting of 48 water molecules in total. The structure of the interfacial water considered herein was assigned either an H-up or H-down orientation. The H-up and H-down water structures were initialized with the structure of the hexagonal ice-like water bilayer first discussed by Bernal and Fowler¹⁶⁸. A schematic of the H-up/H-down water networks is provided in Figure 5.1. DFT simulations are used to optimize the H-up and H-down water networks and to compare the relative energies of each.

The binary H-up/H-down interpretation of the water dipole has been employed successfully in previous work for various surfaces^{37,169,170}.

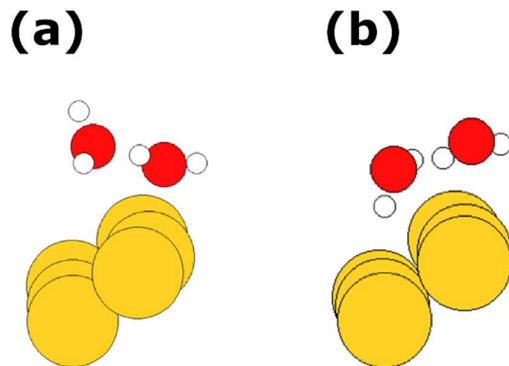


Figure 5.1. (a) H-up water orientation. (b) H-down water orientation. Repeating water molecules in the x , y , and z -directions are omitted for clarity.

While most previous work has modeled the electrochemical double layer with a single layer of aqueous solvent^{170–172}, herein, we use three layers of water on both sides of the periodic surface. The three layers of water used to model the near-electrode environment is reminiscent of the inner and outer Helmholtz planes (IHP and OHP, respectively) which together comprise the region nearest the electrode surface^{27,173}. Water in the third layer was found to be relatively unaffected by changes in the electrode potential, and three layers of water were therefore deemed to be adequate to model the water covered electrode surface (see Figure D.1). The requirement to simultaneously model multiple layers of solvent on both sides of the periodic surface is due to both our treatment of *charged* surfaces (insufficient charge screening will lead to large error in the computed electrostatic potential) and the need to limit the induced dipole normal to the surface. $\Delta G_{\text{H}_2\text{O}}$ is then

$$\Delta G_{\text{H}_2\text{O}} = G_{*/\text{H}_2\text{O}} - G_* - G_{\text{H}_2\text{O}} \quad (5.4)$$

where $G_{*/\text{H}_2\text{O}}$ is the Gibbs free energy of the combined metal/water system, G_* is the Gibbs free energy of metal surface in vacuum, and $G_{\text{H}_2\text{O}}$ is the Gibbs free energy of the water network in the absence of the metal surface. To conserve computational

resources, we apply a similar constant entropic correction analogous to Equation 5.3. For the water molecule, incorporating the change in entropy upon adsorption along with the change in solvation between the bulk and adsorbed states, we obtain an entropy correction of 0.49 eV. A detailed description of the entropy correction scheme is provided in the Appendix D. Therefore, analogous to Equation 5.3 we arrive at the following equation for the Gibbs free energy of water adsorption:

$$\Delta G_{\text{H}_2\text{O}} = \Delta E_{\text{H}_2\text{O}} + 0.49\text{eV} = \frac{1}{N_{\text{H}_2\text{O}}} (E_{*/\text{H}_2\text{O}} - E^* - N_{\text{H}_2\text{O}} E_{\text{H}_2\text{O}}) + 0.49\text{ eV} \quad (5.5)$$

where E_i is the DFT energy for species i .

To draw a qualitative comparison to measured OH_{ad} onset potentials from CO stripping, free energies of hydroxyl formation were also computed for the (110) surfaces of Pt, Ir, Pd, and Rh. The hydroxyl formation energies were computed according to Equation 5.6, while accounting for stabilization by co-adsorbed water in a manner analogous to McCrum and Janik⁴¹.

$$\Delta G_{\text{OH}} = \frac{1}{N_{\text{OH}^*}} (G_{\text{OH}^*/\text{H}_2\text{O}^*} + N_{\text{OH}^*} (G_{\text{H}^+ + e^-}) - G_{\text{H}_2\text{O}^*}) \quad (5.6)$$

where N_{OH^*} is the number of adsorbed hydroxyls present on the surface, $G_{\text{OH}^*/\text{H}_2\text{O}^*}$ is the free energy of the co-adsorbed hydroxyl and water, $G_{\text{H}^+ + e^-}$ is the free energy of the proton-electron pair (equal to $\frac{1}{2} G_{\text{H}_2}$ at equilibrium), and $G_{\text{H}_2\text{O}^*}$ is the free energy of the metal surface with one monolayer (ML) of water adsorbed on the (110) step.

Periodic density functional theory (DFT) calculations were performed using the Vienna ab initio simulation package (VASP, version 5.4.1)⁶³. The RPBE exchange-correlation functional¹⁴⁷ with D3 dispersion corrections¹⁷⁴ was selected because of its good representation of structured water networks and accurate reproduction of the absolute standard hydrogen electrode potential^{175,176}. The core electrons were represented with the projector-augmented wavefunction (PAW) method⁶⁶, and a plane-wave cutoff of 350 eV was used for the valence electrons. The Methfessel–Paxton method of electron smearing was used with a smearing width of 0.1 eV⁶⁸. All geometry optimizations were performed using the quasi-Newton scheme as implemented in VASP. The forces and energies were converged to 0.05 eV Å⁻¹ and

10^{-4} eV, respectively. All calculations were performed with spin-polarization and at the Γ -point. Dipole corrections were applied in the z -direction, normal to the electrode surface. Higher accuracy geometry optimizations on Au(110) were also performed at a plane-wave cutoff of 400 eV and a Monkhorst-Pack k -point mesh⁷⁰ of $3 \times 3 \times 1$, and the adsorption energetics of both the H-up and H-down configurations were found to change by less than 0.05 eV. Upon geometry optimization, computation of the electrostatic potential and Bader charges¹⁷⁷ were done at a plane-wave cutoff of 400 eV and a k -point mesh of $3 \times 3 \times 1$ for all surfaces.

Ab initio molecular dynamics (AIMD) was also performed in VASP to further exploit the water network. The system was treated as an NVT ensemble with dynamics performed at 298 K, with a friction coefficient of $\gamma = 5 \text{ ps}^{-1}$ in a methodology analogous to the one employed by Sakong *et al.* to study a Pt(111)-water system¹⁷⁵. A time step of 1 fs was used and the trajectory was 10 ps in length.

In the current study, the (110) surfaces of Pt, Pd, Ir, Rh, and Au were modeled, along with the (111) surface of Ag. The (110) surfaces of PGMs were chosen since, in previous studies, one of the clearly visible H_{upd} peaks in Pt cyclic voltammetry is the (110) step. The (110) surface was also chosen for Au since its hydrogen binding energy was found to be 0.25 eV more optimal than that of Au (111), suggesting that Au (110) has a higher intrinsic activity and is, therefore, a relevant surface to model. In contrast, Ag (111) was chosen since its hydrogen binding energy was found to be nearly identical to Ag (110), and due to the generally higher fraction of terrace sites. For Cu, the $(2\sqrt{2} \times 2)\text{R}45^\circ\text{-O}$ surface was chosen, as it has been previously identified as the predominant Cu surface at the pHs and electrode potentials of interest herein¹⁷⁸. In all cases, hydrogen is considered to be adsorbed at the most energetically favorable adsorption site on each site: the short bridge on the (110) facet, the *fcc* site of the (111) facet, and the surface oxygen species of the $(2\sqrt{2} \times 2)\text{R}45^\circ\text{-O}$ Cu surface. In all cases, a 3×4 unit cell was used as this produced the least strain in the ice-like water bilayer, except for a 4×4 unit cell used for Cu. An internal vacuum layer of at least 12 Å in the z -direction was inserted for all surfaces in order to extract the absolute

electrode potential. An example of extracting the absolute potential and the corresponding pH from a computed electrostatic potential profile is provided in Appendix D. To manipulate the absolute potential of the electrode, electrons were either added to or subtracted from the neutral unit cell. To directly compare the electronic energies of unit cells of different charge, all energies must be corrected. Herein, we follow the methodology of Taylor *et al.*, described in detail elsewhere¹⁷⁹. The absolute electrode potential is then equal to the converged electrostatic potential, averaged in the *xy*-plane, within the vacuum layer. An example of the electrostatic potential profile is shown in Figure D.2. The absolute electrode potential is then referenced to the standard hydrogen electrode (SHE) by subtracting the absolute potential of the SHE. The value of 4.281 V, determined to be the absolute potential of the SHE in a prior study by Isse *et al.*, is used in this work¹⁸⁰. Lastly, the pH dependence of the adsorption energy of the water structures was elucidated through the Nernst equation, wherein the absolute electrode potential is fundamentally related to the pH as follows²⁷:

$$E = E_0 - 2.303 \frac{RT}{F} \text{pH} \quad (5.7)$$

where E is the absolute electrode potential determined from the electrostatic potential profile, and E_0 is the absolute potential of the SHE equal to 4.281 V. In the range of pH from 0 to 14, the pH at 0 V vs. RHE is directly related to the absolute electrode potential E (corresponding from 0 V vs. SHE to -0.826 V vs. SHE) as determined from the electrostatic potential. Consequently, our underlying assumption is that the effect of pH can primarily be captured by the absolute potential, where the role of water has been isolated through the omission of the electrolyte. This assumption is supported by the observation that the potential of zero charge remains relatively constant (vs. the *SHE* scale) as a function of pH, similarities in spectroscopic features at the same absolute potential, and the universal pH-dependent kinetics of different buffer solutions^{38,181,182}.

5.3 Results

5.3.1 pH-dependent water adsorption on PGMs

Using *ab initio* DFT calculations, we find that the adsorption energy of water on the (110) surfaces of Pt, Ir, Pd, and Rh weakens with increasing pH (*i.e.*, a more negative potential on the SHE scale). The adsorption energies of the H-up and H-down water structures are shown in Figure D.3 for the (110) stepped surfaces of Pt, Ir, Pd, and Rh. In each case, the H-up water orientation is preferred at pH 0. However, as the absolute electrode potential becomes more negative with increasing pH, the H-up orientation gradually becomes less favorable at a rate of (14 ± 3) mV/pH unit for the four metals shown. In the case of Pt, Ir, and Rh, the H-down configuration is more favorable at pH 14. The trend of the water orientation with pH on a typical PGM as evidenced from the DFT simulations is depicted schematically in Figure 5.2b. In all cases, the adsorption energy of water weakens as the pH increases (Figure 5.2a). The consequence for the HOR/HER is that the *apparent* free energy of hydrogen adsorption, strengthens as the pH is increased.

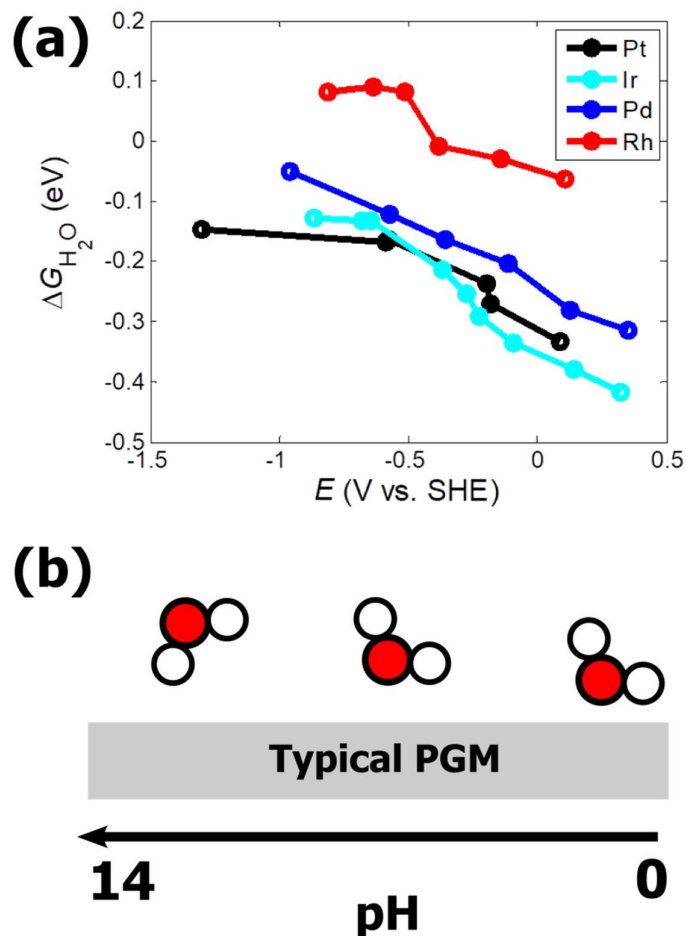


Figure 5.2. (a) Free energies of water adsorption computed from DFT for the (110) surfaces of Pt, Ir, Pd, and Rh, versus the absolute potential. Equation 5.7 relates the absolute potential to the pH. (b) Schematic of the pH-dependent water orientation on the (110) facet of a typical PGM as a function of the pH.

5.3.2 pH-dependent water adsorption on coinage metals

While the H-up water network is the predominant water orientation on PGMs and becomes weaker with increasing pH, the H-down orientation is more stable over the majority of the pH range and becomes more stable with increasing pH for Au (Figure D.4). A similar trend is also seen for Cu (Figure D.5), where the H-down becomes more stable with increasing pH (the H-up network was found to re-orient into the H-down orientation), depicted schematically in Figure 5.3b As a result, the water adsorption energy increases as the pH increases, as shown in Figure 5.3a. Due

to the apparent hydrogen adsorption energy being already too weak at pH 0, the strengthening of the H-down orientation ultimately leads to a further weakening of $\Delta G_{\text{H,app}}$, consequently leading to the observed decrease in HOR activity of Au and Cu with pH (Figure D.12). A prior study incorporating both AIMD and x-ray absorption spectroscopy (XAS) has highlighted the preference of water to adsorb in a H-down configuration on the Au surface¹⁸³. To our knowledge, this work represents the first computational effort on water interacting with the $(2\sqrt{2} \times 2)\text{R}45^\circ\text{-O}$ surface of Cu (100), previously shown to be the preferential Cu surface at HOR/HER conditions¹⁷⁸. However, due to the presence of oxygen species on the Cu surface, the water prefers to orient in the H-down position to increase H-bonding is expected. For the Ag (111) surface, both the H-up and the H-down water network interact weakly with the surface (Figure D.6). In fact, the free energy of water adsorption is positive over the entire pH range as indicated in Figure 5.3a. As a result, our model predicts for Ag (111) that there should be no dependency of $\Delta G_{\text{H,app}}$ on the pH. This result is qualitatively consistent with the measured HOR/HER activities on Ag which demonstrate only a slight dependence on pH. Furthermore, the fact that Ag (111) interacts especially weakly with water may explain why Pt (111) shows a considerably weaker change in the HOR/HER activity with increasing pH^{73,184}.

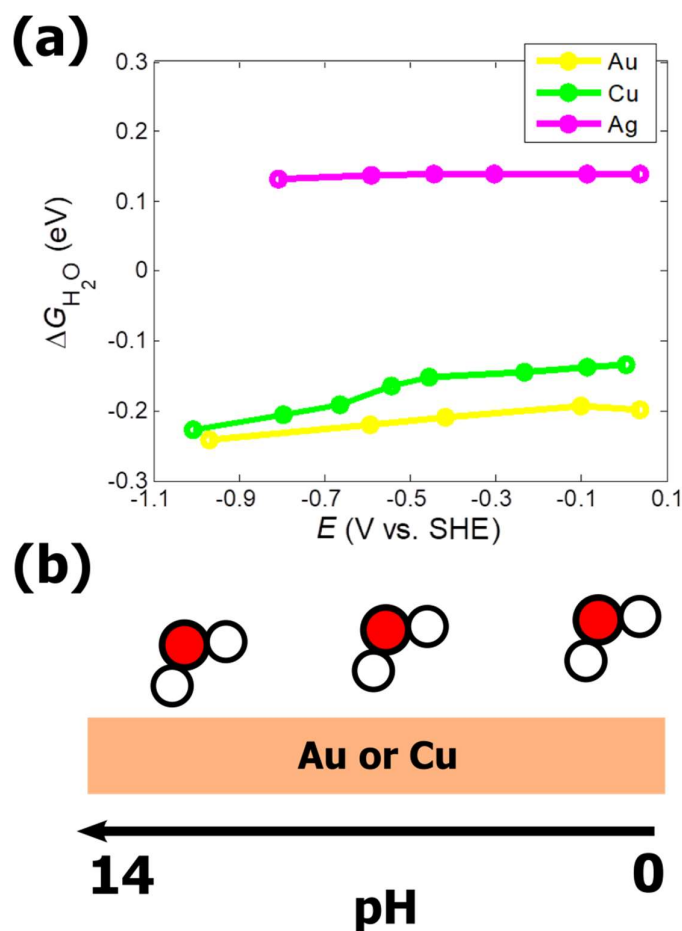


Figure 5.3. (a) Free energies of water adsorption computed from DFT for Au, Cu, and Ag, versus the absolute potential. Equation 5.7 relates the absolute potential to the pH. (b) Schematic of the pH-dependent water orientation on the simulated surfaces of Au or Cu as a function of the pH.

5.3.3 Comparison of simulated $\Delta G_{H,app}$ to H_{upd} peak location

The PGMs (Pt, Ir, Pd, and Rh) have well-defined H_{upd} peak positions. In our recent Perspective³⁶, we show that the CV-measured H_{upd} peak positions are directly related to $\Delta G_{H,app}$. Therefore, it is possible to directly compare the DFT-simulated values of $\Delta G_{H,app}$ to experimentally measured values of $\Delta G_{H,app}$. A parity plot of the simulated and measured $\Delta G_{H,app}$ at all pH values is shown in Figure 5.4. Good quantitative agreement is obtained between the simulated and measured $\Delta G_{H,app}$ for the PGMs. The largest discrepancy between simulated and measured $\Delta G_{H,app}$ is observed for Pd (110) at the low pH regime. It should be noted that the Pd (110)

surface considered herein reconstructs to a missing row geometry as described previously^{185,186}. Moreover, a number of previous studies report on the ability of Pd to form hydrides^{187–190}. Thus, accurate determination of the H_{upd} peak on Pd(110) might not be experimentally feasible. Overall, our computational results are in good agreement with the experimental trend of the H_{upd} peak with varying pH. The coinage metals (Au, Cu, and Ag), on the other hand, do not have clearly visible experimental CV peaks corresponding to H_{upd} adsorption/desorption (Figure D.7). The excellent match between the experimental and computational results on PGMs confirms the reliability of the computational methodology, and thus the calculated pH dependence of $\Delta G_{H, \text{app}}$ for the coinage metals is likely valid.

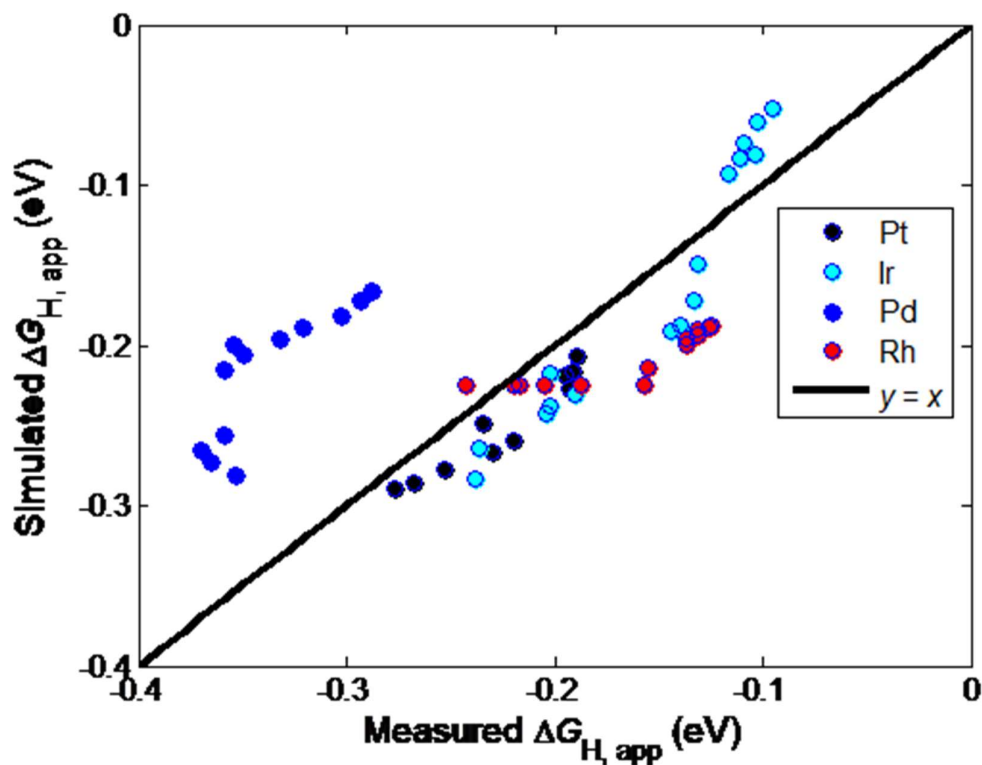


Figure 5.4. Comparison of the simulated $\Delta G_{H, \text{app}}$ from DFT to the experimentally measured $\Delta G_{H, \text{app}}$. Data points span a pH range of 1.4 – 12.8. Experimentally measured $\Delta G_{H, \text{app}}$ for phosphoric buffer, bicarbonate buffer, and 0.1 M KOH were utilized.

Another assessment of the model is comparison to experimental data of the previously measured CVs of CO stripping for Pt, Ir, Pd, and Rh at pH 1.2 – 12.8.³⁸ Based on CO stripping, the onset of OH_{ad} occurs between 0.6 – 0.8 V vs. RHE at pH 1.2 for Pt, Ir, Pd, and Rh. At pH 12.8, however, the OH_{ad} onset occurs earlier at 0.2 – 0.3 V vs. RHE. In Figure 5.5, we observe the same qualitative trend of earlier OH_{ad} onset in base based on computational results. Our model indicates that the reason for earlier OH_{ad} onset in base is the weakening of water adsorption. The destabilization of adsorbed water makes the formation of OH_{ad} relatively more favorable, as shown in the Pourbaix diagrams in Figures D.8-D.11. The onset of the OH_{ad} species estimated here is in especially good agreement with CO stripping data from Garcia, who found the CO stripping onset and peak potentials to be ~0.55 V vs. RHE and 0.62 V vs. RHE, respectively, for the Pt (110) single crystal in alkaline media¹⁹¹. Therefore, in addition to explaining the pH dependence of the H_{upd} desorption peak, the weakening water adsorption with increasing pH for PGMs is also consistent with CO stripping data.

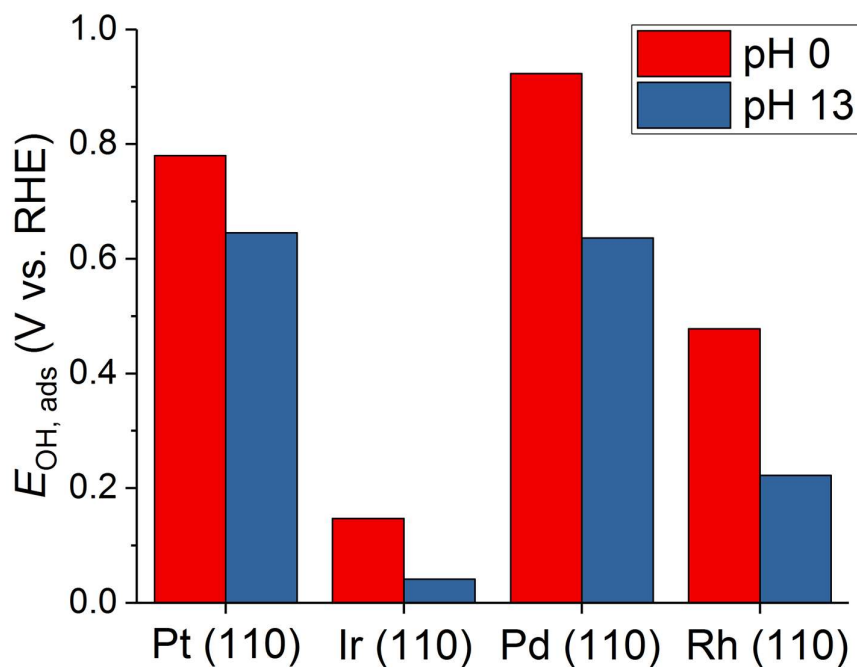


Figure 5.5. Electrode potential (vs. RHE) at which OH_{ad} becomes the most preferential surface species. Determined from computed Pourbaix diagrams of Figures D.8-D.11.

5.3.4 A unified volcano curve for HOR/HER in acid and base

Correlating our first-principles simulations at a given pH with the measured exchange current densities at the same pH, a unified volcano plot is constructed which demonstrates that our theory can incorporate the effect of both the nature of the metal and pH. As expected, the PGMs lie on the strong adsorption branch, whereas the coinage metals (Au, Cu, and Ag) lie on the weak adsorption branch. The measured exchange current densities for the PGMs are taken from Zheng *et al.*³⁶. HOR/HER polarization tests were conducted and exchange current densities were measured for Au, Cu, and Ag (Figures D.12-D.14). The exchange current densities are tabulated in Table D.2. The PGMs, in general, exhibit a greater activity dependence on pH than the coinage metals. In the unified HOR/HER volcano shown in Figure 5.6, the $\Delta G_{\text{H, app}}$ is correlated with the experimentally measured change in activity. As data for

acidic, neutral, and basic electrolytes are all incorporated in Figure 5.6, $\Delta G_{H, app}$ is a suitable *universal* descriptor of the HOR/HER activity trend, regardless of the pH of the electrolyte. Figure 5.6 suggests that Cu has surprisingly low HOR/HER activity given the computed value of $\Delta G_{H, app}$; however, there is a comparatively high degree of uncertainty in the active surface of Cu, as Cu is known to both oxidize *and* reconstruct at the experimental pH and potential of interest. The $(2\sqrt{2} \times 2)\text{R}45^\circ\text{-O}$ surface of Cu (100) modeled here represents an approximation of the experimentally active Cu surface, as the $(2\sqrt{2} \times 2)\text{R}45^\circ\text{-O}$ surface of Cu (100) has been previously shown to be present under HOR/HER conditions.

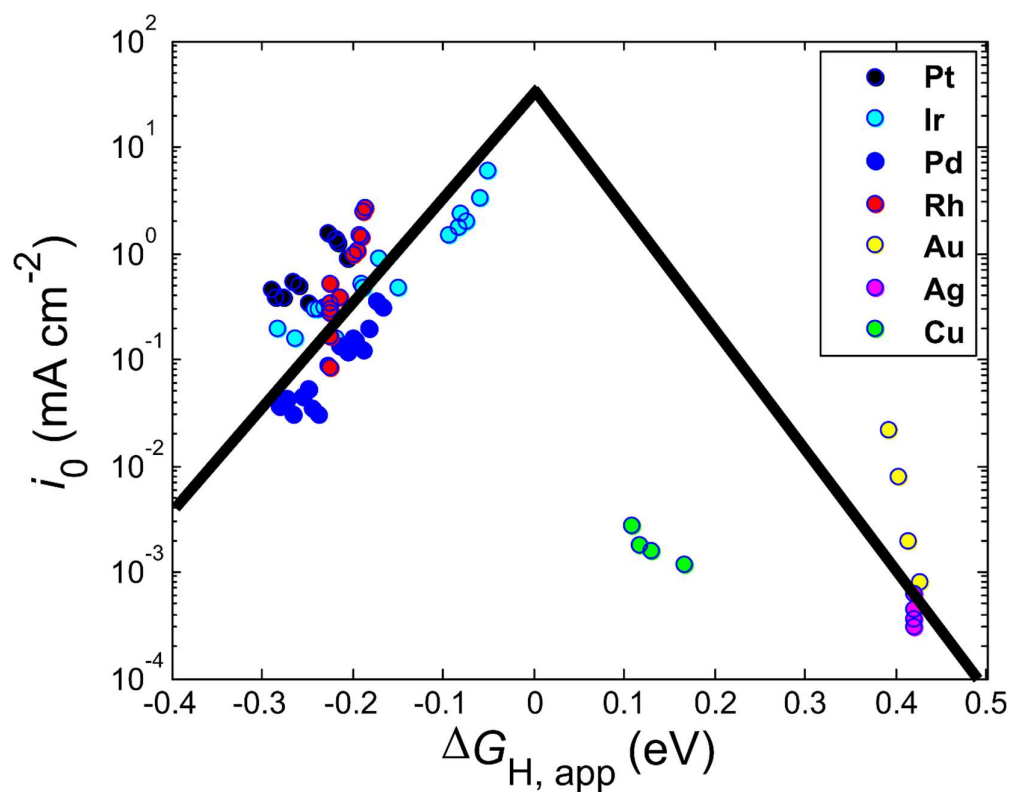


Figure 5.6. Unified volcano plot with novel descriptor $\Delta G_{H, app}$ predicted from DFT for Pt, Ir, Pd, Rh, Au, Cu and Ag.

5.3.5 Discussion

Development of a unified theory explaining the pH-dependence of HOR/HER has proved to be a challenging problem requiring novel insights of the electrode/electrolyte interface. We believe our theory represents a significant step towards a greater fundamental understanding of HOR/HER for *all* catalysts across the *entire* range of pH. The cornerstone of our theory is the establishment of the apparent Gibbs free energy of hydrogen adsorption as a universal descriptor of HOR/HER kinetics across a wide range of metals and the entire range of experimental pH. The ability of a thermodynamic descriptor to describe trends in HOR/HER rates has also been observed by others recently^{192,193}.

Worth noting is that our results, while they represent an advance in understanding of HOR/HER, do not negate prior work which has attempted to explain why the H_{upd} peak and the rate of HOR/HER is dependent on pH. Schwarz *et al.* explained the dependence of the H_{upd} peak of PGMs in terms of the partial oxidation of water on the PGM step sites. Herein, we observe the same behavior for the (110) surfaces of Pt, Pd, Ir, and Rh. The charge transfer and the optimized geometry for Pt (110) and Au (110) are shown as examples in Figure D.16. The H-up water network on Pt is partially oxidized, whereas the H-down water network on Au is partially reduced. Therefore, for the Pt, Pd, Ir, and Rh stepped surfaces, on which the H-up water adsorption is preferred, the adsorption energy of water weakens with increasing pH. In contrast, the H-down water orientation is preferred for Au and Cu, and thus, the adsorption energy of water on Au (110) *strengthens* with increasing pH. The partial oxidation (reduction) of H-up (H-down) water is a result of the electronic structure of the water molecule. The highest occupied molecular orbital (HOMO) of water is the $1b_1$ orbital, which is primarily localized around the oxygen atom and is associated with lone pair effects¹⁹⁴. The lowest unoccupied molecular orbital (LUMO) of water, however, is the $4a_1$ orbital and is localized along the O-H bond¹⁹⁴. Therefore, as the electrode surface becomes more electron-rich at negative electrode

potentials (i.e., increasing pH), electron transfer from the metal into the LUMO of water occurs.

To support the findings of our DFT study wherein we assign an initial H-up or H-down configuration to the water network, *ab initio* molecular dynamics (AIMD) were also performed. The resulting distribution of H atoms along the *z*-direction is shown in Figure D.17. Comparison of the AIMD simulation to the static H-down structure optimized with DFT indicates good agreement in both the position and number of the hydrogen atoms most proximal to the electrode surface. Furthermore, the water molecules located further away from the electrode surface have a greater standard deviation in their position over time. This suggests that water further away from the surface (*i.e.*, in approximately the third solvation shell) behaves in a more “bulk-like” fashion, whereas the water nearest the surface has a comparatively higher degree of order. The assertion that the electrode has a small effect on water outside of the third solvation shell is also supported by charge density differences from static DFT calculations (Figure D.1). Furthermore, the ordered nature of water at electrified interfaces has been a subject of numerous studies^{171,183,195,196}. AIMD simulations were also done on Au (110) starting from an H-up water network, and the system was shown to evolve toward the H-down orientation (Figure D.18).

Our unified theory is also consistent with the observation that improved HOR/HER activity is observed when a hydrophilic material (*e.g.*, Ni(OH)₂) is deposited on Pt^{19,39}. The surface OH_{ad} species likely interacts strongly with H-up oriented water due to a stabilizing hydrogen-bonding effect. Consequently, the adverse effect of weakening the adsorption of H-up water with increasing pH (as is the case for PGMs) can be partially mitigated. Evidence for this hypothesis has been observed experimentally where the near-electrode water dipole orientation for Ni(OH)₂ deposited on Pt has been shown to significantly differ from that on Pt alone¹⁹⁷.

5.4 Conclusions

Herein, we defined a universal thermodynamic descriptor, the apparent free energy of hydrogen adsorption, for the HOR/HER kinetics. Through our DFT investigation, the free energy of water adsorption was found to depend on the pH. Whether water adsorption weakens or strengthens with increasing pH depends on the preferred orientation of the water network; the H-down (up) oriented water network becomes more (less) favorable with increasing pH. Consequently, with increasing pH, the apparent Gibbs free energy of hydrogen adsorption strengthens on the (110) surfaces of Pt, Pd, Ir, and Rh, but weakens on Au and Cu, and stays the same on Ag. The DFT-calculated values of the apparent free energy of hydrogen adsorption were found to correspond well to the H_{upd} peak as measured via cyclic voltammetry. Finally, a unified HOR/HER volcano was constructed which demonstrates that the apparent free energy of hydrogen adsorption is a universal descriptor for the HOR/HER kinetics regardless of pH. Through the identification of this novel thermodynamic descriptor for HOR/HER, we hope to illuminate a path toward rational design of catalysts with kinetics in basic electrolytes comparable to those in acidic electrolytes.

5.5 Acknowledgements

S.A.G. and M.L. contributed equally to this work. B.X., D.G.V. and Y.Y. conceived the idea. S.A.G. and D.G.V. performed the DFT calculations and analyzed the computational data. M.L. performed the electrochemical tests of the coinage metals with the assistance from J.N. and J.Z. S.A.G., D.G.V., and Y.Y. wrote the manuscript. All authors discussed the results and commented on the manuscript.

The computational work was financially supported from the Catalysis Center for Energy Innovation, an Energy Frontier Research Center funded by the US Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number DE-SC0001004. This research used resources of the National Energy Research Scientific Computing Center, a DOE Office of Science User Facility

supported by the Office of Science of the US Department of Energy under Contract No. DE-AC02-05CH11231. The experimental work was financially supported from DE-AR-0000009.

Chapter 6

UNDERSTANDING THE pH DEPENDENCE OF MECHANISM AND ACTIVITY OF HYDROGEN OXIDATION/EVOLUTION REACTION ON AN RU CATALYST

6.1 Introduction

Fuel cells, especially the low-temperature hydrogen proton exchange membrane fuel cells (PEMFCs), are considered to be efficient and environmentally friendly energy conversion devices^{45,198}. To date, the state-of-the-art hydrogen oxidation reaction (HOR) and oxygen reduction reaction (ORR) catalysts for PEMFCs are Pt and Pt-based alloys⁴⁶. However, the commercialization of PEMFCs is hampered by the high loading and the high price of Pt. Switching from an acidic fuel cell (PEMFCs) to an alkaline version (hydroxide exchange membrane fuel cells, HEMFCs) can lower the cost of catalysts at the cathode by using non-precious metal ORR catalysts. Recently, non-precious metal ORR catalysts (such as Fe-based¹⁹⁹, carbon nanotube/nanoparticle composite⁴⁹, and perovskite-based²⁰⁰ catalysts) have been widely investigated, and show comparable activity in base as Pt in acid. However, HEMFCs still show lower power density than PEMFCs^{201,202}. The sluggish HOR rate in alkaline environment is one of the key contributors to the low performance of HEMFCs¹⁰. The exchange current densities (i_0) of the most active HOR catalysts Pt, Ir, Pd and Rh are lower by one to two orders of magnitude in base than in acid^{17,38,203,204}. Strmcnik *et al.* showed that the HOR activity could be enhanced by the introduction of a more oxophilic metal (such as Ru) into Pt, and proposed that the enhanced activity is due to adsorbed OH (OH_{ad}) on more oxophilic sites being able to react with the adsorbed H (H_{ad}) to facilitate HOR¹⁹. However, other studies suggest that the difference of HOR activities between acid and base is due to the modification of the hydrogen binding energy (HBE)^{38,54,89,203,205,206}. The ligand effect instead of bifunctional effect was demonstrated to be responsible for enhanced

HOR/HER activity in an alkaline electrolyte based on the observation that the fully Pt covered Ru nanoparticles show higher activity than partially Pt covered Ru²⁰⁵. More recently, Lu and Zhuang showed that PtNi nanoparticles and acid washed PtNi nanoparticles with same HBE but greatly different OH binding energy exhibited similar HOR/HER activities in base, which excluded the promotional role of adsorbed OH²⁰⁶. Alternatively, the interfacial water reorganization has also been proposed to be a pH-dependent descriptor for HER rate on Pt¹⁹⁷. Previous studies showed the HOR activity is correlated with the apparent HBE (HBE_{app}), which is a combination of the intrinsic HBE and the surface water adsorption energy, measured by cyclic voltammograms (CVs) at different pH electrolytes^{36,38}.

As a member of the PGMs, Ru seems to have a unique HOR behavior in base compared with Pt, Ir, Pd, and Rh. It is reported that Ru supported on carbon (Ru/C) exhibits higher HOR activity in base than in acid²⁰⁷, which is opposite to Pt, Ir, Pd, and Rh. Ru/C also showed high performance in HEMFCs as the HOR catalyst which was comparable to that of a commercial Pt/C catalyst²⁰⁸. Moreover, another benefit of using Ru as the HOR catalyst of a HEMFC is the less carbon corrosion at the cathode compared with Pt, Ir, and Pd caused by reverse-current decay, owing to the lower ORR activity of Ru²⁰⁹. In this work, the effect of pH on the HOR/HER activity, the reaction mechanism, and the ease of Ru oxidation are investigated. The HOR/HER activity of Ru/C is presented as the exchange current density obtained by modeling the kinetic polarization curve with the Butler-Volmer equation. The ease of Ru oxidation is investigated by using the potential at the maximum current of HOR polarization curve obtained by rotating disk electrode (RDE) method. Density functional theory (DFT) calculations indicate that the apparent hydrogen binding energy is the fundamental descriptor of HOR/HER activity on Ru over the entire pH range. The DFT calculations also reveal that the experimental V-shaped HOR/HER activity dependence on pH is a result of the decreasing activity of Ru terrace sites with increasing pH, but increasing activity of hydroxylated Ru edges with pH.

6.2 Methods

6.2.1 Experimental

6.2.1.1 Materials and preparation of electrolytes

Ru/C (20 wt.% Ru supported on Vulcan XC-72, Premetek Co.) was obtained commercially and used as received. 0.1 M and 1 M sulfuric acid (H_2SO_4), 0.2 M phosphoric acid (H_3PO_4), and 0.2 M acetic acid (CH_3COOH) were prepared by diluting 95 wt.% H_2SO_4 (EMD), 80 wt.% H_3PO_4 (Sigma Aldrich), and 99.9 wt.% CH_3COOH (Sigma Aldrich) with DI water, respectively. 0.1 M and 3.7 M potassium hydroxide (KOH), 0.2 M citric acid ($\text{C}_6\text{H}_8\text{O}_7$), and 0.2 M boric acid (H_3BO_3) were prepared from KOH tablets (85 wt.%, 99.99 % metal trace, Sigma Aldrich), $\text{C}_6\text{H}_8\text{O}_7$ powder (99 wt.%, Sigma Aldrich), and H_3BO_3 powder (99 wt.%, Sigma Aldrich), with DI water, respectively. Buffer solutions were prepared by adding different amounts (1-18 mL) of 3.7 M KOH into 100 mL of 0.2 M H_3PO_4 , 0.2 M $\text{C}_6\text{H}_8\text{O}_7$, 0.2 M CH_3COOH , or 0.2 M H_3BO_3 solutions.

6.2.1.2 Electrochemical measurements

The electrochemical measurements were performed in a three-electrode cell with a silver-silver chloride (Ag/AgCl) double junction reference electrode, a Pt wire counter electrode, and a glassy carbon electrode working electrode which is attached to a rotator (PINE instruments) controlled by a multichannel potentiostat (Princeton Applied Research). All the potentials used in this work were converted to the reversible hydrogen electrode (RHE) scale. The Ru/C (1 $\text{mg}_{\text{Ru/C}}/\text{mL}$) ink solution was prepared by dispersing Ru/C (20 wt.%) in a 0.05% Nafion in DI water solution followed by ultrasonication for 1 h. The ink was pipetted onto the glassy carbon electrode (5 mm diameter, 0.196 cm^2) with a final metal loading of $20 \mu\text{g}_{\text{Ru}}/\text{cm}_{\text{disk}}^2$.

CVs for Ru/C were obtained in Ar-purged buffered electrolytes with different pHs at room temperature (293 K) with a scanning rate of 50 mV/s from 0.05 to 0.9 V vs. RHE without rotating. The HOR polarization was performed in H_2 saturated

buffered electrolytes with different pHs at a scanning rate of 50 mV/s and a rotation speed of 1600 rpm for several cycles until a stable polarization curve was obtained. The scanning rate was changed to 10 mV/s, and the obtained anodic polarization curves were reported in this paper. The iR -free potential ($E_{iR\text{-free}}$) was obtained by correcting the voltage using the internal resistance (R_s) measured by electrochemical impedance spectroscopy (EIS) according to the following equation:

$$E_{iR\text{-free}} = E - iR_s \quad (6.1)$$

where E is the measured potential, and i is the corresponding current. The pH values of electrolytes were calculated from the HOR/HER reversible potential (potential at current equals zero) based on the Nernst equation:

$$E_{\text{H}_2/\text{H}^+}(\text{vs. } E_{\text{Ag}/\text{AgCl}}) = -E_{\text{Ag}/\text{AgCl}} - \frac{2.303RT}{F} \text{pH} \quad (6.2)$$

where $E_{\text{Ag}/\text{AgCl}}$ is the standard potential for the silver-silver chloride electrode (Ag/AgCl , -0.199 V), R is the universal gas constant ($8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$), T is the temperature in Kelvin, and F is Faraday constant ($96,485 \text{ C}\cdot\text{mol}^{-1}$). The HOR/HER activity is represented by the exchange current density (i_0), which was obtained by fitting kinetic current (i_k) with the Butler-Volmer equation:

$$i_k = i_0 A_s \left[\exp\left(\frac{\alpha_a F \eta}{RT}\right) - \exp\left(\frac{-\alpha_c F \eta}{RT}\right) \right] \quad (6.3)$$

where α_a and α_c are the transfer coefficients, A_s is the electrochemical surface area of Ru/C, and η is the overpotential. i_k is calculated by the Koutecky-Levich equation²¹⁰:

$$\frac{1}{i} = \frac{1}{i_k} + \frac{1}{i_d} \quad (6.4)$$

where i is the measured current, i_k is the kinetic current, and i_d is the diffusion limited current. i_d is defined from the following equation:

$$i_d = i_{\text{lim}} \left[1 - \exp\left(-\frac{2F}{RT}\right) \right] \quad (6.5)$$

where η is the overpotential and i_{lim} is the maximum current obtained from polarization curves.

Cu underpotential deposition (Cu_{upd}) stripping voltammetry was performed for determining the surface area (A_s) of Ru/C. Cu stripping voltammetry was performed in Ar-purged 0.1 M H_2SO_4 solution containing 2 mM CuSO_4 from 0.3 – 0.9 V vs. RHE at 20 mV/s. Ru/C was pretreated by cycling from 0.05 to 1 V vs. RHE at 100 mV/s in 0.1 M H_2SO_4 until the CV was stable, and then the scanning rate was changed to 10 mV/s. The CV from 0.05 – 0.9 V vs. RHE at 20 mV/s was served as the background for the corresponding Cu_{upd} stripping voltammogram.

6.2.2 Theoretical

6.2.2.1 Dual-pathway kinetic model of HOR/HER

The HOR/HER is believed to go through two of the three elemental steps (Tafel-Volmer pathway or Heyrovsky-Volmer pathway). In Equations 6.6-6.8, we assume the catalyst surface to be covered by water:



Wang *et al.* has established a kinetic model of two pathways (Tafel-Volmer pathway and Heyrovsky-Volmer pathway) with the three elementary reaction steps and derived a dual-pathway kinetic equation using four standard Gibbs free energies as the adjustable parameters^{211–213}. The four kinetic parameters are the apparent Gibbs free energy of hydrogen adsorption at 0 V vs. RHE ($\Delta G_{\text{H,app}}^0$), and the standard activation Gibbs free energies for the three elementary reaction steps (ΔG_{+T}^{*0} , ΔG_{+H}^{*0} , and ΔG_{-V}^{*0}). Though the Heyrovsky step and the Volmer step have different reaction equations in acid and base, the adsorbed reaction intermediate species (H^*) is the same in acid and base, thus the dual-pathway equation is the same for HOR/HER intermediates in both

electrolytes. By fitting the kinetic curves of HOR/HER to the dual-pathway kinetic equation, the activation Gibbs free energies of Tafel step (ΔG_{+T}^{*0}), Heyrovsky step (ΔG_{+H}^{*0}), and Volmer step (ΔG_{-V}^{*0}) on Ru/C in different pH electrolytes were obtained. The key assumption from this model is: $\frac{d\theta}{dt} = 2v_T + v_H - v_V = 0$, where θ is the coverage of H^* , and v_T , v_H and v_V are the reaction rate for Tafel, Heyrovsky and Volmer steps, respectively. The four free energy parameters vary because they depend on both properties of catalysts and the pH of electrolytes. With both HOR and HER under consideration, T/H/V with + and – signs indicate HOR and HER, respectively.

The total kinetic current of HOR/HER is described as the following equations:

$$j_k = j_T + j_H \quad (6.9)$$

$$j_T = j_{+T} - j_{-T} = j^* e^{-\frac{\Delta G_{+T}^{*0}}{kT}} [(1 - \theta)^2 - e^{\frac{2\Delta G_{H,app}^0}{kT}} \theta^2] \quad (6.10)$$

$$j_H = j_{+H} - j_{-H} = j^* e^{-\frac{\Delta G_{+H}^{*0}}{kT}} [e^{\frac{0.5\eta}{kT}} (1 - \theta) - e^{\frac{2\Delta G_{H,app}^0}{kT}} e^{-0.5\eta/kT} \theta] \quad (6.11)$$

where $j^*=1000 \text{ A}\cdot\text{cm}^{-2}$ is a fixed reference prefactor, and $kT = 25.51 \text{ meV}$ at 298 K. θ is the coverage for H^* , which is derived by solving the steady state equation: $\frac{d\theta}{dt} =$

$$2v_T + v_H - v_V = 0, \text{ where } v \text{ is reaction rate. The solution can be expressed as:} \\ \theta = \frac{-B - \sqrt{B^2 - 4A}}{2A}, A \neq 0; \theta = -\frac{C}{B}, A = 0 \quad (6.12)$$

Where,

$$A = 2g_{+T} - 2g_{-T}; B = -4g_{+T} - g_{+H} - g_{-H} - g_{+V} - g_{-V};$$

$$C = 2g_{+T} + g_{+H} + g_{-V}.$$

The expressions are shown as follows:

$$g_{+T} = e^{-\Delta G_{+T}^{*0}/kT}; g_{-T} = e^{-(\Delta G_{+T}^{*0} - 2\Delta G_{H,app}^0)/kT};$$

$$g_{+H} = e^{-(\Delta G_{+H}^{*0} - 0.5\eta)/kT}; g_{-H} = e^{-(\Delta G_{+H}^{*0} - 2\Delta G_{H,app}^0 + 0.5\eta)/kT};$$

$$g_{+V} = e^{-(\Delta G_{-V}^{*0} - \Delta G_{H,app}^0 - 0.5\eta)/kT}; g_{-V} = e^{-(\Delta G_{-V}^{*0} + 0.5\eta)/kT};$$

6.2.2.2 DFT calculations

In the DFT study conducted herein, we investigate the ability of the apparent hydrogen binding energy to universally explain HOR/HER activity trends over the entire range of pH. The apparent hydrogen binding energy is defined as

$$\Delta G_{\text{H,app}} = \Delta G_{\text{H}} - \Delta G_{\text{H}_2\text{O}} \quad (6.13)$$

where ΔG_{H} is the Gibbs free energy of hydrogen adsorption in vacuum and $\Delta G_{\text{H}_2\text{O}}$ is the Gibbs free energy of water adsorption normalized on a per water molecule basis. The Gibbs free energy of hydrogen adsorption in vacuum is defined with reference to the gas-phase hydrogen molecule

$$\Delta G_{\text{H}} = G_{\text{H}^*} - G_* - \frac{1}{2} G_{\text{H}_2} \quad (6.14)$$

where G_{H^*} is the Gibbs free energy of the electrode surface with hydrogen adsorbed, G_* is the Gibbs free energy of the clean electrode surface, and G_{H_2} is the Gibbs free energy of the gas phase hydrogen molecule. In this work, we have applied a constant entropic correction of 0.24 eV as suggested by Nørskov *et al.*³⁵ to the electronic energies obtained from DFT. Therefore, Equation 6.14 is rewritten as

$$\Delta G_{\text{H}} = \Delta E_{\text{H}} + 0.24 \text{ eV} = E_{\text{H}^*} - E_* - \frac{1}{2} E_{\text{H}_2} + 0.24 \text{ eV} \quad (6.15)$$

where E represents the DFT energy. The computation of $\Delta G_{\text{H,app}}$ was performed for three characteristic Ru surfaces: a Ru (0001) terrace, a clean Ru (0001) step, and a hydroxylated Ru (0001) step. The model of the Ru (0001) step utilized herein has been the subject of prior theoretical investigation by Nørskov *et al.* The Ru (0001) step was found to be present experimentally during the electrochemical synthesis of ammonia on Ru nanoparticles²¹⁴. Thus, we expect the Ru (0001) step modeled herein to be equally relevant for HOR/HER occurring on Ru nanoparticles.

To compute $\Delta G_{\text{H}_2\text{O}}$, we use an extended hydrogen-bonded water network consisting of 48 water molecules in total. The structure of the interfacial water considered herein was assigned either an H-up or H-down orientation. The H-up and H-down water structures were initialized with the structure of the hexagonal ice-like

water bilayer first discussed by Bernal and Fowler¹⁶⁸. The binary H-up/H-down interpretation of the water dipole has been employed successfully in previous work for various surfaces^{37,169,170}. While most previous work has modeled the electrochemical double layer with a single layer of aqueous solvent^{170–172}, herein, we use three layers of water on both sides of the periodic surface. The requirement to simultaneously model multiple layers of solvent on both sides of the periodic surface is due to both our treatment of a *charged* Ru surface (insufficient charge screening will lead to large error in the computed electrostatic potential) and the need to limit the induced dipole normal to the surface. $\Delta G_{\text{H}_2\text{O}}$ is then

$$\Delta G_{\text{H}_2\text{O}} = G_{*/\text{H}_2\text{O}} - G_* - G_{\text{H}_2\text{O}} \quad (6.16)$$

where $G_{*/\text{H}_2\text{O}}$ is the Gibbs free energy of the combined Ru/water system, G_* is the Gibbs free energy of Ru surface in vacuum, and $G_{\text{H}_2\text{O}}$ is the Gibbs free energy of the water network in the absence of the Ru surface. Analogous to Equation 6.15, we arrive at the following equation for the Gibbs free energy of water adsorption:

$$\Delta G_{\text{H}_2\text{O}} = \Delta E_{\text{H}_2\text{O}} + T\Delta S_{\text{H}_2\text{O}} = E_{*/\text{H}_2\text{O}} - E_* - E_{\text{H}_2\text{O}} + T\Delta S_{\text{H}_2\text{O}} \quad (6.17)$$

where E represents the DFT energy, T is the temperature, and $\Delta S_{\text{H}_2\text{O}}$ is change in the entropy of H_2O upon adsorption onto the electrode surface. This quantity was found to be surface-dependent: 0.15 eV for terrace sites, 0.21 eV for clean steps, and 0.10 eV for hydroxylated steps, all at 293 K.

Following the computation of $\Delta G_{\text{H}, \text{app}}$ for each Ru surface, we predict the exchange current density of a Ru nanoparticle as a function of the pH. In order to compute the exchange current density using the adsorption energies from DFT, we utilize the universal scaling relationship between the underpotential deposited hydrogen (H_{upd}) peak and the measured exchange current density. The universal scaling relationship takes the form,

$$i_{0,j} = A e^{-\Delta G_{\text{H}, \text{app}, j} / kT} \quad (6.18)$$

where A is a constant prefactor previously determined from pH scans in numerous buffered solutions on carbon-supported Pt, Ir, Pd, and Rh catalysts to be $35 \text{ mA cm}^{-2}_{\text{metal}}$. Note that because the prefactor A originates from the *universal* scaling relationship of the H_{upd} peak and the measured exchange current density, the A prefactor remains approximately constant for all surfaces. Furthermore, because the hydrogen adsorption is computed herein at low coverage, the apparent Gibbs free energies of hydrogen adsorption presented herein are expected to be closely analogous to the experimental H_{upd} .

The overall exchange current density of the Ru nanoparticle is thus defined to be the site-weighted average of the propensity of each site (i.e., a Gillespie average)¹²⁴,

$$\bar{i}_0 = \sum_{j=1}^{\# \text{surfaces}} x_j i_{0,j} \quad (6.19)$$

where x_j is the fractional abundance of surface j . In order to fully specify Equation 6.19, a fractional abundance of total edge sites (both clean and hydroxylated) must be assumed. The fraction of edge sites present is primarily a function of the nanoparticle size, and previous work has suggested that nanoparticles with a diameter of $\sim 3 \text{ nm}$ (such as the ones synthesized herein) contain approximately 10% edge sites.

Because the formation of adsorbed hydroxyl can have a strong impact on both hydrogen and water adsorption, the formation energies of hydroxyl were also computed for each Ru surface. The hydroxyl formation energies were computed according to Equation 6.20, while accounting for stabilization by co-adsorbed water in a manner analogous to McCrum and Janik,

$$\Delta G_{\text{OH}} = \frac{1}{N_{\text{OH}^*}} (G_{\text{OH}^*/\text{H}_2\text{O}^*} + N_{\text{OH}^*} (G_{\text{H}^+ + e^-}) - G_{\text{H}_2\text{O}^*}) \quad (6.20)$$

where N_{OH^*} is the number of adsorbed hydroxyls present on the surface, $G_{\text{OH}^*/\text{H}_2\text{O}^*}$ is the free energy of the co-adsorbed hydroxyl and water where N_{OH^*} of the initially adsorbed water species have been oxidized into OH^* , $G_{\text{H}^+ + e^-}$ is the free energy of the proton-electron pair (equal to $\frac{1}{2} G_{\text{H}_2}$ at equilibrium), and $G_{\text{H}_2\text{O}^*}$ is the free energy of the Ru surface with adsorbed water.

On the basis of the hydroxyl formation energies, the surface coverage of hydroxyl was computed as,

$$\theta_{\text{OH}^*} = \sum_i^{\# \text{ of surfaces}} \theta_{\text{OH}^*,i} e^{-\Delta G_i/k_B T} \quad (6.21)$$

where the surfaces include adsorbed hydrogen, adsorbed hydroxyl at coverages of $\frac{1}{4}$ ML, $\frac{1}{2}$ ML, and 1 ML, and adsorbed water. $\theta_{\text{OH}^*,i}$ is the corresponding coverage of adsorbed hydroxyl for surface i (zero for the adsorbed hydrogen and adsorbed water surfaces), ΔG_i is the free energy of formation of surface i (which is dependent on the potential and the pH), k_B is the Boltzmann constant, and T is the temperature in Kelvin.

Periodic DFT calculations were performed using the Vienna ab initio simulation package (VASP, version 5.4.1).⁶³ The RPBE exchange-correlation functional¹⁴⁷ with D3 dispersion corrections¹⁷⁴ was selected because of its good representation of structured water networks and accurate reproduction of the absolute standard hydrogen electrode potential^{175,176}. The core electrons of Ru were represented with the projector-augmented wavefunction (PAW) method⁶⁶, and a plane-wave cutoff of 400 eV was used for the valence electrons of Ru. The Methfessel–Paxton method of electron smearing was used with a smearing width of 0.1 eV⁶⁸. All geometry optimizations were performed using the quasi-Newton scheme as implemented in VASP. The forces and energies were converged to 0.05 eV Å⁻¹ and 10⁻⁴ eV, respectively. All calculations were performed with spin-polarization and at the Γ -point. Dipole corrections were applied in the z -direction, normal to the electrode surface.

6.3 Results

6.3.1 Tafel-Volmer or Heyrovsky-Volmer

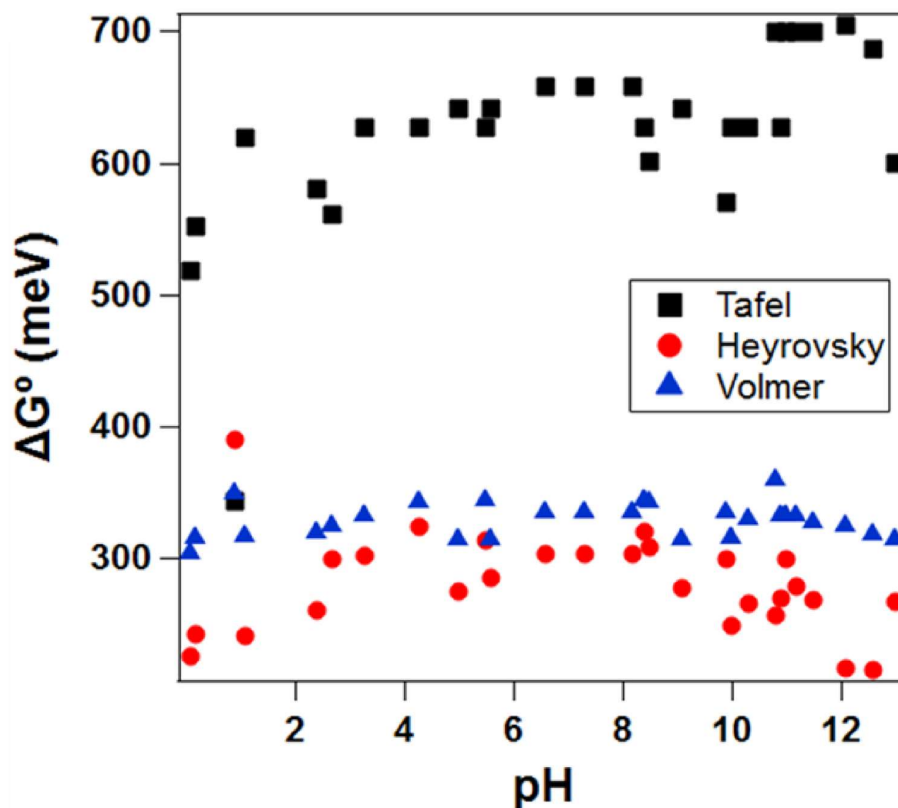


Figure 6.1. Gibbs free energy of activation of the Tafel step, Heyrovsky step, and Volmer step of HOR/HER on Ru/C obtained from the dual pathway model as a function of electrolyte pH.

The HOR/HER specific kinetic currents of Ru/C in electrolyte with different pHs from -30 to 40 mV vs. RHE were modeled with a dual-pathway model (an example of HOR/HER kinetic current at $\text{pH} = 4.3$ is shown in Figure E.3), and the Gibbs free energy of activation of the Tafel, Heyrovsky and Volmer steps were plotted as a function of pH (Figure 6.1). Since the HOR/HER goes through either a Heyrovsky-Volmer or a Tafel-Volmer pathway, the significantly lower Gibbs free energy of activation of the Heyrovsky step than the Tafel step indicates that the

Heyrovsky step is greatly favored for HOR/HER on Ru/C, thus making Heyrovsky-Volmer the dominating reaction pathway. Additionally, the Gibbs free energy of activation of the Volmer step is higher than that of Heyrovsky step, indicating that the Volmer step is the rate-determining step. Therefore, the reaction mechanism of HOR/HER on Ru/C in all pHs is Heyrovsky-Volmer with the Volmer step being the rate-determining step.

Exchange current densities of HOR at different pHs were obtained by fitting the kinetic current density into the Butler-Volmer equation. The polarization curves for phosphoric acid (pH=2), phosphoric acid buffer (pH=6.7), and 0.1 M KOH (pH=13) fitted to the Butler-Volmer equation are shown in Figure E.4-E.6. For 0.1 M KOH, it is demonstrated in Figure E.6 that $\alpha_a + \alpha_c = 2$ has better agreement with experimental data, with $\chi^2=30.3$ compared to $\chi^2=279.9$ for $\alpha_a + \alpha_c = 1$, which indicates that the mechanism is a Heyrovsky-Volmer(RDS) mechanism. This is consistent with the dual pathway modeling. From the polarization curve, the current reaches a maximum during the polarization curve. Previous literature examined relative importance of the two reaction pathways on Pt and Ru catalyst. They demonstrated the relative importance of the Heyrovsky-Volmer mechanism for Ru which is different from Pt which showed a Tafel-Volmer(RDS) mechanism²¹⁵. The transfer coefficient α_a is 1.15 ± 0.06 from the Butler-Volmer fitting on Ru/C in all pH electrolytes.

6.3.2 Experimental exchange current density

In the previous study on the pH dependence of HOR/HER on Pt, Ir, Pd, and Rh nanoparticles, we observed a universal scaling relationship between the H_{upd} desorption peak and the HOR/HER exchange current density. In the cases of Pt, Ir, Pd, and Rh, the H_{upd} desorption peak was shown to monotonically shift to more positive electrode potentials as the pH was increased. The shift corresponded to a strengthened apparent hydrogen binding energy (i.e., incorporating effects of water

adsorption, electrolyte, etc.), and led to a monotonic decrease of the exchange current density with increasing pH.

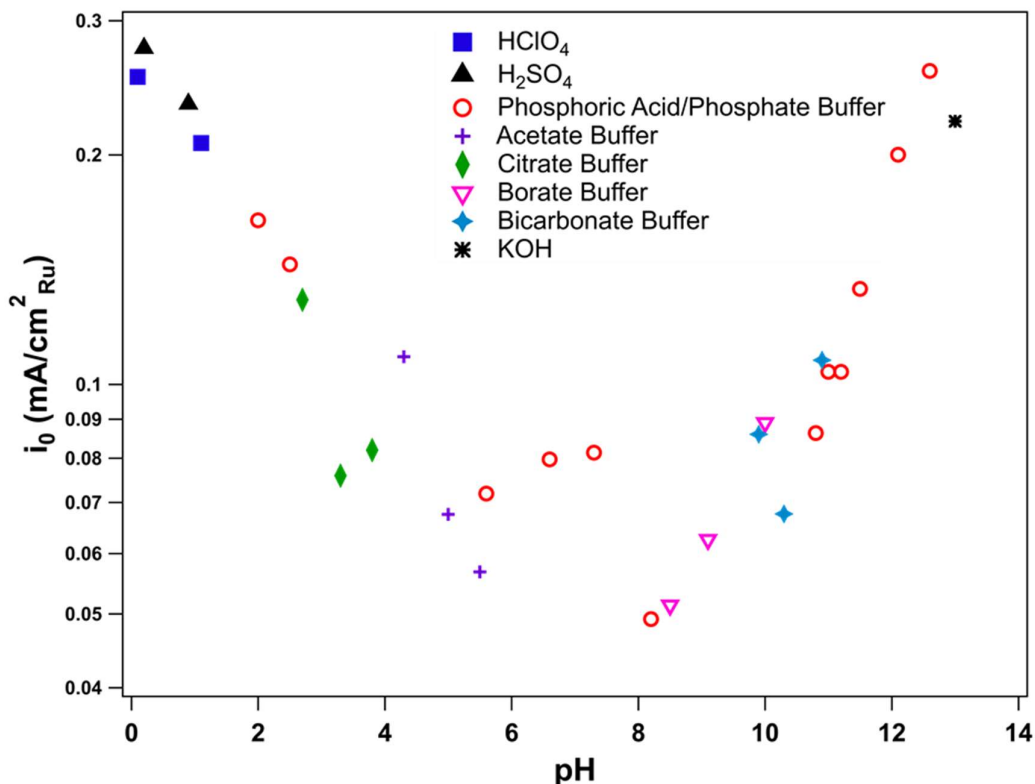


Figure 6.2. Exchange current density of Ru/C in buffers at a variety of different pHs. HOR/HER polarization curves were measured at a scan rate of 10 mV/s and a rotation rate of 1600 rpm at 293 K. Ru/C loading is 20 $\mu\text{g}_{\text{Ru}}/\text{cm}^2$.

However, the HOR/HER exchange current density (i_0) on Ru/C exhibits a fundamentally different dependency on pH than the other monometallics tested to date. We observe that i_0 on Ru/C decreases as the pH of the electrolyte increases from about 0 to 7 and increases as pH increases from 7 to 13, resulting in a “V-shaped” relationship between i_0 and electrolyte pH (Figure 6.2), which is different from the other PGMs (Pt, Ir, Pd, and Rh)^{38,89}. The HOR/HER exchange current density on Ru/C in 0.1 M KOH in this study is 0.22 mA/cm²_{Ru}, which more than triples the value reported on 3 nm Ru nanoparticles in 0.1 M NaOH at 25 °C (about 0.065

$\text{mA}/\text{cm}^2_{\text{Ru}})^{207}$. Similar HOR/HER activities were obtained in HClO_4 or H_2SO_4 with $\text{pH} = 1$ with $i_0 \approx 0.21$ to $0.24 \text{ mA}/\text{cm}^2_{\text{Ru}}$, which is also significantly higher than the value reported in the literature for $0.1 \text{ M H}_2\text{SO}_4$ ($0.05 \text{ mA}/\text{cm}^2_{\text{Ru}})^{207}$. The HOR/HER activities of Ru/C in acid ($\text{pH}=0$) and in base ($\text{pH}=13$) are five times higher than in the neutral electrolytes ($\text{pH}=5-9$).

Figure E.7 shows the CVs of Ru/C in Ar-saturated buffer solutions with different pH values. Similar shape of CVs have been reported previously for bulk Ru in acid²¹⁶, and Ru nanoparticles supported on carbon in base²⁰⁷. Because of the overlap of the H_{upd} and the surface Ru oxidation, $\Delta G_{\text{H,app}}$ cannot be obtained from the CVs. The occurrence of Ru oxidation in the H_{upd} adsorption/desorption region also makes it inappropriate to determine surface area from the H_{upd} peak. Therefore, Cu_{upd} stripping is adopted to determine surface area²¹⁷. The electrochemical active surface area (ECSA) of Ru calculated from Cu stripping (Figure E.8) is $77.0 \text{ m}^2/\text{g}_{\text{Ru}}$.

The limiting current density (i_{lim}) on the HOR/HER polarization curves increases with the rotation speeds increasing from 900 rpm to 3600 rpm (Figure 6.3). The number of electrons transferred (n) is determined to be ~ 1.86 from Koutecky-Levich plot (Figure 6.3 inset) indicated by the Levich equation with $i_{\text{lim}} = 0.62nFD^{2/3}\nu^{1/6}c_0\omega^{1/2}$, where F is Faraday constant, D is the diffusivity of hydrogen in 0.1 M KOH ($3.7 \times 10^{-5} \text{ cm}^2/\text{s}$), ν is the kinematic viscosity of the 0.1 M KOH electrolyte ($1.01 \times 10^{-2} \text{ cm}^2/\text{s}$), c_0 is the solubility of H_2 in 0.1 M KOH ($7.33 \times 10^{-4} \text{ M}$), and ω is the rotation rate in radians²¹⁸. This result indicates the number of electrons transferred in HOR on Ru/C is close to 2, which is consistent with the Heyrovsky-Volmer pathway in Figure 1, $\alpha_a + \alpha_c = 2$ from the Butler-Volmer model, and the previous study²⁰⁷.

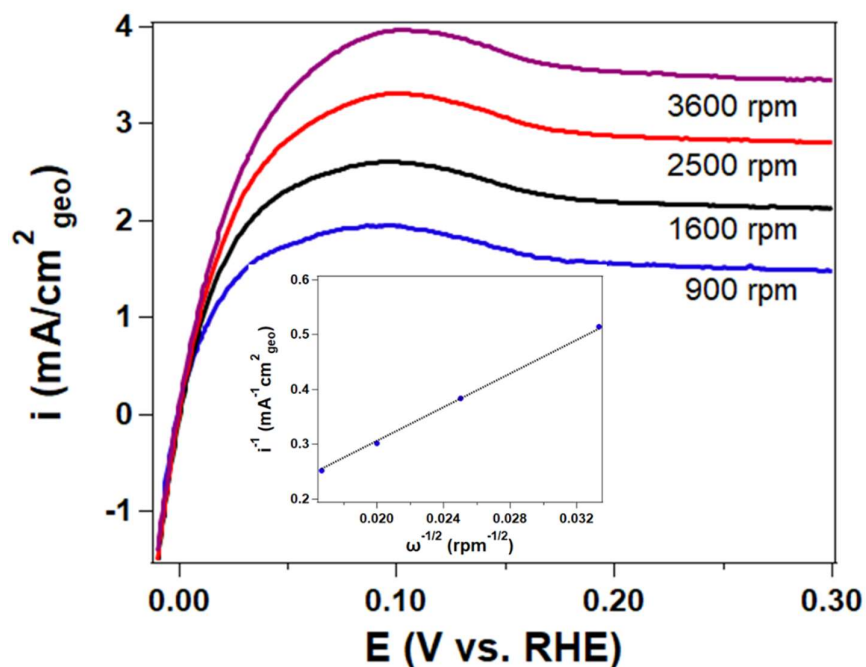


Figure 6.3. HOR/HER polarization curves of Ru/C at different rotation rates in H₂-saturated 0.1 M KOH. Inset is the Koutecky-Levich plot for the current at 0.1 V vs. RHE where the plot is inverse maximum current vs. inverse rotation rate. The number of electrons transferred is determined to be ~1.86.

For the HOR polarization curves shown in Figure 6.4a, a maximum in the HOR current (located at $E_{\max}$) is observed at all pH conditions. The potentials at maximum HOR current ($E_{\max}$) in electrolytes with different pHs - determined from their corresponding HOR/HER polarization curves (Figure 6.4a) – increases initially as pH increases from 0 to 7 and then decreases afterward, resulting in a reverse “V”-shaped relationship between $E_{\max}$ and pH (Figure 6.4b). The decrease of the polarization current at potentials greater than $E_{\max}$ (which would otherwise plateau at the limiting current) is a consequence of the decrease of HOR activity due to the loss of active surface sites from oxidation of surface Ru. Therefore, $E_{\max}$ could be indicative of the easiness of surface oxidation; however, because both hydrogen oxidation and hydroxide adsorption are likely contributing to the kinetic current, isolating hydroxide adsorption in the polarization curves is non-trivial. Consequently,

we invoke *ab initio* simulations of the electrode interface to clarify our understanding of the role of oxidation in determining the HOR/HER activity of Ru.

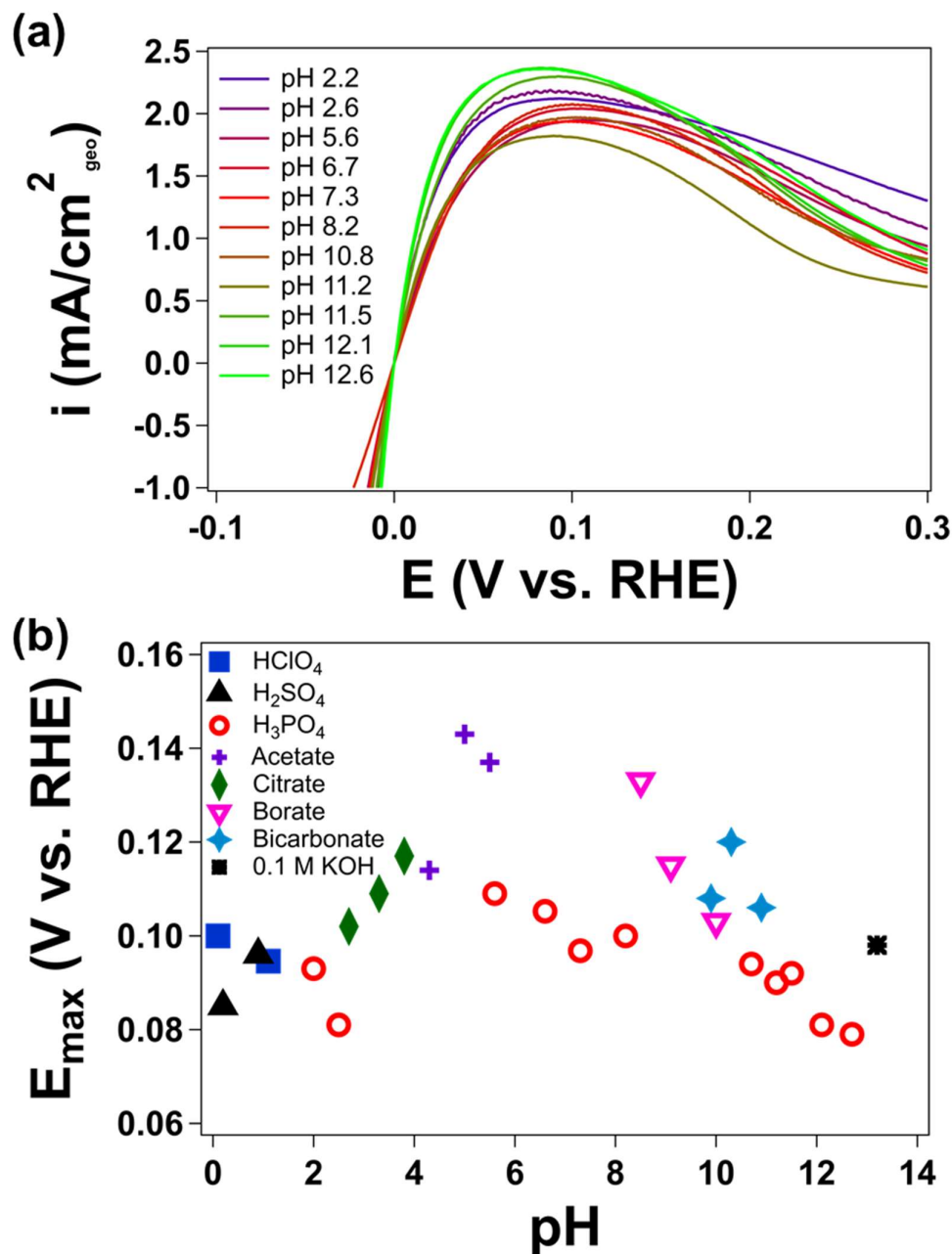


Figure 6.4. (a) Representative polarization curves for Ru in a variety of pHs. HOR/HER polarization curves were measured at scan rate of 10 mV/s and rotation rate of 1600 rpm at 293 K. Ru/C loading is 20 $\mu\text{g}_{\text{Ru}}/\text{cm}^2$. (b) The peak potential in the HOR polarization curve in different buffer solutions at a variety of pHs. The E_{max} shows the inverse trend to the exchange current density with pH trend.

6.3.3 DFT investigation

In lieu of being able to directly measure the apparent hydrogen binding energy from the CVs on Ru, a DFT investigation was performed to elucidate at the atomistic level the pH behavior of Ru under HOR/HER conditions. On the basis of the pH dependence of the polarization curves shown in Figure 6.4, along with a body of research indicating the ease of Ru oxidation under mild oxidation conditions, we hypothesize that incipient Ru oxidation (i.e., hydroxylation of the Ru surface) is responsible for the non-monotonic activity trend with respect to pH. To determine the validity of the surface oxidation hypothesis, we compute specific adsorption energy of protons and hydroxide ions at 0 V vs. RHE. On Ru (0001) terraces (Figure 6.5a), we find that the formation of adsorbed hydrogen at 0 V vs. RHE is preferential (free energy of adsorption of -0.37 eV) to the formation of adsorbed hydroxyl (free energy of adsorption of +0.22 eV). Importantly, on an RHE scale, the adsorption of a proton or a hydroxide ion is pH *independent*. Based on these results, H* is preferential to OH* on Ru (0001) terraces until ~ 0.3 V vs. RHE, and surface oxidation should play no major role in determining the HOR/HER activity of Ru terrace sites. A different situation, however, transpires on the Ru steps. On Ru steps, however, the formation of adsorbed hydroxide is preferential to an adsorbed proton at 0 V vs. RHE (Figure 6.5b). Furthermore, adsorbed water at pH 14 is more weakly bound to Ru steps than at pH 0, the same trend found on the (110) surfaces of Pt, Ir, Pd, and Rh. The consequence of weakening water adsorption on Ru at high pH is two-fold: 1) the apparent hydrogen binding energy strengthens, and 2) the formation of adsorbed hydroxide becomes more preferential. Thus, Ru step sites seem to be susceptible to increased formation of adsorbed hydroxide with increased pH.

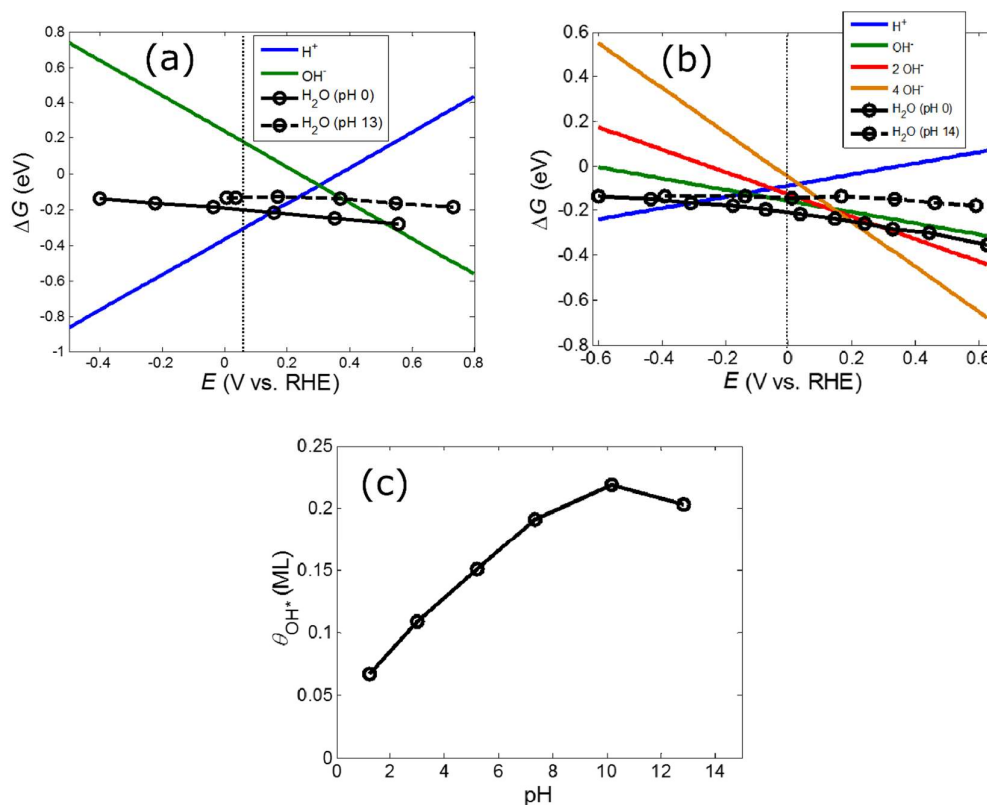


Figure 6.5. (a) Surface Pourbaix diagram for Ru (0001) terraces at 293 K. The dashed vertical line indicates the equilibrium potential for the HOR/HER. (b) Surface Pourbaix diagram for Ru step/edges at 293 K. OH^- , $2 OH^-$, and $4 OH^-$ correspond to $\frac{1}{4}$ monolayer (ML), $\frac{1}{2}$ ML, and 1 ML, respectively. The dashed vertical line indicates the equilibrium potential for the HOR/HER. (c) Fractional coverage of hydroxide on Ru steps at 0 V vs. RHE and 293 K as a function of pH.

Upon employing Equation 6.21 to determine the surface oxidation state, we find that, indeed, the coverage of adsorbed hydroxide triples on Ru steps at pH 13 compared to pH 1 (Figure 6.5c). The consequence of weakening water adsorption on Ru steps is that adsorption of hydroxide onto Ru steps becomes more preferential as the pH is increased. Therefore, in order to model the pH-dependent behavior of Ru, the pH-dependent hydroxide adsorption on Ru steps must be accounted for.

Thus, the adsorption energies were computed of both H-up and H-down water networks over the pH range for a Ru (0001) terrace, a Ru (0001) step, and a Ru (0001) hydroxylated step. The computed pH-dependent water adsorption energies, together with the standard HBE for each surface (as defined in Equation 6.15), results in the

trend in apparent HBE shown in Figure 6.6a. For each of the three characteristic Ru surfaces, the same general trend of strengthening apparent HBE is observed as the pH is increased. However, the absolute values of the apparent HBE for each surface are in stark contrast. Whereas the apparent HBE on a Ru terrace and a *clean* Ru step are nearly identical in both magnitude and trend, the apparent HBE on a *hydroxylated* Ru step is approximately 0.25 eV weaker at all pH values than either the terrace or the clean step. As a result, the weakening of water adsorption with increasing pH on a hydroxylated Ru step leads to the apparent HBE approaching its theoretical optimal value for HOR/HER of 0 eV.

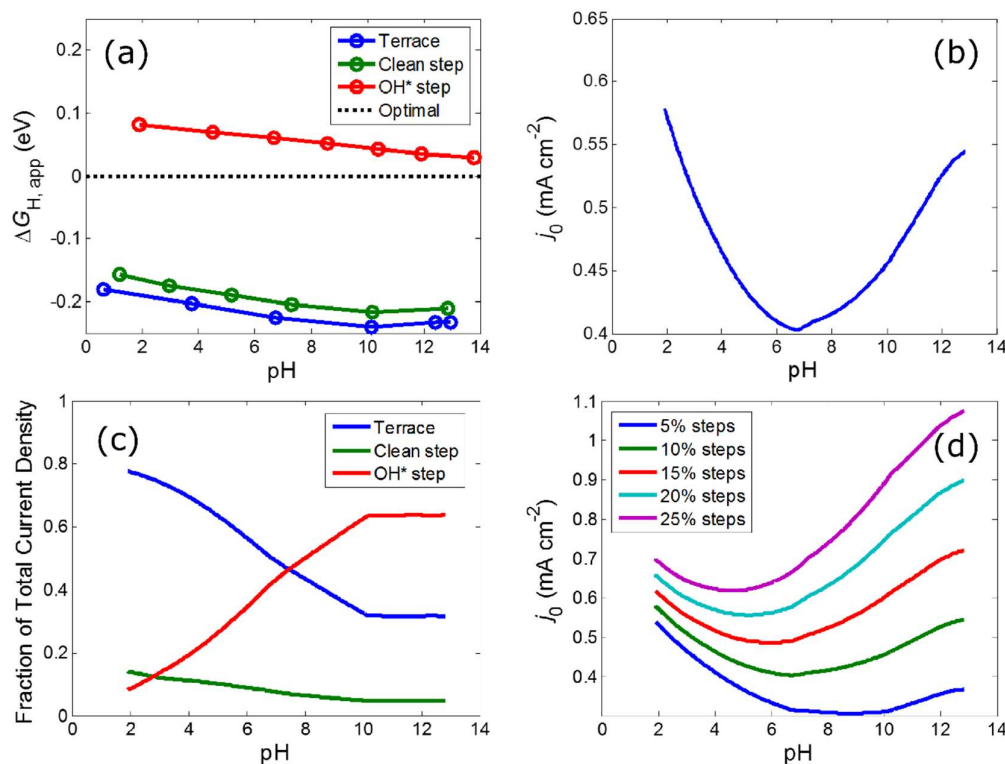


Figure 6.6. (a) Dependence of apparent Gibbs free energy of hydrogen adsorption for a Ru terrace, a Ru step, and a hydroxylated Ru step. (b) Predicted HOR/HER exchange current density as a function of the pH for a representative Ru nanoparticle. The results were computed assuming a nanoparticle with 10% step/edge sites, and a reaction symmetry factor of 0.575. (c) Relative contributions of each Ru surface (terrace, step with and without OH*) to the overall nanoparticle activity. (d) Dependence of HOR/HER exchange current density on the fraction of total step/edge sites (both clean and hydroxylated).

The predicted exchange current density of a Ru nanoparticle with 10% hydroxylated step/edge sites is shown in Figure 6.6b. The trend in the predicted exchange current density is in excellent qualitative agreement with the experimentally measured exchange current densities shown in Figure 6.2. Partitioning the overall current density into contributions from Ru terraces, clean Ru steps, and hydroxylated Ru steps, the minimum HOR/HER activity in Figure 6.6b is shown to approximately coincide with the Ru terraces and the hydroxylated Ru steps contributing equally to the overall Ru HOR/HER activity (Figure 6.6c). Past this critical pH, the hydroxylated Ru steps are further activated and the overall Ru HOR/HER activity begins to increase. Thus, as the number of Ru steps are increased (e.g., with smaller nanoparticle sizes), the HOR/HER activity is further improved and the critical pH of minimum HOR/HER activity decreases (Figure 6.6d).

Using the knowledge gained herein regarding the pH-dependent electrochemical behavior of Ru, together with Butler-Volmer kinetic modeling and first-principles DFT simulations of the solvated electrode interface, we propose the mechanism shown in Figure 6.7 as explaining the pH-dependent HOR/HER on Ru. Under low pH conditions (Figure 6.7a), Ru is observed to have high HOR/HER activity, with the Heyrovsky energy barrier being low and the terrace sites contributing nearly 80% of the overall activity. The low energy barrier of the Heyrovsky step is due to the strong water adsorption at low pH, and consequently the ability of the water molecule to serve as a proton shuttle during adsorption of H_2 , as depicted in Figure 6.7a²¹⁹. However, water adsorption weakens as the pH is increased. The weakening of water adsorption is directly related to the lengthening of the hydrogen bond between H_2O and the adsorbed H_2 (H_2^*). As a result, the hydrogen bond between H_2O and H_2^* , crucial for lowering the energy of the Heyrovsky transition state, is weakened and the energy barrier is consequently increased as shown in Figure 6.1.

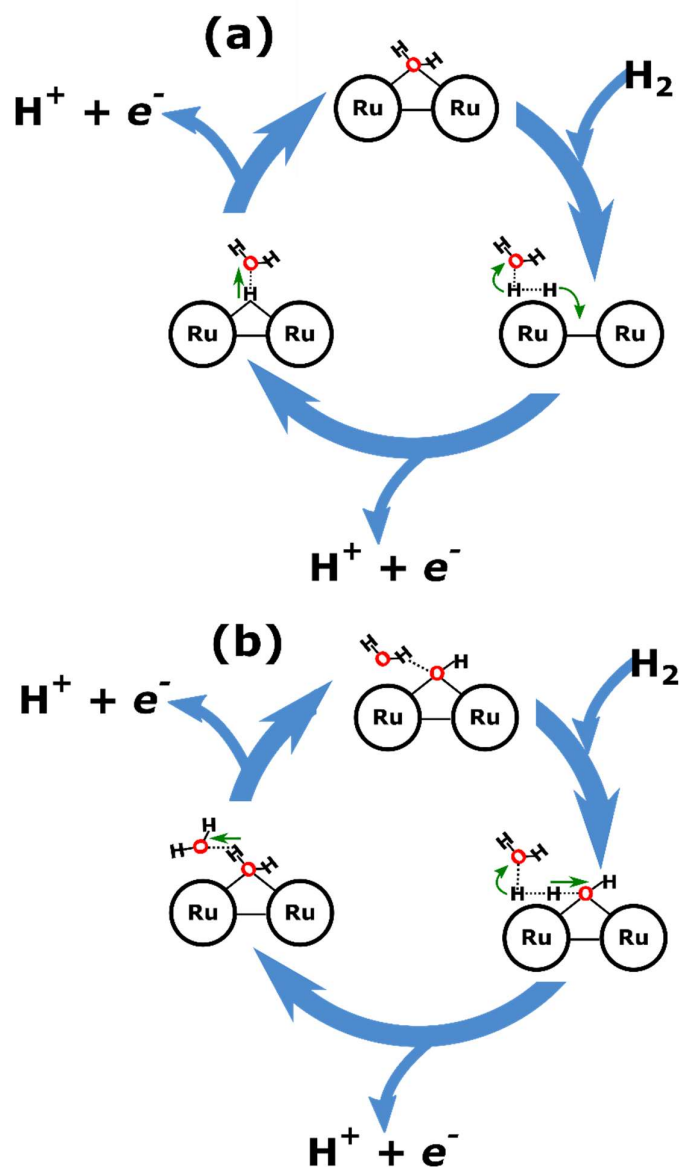


Figure 6.7. (a) The proposed reaction pathway occurring under acidic conditions. At these conditions, Ru terrace sites primarily contribute to the HOR/HER activity (Figure 6.6c). (b) The proposed reaction pathway occurring under basic conditions. This pathway occurs only on Ru steps, where incipient surface oxidation begins prior to 0 V vs. RHE at high pH. The green arrows depict the movement of the H atoms following the formation of the activated complex.

However, as the pH is increased, hydroxide begins to adsorb on Ru steps. The newly adsorbed hydroxide provides a second hydrogen bond in the Heyrovsky transition state (Figure 6.7b). The second hydrogen bond compensates for the weakening of the hydrogen bond depicted in Figure 6.7a. Consequently, Ru steps with

adsorbed hydroxide become the primary active sites at basic conditions, as they are instrumental in lowering the barrier of the Heyrovsky step.

6.4 Conclusions

The HOR/HER activity of Ru/C determined by the RDE method shows a V-shaped dependence of pH from pH 0 to pH 13. The potential of maximum current in the HOR polarization curves was found to be inversely related to the HOR/HER activity, leading to the hypothesis that oxidation of the Ru nanoparticles may be having an effect on the HOR/HER activity. The *ab initio* DFT simulations used to test our hypothesis indicated that hydroxylation of Ru steps becomes more facile as the pH is increased. Furthermore, the apparent hydrogen binding energy indicates that hydroxylated Ru steps are highly active under basic conditions, therefore leading to the experimentally observed increase in HOR/HER activity. Using the apparent hydrogen binding energy as the single HOR/HER kinetic descriptor, we reproduce the experimental activity trend as a function of the pH. At the mechanistic level, the increase in HOR/HER activity is presumed to result from the OH*-mediated stabilization of the Heyrovsky transition state, due to the Heyrovsky-Volmer pathway being the preferred reaction route at all pHs based on a dual-pathway kinetic model.

6.5 Acknowledgments

‡ S. A. Giles, J. Nash, and Y. Wang contributed equally to this work. Y. Wang was supported by the Shanxi Scholarship Council of China.

Chapter 7

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

7.1 Modeling of Nanoparticles and Supported Nanoparticles for Electrocatalysis

Nanoparticle electrocatalysts offer a high degree of catalyst utilization and are therefore desirable when maximizing efficiency of an electrochemical system. However, nanoparticles generally offer a multitude of adsorption sites with their own reactive properties, in addition to being affected strongly by the choice of catalyst support. In this thesis, we employ first-principles density functional theory (DFT) simulations of nanoparticles supported on graphene and graphene doped with nitrogen or boron to elucidate the role of the support on catalysis occurring on the nanoparticles. We also employ DFT calculations to understand differences in adsorption energetics on terrace and step sites of nanoparticle metal oxides.

In Chapter 2, the effect of the support is experimentally demonstrated through the synthesis of Ni nanoparticles support on carbon nanotubes and nitrogen-doped carbon nanotubes. The doping of nitrogen into the carbon nanotube support was found to yield a threefold increase in the HOR/HER exchange current density. DFT simulations of Ni nanoclusters on graphene and N-doped graphene revealed that the doping of nitrogen into the graphene support stabilizes the Ni nanoparticle against reconstruction. This result agrees with experimental observations that doping of the carbon nanotube supports limits sintering of the Ni nanoparticles by “tethering” them to the carbon nanotube framework.

In Chapter 3, we further explore the effects of graphene and doped graphene supports by considering graphene, nitrogen-doped graphene, and boron-doped graphene as supports for Ni, Cu, and Ag nanoparticles. Specific novelties included:

1. *Modeling of nanoparticle-support interactions between Ni, Cu, and Ag nanoparticles and graphene, nitrogen-doped graphene, and boron-doped graphene.* We find that in each case we consider, that nitrogen-doped graphene and boron-doped graphene supports interact more strongly with each nanoparticle. The stronger nanoparticle-support interaction consequently stabilizes the nanoparticles against sintering and increases monodispersity, a widely observed experimental phenomenon that highlights a key advantage of doped and defected supports in general.
2. *Visualization of the complex site heterogeneity of the supported nanoparticles through heat maps indicating site-to-site variations in hydrogen adsorption and HOR activity.* Doping of nitrogen or boron into the graphene support is observed to greatly increase the HOR activity of Ni nanoparticle sites near the support. In contrast, and interestingly, doping of nitrogen or boron into the graphene is predicted to decrease the HOR activity of Cu and Ag nanoparticles. This observation is rationalized through the universal weakening of hydrogen adsorption of nanoparticles supported on doped graphene. To our knowledge, this is the first time that dopant effects on volcano curves are analyzed.
3. *Quantitative comparison of intrinsic site reactivity properties to those induced by dopants.* Our findings show that the dopant-induced change in hydrogen adsorption for a given site can equal or exceed the importance of site type (e.g., edge, terrace, etc.) in determining the strength of hydrogen adsorption at a site, and hence the HOR activity. The dopant-induced change is shown to be most dominant for the supported Ni nanoparticles and least dominant for the supported Ag nanoparticles, which corresponds to the observed trend of the nanoparticle-support interaction being strongest for Ni and weakest for Ag.
4. *Prediction of the site-dependent hydrogen adsorption through the first-of-its-kind principal component analysis (PCA) that automatically identifies novel descriptors of reactivity.* The PCA adsorption model performs well for a variety of supported nanoparticles and site types. Strikingly, we discover that while the PCA adsorption model involves a linear term related to the d band center, a descriptor

frequently employed in catalysis, non-linear terms and the local coordination environment contribute significantly to reactivity as well. Furthermore, we show that the recent generalized coordination number model introduced by Sautet and co-workers breaks down for moderate size supported nanoparticles.

5. *Development of a size-dependent activity model that yields quantitative agreement with the experimental system.* The size-dependent activity model accepts a distribution of nanoparticle sizes as an input, chosen from experimental data. Together with first-principles density functional theory simulations of sites nearest the support, more realistic predictions of catalytic activity are obtained.

In Chapter 4, the modeling of nanoparticles was extended to Fe_3O_4 nanoparticles for oxygen evolution. On the basis of microscopy images of the synthesized Fe_3O_4 nanoparticles, the nanoparticles were determined to be cuboctahedral in shape, exposing the (100) and (111) facets, along with the (211) edge. The experimental activity of the Fe_3O_4 nanoparticles was determined to vary linearly with the edge length of the nanoparticles. DFT+ U simulations were performed and found that the (211) edge had the lowest overpotential for the oxygen evolution reaction. From the DFT simulations, the conversion of O^* to OOH^* on the Fe_3O_4 (211) facet was found to be the potential-determining step. Further experimental synthesis of amorphous FeO_x and amorphous NiFeO_x was performed, with the NiFeO_x catalyst having the highest activity.

7.2 Modeling of the pH-dependent Electrochemical Interface

Ab initio simulations of the solvated electrochemical interface have become a key area of interest. The electrochemical interface is complex system which, due to the time scales involved in a reactive, solvated electrochemical system, poses challenges to computational studies. In this thesis, we employ *ab initio* simulations on static water networks with different dipole orientations to capture the dependence of water adsorption on the pH and potential.

In Chapter 5, *ab initio* simulations of the electrochemical interface indicate that water adsorption varies as a function of the pH. Specific novelties included:

1. *Experimentally measured pH-dependent HOR/HER activities of Au, Cu, and Ag electrocatalysts.* We have previously demonstrated that the HOR/HER activity of platinum group metals, including Pt, Ir, Pd, and Rh, universally decreases with increasing pH. In this work, we have extended this analysis to coinage group metals, including Au, Cu, and Ag. Here we find that the HOR/HER activity of Au, Cu, and Ag also decreases with increasing pH. Interestingly, the activity of Au, Cu, and Ag decreases with increasing pH despite each of these metals being widely accepted as residing on the opposite branch of the HOR/HER volcano from the platinum group metals.
2. *Simulation of the Gibbs free energy of water adsorption as a function of pH for Pt, Ir, Pd, Rh, Au, Cu, and Ag catalysts.* To investigate our hypothesis that the inclusion of water adsorption is an essential feature to explain the experimentally observed HOR/HER activities and underpotential-deposited hydrogen (H_{UPD}) peak potentials, we compute from first-principles the pH dependence of water adsorption. For Pt, Ir, Pd, and Rh, we find that water adsorption weakens with increasing pH, while water adsorption strengthens with increasing pH for Au and Cu. The opposite pH-dependent trend of water adsorption observed here is significant since Au and Cu reside on the opposite branch of the HOR/HER volcano from the platinum group metals, as mentioned above. Moreover, water adsorption on Ag was found to be approximately pH independent, in agreement with Ag exhibiting the weakest pH dependence of the HOR/HER activity for the metals studied here.
3. *Direct comparison of the pH-dependent apparent Gibbs free energy of hydrogen adsorption, as computed from DFT, to experimentally measured values of the $H-UPD$ peak position for Pt, Ir, Pd, and Rh.* For Pt, Ir, Pd, and Rh catalysts, we previously shown that the experimentally measured HUPD peak position shifts to more positive potentials. Our first-principles simulations of the apparent Gibbs free energy of hydrogen adsorption are shown to be in good quantitative agreement with

the previously measured H_{UPD} peak potentials measured from cyclic voltammetry. Consequently, the thermodynamic descriptor of HOR/HER that we have previously proposed and compute for the first time herein is confirmed to match well with available experimental data for the catalysts studied here.

4. *Prediction of onset potentials for the adsorbed hydroxyl (OH_{ad}) species which are consistent with experimental carbon monoxide (CO) stripping data available for Pt, Ir, Pd, and Rh catalysts.* CO stripping cyclic voltammetry is a commonly employed electrochemical technique which indicates the potential at which the OH_{ad} species forms on the electrode surface. Recently, some groups have proposed that OH_{ad} is responsible for displacing the HUPD species. Consequently, this hypothesis proposes that OH_{ad} forms at later potentials as the pH is increased. However, this hypothesis is in qualitative disagreement with the experimentally observed earlier onset of CO stripping for Pt, Ir, Pd, and Rh. By computing the free energies of formation of adsorbed hydrogen, hydroxyl, and water over the entire pH range, we demonstrate that our theory is consistent with experimental data available for Pt, Ir, Pd, and Rh catalysts.

5. *Construction of a first-of-its-kind volcano plot demonstrating the apparent Gibbs free energy of hydrogen adsorption to be a universal descriptor of HOR/HER.* Previous work by our group and others have frequently implemented the DFT-computed hydrogen binding energy as a descriptor for the HOR/HER activity; however, the hydrogen binding energy cannot explain either the widely observed phenomena of decreasing HOR/HER activity with increasing pH or the shift in the H_{UPD} peak in cyclic voltammograms. We show that comparing the Gibbs free energy of hydrogen adsorption computed from DFT to electrochemical measurements of the exchange current density at the same pH, that all catalysts studied herein (Pt, Ir, Pd, Rh, Au, Cu, and Ag) follow a universal volcano trend.

In Chapter 6, the methodology used for studying the pH-dependent water adsorption in Chapter 5 is extended to study the pH-dependence of HOR on Ru nanoparticles. Specific novelties included:

1. *Experimentally measured pH-dependent HOR/HER activities of Ru nanoparticles.* We have previously demonstrated that the HOR/HER activity of platinum group metals, including Pt, Ir, Pd, and Rh, universally decreases with increasing pH. In this work, we have extended this analysis to Ru. Here we find, interestingly, the HOR/HER activity of Ru decreases from $\sim$ pH 1-7, and then increases from $\sim$ pH 7-13. Importantly, the Ru catalyst has an HOR/HER activity in alkaline media (pH 13) which is nearly equal to its activity in acidic media (pH 1). This behavior is highly promising for the design of alkaline HOR/HER catalysts which rival the activity of acidic HOR/HER catalysts.
2. *Computing the kinetic barriers of the Tafel-Heyrovsky-Volmer HOR/HER mechanism on Ru as a function of the electrolyte pH.* Using a previously established methodology of computing the barriers of the Tafel, Heyrovsky, and Volmer steps based on experimental HOR/HER polarization curves, we show here for the first time that the HOR/HER on Ru follows a Heyrovsky-Volmer mechanism, where Volmer is the rate-determining step. Although the Volmer step remains the rate-determining step throughout the entire pH range, the energy barrier for the Heyrovsky step is demonstrated to be more sensitive to the pH. This phenomenon of distinct sensitivity of the Heyrovsky step is later rationalized through a proposed mechanism in which the Heyrovsky step takes place primarily on vacant terrace sites at low pH, but primarily on hydroxylated step sites at high pH.
3. *First-principles simulations of interfacial water and the apparent Gibbs free energy of hydrogen adsorption on Ru terraces, steps, and hydroxylated steps under an applied potential and pH.* For each Ru surface, water adsorption was computed as a function of the pH and potential. Furthermore, because Ru is known to be highly oxophilic, the adsorption energy of hydroxide, along with the proton adsorption energy, were computed as a function of the pH. While the formation of adsorbed hydroxyl was determined to not be energetically favorable on the Ru terrace, the formation of adsorbed hydroxyl was deemed energetically favorable at the HOR/HER equilibrium potential on Ru step sites. Consequently, the coverage of hydroxyl on Ru

steps is found to increase significantly as the pH is increased. Furthermore, upon computing the apparent Gibbs free energy of hydrogen adsorption on Ru terraces, steps, and hydroxylated steps, the intrinsic activities of the terrace and clean step sites were found to decrease with increasing pH, while the intrinsic activity of the hydroxylated step was found to increase with increasing pH.

4. *First-principles prediction of the pH-dependent exchange current density of Ru which matches well the trend of the experimentally measured exchange current density with pH.* Using the apparent Gibbs free energy of hydrogen adsorption computed from first-principles using density functional theory (DFT) of each Ru surface considered herein (terrace, clean step, and hydroxylated step), the pH-dependent HOR/HER activity of Ru is predicted and found to match closely with the experimental trend of decreasing activity from $\sim$ pH 1-7 and increasing activity from $\sim$ pH 7-13. Further, to estimate the HOR/HER activity of Ru in a model which considers both Ru terrace sites, Ru step sites, and hydroxylated Ru step sites, a fraction of step sites (related directly to nanoparticle size) was assumed. An activity model assuming 10% step sites was found to give the best qualitative agreement with the observed experimental trend; this percentage of step sites was found to correspond to an $\sim$ 3 nm diameter nanoparticle, in exceptional agreement with the 2.6 ± 0.6 nm Ru nanoparticle size distribution determined from transmission electron microscopy (TEM).

5. *Proposed mechanism for the pH-dependent HOR/HER on Ru which incorporates kinetic modeling of the pH-dependent HOR/HER polarization curve and first-principles modeling of the pH-dependent apparent Gibbs free energy of hydrogen adsorption.* Based on the kinetic modeling of the HOR/HER polarization curve which indicated the Heyrovsky-Volmer mechanism to be predominant over the entire pH range, along with the first-principles DFT simulations which indicate Ru terraces as the active site at low pH and hydroxylated Ru steps to be the active site at high pH, we propose a mechanism for the progression of HOR/HER on Ru which is consistent with our findings.

7.3 Recommendations

Predicting the structure and reactivity properties of nanoparticles is of widespread interest not only in electrochemistry, but in catalysis research in general. Wulff constructions coupled with DFT-predicted energies of surface facets have been used recently to predict the equilibrium shape of nanoparticles^{105,220,221}. However, these studies are typically confined to the ultrahigh vacuum regime where adsorbate coverage on the nanoparticle is negligible. The prediction of nanoparticle structure under reaction conditions is generally more complicated as oxidation of the nanoparticle can occur, along with entropy-induced deviation from the Wulff equilibrium structure due the experimental system operating at a finite temperature^{222,223}. In an electrochemical system, operation at a certain applied electrode potential and pH can induce changes in the nanoparticle structure and adsorbate coverages.

While the DFT methods used in this thesis are approximate in nature and have their own error associated with them²²⁴, these errors often cancel each other out when computing energy differences (e.g., reaction energies or kinetic barriers)²²⁵. However, if a wrong or irrelevant surface is chosen and modeled with DFT, the predictions will likely have little, if any, agreement with experiment. Consequently, future work on nanoparticle catalysis will likely focus on predicting the structure of nanoparticles under a given set of reaction conditions, including specific applied potentials and pHs.

Future studies on the pH dependence of HOR/HER will likely focus on the dynamic behavior of the electrode-electrolyte interface. The value of the methodology used in this thesis is that all energetics are computed *ab initio* at the quantum level. However, the use of computationally-expensive density functional theory confines us to directly compute only the thermodynamics the HOR/HER process. To allow for direct computation of the HOR/HER *kinetics*, the water near the electrode must be treated dynamically (i.e., through either classical or *ab initio* molecular dynamics) to capture the solvent reorganization known to accompany charge transfer reactions

The dynamic treatment of the electrode-electrolyte interface brings its own set of challenges, however. First, the dynamic trajectory must be performed over a sufficiently long time scale in order to capture the entirety of the solvent reorganization process. Simulations of adsorbed water networks on a Pt surface indicate that the reorganization of the solvent occurs over a time scale on the order of nanoseconds²²⁶. Moreover, the time steps for such simulations of water networks are typically around one femtosecond. As a result, one should expect to perform at least 10^6 time steps in order to capture a single charge transfer and solvent reorganization process.

Nevertheless, there is a bright future for being able to compute directly the reaction kinetics of HOR/HER in solvated, electrified systems. Numerous recent advances have been made on the application of metadynamics to computing the free energy profile of various reactions^{227–230}. One such study involved computing the reaction pathway of CO reduction on Cu (100) using a combination of *ab initio* molecular dynamics and metadynamics²³¹. However, due to the computational expense of *ab initio* molecular dynamics, trajectories were simulated only on the order of picoseconds, thereby potentially missing slower solvent reorganization.

Central to this work, future studies will also need to capture the pH-dependence of HOR/HER. The method discussed herein of modulating the charge of the electrode, thereby changing the electrode potential and relating to pH through the Nernst equation, could be extended to future studies where the water is treated dynamically. If classical molecular dynamics is employed (where a force field is assumed *a priori*), one could mimic changes in the electrode potential and pH by imposing a Gaussian charge distribution on the electrode surface. Alternatively, protons, hydroxide ions, and counterions could be explicitly included in the water network. Each approach has its merits and drawbacks, and future research should focus on establishing a protocol on how the experimental pH is best captured within the limitations of computational resources.

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**NICKEL SUPPORTED ON NITROGEN-DOPED CARBON NANOTUBES AS
HYDROGEN OXIDATION REACTION CATALYST IN ALKALINE
ELECTROLYTE**

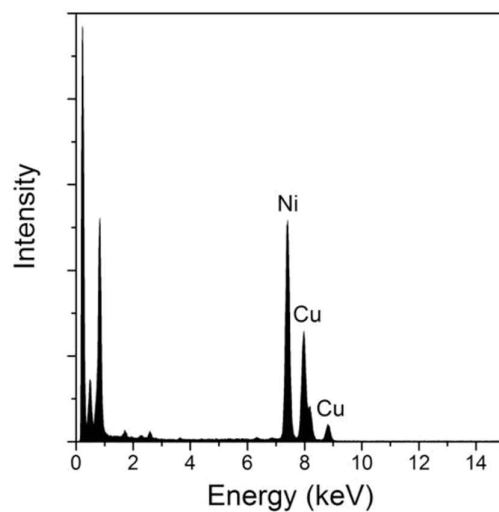


Figure A.1. EDS spectra of the Ni/N-CNT catalysts obtained on the JEOL JEM-3010 TEM equipped with EDS. The Cu peaks come from the copper grid.

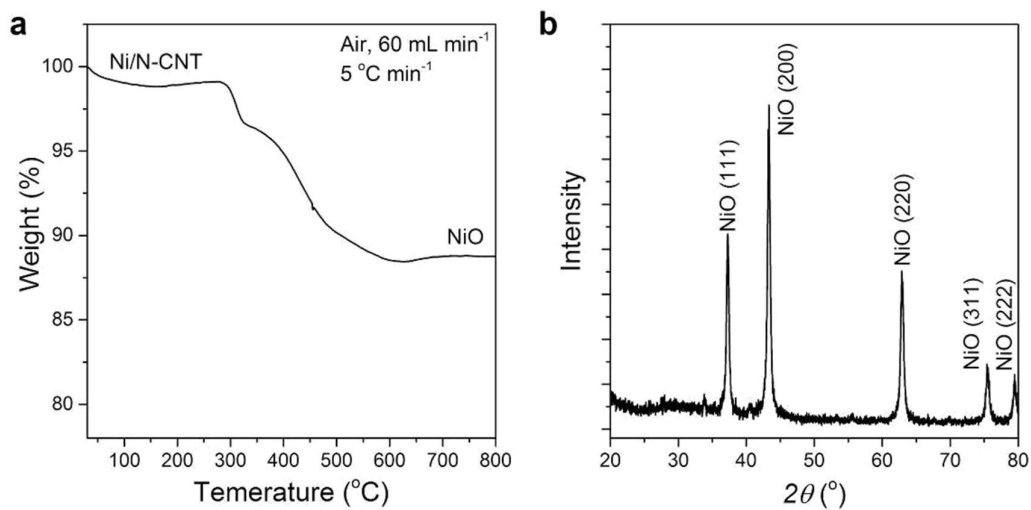


Figure A.2. (a) TGA curve of the Ni/N-CNT catalyst. (b) XRD pattern of the residue after TGA test. The TGA was performed under air atmosphere. N-CNTs were burned off and Ni was oxidized to NiO, which was confirmed by the XRD pattern (JCPDS card No. 47-1049). The weight remained after the TGA test is 88.7 wt %. Based on the formula of NiO, 78.6 wt % of NiO comes from Ni. Thus the Ni loading in Ni/N-CNT is $88.7 \text{ wt \%} \times 78.6 \text{ wt \%} = 70 \text{ wt \%}$.

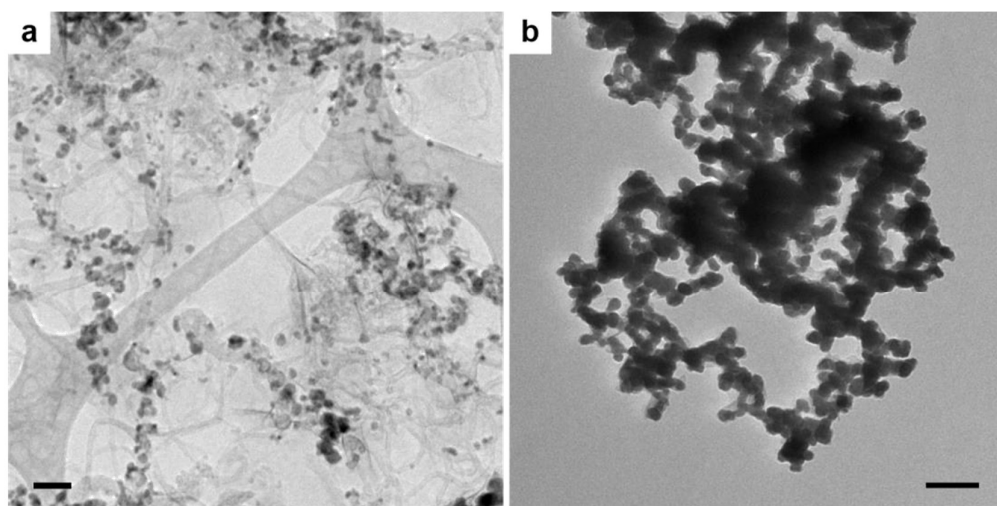


Figure A.3. TEM images of (a) Ni/CNT, (b) Ni. The scale bars, 100 nm.

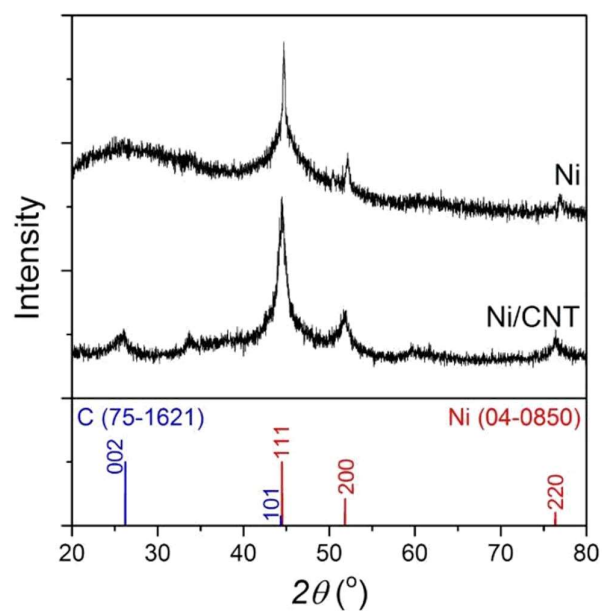


Figure A.4. XRD patterns of Ni/CNT and Ni. The standard pattern of Ni (JCPDS card No. 04-0850) and graphite (JCPDS card No. 75-1621) are shown beneath the plots.

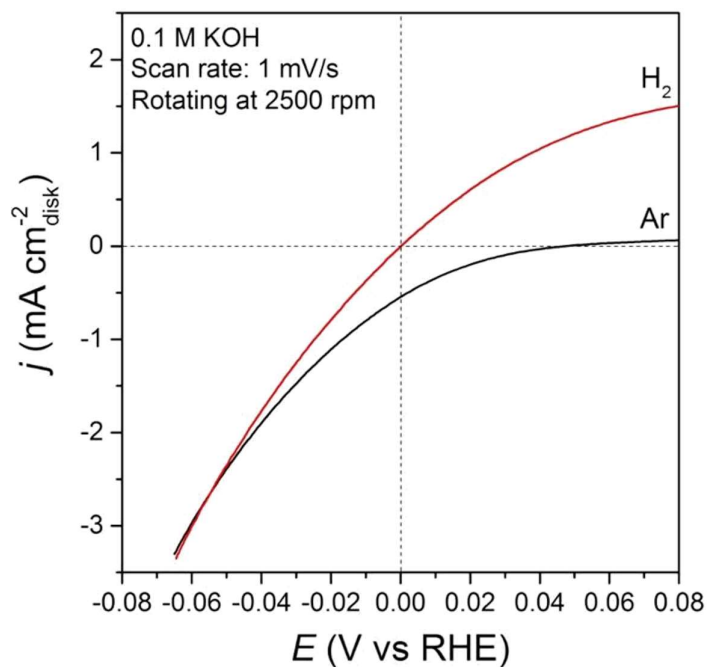


Figure A.5. Polarization curves of Ni/N-CNT in H₂ or Ar-saturated 0.1 M KOH at a scan rate of 1 mV s⁻¹ and rotating speed of 2500 rpm. To confirm the anodic current comes from HOR, we further tested the samples in an Ar-saturated solution. No anodic current was found when H₂ was replaced by Ar, indicating that H₂ is a reactant for the reaction. However, a cathodic current below 0 V was also observed in Ar atmosphere, which is similar in H₂ atmosphere. This cathodic current is attributed to the HER in which water is the reactant, and thus can be observed in both atmospheres.

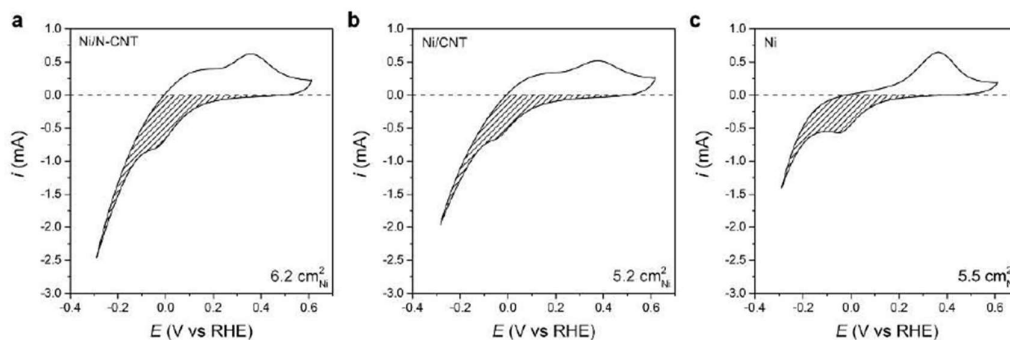


Figure A.6. Cyclic voltammetry (CV) of the catalysts in Ar-saturated 0.1 M KOH at a scan rate of 50 mV s^{-1} : (a) Ni/N-CNT, (b) Ni/CNT, (c) Ni. The patterned parts of the CV represent the area integrated to estimate the electrochemical surface area (ECSA) of Ni. The calculated ECSA of each catalyst are shown at lower right corner, respectively. The ECSA of Ni is calculated from the charge of the reduction of Ni(OH)_2 to Ni. The cathodic current at the backward scan not only comes from the reduction of Ni(OH)_2 , but also captures hydrogen evolution current. We subtract the HER current, which is estimated from the cathodic current at the forward scan. Thus only the patterned areas were integrated, which is the charge from the reduction of Ni(OH)_2 without HER. The ECSAs were calculated from the integrated area using a charge density of $514 \text{ } \mu\text{C cm}_{\text{Ni}}^{-2}$ for one monolayer of OH adsorption on Ni.

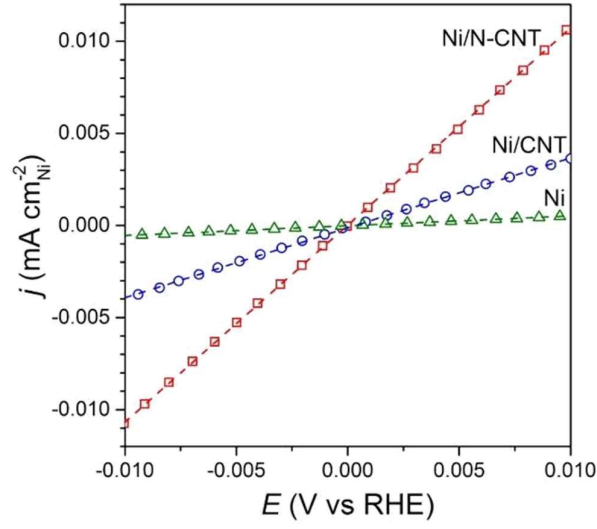


Figure A.7. Micro-polarization region (–10 mV to 10 mV) of Ni/N-CNT, N/CNT and Ni, respectively. The dash lines indicate the linear fitting.

In the micro-polarization region, the Butler-Volmer equation can be simplified to

$$j_0 = \frac{j}{\eta} \frac{RT}{F} \quad (\text{A.1})$$

where R is the universal gas constant, T is the temperature, F is Faraday's constant and j is the measured current density. Thus the exchange current density can be obtained from the slope of the linear fitting of j vs η . The obtained j_0 are listed in Table A.1, which are similar to the Butler-Volmer fitting results.

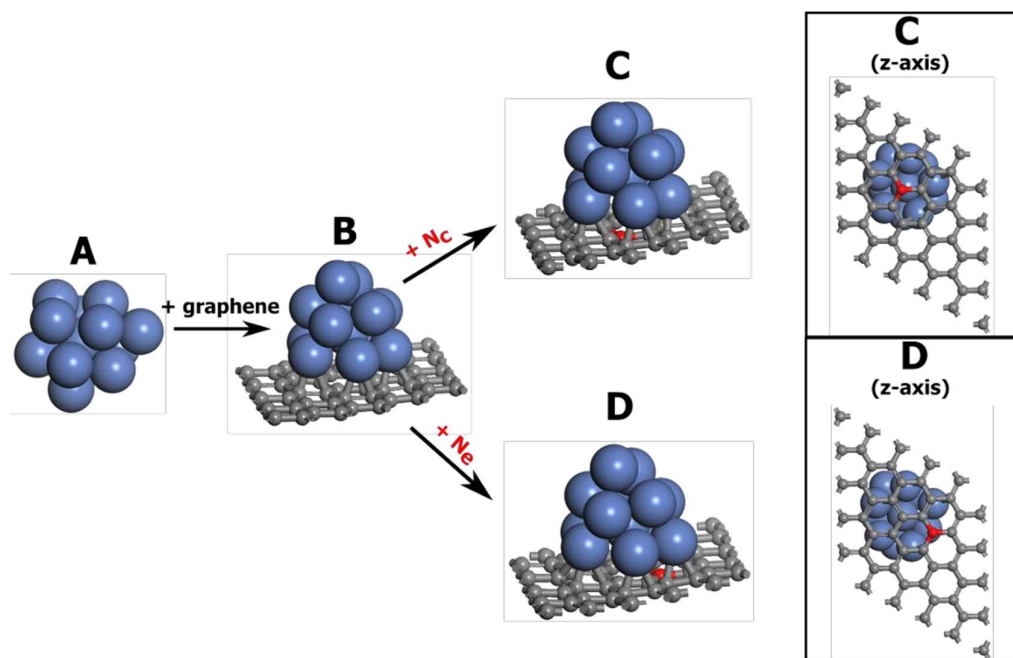


Figure A.8. Graphical depiction of the model systems considered in the current study. A: unsupported Ni_{13} , B: $\text{Ni}/\text{graphene}$, C: $\text{Ni}/\text{N}_c\text{-graphene}$, D: $\text{Ni}/\text{N}_e\text{-graphene}$ (N_c and N_e are center and edge nitrogen, respectively). Inset shows viewpoint from the z-axis to visualize the nitrogen doping location. Blue, gray, and red spheres represent Ni, C, and N atoms, respectively.

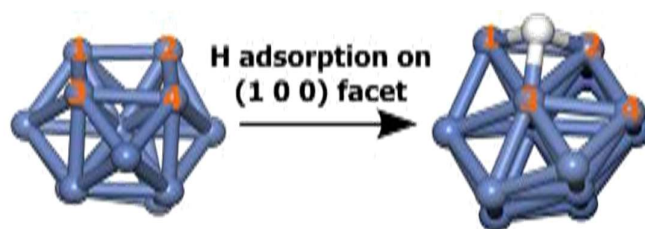


Figure A.9. Example of Ni reconstruction following hydrogen binding. Blue and white spheres represent Ni and H atoms, respectively.

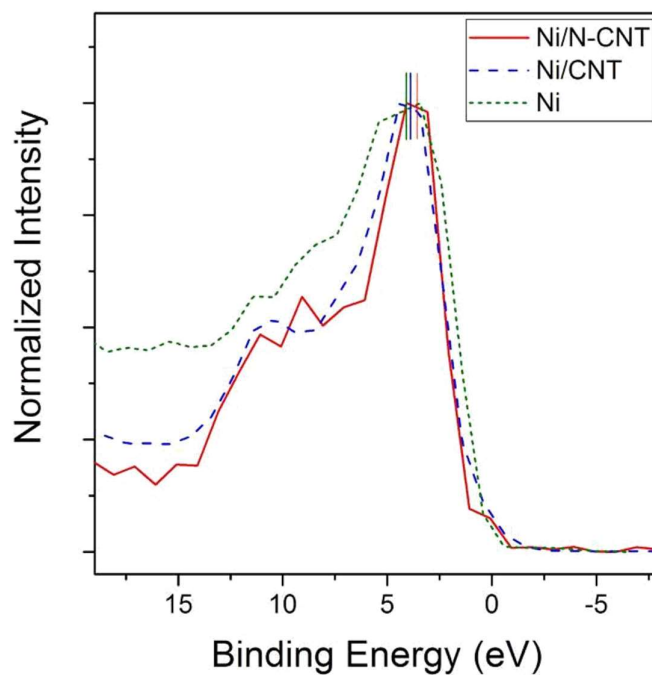


Figure A.10. Normalized XPS valence band spectra of Ni/N-CNT, Ni/CNT and Ni. The vertical lines represent the *d*-band centers. It can be observed that the valence band spectrum of Ni/N-CNT is narrower than those of Ni and Ni/CNT. The *d*-band center relative to the Fermi level follows the sequence of Ni (−4.0 eV) < Ni/CNT (−3.9 eV) < Ni/N-CNT (−3.7 eV), which is consistent with the DFT calculation results. The differences to the calculated *d*-band center shown in Figure 2.4c are mainly due to that the XPS measures the *d*-band of the whole nanoparticle, but only the *d*-band of the local sites affected by the N dopant calculated and shown in Figure 2.4c.

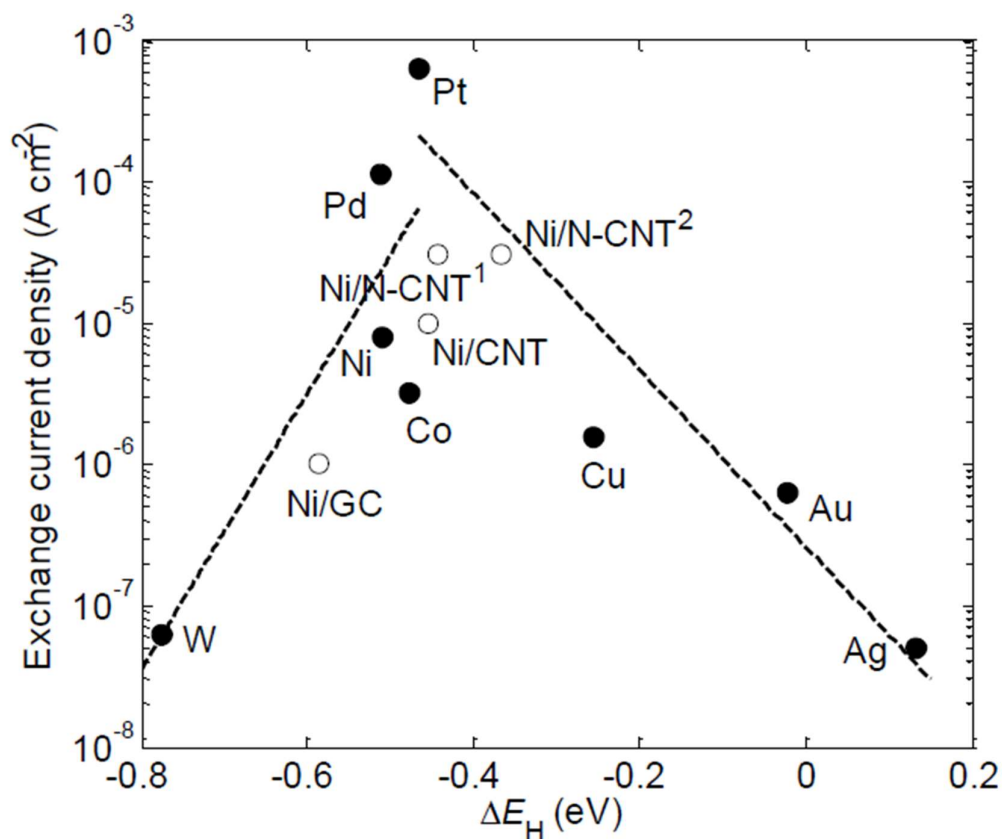


Figure A.11. Volcano plot showing *measured* exchange current densities as a function of the calculated hydrogen binding energy. Filled circles are single metal surfaces, using experimental data from Sheng *et al.*¹⁸, used in the regression to find the α and β parameters. Open circles represent the site-averaged binding energy of the nanocluster along with the measured activity of the experimental catalysts. The model systems are labeled according to their experimental counterparts, therefore: Ni/GC is unsupported Ni₁₃, Ni/CNT is Ni/graphene, Ni/N-CNT¹ is the Ni₁₃ nanocluster supported on N_c-graphene, and Ni/N-CNT² is the Ni₁₃ nanocluster supported on N_c-graphene. Fitting parameters for the ascending branch: $\alpha = 9.799\ A\ cm^{-2}\ eV^{-1}$, $\beta = 0.384\ A\ cm^{-2}$; Fitting parameters for the descending branch: $\alpha = -6.254\ A\ cm^{-2}\ eV^{-1}$, $\beta = -6.586\ A\ cm^{-2}$.

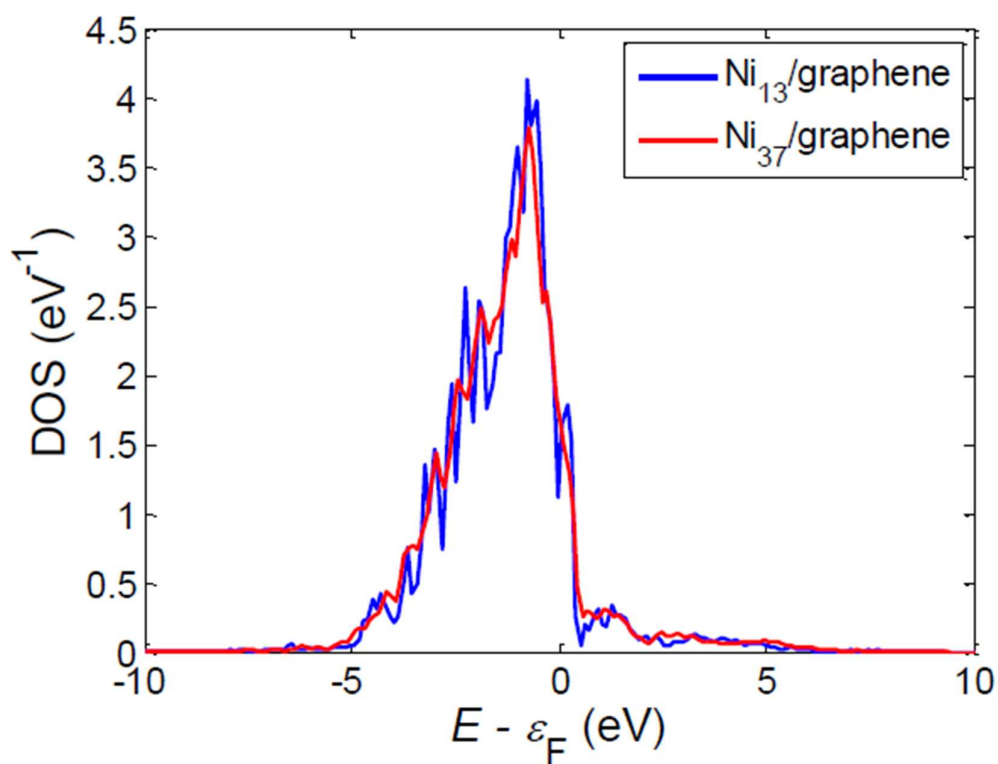


Figure A.12. Comparison of the d density of states (DOS) for the Ni₁₃ and the Ni₃₇ nanoparticles. The calculated *d*-band centers are -1.28 eV and -1.27 eV for the Ni₁₃ and Ni₃₇, respectively. The Fermi level is the energy reference.

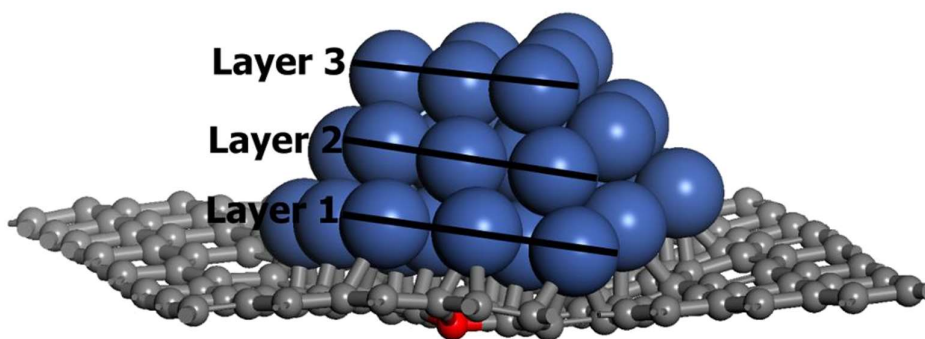


Figure A.13. Ni₃₇ nanoparticle model supported on N-graphene with an edge nitrogen dopant. Blue, gray, and red spheres represent Ni, C, and N atoms, respectively.

Table A.1. Summary of the mass activity at 50 mV vs RHE and exchange current density of Ni/N-CNT, Ni/CNT and Ni. The exchange current densities are calculated by Butler-Volmer fitting and micro-polarization methods.

Catalyst	Mass activity at 50 mV	Exchange current density ($\text{mA cm}_{\text{Ni}}^{-2}$)	
		Butler-Volmer fitting	Micro-polarization
Ni/N-CNT	9.3	0.028	0.027
Ni/CNT	1.9	0.0092	0.0097
Ni	0.28	0.0013	0.0013

Table A.2. Benchmark HOR mass activities of the PGM-free catalysts.

Catalyst	Electrolyte	Temperature ($^{\circ}\text{C}$)	Mass activity at 50 mV (mA mg^{-1})	Reference
Ni/N-CNT	0.1 M KOH	r. t.	9.3	This work
Ni/CNT	0.1 M KOH	r. t.	1.9	This work
Ni	0.1 M KOH	r. t.	0.28	This work
Raney Ni	6 M KOH	r. t.	0.15	2
Raney Ni	6 M KOH	23	0.11	3
Raney Ni/PTFE	25 wt % KOH (~5.5 M)	25	0.07	4
Raney-Ni/PTFE	25 wt % KOH (~5.5 M)	25	0.43	5
Raney Ni/PTFE	25 wt % KOH (~5.5 M)	25	0.27	6
Raney Ni/PTFE	30 wt % KOH (~6.9 M)	25	0.36	7
Ni-Mo	6 M KOH	23	1.8	6
Ni-Fe	6 M KOH	23	0.51	6
Ni-Ti	6 M KOH	23	1.5	6
Ni-Ti	6 M KOH	30	0.3	8
Ni-Mo	6 M KOH	30	5.3	9
Ni-W	6 M KOH	32	0.48	9
Raney Ni	6 M KOH	60	2.0	10
Raney Ni	6 M KOH	60	0.5	11
Ni-Ti	6 M KOH	60	1.4	11
Ni-Cr	6 M KOH	60	2.5	11
Ni-Cu	6 M KOH	60	0.9	11

Ni-Fe	6 M KOH	60	0.8	11
Ni-La	6 M KOH	60	2.0	11
Ni-Cr	6 M KOH	60	2.2	12
Ni-Ti	6 M KOH	60	1.8	12
Ni-Co	6 M KOH	80	4.0	13

Table A.3. Benchmark HOR exchange current densities of the PGM and PGM-free catalysts.

Catalyst	Electrolyte	Temperature (°C)	Exchange current density (mA cm _{metal} ⁻²)	Reference
Ni/N-CNT	0.1 M KOH	r.t.	0.028	This work
Ni/CNT	0.1 M KOH	r.t.	0.0092	This work
Ni	0.1 M KOH	r.t.	0.0013	This work
NiCoMo	0.1 M KOH	r.t.	0.015	14
Pd/Au	0.1 M NaOH	20	0.023	15
Pt(pc) ^a	0.1 M NaOH	20	0.55	16
Pt(pc) ^a	0.1 M KOH	21	0.69	17
Pt/C	0.1 M KOH	21	0.57	17
Pt/C	0.1 M NaOH	40	1.0	18
Pd/C	0.1 M NaOH	40	0.06	18
Ir/C	0.1 M NaOH	40	0.37	18

^a: pc = polycrystalline disk

Table A.4. Calculated *d*-band centers for undoped and doped cases for each layer of the Ni₃₇ model. To explore the locality of the effect of the dopant, only the *d*-band centers of the three nearest neighbor Ni atoms for each layer shown above were taken into account.

Layer	Undoped: $\epsilon_d - \epsilon_F$ (eV)	Doped: $\epsilon_d - \epsilon_F$ (eV)	$\Delta(\epsilon_d - \epsilon_F)$ (eV)
1	-1.290	-1.233	+0.047
2	-1.271	-1.278	-0.007
3	-1.313	-1.315	-0.002

Appendix A: Note 1

Calculation of the Exchange Current Density from the Volcano Plot.

Figure A.11 shows the volcano plot used to correlate the calculated, site-dependent hydrogen binding energies to exchange current density by obtaining the α and β parameters of Equation A.3. The regression in Equation A.3 was performed with respect to the close-packed surfaces of single metals (Ni, Pt, Co, etc.) for which exchange current density data was available (filled points in Figure A.11).¹ For each of the threefold hollow sites on the four Ni₁₃ model systems, the hydrogen binding energy was calculated from Equation A.2. In Figure A.11, the open points representing the *site-averaged* binding energies for unsupported Ni, Ni/graphene, Ni/N_c-graphene, and Ni/N_e-graphene are shown with the experimentally measured exchange current densities of Ni/C, Ni/CNT, and Ni/N-CNT, respectively (note that no distinction is made experimentally between the N_c-graphene and N_e-graphene systems). Figure A.11 indicates that binding energies between -0.3 and -0.5 eV were found to be optimal for HOR, in agreement with previous studies in acidic and alkaline solutions.

Appendix A: Note 2

Calculations on a Larger Ni₃₇ Nanoparticle. In order to evaluate the ability of the Ni₁₃ model to capture the thermochemical and electronic properties of the large experimental nanoparticles, we compared the results with those on a Ni₃₇ (truncated cuboctahedron) nanoparticle with a diameter of ~ 1.0 nm. The d density of states for the two models are compared in Figure A.12 and the structural model of the Ni₃₇ is shown in Figure A.13. The d -orbitals of the Ni₁₃ cluster correspond well to the larger

Ni₃₇ model. Importantly, the difference in the calculated *d*-band center is only 0.01 eV for the two nanoparticles. Activity predictions for the two models are also in close agreement: the exchange current density was predicted to be $6.7 \times 10^{-3} \text{ mA cm}^{-2}$ and $7.2 \times 10^{-3} \text{ mA cm}^{-2}$ for the Ni₃₇/graphene and the Ni₁₃/graphene, respectively.

Next, we explore the electronic effect of the nitrogen-doped support of the N_e-graphene for the two nanoparticles. Table A.4, corresponding to the structural model in Figure A.13, clearly shows that only the first layer of the Ni₃₇ nanoparticle is significantly affected by the presence of the dopant. This provides evidence that the dopant has a *local electronic effect only* on the adsorption sites of the nearby Ni atoms. As a result, it is no surprise that the smaller Ni₁₃ model exhibits a corresponding upshift in the *d*-band center with an edge nitrogen present.

Appendix A: Supplementary Methods

Hybrid Activity Model for Hydrogen Oxidation.

For each adsorption site *i*, the hydrogen binding energies are calculated according to Equation A.2,

$$\Delta E_{\text{H}} = E_{\text{metal+support}} - E_{\text{metal+support}} - \frac{1}{2} E_{\text{H}_2} \quad (\text{A.2})$$

where $E_{\text{metal+support}}$ is the total energy of the nanoparticle and support with a hydrogen atom adsorbed, $E_{\text{metal+support}}$ is the energy of the nanoparticle and support, and E_{H_2} is the energy of a hydrogen molecule in the gas phase.

In order to estimate the overall exchange current density for a given model system, the ascending and descending branch of the volcano curve are correlated to

the hydrogen binding energy at site i , $\Delta E_{H,i}$, via a linear scaling relationship with α and β as fitting parameters

$$\log j_{0,i} \text{ (mA cm}^{-2}\text{)} = \alpha \times \Delta E_{H,i} + \beta \quad (\text{A.3})$$

Given the site heterogeneity of the Ni₁₃ nanocluster, the local exchange current densities for each binding site are averaged according to the stochastic method of Gillespie.²⁰

$$\bar{j}_0 = \frac{1}{n} \sum_{i=1}^n j_{0,i} \quad (\text{A.4})$$

In Equations A.3 and A.4, $j_{0,i}$ is the exchange current density of binding site i as predicted by the volcano relationship given the hydrogen binding energy at that site, and n is the number of threefold Ni binding sites present on the nanoparticle surface, since atomic hydrogen preferentially binds on threefold hollow sites in our nanoparticle models.

Appendix A

EFFECT OF SUBSTITUTIONALLY DOPED GRAPHENE ON THE ACTIVITY OF NANOPARTICLE METAL CATALYSTS FOR THE HYDROGEN OXIDATION REACTION

Upon identifying the shift in the d band center as a sufficient qualitative descriptor for the shift in adsorption energy, we next consider whether small metal clusters can be used to quickly screen supported catalysts. A number of previous theoretical studies have attempted to rationalize the interaction between carbon-based supports and nanoparticles by considering metal clusters of only a few atoms (e.g., $n = 1-4$)¹¹⁶⁻¹¹⁸. Therefore, we consider the adsorption of metal adatoms on N-graphene and compare their d band centers to the adatom on pristine graphene. As we show in Figure S1, the d band center of the Ag adatom is upshifted by the presence of nitrogen, the opposite of what is observed for the larger nanoparticle. Furthermore, the Cu adatom has its d -band unaffected by the dopant, whereas a significant downshift is observed for the 37-atom Cu nanoparticle. Therefore, we conclude that metal adatoms interact with the support in a qualitatively different fashion than do larger nanoparticles, and therefore cannot be used to reliably predict how the reactivity properties of larger than sub-nanometer catalysts will change as a function of the support.

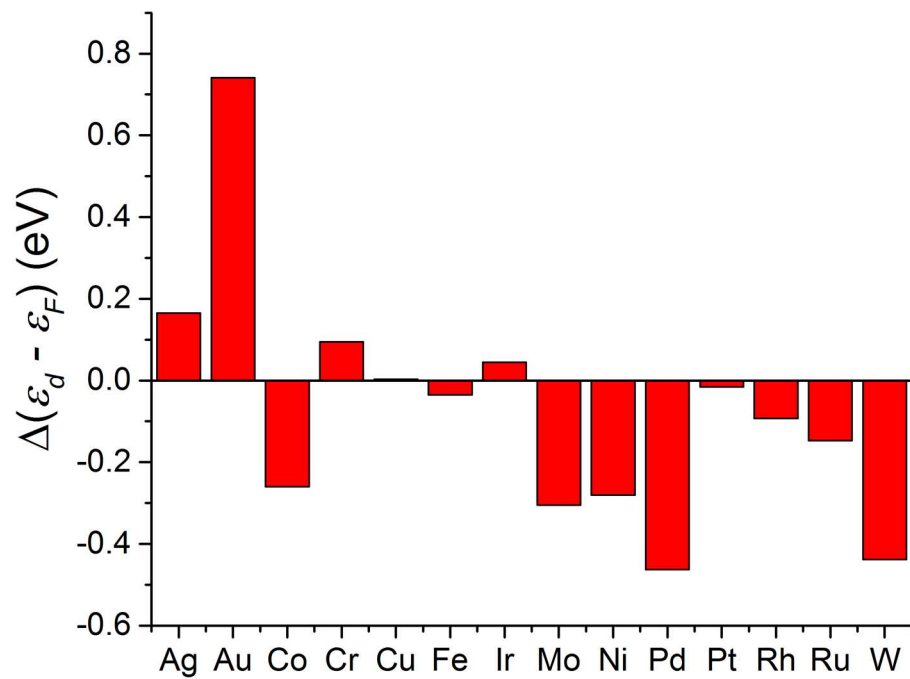


Figure B.1. Shift in the d band center relative to the Fermi level for a variety of metal adatoms due to nitrogen doping. The change in the d band center of the metal adatom is computed relative to the d band center of the metal adatom on undoped graphene.

Table B.1. Comparison of the local charge on graphitic and pyridinic nitrogen dopants as determined from a Bader charge analysis.

Support	Charge on dopant atom (e^-)
N _{graphitic} -graphene	-1.34
N _{pyridinic} -graphene	-1.32

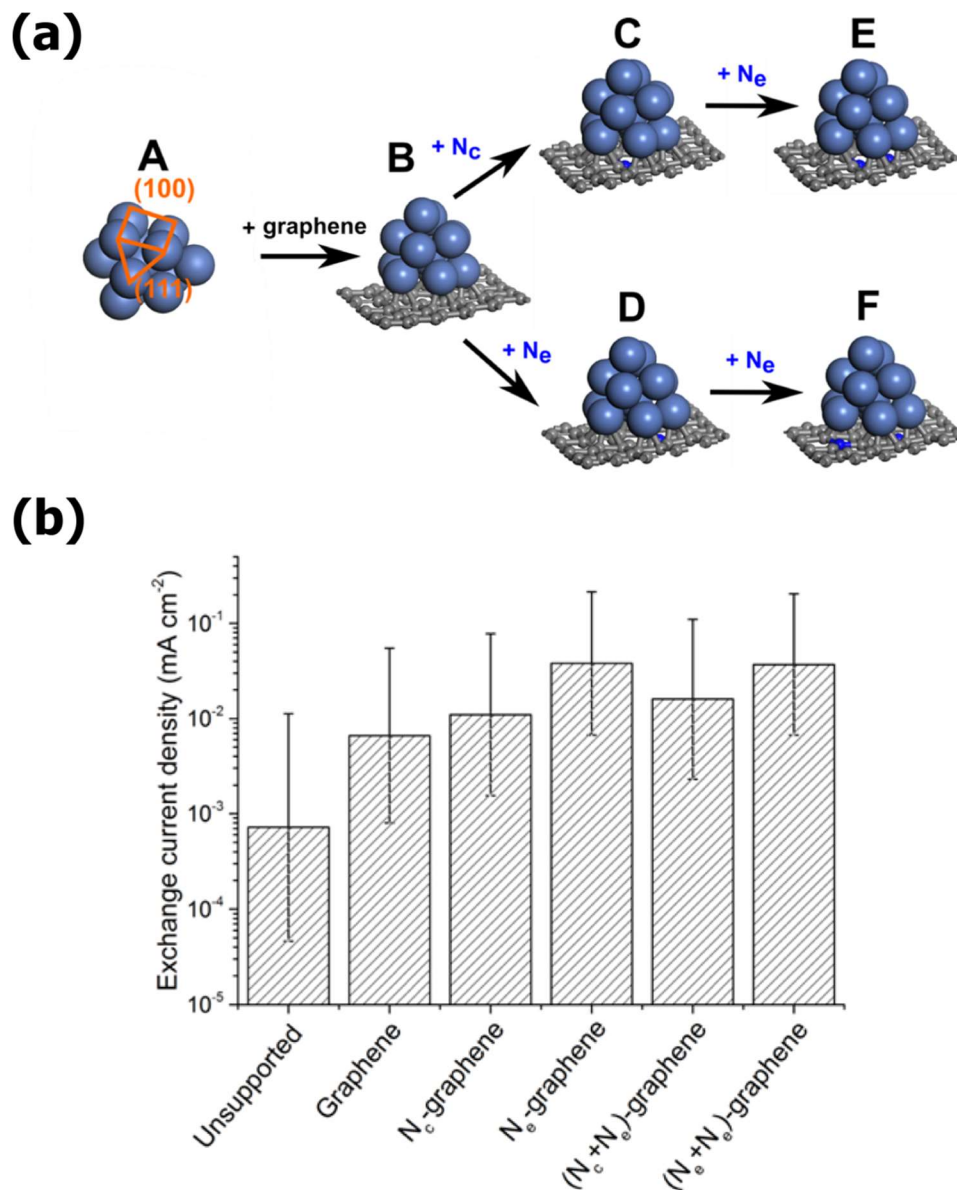


Figure B.2. (a) Graphical depiction of the model systems (one and two dopants located at either center or edge) considered in the current study – N_c: nitrogen at center location, N_e: nitrogen at edge location. A: unsupported Ni₁₃, B: Ni/graphene, C: Ni/N_c-graphene, D: Ni/N_e-graphene, E: Ni/(N_c + N_e)-graphene, F: Ni/(N_e + N_e)-graphene. (b) Predicted exchange current densities based on the volcano relationship for each model system. Error bars are 75% confidence intervals resulting from the linear regression of the HOR/HER volcano.

In addition to studying the effect of a dopant located at the edge of the nanoparticle adjacent to its (111) face, we also studied the charge transfer for four other dopant locations: edge of the (100) face, corner (i.e., the intersection of the (111) and (100) faces), center, and distant (i.e., not in direct coordination with the nanoparticle). The specific locations of these dopants are indicated in Figure B.3, shown from the perspective of the underside of the nanoparticle-support system. The relative energies of nanoparticle/support systems are shown for each case in Table B.2. There is little energetic preference for any particular nitrogen location, but the dopant located at the (111) edge is deemed to be the most energetically stable.

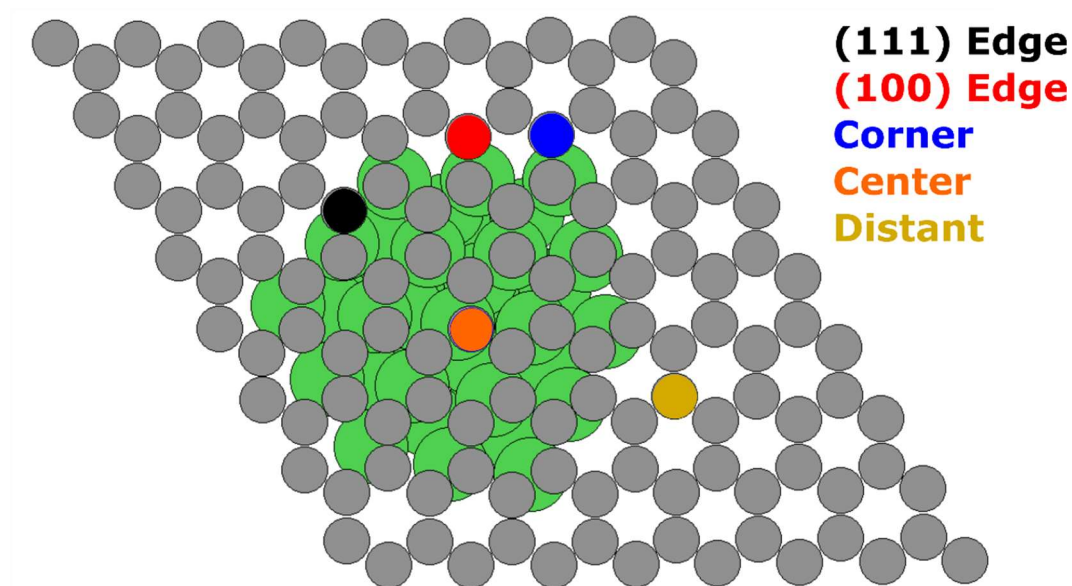


Figure B.3. Locations of dopants for which energy and charge transfer properties were calculated. Because the (111) edge is the most stable location, the results for this location are given in Chapter 3 unless otherwise stated.

Table B.2. Energies of the Ni/N-graphene system as a function of the location of the nitrogen dopant. Energies are shown relative to the most stable location, the (111) edge.

Nitrogen location	Energy relative to N at (111) edge (eV)
(111) edge	—
(100) edge	+0.04
Corner	+0.07
Center	+0.06
Distant	+0.09

The charge on a supported Ni₃₇ nanoparticle is shown in Figure B.4 as a function of position of each dopant. We observe that, in all cases, dopants located at the edge of the (111) face, the (100) face, and the corner of the nanoparticle induce similar charge transfer behavior. Conversely, dopants located at either the center of or distant from the nanoparticle can lead to different charge transfer behavior. We rationalize the effect of dopant location as a result of the nanoparticle being coordinated with partially charged carbons near the dopant. In the case of Ni₃₇ supported on N-graphene, the graphene maintains its sp² character, and thus, the nitrogen atom acts as an electron withdrawing group. The carbon atoms surrounding the nitrogen dopant, however, become electron donating. As a result, when the nitrogen is located at the center and distant positions, the nanoparticle is more coordinated with electron donating carbons, becoming more negatively charged. Consistent with the role of the carbon atoms in determining the nanoparticle charge, we see the reverse trend for the B dopant located at the center of the nanoparticle. When substituted into the two-dimensional graphene structure, B acts as an electron

donating group. Our observation that the neighboring carbon atoms also play a key role in determining the charge transfer is in agreement with recent experimental findings which demonstrated the nearest neighbor carbon atoms to the dopant are the active sites for the oxygen reduction reaction (ORR)²³².

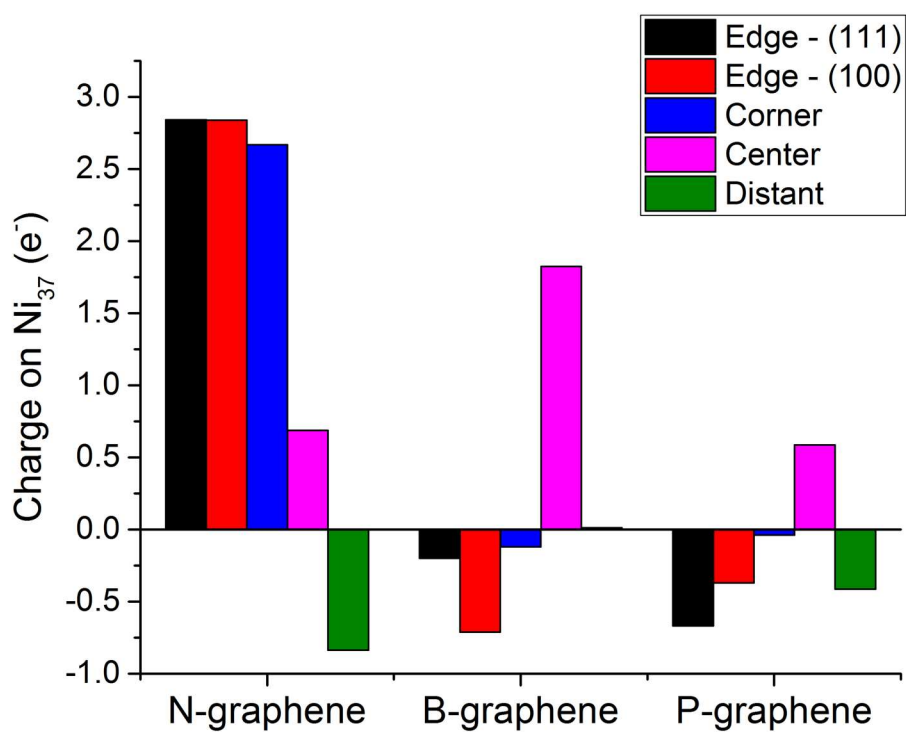


Figure B.4. Charge of the Ni nanoparticle as function of the dopant and dopant location.

Correlation of hydrogen binding energy to measured exchange current density

The hydrogen adsorption energies of the close-packed surfaces (the (111) facet for *fcc* metals, and the (0001) facet for *hcp* metals) were computed and correlated via Equation 3.1 to experimentally measured exchange current densities in 0.1 M KOH for W, Ni, Co, Pd, Pt, Ir, Cu, Au, and Ag available in prior work¹⁸. The linear regressions for the strong and weak adsorption branch of the HOR/HER volcano were determined to be, respectively,

$$j_0 \text{ (mA cm}^{-2}\text{)} = 13.856 \times \Delta E_{\text{H}} \text{ (eV)} + 3.257$$

$$j_0 \text{ (mA cm}^{-2}\text{)} = -7.242 \times \Delta E_{\text{H}} \text{ (eV)} - 6.575$$

For sites with ΔE_{H} stronger than Pt (111) ($\Delta E_{\text{H,Pt(111)}} = -0.466$ eV), the regression equation for the strong adsorption branch is used. For sites more weakly adsorbing than Pt (111), the regression equation for the weak adsorption branch is used. The positive slope of the regression of the strong adsorption branch of the volcano indicates that the activity of a strong adsorption site increases with decreasing hydrogen binding. The negative slope of the weak adsorption branch of the volcano indicates that the activity of a weak adsorption site decreases with further weakening of the hydrogen binding energy.

Estimating the Fraction Nanoparticle Sites Captured by the DFT Model

The fraction of nanoparticle sites affected by the support, and thus captured in the DFT model, is given in Equation 3.6. This equation is obtained by assuming geometric similarity between nanoparticles of different sizes, where each nanoparticle is approximated as a hemisphere in accordance with microscopy images for Ni/CNT

and Ni/N-CNT⁹⁵. The fraction of the nanoparticle captured by the DFT model, x_{NP} , is defined as

$$x_{\text{NP}} \equiv \frac{A_{\text{NP}}}{A_{\text{total}}}$$

where A_{NP} is the area of the nanoparticle captured by DFT (i.e., the three atomic layers nearest the support), and A_{total} is the total area of hemispherical nanoparticle, equal to $\frac{1}{2}\pi d^2$. A differential surface area element dA is equal to $r^2 \sin \varphi \, d\varphi \, d\theta$, or equivalently, $\frac{1}{4}d^2 \sin \varphi \, d\varphi \, d\theta$. Therefore, A_{NP} is calculated as,

$$A_{\text{NP}} = \frac{1}{4}d^2 \int_{\frac{\pi}{2} - \frac{2d_{\text{M-M}}(N_{\text{layers}}-1)}{d}}^{\frac{\pi}{2}} \sin \varphi \, d\varphi \int_0^{2\pi} d\theta$$

where $\frac{2d_{\text{M-M}}(N_{\text{layers}}-1)}{d}$ is the angle subtended by the regime of the nanoparticle captured by the DFT structural model. Consequently, the angle approaches zero as the nanoparticle diameter d approaches infinity. A schematic is provided in Figure B.5.

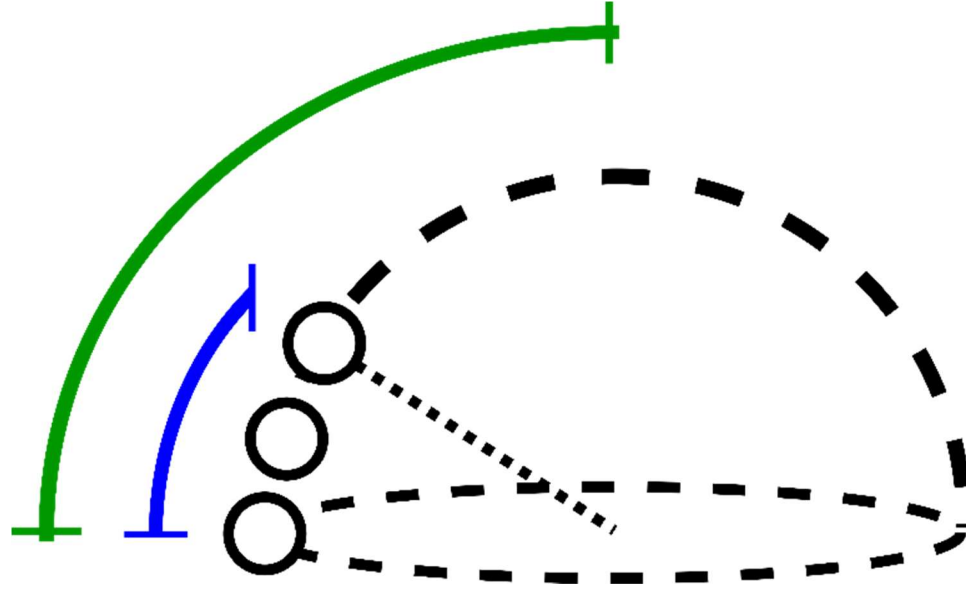


Figure B.5. Hemispherical supported nanoparticle model. The blue arc represents the sites which are captured in the DFT model (the three atomic layers nearest to the support). The green arc represents the distance from $\varphi = \frac{\pi}{2}$ to $\varphi = 0$, or $\frac{1}{4}\pi d$.

As an example, suppose one wishes to calculate x_{NP} for a nanoparticle of diameter 20 nm. The total area of the hemispherical nanoparticle is:

$$A_{\text{total}} = \frac{1}{2}\pi d^2 = 628.32 \text{ nm}^2$$

The area of the regime captured by the DFT structural model is:

$$A_{\text{NP}} = \frac{1}{4}d^2 \int_{\frac{\pi}{2} - \frac{2d_{\text{M-M}}(N_{\text{layers}}-1)}{d}}^{\frac{\pi}{2}} \sin \varphi \, d\varphi \int_0^{2\pi} d\theta$$

$$\begin{aligned} A_{\text{NP}} &= \frac{1}{4}(20 \text{ nm})^2 \cdot 2\pi \cdot \left\{ \left[-\cos\left(\frac{\pi}{2}\right) \right] - \left[-\cos\left(\frac{\pi}{2} - \frac{2d_{\text{M-M}}(N_{\text{layers}}-1)}{d}\right) \right] \right\} \\ &= 31.40 \text{ nm}^2 \end{aligned}$$

$$\therefore x_{\text{NP}} = \frac{A_{\text{NP}}}{A_{\text{total}}} = 0.05$$

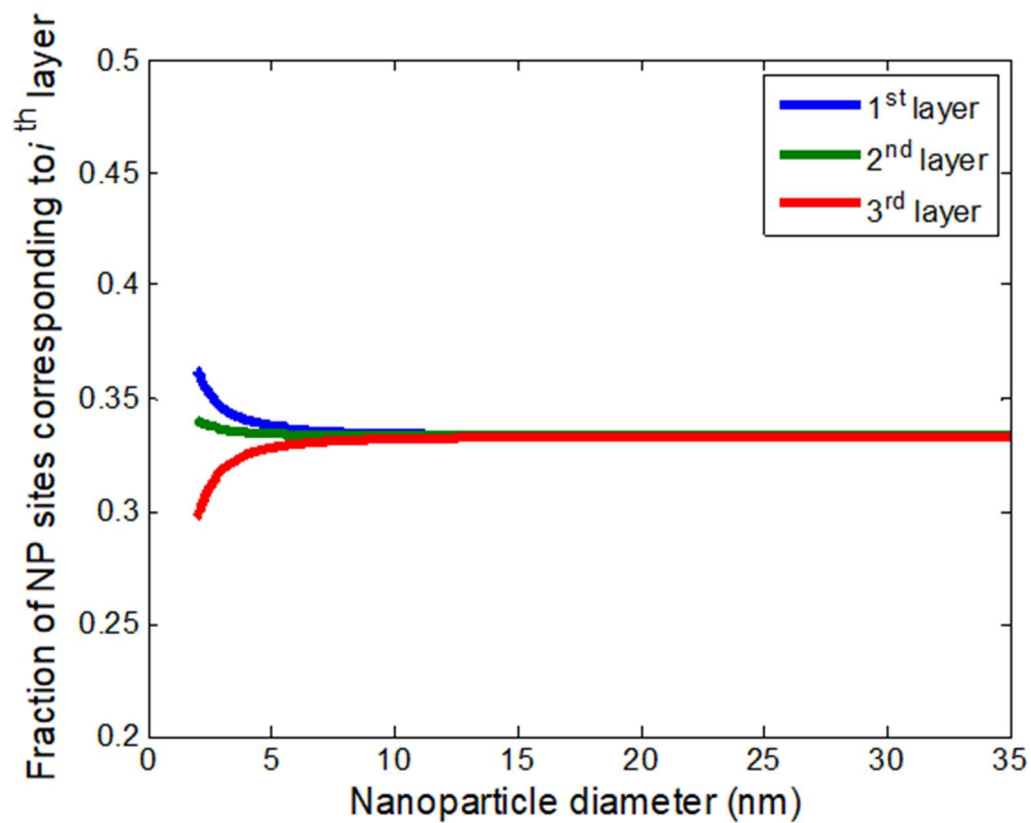


Figure B.6. Relative fractions 1st, 2nd, and 3rd layer sites comprising the nanoparticle regime as a function of the nanoparticle diameter. The fractions were computed by integrating on a per layer basis, analogous to the computation of x_{NP} .

Effect of Graphene Support on Nanoparticle Structure

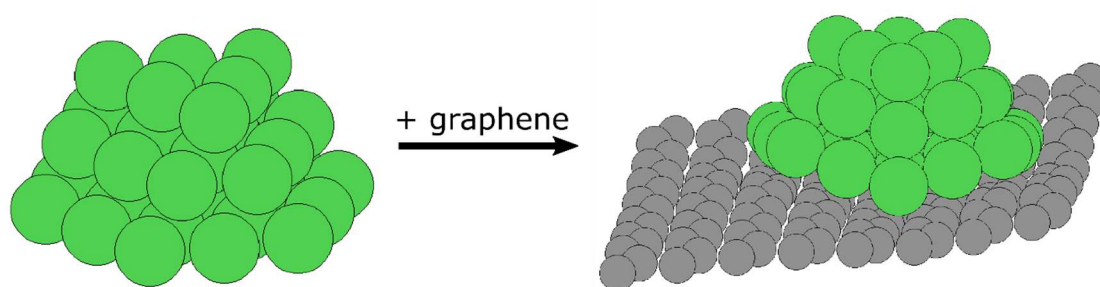


Figure B.7. The initial unsupported cuboctahedral Ni nanoparticle, along with the supported Ni nanoparticle. The presence of the graphene support leads to the nanoparticle preferentially exposing the (111) exclusively.

Laplacian of Charge Density Between Nanoparticle and Support

To explain the stronger nanoparticle-support interaction energy for the case of doped supports, the Laplacian of the charge density was computed for the supported Ni nanoparticles. The value of the Laplacian is shown in Figure B.8 between the nitrogen or boron dopant (or the corresponding carbon atom, in the case of undoped graphene) and the nearest neighbor Ni atom. In regions of electron concentration, the Laplacian of the charge density is negative; in regions of electron depletion, the Laplacian is positive. The Laplacians of the charge density between undoped graphene and N-graphene are quite similar, possibly indicating why graphene and N-graphene supports lead to relatively similar interaction energies with the nanoparticle (Figure 3.3). In contrast, the Laplacian of the charge density between the boron dopant and Ni indicates a much larger degree of electron concentration near the boron dopant. The stronger electronic interaction between B-graphene and the nanoparticle consequently leads to the significantly stronger interaction energies between B-graphene and each of the nanoparticles modeled.

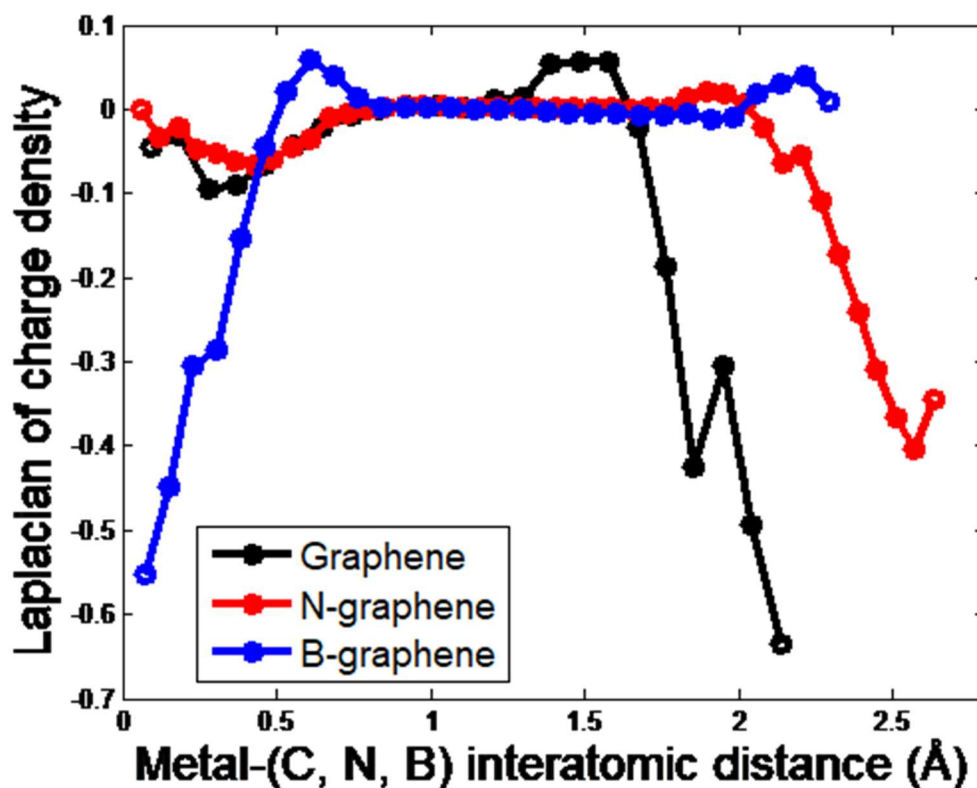


Figure B.8. The value of the Laplacian of the charge density as a function of the distance between the nearest neighbor Ni atom and the carbon, nitrogen, or boron atom in graphene, N-graphene, and B-graphene, respectively. Laplacian values smaller than zero indicate charge concentration, whereas values larger than zero indicate charge depletion.

Hydrogen Adsorption Energy and Activity Heat Maps: Cu and Ag Supported Nanoparticles

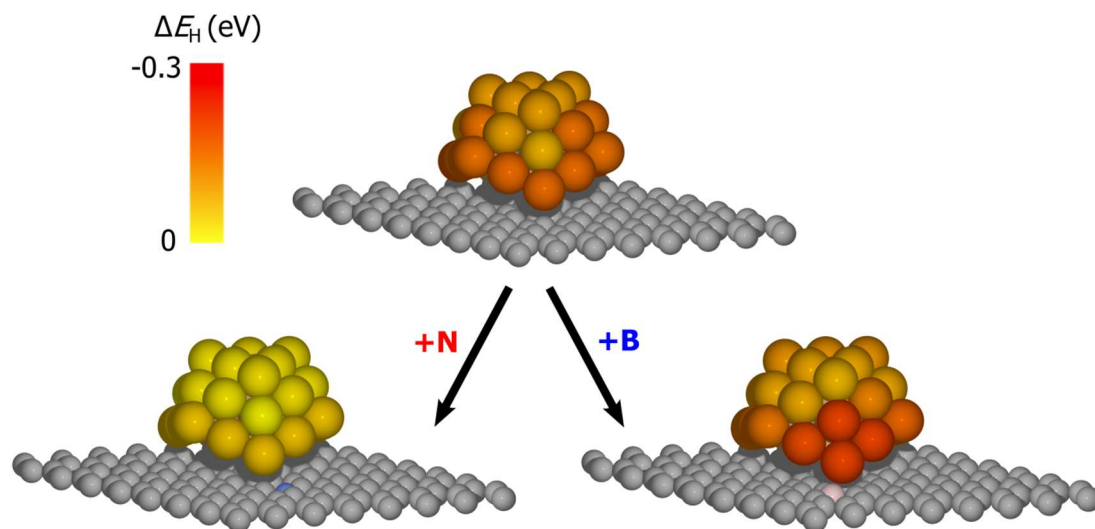


Figure B.9. Heat map of the local hydrogen adsorption energy for Cu/graphene (top), Cu/N-graphene (bottom left), and Cu/B-graphene (bottom right).

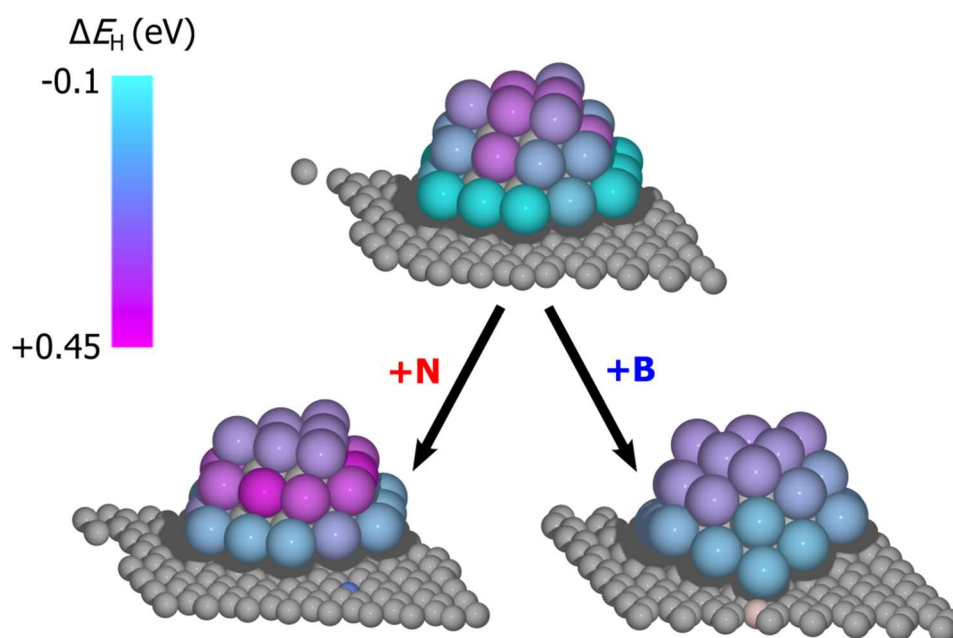


Figure B.10. Heat map of the local hydrogen adsorption energy for Ag/graphene (top), Ag/N-graphene (bottom left), and Ag/B-graphene (bottom right).

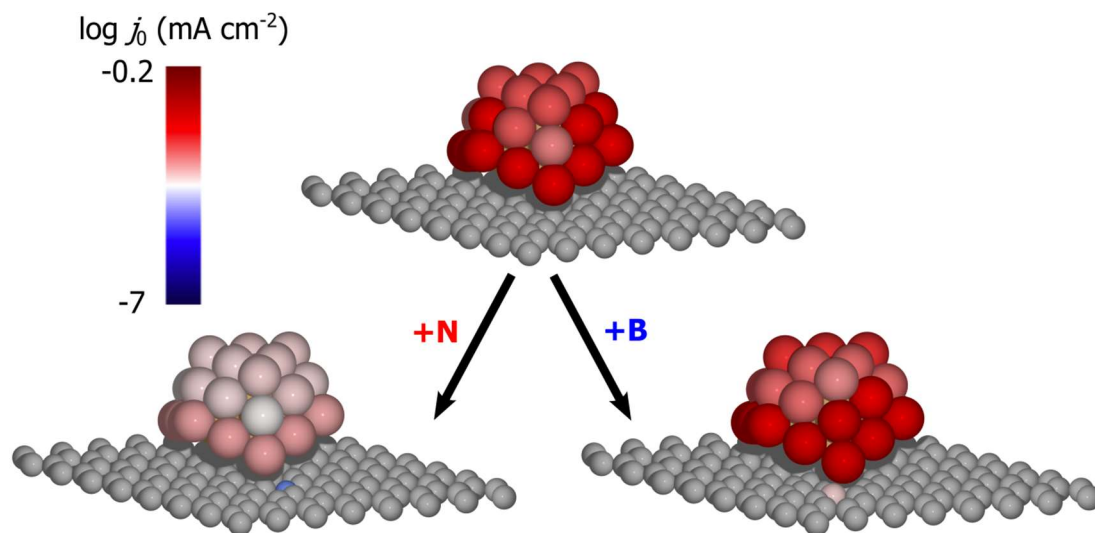


Figure B.11. Heat map of the local HOR/HER exchange current density for Cu/graphene (top), Cu/N-graphene (bottom left), and Cu/B-graphene (bottom right).

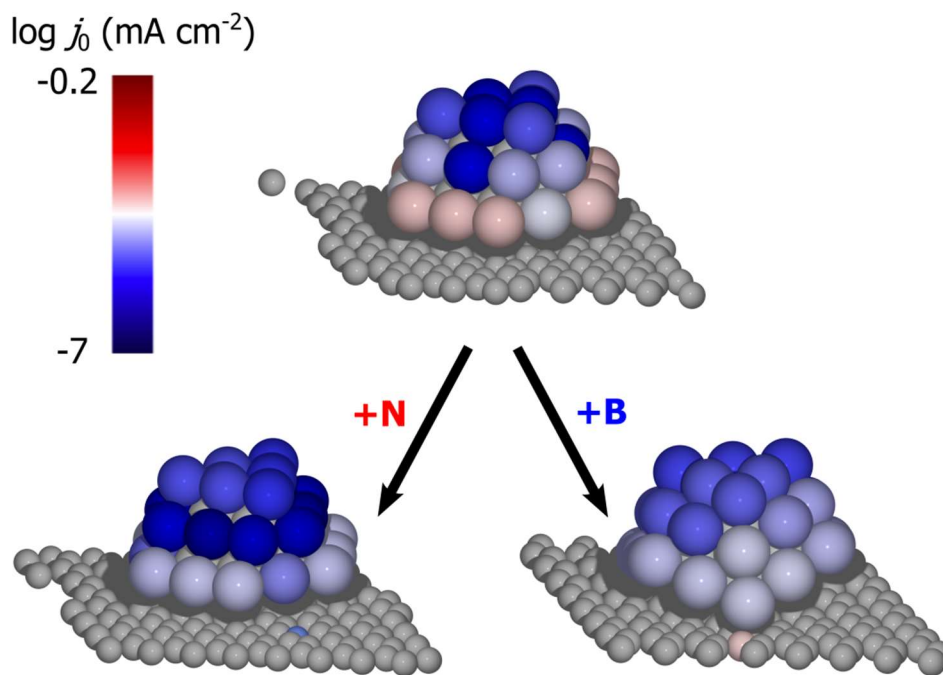


Figure B.12. Heat map of the local HOR/HER exchange current density for Ag/graphene (top), Ag/N-graphene (bottom left), and Ag/B-graphene (bottom right).

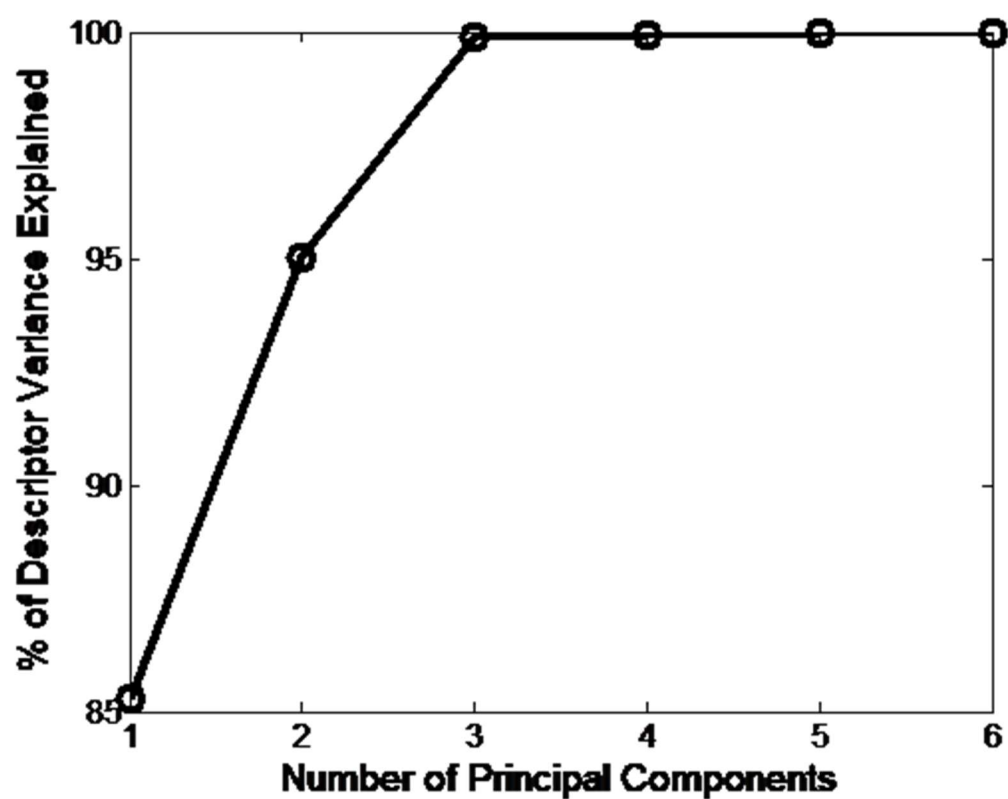


Figure B.13. Percentage of variance in descriptors explained as a function of the number of principal components.

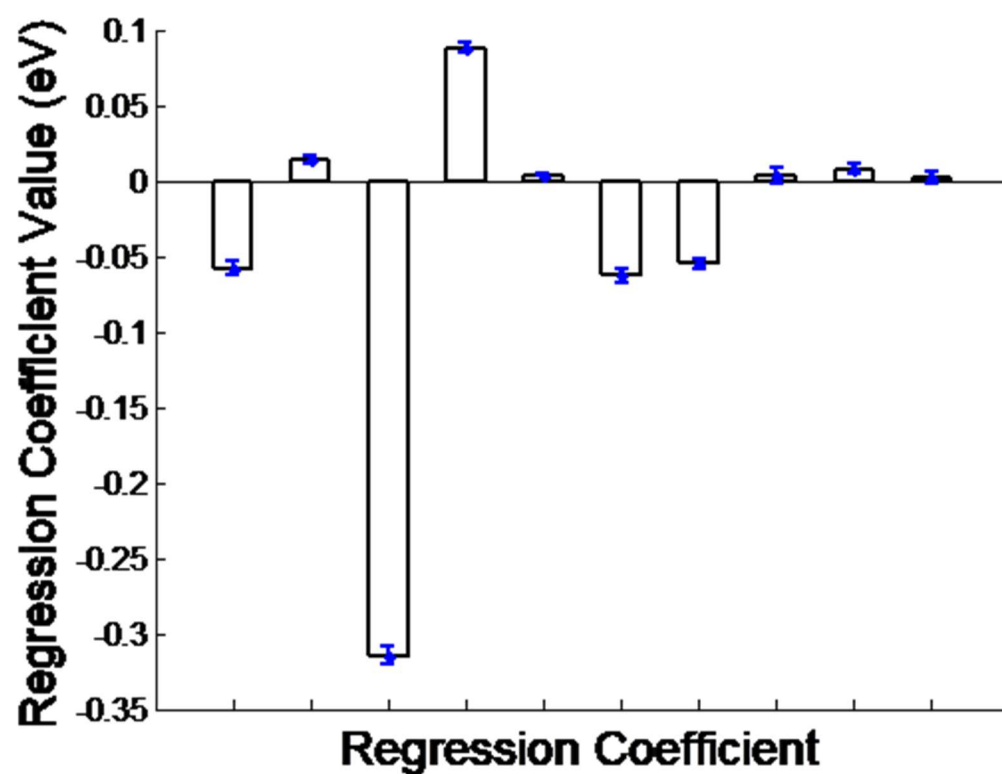


Figure B.14. Value of regression coefficients in the PCA adsorption model. Blue bars represent the standard error. Coefficients are shown in the following order: intercept, x_1 , x_2 , x_3 , x_1^2 , x_2^2 , x_3^2 , x_1x_2 , x_1x_3 , and x_2x_3 .

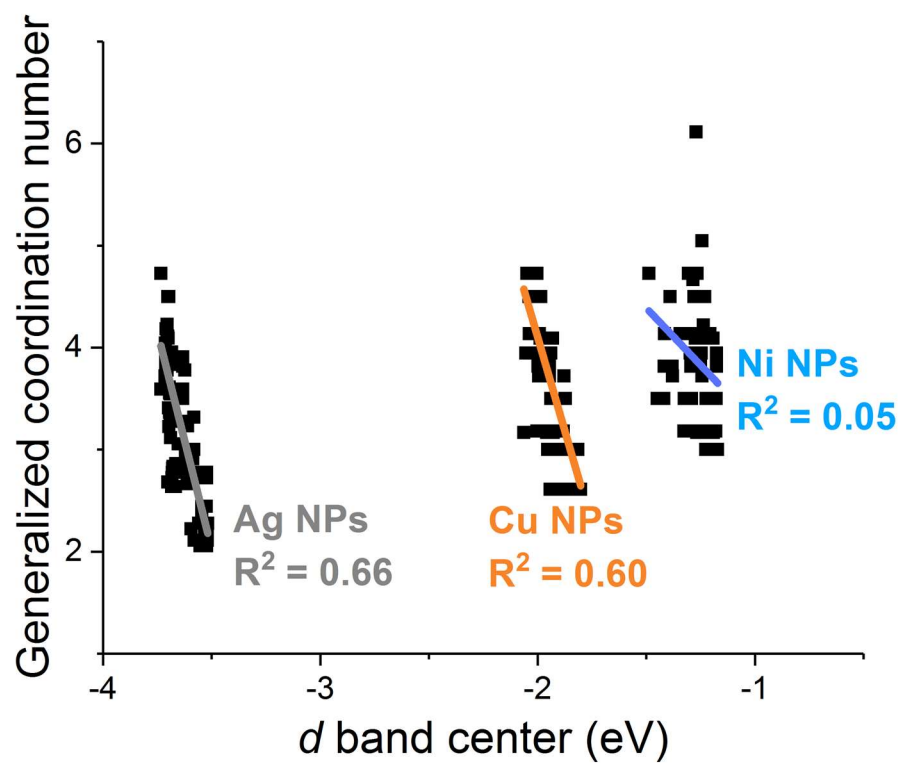


Figure B.15. Correlation of the generalized coordination number with the computed d band center of each site for Ni/x-graphene, Cu/x-graphene, and Ag/x-graphene. Effectively no correlation is seen for the Ni nanoparticles which have the strongest interaction with the support.

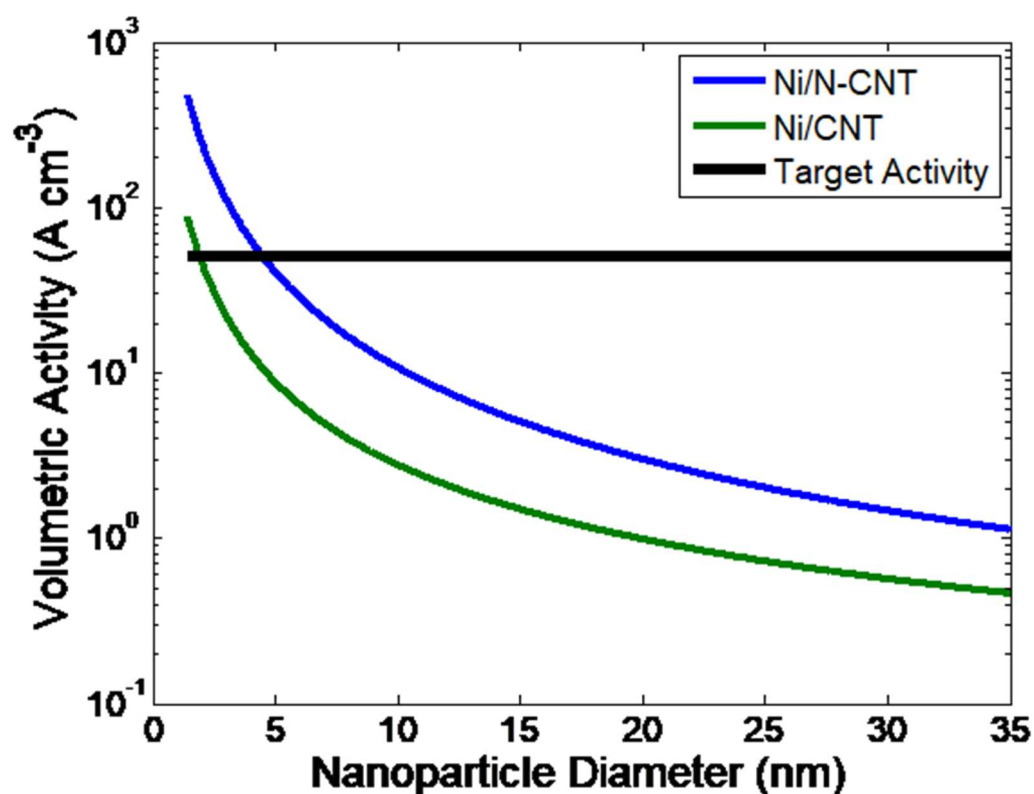


Figure B.16. Volumetric activity of the Ni/CNT and Ni/N-CNT nanoparticles as a function of nanoparticle diameter. The target activity is the estimated HOR activity needed to satisfy the 1 W cm^{-2} DOE power density target for HEMFCs¹⁰. The volume fraction of the supported catalyst is assumed to be constant.

Appendix B

IDENTIFYING ACTIVE SITES OF METAL OXIDES FOR OXYGEN EVOLUTION USING MONODISPERSE NANOPARTICLES

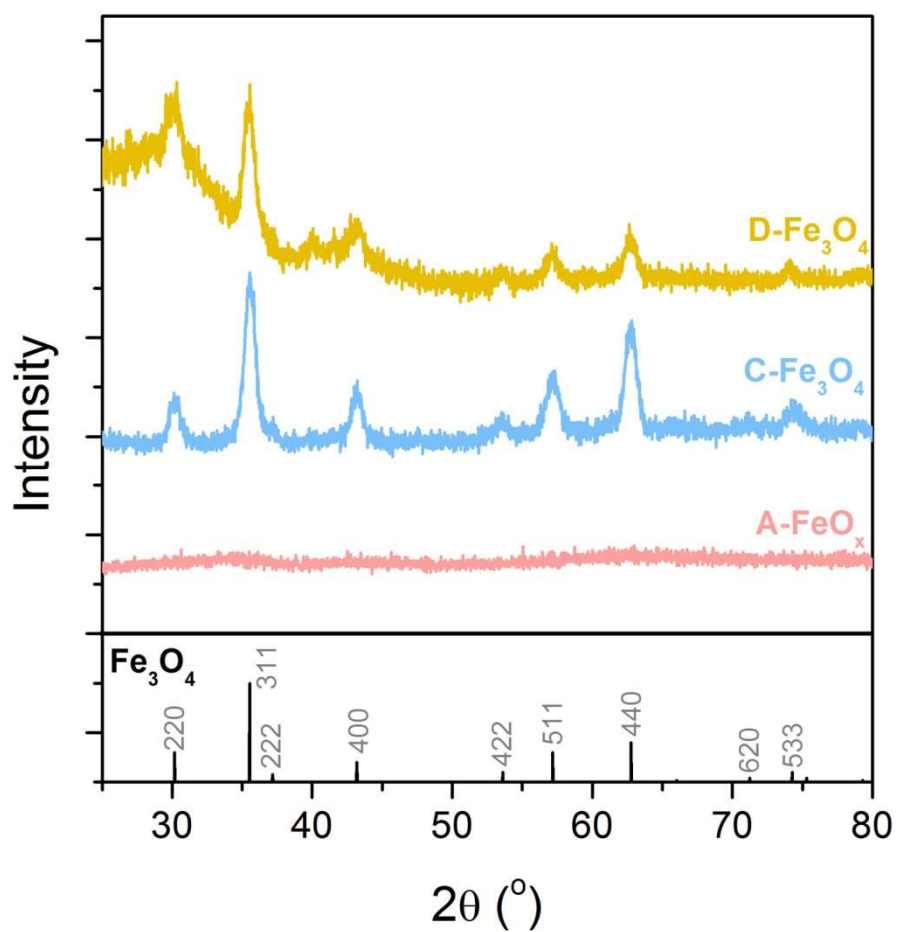


Figure C.1. XRD patterns of the iron oxide nanoparticles. The standard pattern of Fe₃O₄ (JCPDS card No. 65-3107) is shown beneath the plot.

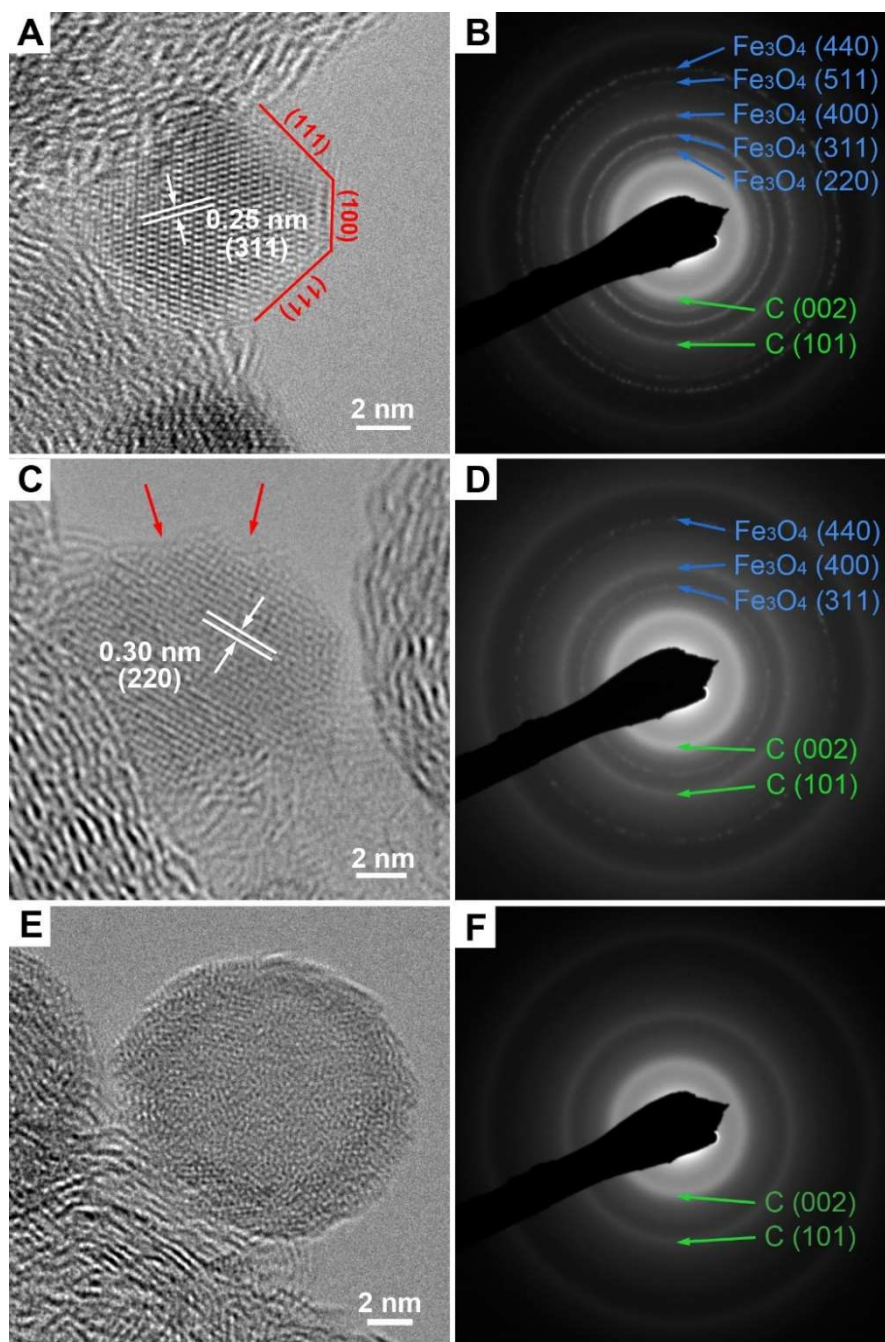


Figure C.2. HRTEM images and the corresponding SAED pattern of the nanoparticle supported on carbon after calcination in air. (A, B) C-Fe₃O₄/C. The lattice spacing of 0.25 nm corresponding to the (311) plane of Fe₃O₄. The nanoparticle expose (111) and (100) surfaces. The diffraction rings in the SAED pattern can be indexed as carbon or Fe₃O₄. (C, D) D-Fe₃O₄/C. The lattice spacing of 0.30 nm corresponds to the (220) plane of Fe₃O₄. The defects on the surface are indicated by red arrows. The diffraction rings in the SAED pattern can be indexed as carbon or Fe₃O₄. (E, F) A-FeO_x/C. No clear lattice fringe can be seen in the HRTEM images. The SAED pattern only shows the diffraction rings from carbon support.

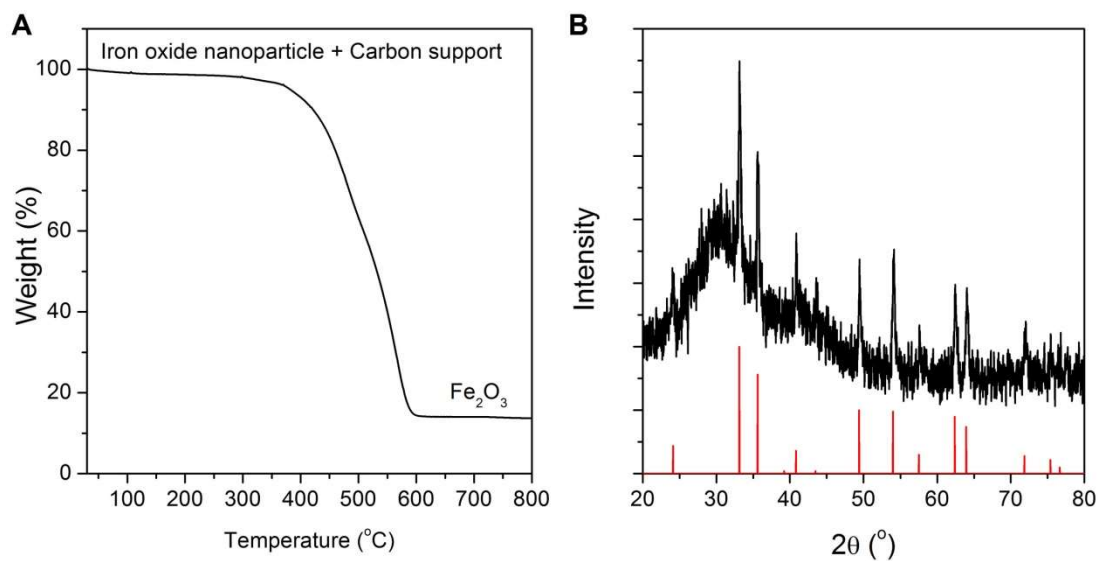


Figure C.3. (A) A typical TGA curve of the carbon supported iron oxide nanoparticles. (B) XRD pattern of the residue after TGA test. The standard pattern of $\alpha\text{-Fe}_2\text{O}_3$ (JCPDS card No. 85-0597) was shown beneath the plot.

The TGA was performed under an air atmosphere. Carbon supports were burned off and the iron oxide was further oxidized to $\alpha\text{-Fe}_2\text{O}_3$, which was confirmed by the XRD pattern. Thus the iron content can be obtained from the TGA curves.

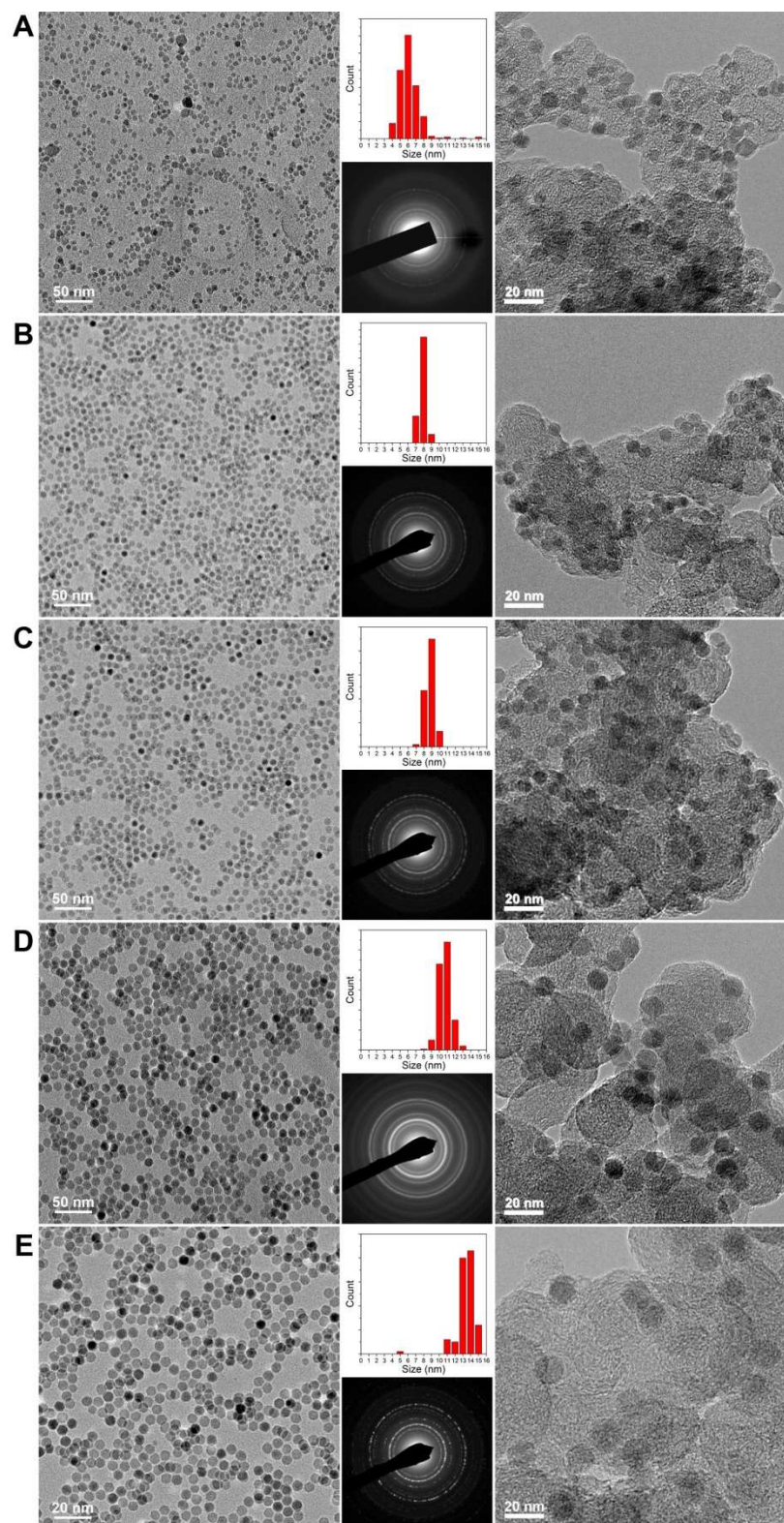


Figure C.4. TEM image, Size distribution, SEAD pattern of C-Fe₃O₄ nanoparticles and TEM image of the carbon supported C-Fe₃O₄ nanoparticles. (A) 6.0 nm. (B) 7.9 nm. (C) 8.8 nm. (D) 10.7 nm. (E) 13.3 nm.

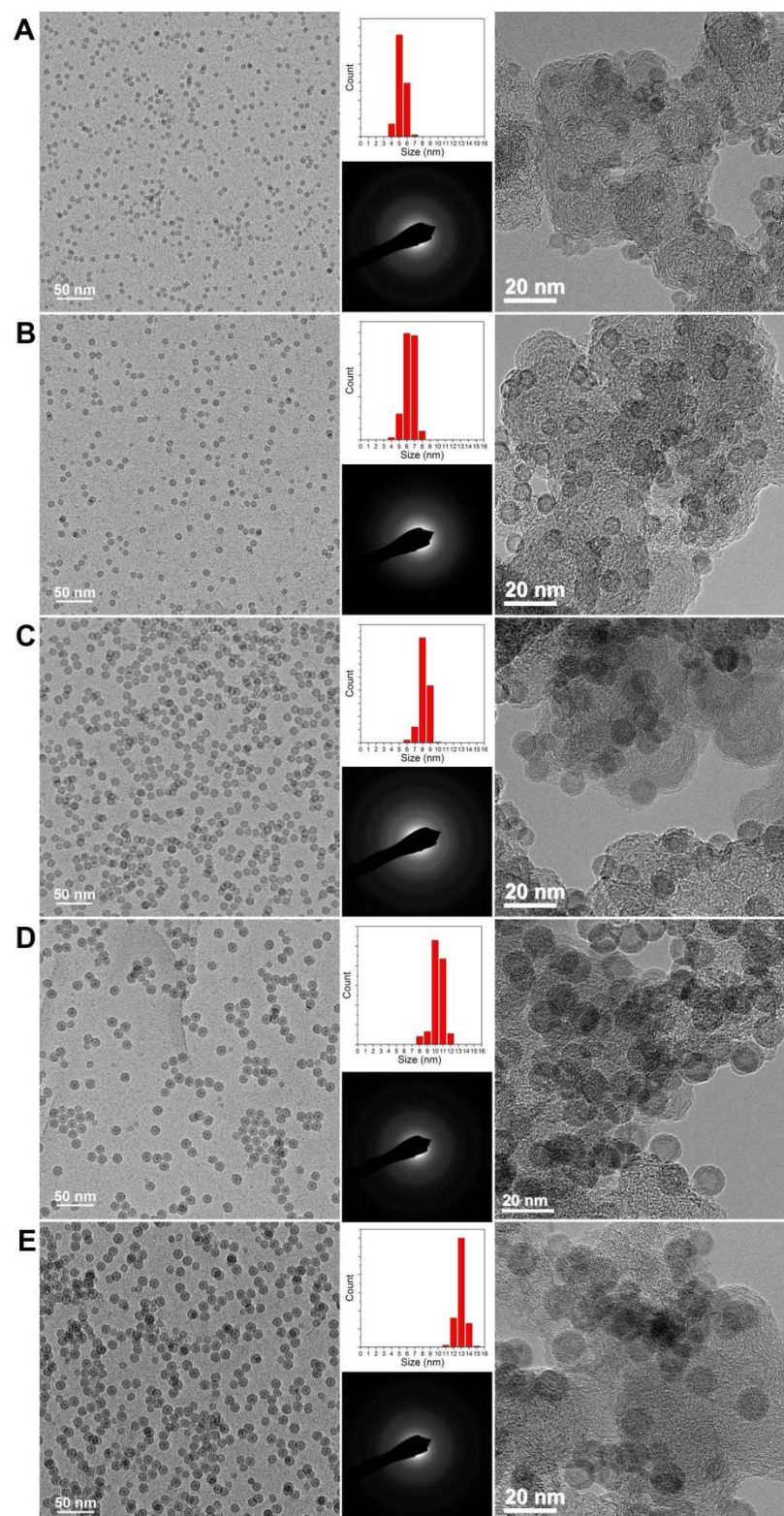


Figure C.5. TEM image, Size distribution, SEAD pattern of the A-FeO_x nanoparticles and TEM image of the carbon supported A-FeO_x nanoparticles. (A) 5.2 nm. (B) 6.4 nm. (C) 8.2 nm. (D) 10.4 nm. (E) 13.0 nm.

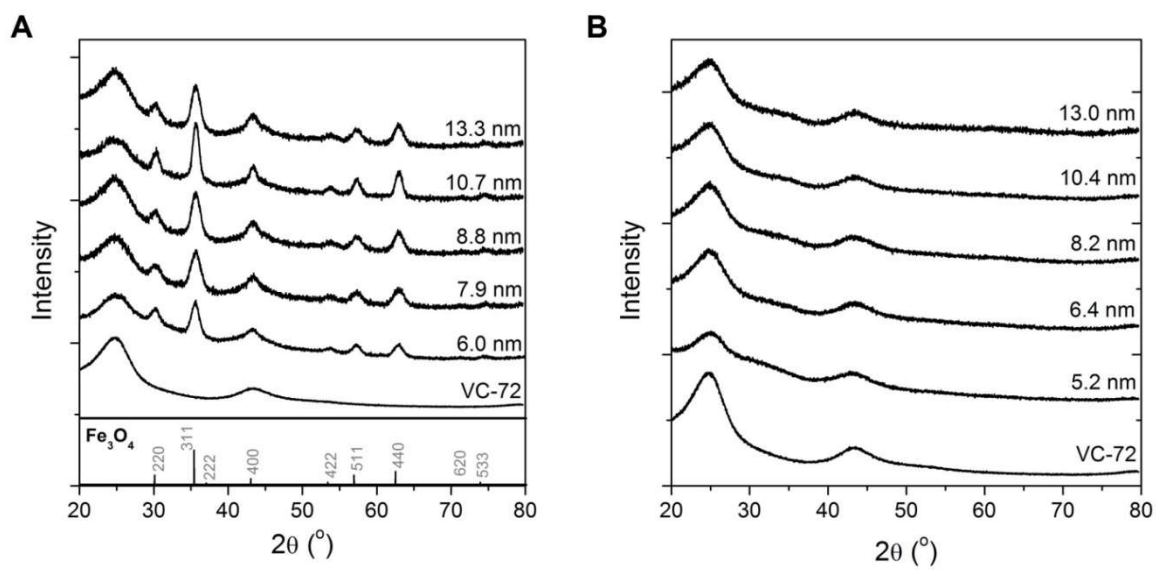


Figure C.6. XRD patterns of the carbon supported nanoparticles. (A) C-Fe₃O₄ nanoparticle series. (B) A-FeO_x nanoparticle series. The XRD pattern of carbon support (VC-72) is also shown in both plots

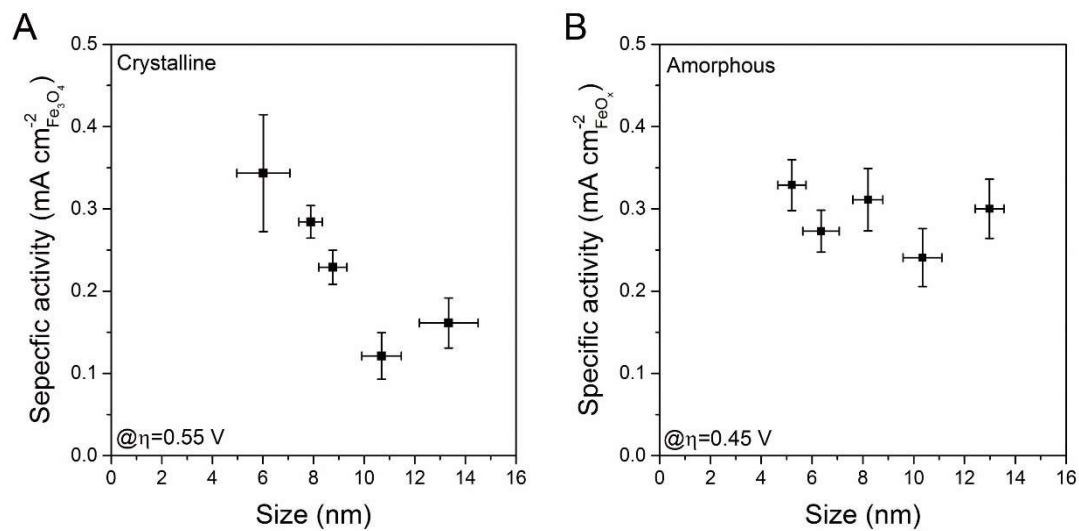


Figure C.7. Surface area specific activity of the nanoparticle series. (A) C-Fe₃O₄ nanoparticles. (B) A-FeO_x nanoparticles. The overpotential is marked at the lower left corner. Note, the current densities for A-FeO_x nanoparticles are obtained at a relative lower overpotential (0.45 V) than the C-Fe₃O₄ nanoparticles (0.55 V), due to the A-FeO_x nanoparticles have higher OER activities.

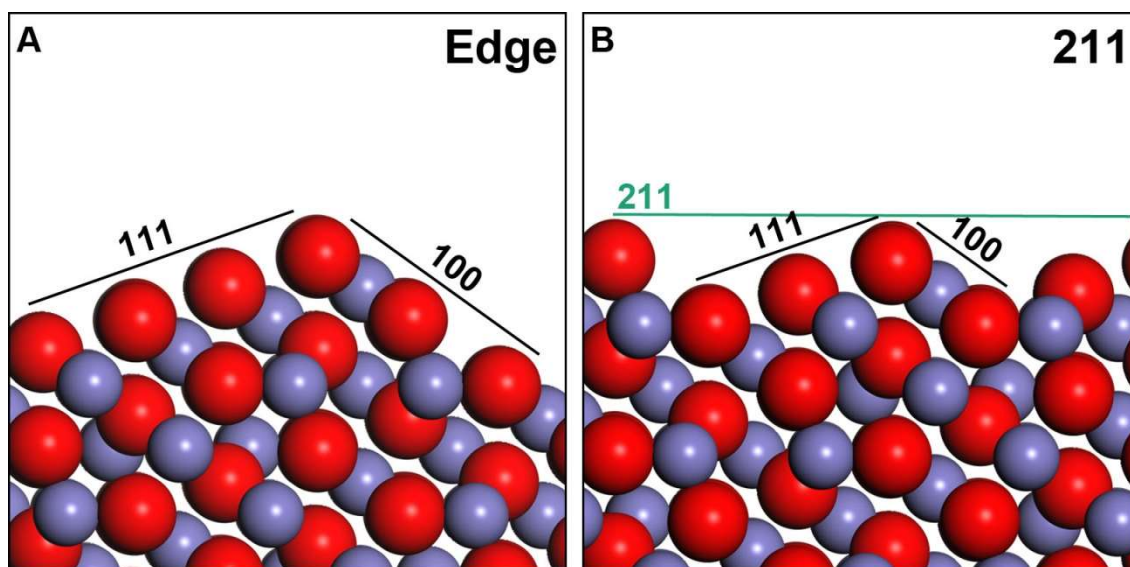


Figure C.8. Scheme of the structure of Fe₃O₄. (A) Cuboctahedral edge. (B) (211) surface. Blue spheres represent Fe atoms and red spheres represent O atoms.

The edge sites of a cuboctahedral nanoparticle are bounded by (111) and (100) surfaces. For the (211) surface, it is a stepped surface, which exhibits regular single-atom steps of (100), separated by two-atom wide terraces of (111). The steps on the (211) surface have an analogous structure to the edge of the cuboctahedron. Thus, it is reasonable to use the (211) surface to mimic the edge sites.

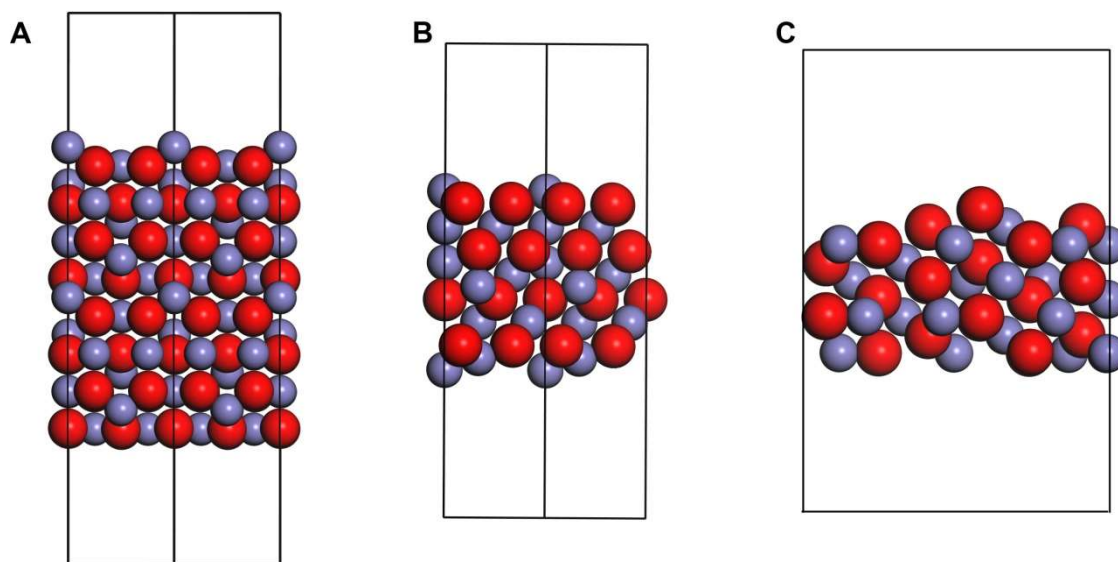


Figure C.9. Side views of the lowest energy terminations of Fe₃O₄. (A) (100) surface. (B) (111) surface. (C) (211) surface. Blue spheres represent Fe atoms and red spheres represent O atoms.

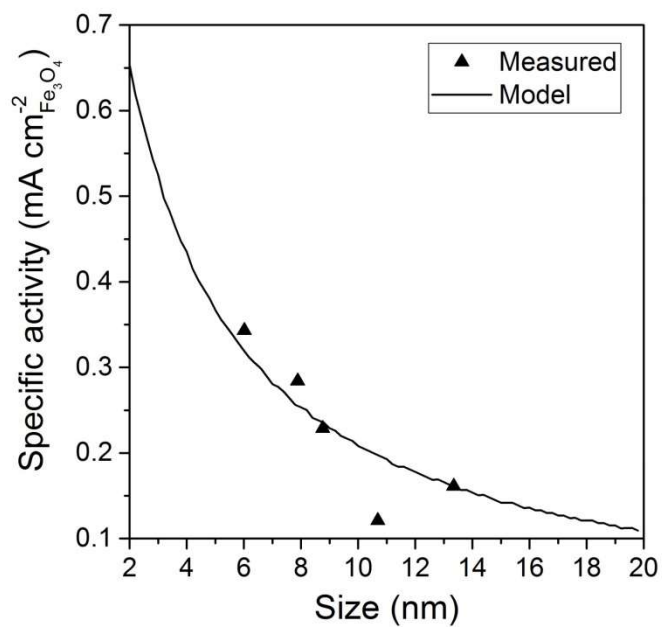


Figure C.10. Predicted specific current density (solid line) of the C-Fe₃O₄ nanoparticle at the calculated overpotential of 0.66 V. The measured data is experimentally observed at an overpotential of 0.55 V.

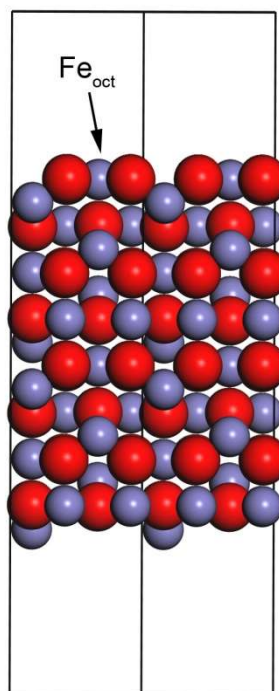


Figure C.11. Side views of the Fe_{oct} -terminated (100) surface.

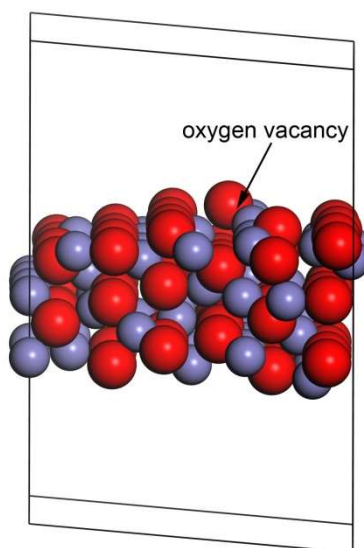


Figure C.12. Model of the (211) surface with an oxygen vacancy.

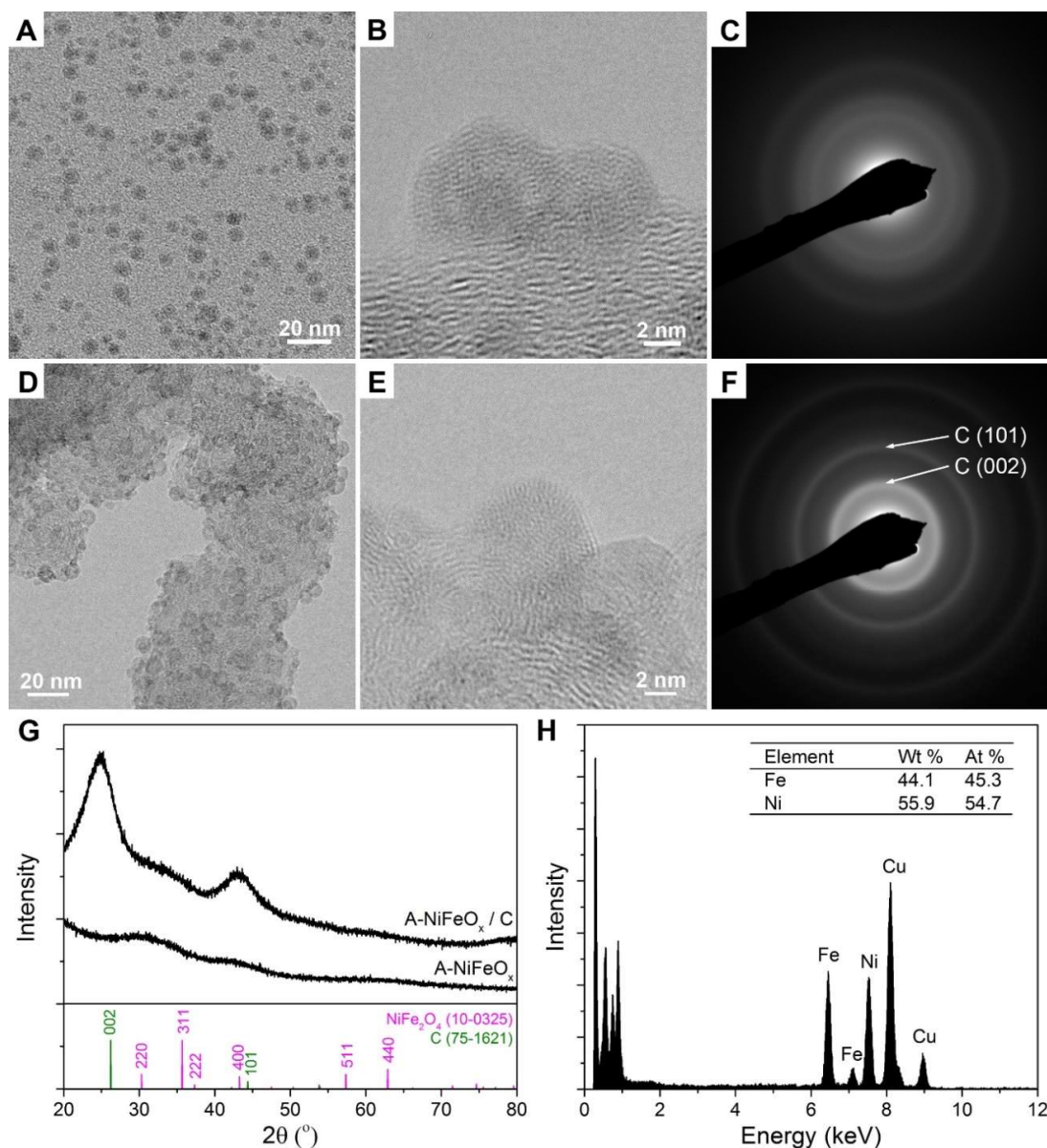


Figure C.13. Characterization of the A-NiFeO_x NPs catalysts. (A) TEM image of the A-NiFeO_x NPs. (B) HRTEM image of an A-NiFeO_x NP. (C) SAED pattern of the A-NiFeO_x NPs. (D) TEM image of the A-NiFeO_x NPs supported on carbon (A-NiFeO_x/C). (E) HRTEM image of an A-NiFeO_x NP supported on carbon. (F) SAED pattern of the A-NiFeO_x/C. (G) XRD patterns of A-NiFeO_x NP and A-NiFeO_x/C. For A-NiFeO_x NP, only very broad humps shown in the pattern. For A-NiFeO_x/C, the two broad peaks are attributed from carbon support (JCPDS card No.75-1621). (H) EDS pattern of the A-NiFeO_x NPs. The signals attribute to Cu come from the copper grid.

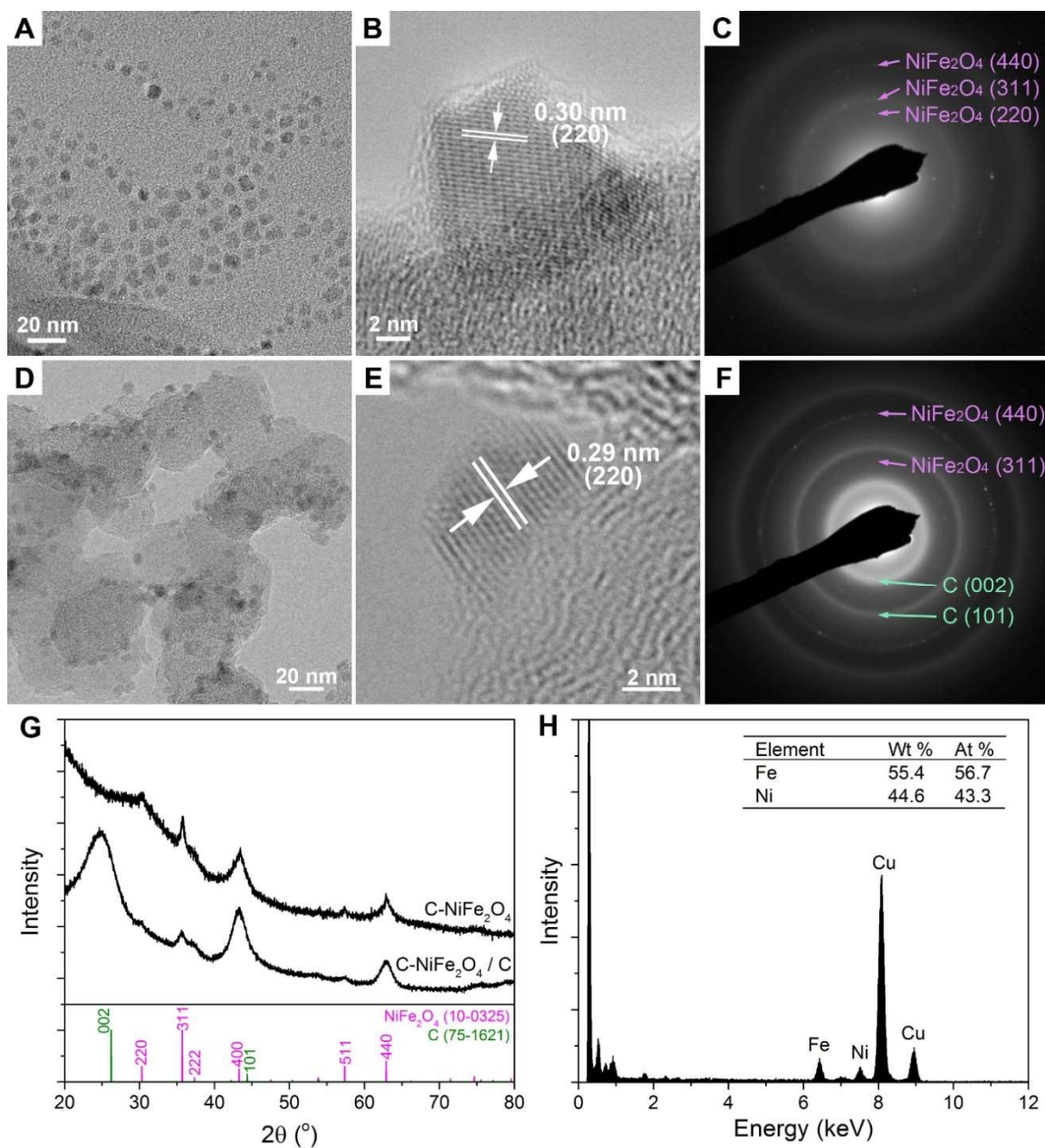


Figure C.14. Characterization of the C-NiFe₂O₄ NPs catalysts. (A) TEM image of the C-NiFe₂O₄ NPs. (B) HRTEM image of a C-NiFe₂O₄ NP. The lattice fringe with a spacing of 0.30 nm corresponds to the (220) facet of NiFe₂O₄. (C) SAED pattern of the C-NiFe₂O₄ NPs. (D) TEM image of the C-NiFe₂O₄ NPs supported on carbon (NiFe₂O₄/C). (E) HRTEM image of a C-NiFe₂O₄ NP supported on carbon. The lattice fringe with a spacing of 0.29 nm corresponds to the (220) facet of NiFe₂O₄. (F) SAED pattern of the C-NiFe₂O₄/C. (G) XRD patterns of C-NiFe₂O₄ NPs and C-NiFe₂O₄/C. For C-NiFe₂O₄ NPs, all the diffraction peaks can be indexed as the cubic phase of NiFe₂O₄ (JCPDS card No.10-0325). For C-NiFe₂O₄/C, the additional peaks to NiFe₂O₄ can be indexed to carbon (JCPDS card No.75-1621). (H) EDS pattern of the C-NiFe₂O₄ NPs. The signals attributed to Cu come from the copper grid.

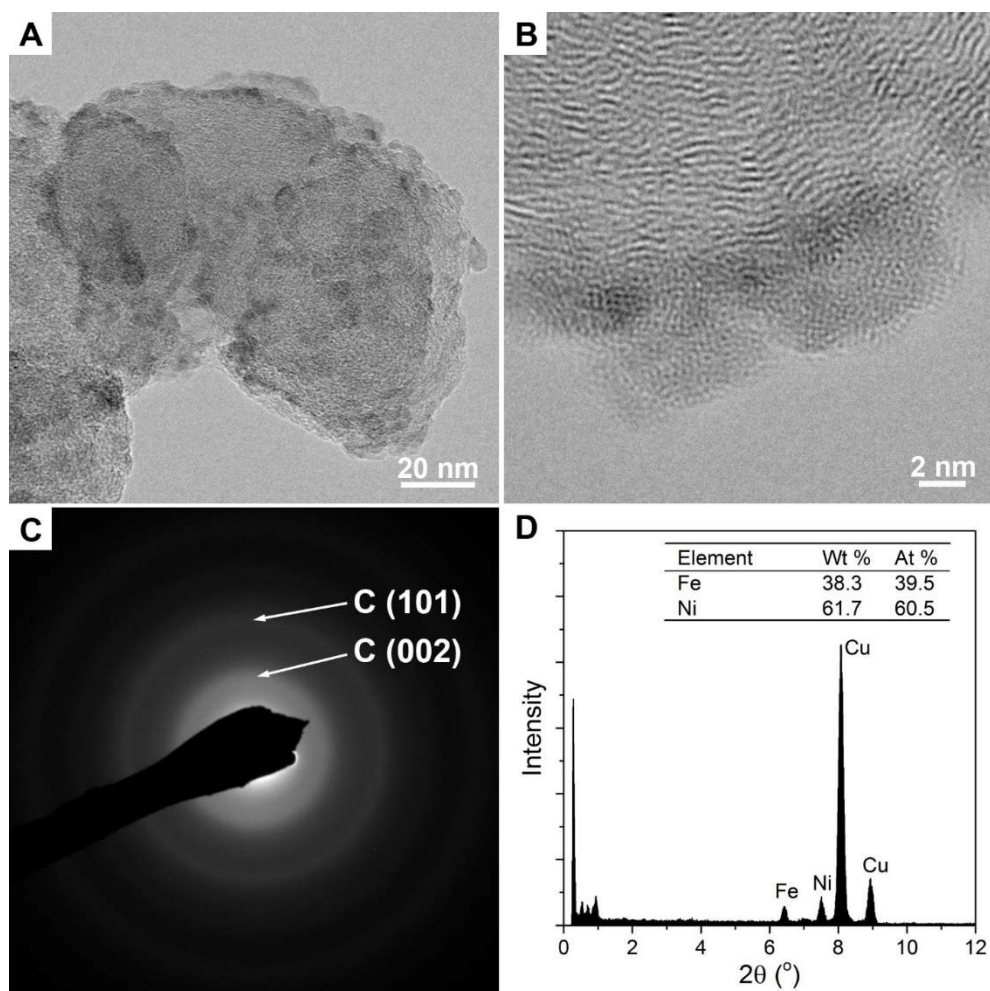
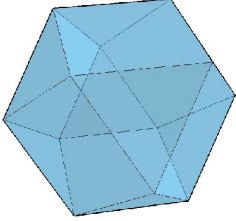
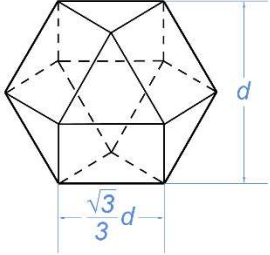
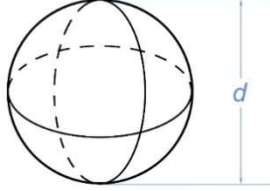


Figure C.15. A-NiFeO_x catalysts after a 5 h chronopotential test under an OER current density of 10 mA cm⁻². (A) TEM image of the A-NiFeO_x/C catalyst. (B) HRTEM image of the A-NiFeO_x nanoparticles. There is no clear lattice fringe that can be identified, which implies the amorphous structure. (C) SAED pattern of the A-NiFeO_x/C. No clear diffraction rings related to nickel iron oxides can be detected. (D) EDS pattern of the A-NiFeO_x/C. The signals attributed to Cu come from the copper grid.

Table C.1. Relationship of edge length or surface area to particle size.

Object	Cuboctahedron	Sphere
3D model		
2D projection		
Size	d	d
Edge length / Girth	$8\sqrt{3} d \approx 13.86 d$	$\pi d \approx 3.14 d$
Surface	$\left(2 + \frac{2\sqrt{3}}{3}\right) d^2 \approx 3.15 d^2$	$\pi d^2 \approx 3.14 d^2$
Volume	$\frac{5\sqrt{6}}{27} d^3 \approx 0.454 d^3$	$\frac{1}{6} \pi d^3 \approx 0.524 d^3$
Volume normalized edge length / girth	$\frac{108\sqrt{2}}{5} \frac{1}{d^2} \approx 30.54 \frac{1}{d^2}$	$6 \frac{1}{d^2}$
Volume normalized surface area	$\frac{9(\sqrt{2} + \sqrt{6})}{5} \frac{1}{d} \approx 6.95 \frac{1}{d}$	$6 \frac{1}{d}$

The volume normalized edge length / girth is inversely proportional to the square of the size. However, the volume normalized surface area is inversely

proportional to size. Thus, it is possible to locate the active sites on the edge or the surface by using nanoparticles with different sizes.

Table C.2. Experimental results of the C-Fe₃O₄ nanoparticle series.

Size (nm)	Volume normalized edge length (nm nm _{Fe₃O₄} ⁻³)	Volume normalized surface area (nm ² nm _{Fe₃O₄} ⁻³)
6.0 ± 1.0	0.92 ± 0.30	1.19 ± 0.20
7.9 ± 0.5	0.50 ± 0.060	0.88 ± 0.053
8.8 ± 0.6	0.40 ± 0.051	0.79 ± 0.050
10.7 ± 0.8	0.27 ± 0.041	0.65 ± 0.048
13.3 ± 1.1	0.18 ± 0.088	0.53 ± 0.082

Table C.3. Experimental results of the A-FeO_x nanoparticle series.

Size (nm)	Volume normalized girth (nm nm _{FeO_x} ⁻³)	Volume normalized surface area (nm ² nm _{FeO_x} ⁻³)
5.2 ± 0.6	1.17 ± 0.13	1.01 ± 0.23
6.4 ± 0.7	0.96 ± 0.12	0.68 ± 0.18
8.2 ± 0.6	0.74 ± 0.056	0.40 ± 0.064
10.4 ± 0.8	0.58 ± 0.048	0.25 ± 0.044
13.0 ± 0.6	0.46 ± 0.021	0.16 ± 0.014

Table C.4. Calculated free energy for each OER elemental step at 0 V overpotential for OER (the step with highest free energy is marked as red).

	(100) - Fe _{tet}	(100) - Fe _{oct}	(111)	(211)
$\text{H}_2\text{O} + * \rightarrow \text{OH}^* + \text{H}^+ + \text{e}^-$	-2.37	-0.65	-1.121	-0.133
$\text{OH}^* \rightarrow \text{O}^* + \text{H}^+ + \text{e}^-$	-0.161	-0.161	0.96	-0.087
$\text{O}^* + \text{H}_2\text{O} \rightarrow \text{OOH}^* + \text{H}^+ + \text{e}^-$	0.646	0.646	-0.501	0.66
$\text{OOH}^* \rightarrow \text{O}_2 + \text{H}^+ + \text{e}^-$	1.885	0.165	0.662	-0.44

Table C.5. Calculated free energy for each OER elementary step at 0 V overpotential, with the OER proceeding through a Mars-van Krevelen mechanism.

	(211)
$\text{H}_2\text{O} + V_{\text{O}} \rightarrow \text{OH}^* + \text{H}^+ + \text{e}^-$	-1.869
$\text{OH}^* \rightarrow \text{O}^* + \text{H}^+ + \text{e}^-$	-0.231
$\text{O}^* + \text{H}_2\text{O} \rightarrow \text{OOH}^* + \text{H}^+ + \text{e}^-$	-1.55
$\text{OOH}^* \rightarrow \text{O}_2 + V_{\text{O}} + \text{H}^+ + \text{e}^-$	3.65

Table C.6. Summary of previously reported OER catalyst activities.

Catalyst	Loading (mg cm ⁻²)	Electrolyte	E@10 A g ⁻¹ (V vs RHE)	E@10 mA cm ⁻² (V vs RHE)	Ref.
NiFeO _x	0.1	0.1 M KOH	1.47	1.51	This work
IrO ₂	0.1	0.1 M KOH	1.52	1.59	This work
NiFe-LDH/CNT	0.2	0.1 M KOH	1.511	1.538	5
Mn ₃ O ₄ /CoSe ₂	0.2	0.1 M KOH		1.59	6
α-Ni(OH) ₂	0.2	0.1 M KOH		1.561	7
Ba _{0.5} Sr _{0.5} Co _{0.8} Fe _{0.2} O _{3-δ}	0.25	0.1 M KOH	1.55		8
Pr _{0.5} Ba _{0.5} CoO _{3-δ}	0.25	0.1 M KOH		1.58	9
NG-CNT	1.75	0.1 M KOH		1.71	10
Ni _x Co _{2-x} O ₄	2.3	1.0 M NaOH	1.60	1.62	11
LT-LiCoO ₂	0.25	0.1 M KOH	1.59	1.60	12
Exfoliated NiFe-LDH	0.07	1.0 M KOH		1.53	13
De-LiCoO ₂	0.1	0.1 M KOH		1.54	14
NiFeAlO ₄	0.125	0.1 M KOH	1.53		15
Ni _{0.2} Co _{0.3} Ce _{0.5} O _x	~ 0.1	1.0 M KOH		1.54	16
Amorphous CoFe ₂ O _n	0.051	0.1 M KOH	1.57		17
Ni _{0.9} Fe _{0.1} O _x	0.00117	1.0 M KOH		1.566	18
Co _{1-x} Fe _x (OOH)	0.01	1.0 M KOH		1.56	19
G-FeCoW	0.21	1.0 M KOH		1.453	20

Appendix C

A UNIVERSAL DESCRIPTOR FOR HYDROGEN OXIDATION AND EVOLUTION REACTIONS OVER PLATINUM GROUP AND COINAGE METALS

Experimental Methods

Chemicals

Buffer electrolytes were prepared by adding 1, 5, 10 and 14 mL of 4 M potassium hydroxide (KOH) solution prepared from KOH tablet (99.99% metal trace, Sigma Aldrich) to 100 mL of 0.2 M phosphoric acid (H_3PO_4 , 99.99%, Sigma Aldrich) solution and 100 mL of 0.2 M potassium bicarbonate (KHCO_3 , 99.7%, Sigma Aldrich) solution, respectively. All chemicals were used as received without further purification.

Electrochemical Measurements

All the electrodes used in this work are 5-mm diameter polycrystalline disks with a geometric area of 0.196 cm^2 . The polycrystalline metal electrodes, mounted on a rotating disk electrode assembly (RDE, Pine instrument), were transferred into a typical three-electrode glass jacketed cell (PINE instruments) for electrochemical measurements. The clean procedure of the cell included soaking in a mixture of H_2SO_4 and Nochromix for four hours and rinsing well with deionized water ($18.2 \text{ M}\Omega \text{ cm}$). A gold foil (Aldrich) instead of a Pt wire was used as counter electrode to avoid any contamination of Pt. The Ag/AgCl reference electrode (PINE instruments) was used,

but all potentials in this paper are given with respect to the reversible hydrogen electrode (RHE). Before measurements, the working electrodes were polished with a 0.05 μm Al_2O_3 particle-suspension on a moistened polishing cloth followed by sonicating and rinsing with deionized water.

Cyclic voltammetry measurements were performed in Ar-saturated buffer electrolytes. Before recording, several cycles at a scanning rate of 100 mV s^{-1} were used to clean and reconstruct the electrode surfaces until steady state CVs were obtained. The oxide reduction peak of Au and oxide formation peaks of Ag and Cu were used to determine the electrochemical surface areas (ECSAs) of the electrodes. Detailed experimental procedures and ECSA calculations are provided below. The HER polarization curves were recorded in H_2 -saturated buffer electrolytes at a rotating speed of 2500 rpm and a scanning rate of 10 mV s^{-1} . For all polycrystalline electrodes, the upper potential limits were chosen to be 0.2 V (vs. RHE) so as to minimize the dissolution and oxidation of working electrode materials. Also, the HER current densities were controlled not to exceed $-5 \text{ mA/cm}_{\text{disk}}^2$ to avoid significant bubble formation and extended dissolution of the counter electrode materials. The given HER polarization curves were corrected for solution resistance determined by a.c.-impedance spectroscopy method (the method and resistance values for various buffer electrolytes are provided below). For CO stripping measurements, the electrodes were firstly transferred into the buffer electrolytes at a potential of 0.1 V (vs. RHE) while purging the electrolyte with CO gas for about 10 min. Afterwards, the electrolyte was purged with pure Ar for another 10 min to completely remove CO from the solution. Starting from 0.1 V the potential was cycled in a given potential region at 20 mV s^{-1} . The second CV was used as the background.

Determination of solution pH

The pH values of buffer electrolytes were calculated from the HOR/HER reversible potential (potential at current is equal to zero, $E_{\text{H}_2/\text{H}^+}$ versus Ag/AgCl) based on the Nernst equation:

$$\text{pH} = \frac{-E_{\text{H}_2/\text{H}^+ \text{ versus Ag/AgCl}} - E_{\text{Ag/AgCl}}}{2.303RT/F}$$

where R is the universal gas constant, T is the temperature in Kelvin, F is the Faraday constant and $E_{\text{Ag/AgCl}}$ is the standard potential for Ag/AgCl reference electrode.

Electrochemical Surface Area (ECSA) Measurements using Cyclic Voltammetries

Au: After obtaining a stable CV scanned from 0 to 1.6 V versus RHE at a sweep rate of 50 mV s⁻¹ in Ar saturated buffer solutions, the reduction peak centered between 1.1 to 1.2 V, which is due to the reduction of AuO and corresponds to a charge density of 390 μC/cm²_{Au}, was used to determine the ECSAs of Au disk in buffer solutions with different pH values.

Cu: Because of the dissolution problems of Cu disk in low-pH electrolytes, the ECSA of Cu disk determined from the CV in 0.1 M KOH solution was applied to the low-pH buffer solutions. The CV was performed in Ar saturated 0.1 M KOH solution from -0.5 V to 1.65 V versus RHE at a scan rate of 20 mV s⁻¹. The broad positive going peak between 0.5 V and 0.71 V, which corresponds to the cover of one monolayer of Cu₂O with a charge density of 360 μC/cm²_{Cu}, was used to calculate the ECSA of Cu electrode.

Ag: The CV was scanned from 0 to 1.6 V versus RHE at a sweep rate of 100 mV s⁻¹ in 0.1 M KOH electrolyte saturated with Ar. The anodic peak centered at about 1.25V, which is attributed to the formation of one monolayer of AgOH or Ag₂O with a charge density of 400 μC/cm²_{Ag}, was used to calculate the ECSA of Ag disk.

Determination of Solution Resistance using Impedance Spectroscopy

The solution resistance was determined after each HER measurements by a.c.-impedance spectra. For the measurement, a potential amplitude of 10 mV was applied with frequencies starting from 200 kHz to 100 mHz. The real component value of the impedance at 1 kHz was used as the Ohmic resistance of the system. The obtained solution resistances of used buffer electrolytes were shown in Table D.1.

Table D.1. Solution resistances of phosphoric acid/phosphate buffer and bicarbonate/carbonate buffer electrolyte.

Buffer electrolyte	Solution pH	Solution resistance (Ω)
Phosphoric acid/phosphate	1.8	65 ± 1
	5.6	62 ± 1
	8.7	35 ± 1
	12.1	27 ± 1
Bicarbonate/carbonate	10.8	32 ± 1
	12.1	21 ± 1
	13.2	19 ± 1

Charge Density Differences within the Water Network

An adequate amount of water must be explicitly simulated to capture the physics of the metal-water interface. To verify that three layers of water molecules is adequate, charge density differences between low and high pH were computed for the same surface and water orientation. The resulting charge density difference for Pt (110) is shown in Figure D.1. The initial charge density was taken to be at pH ~ 1 , and

the final charge density was taken to be at pH ~ 10 . The majority of the differences in charge density are shown to occur within the first layer of the water network. Charge differences occurring in the third layer are primarily due not to charge transfer, but rather on minor differences in the position of the water molecules.

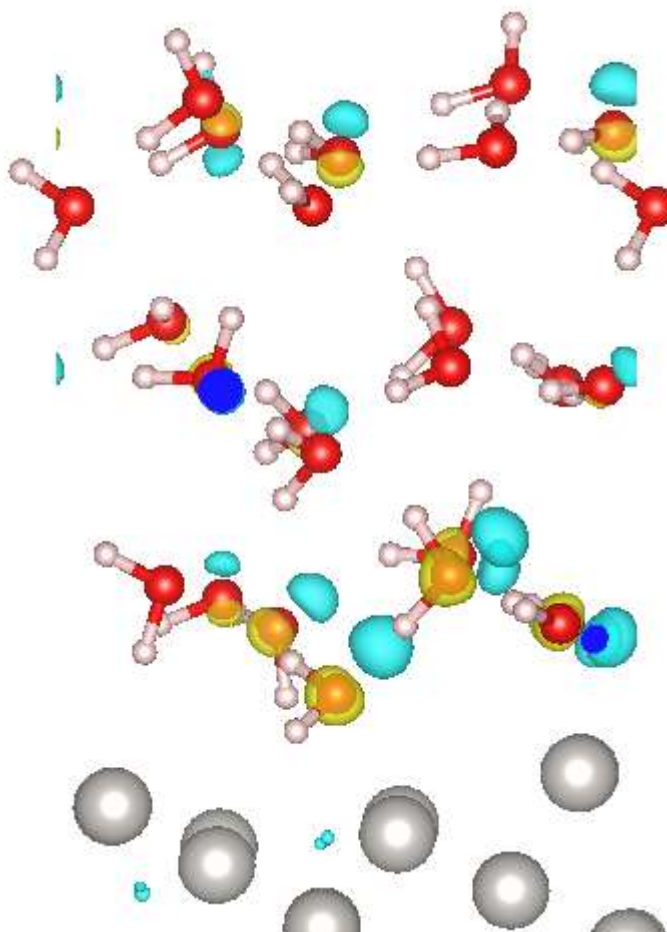


Figure D.1. Charge density difference between pH ~ 1 and pH ~ 10 for the H-up water network on Pt (110). Yellow and blue regions depict areas of charge accumulation and charge depletion, respectively. The charge density isosurfaces represent a value of $\pm 0.03 e/\text{\AA}^3$.

Entropy Correction Scheme for the Water Molecule

To obtain the Gibbs free energy of adsorption for the H-up/H-down water networks, we account for the change in both the entropy and the solvation of the water molecule. The expression for estimating Gibbs free energies from DFT energies for the water molecule is as follows:

$$G_{*/\text{H}_2\text{O}} = E_{*/\text{H}_2\text{O}} + \text{ZPE}_{*/\text{H}_2\text{O}} - TS_{*/\text{H}_2\text{O, vib}}$$
$$G_{\text{H}_2\text{O}} = E_{\text{H}_2\text{O}} + \text{ZPE}_{\text{H}_2\text{O}} - TS_{\text{H}_2\text{O, tot}} + \Delta G_{\text{H}_2\text{O}}^{\text{solv}}$$

where $\text{ZPE}_{*/\text{H}_2\text{O}}$ and $S_{*/\text{H}_2\text{O, vib}}$ is the zero-point energy and vibrational entropy, respectively, of the water network adsorbed on the metal surface, $\text{ZPE}_{\text{H}_2\text{O}}$ and $S_{\text{H}_2\text{O, tot}}$ are the zero-point energy and total entropy (vibrational, rotational, and translational components), respectively.

The entropy change of a water molecule upon adsorption has been thoroughly studied by Kolb *et al*¹⁷¹. Upon modeling multiple structured water networks, Kolb et al. found the entropy change between the free and adsorbed states to be 0.21 ± 0.01 eV. The solvation of the adsorbed water network is implicitly accounted for when DFT is performed on the extended hydrogen-bonded water networks discussed herein. The free energy of solvation of the water molecule is well-documented, and herein we use a value of -0.28 eV. This leads to the following correction to the DFT water adsorption energy to yield the water adsorption free energy:

$$\Delta G_{\text{H}_2\text{O}} = \Delta E_{\text{H}_2\text{O}} + \Delta(\text{ZPE} - \text{TS})_{\text{H}_2\text{O}} - \Delta G_{\text{H}_2\text{O}}^{\text{solv}} = \Delta E_{\text{H}_2\text{O}} + 0.49 \text{ eV}$$

Extraction of Absolute Potential and pH from DFT Calculations

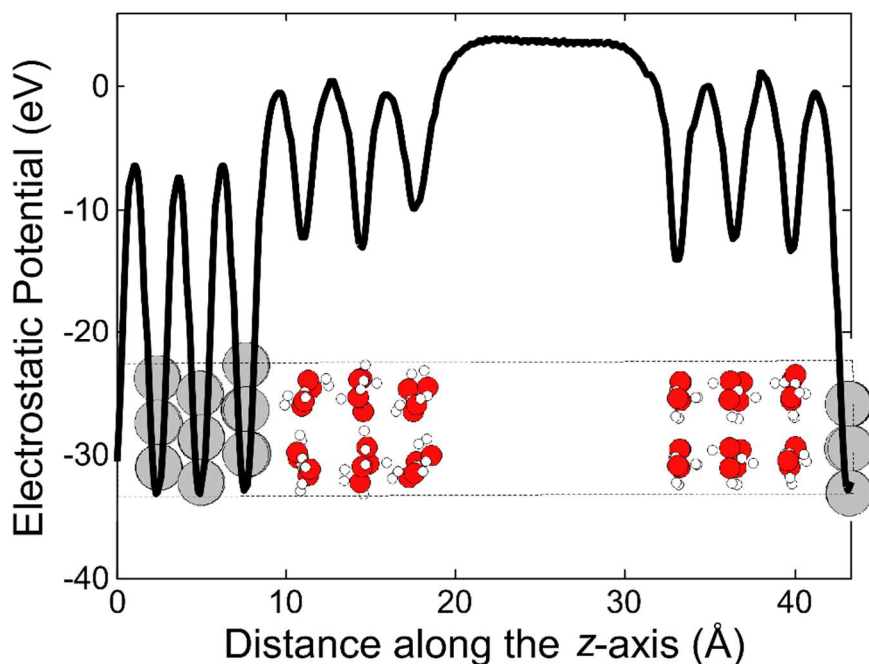


Figure D.2. Example of an electrostatic potential profile of an H-down water network on Ag (111) at a charge of $-0.5 e^-$.

The result of computing the electrostatic potential profile for an atomic system is shown in Figure D.2. The electrostatic potential shown has been referenced to the Fermi level. The resulting work function of 3.54 eV as measured in the vacuum region of Figure D.2 is consequently related to the absolute potential and pH in the following manner:

$$E \text{ (V vs. SHE)} = \frac{3.536 \text{ V}}{e} - 4.281 \text{ V} = \mathbf{-0.745 \text{ V vs. SHE}}$$

$$\text{pH} = \frac{-0.745 \text{ V vs. SHE}}{-0.0592 \text{ V/pH}} = \mathbf{12.6}$$

Adsorption Energies of H-up and H-down Water Networks on Pt, Ir, Pd, and Rh

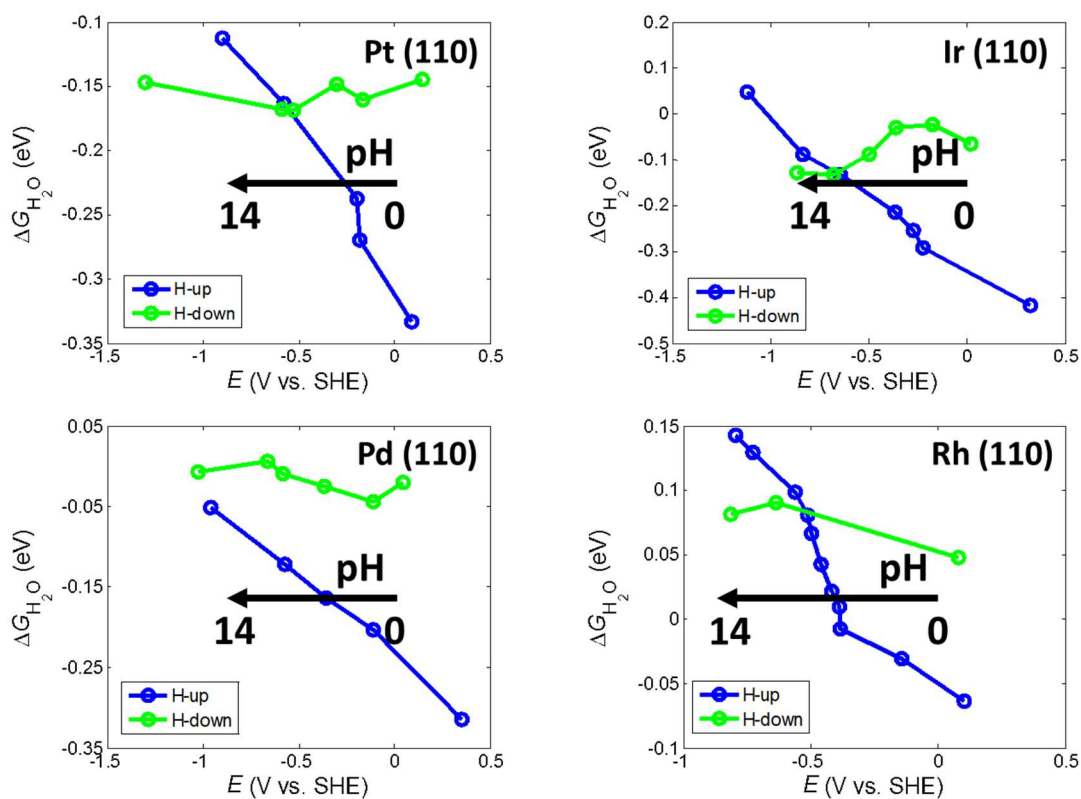


Figure D.3. Free energies of water adsorption for H-up and H-down orientations on the (110) surfaces of Pt, Ir, Pd, and Rh.

Adsorption Energies of H-up and H-down Water Networks on Au, Cu, and Ag

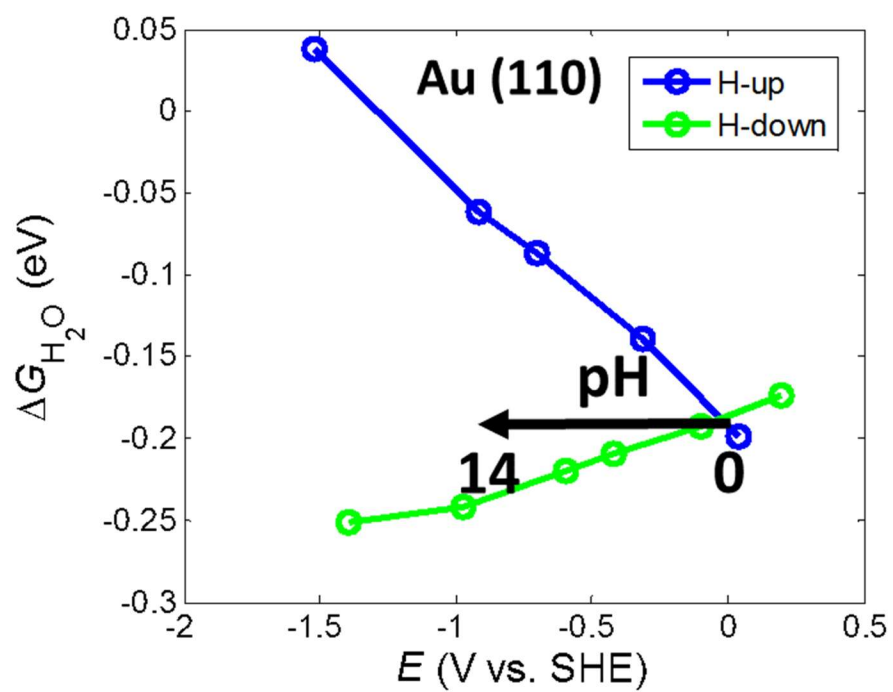


Figure D.4. Free energy of water adsorption for the H-up and the H-down orientation on Au (110).

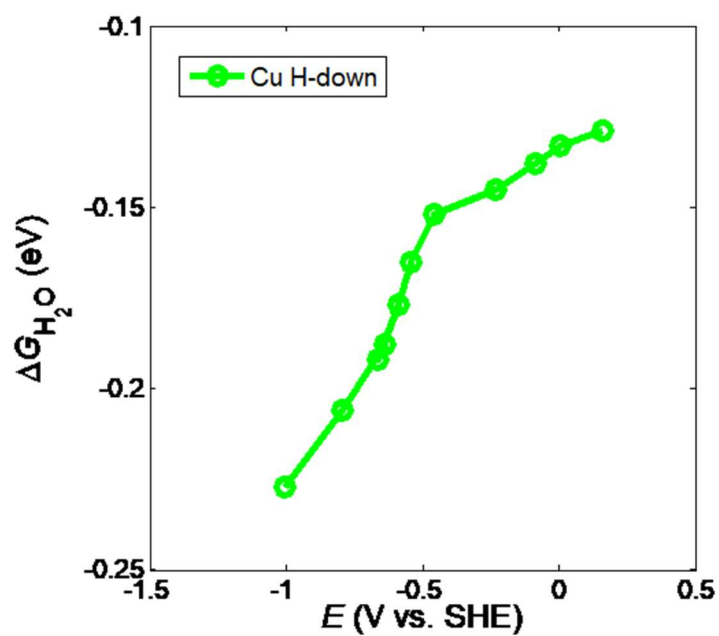


Figure D.5. Free energy of water adsorption for the H-down orientation on Cu (100)- $(2\sqrt{2} \times 2)R45^\circ$ -O. The H-up was found to preferentially re-orient into the H-down orientation.

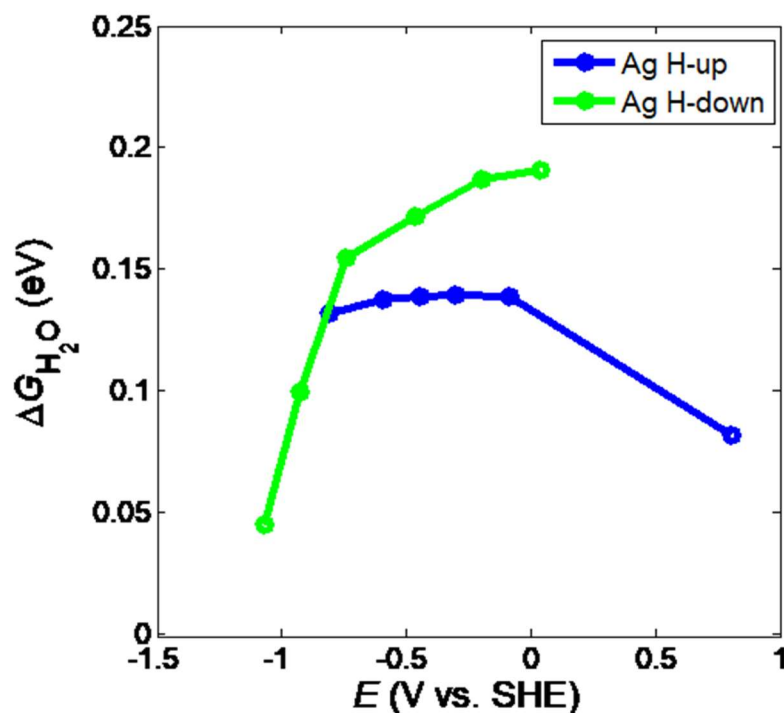


Figure D.6. Free energy of water adsorption for the H-up and the H-down orientation on Ag (111).

Cyclic Voltammograms of Au, Cu, and Ag at Different pH

Figure D.7 shows the CVs of Au (a) and Cu (b) in 0.2 M phosphoric acid/phosphate buffer electrolyte. Due to the high solubility of Ag in the phosphoric acid/phosphate buffer solution, stable CV could not be obtained through the whole pH range. The CVs of Ag polycrystalline electrode measured in bicarbonate/carbonate buffer electrolyte are shown in Figure D.7c. The profiles of all the CVs in buffer solutions are similar with the typical CVs of Au, Cu and Ag polycrystalline electrodes in extreme acid or base: a wide double-layer potential region is followed by the featured oxidation/reduction peak^{233–235}. In our previous study of platinum group metals (PGMs), we demonstrated that the shift of hydrogen under-potential

deposition/adsorption peak potential (E_{peak}) vs. RHE from the CV directly reflects the change of HBE of the electrode materials in the buffer electrolytes with different pH values⁸⁹. However, the hydrogen redox peaks were not shown in the CVs of Au, Cu and Ag because the interactions between hydrogen and these metals were too weak. It is therefore not possible to tell the pH effect on the HBE of the weakly binding metals by regular RDE experiments.

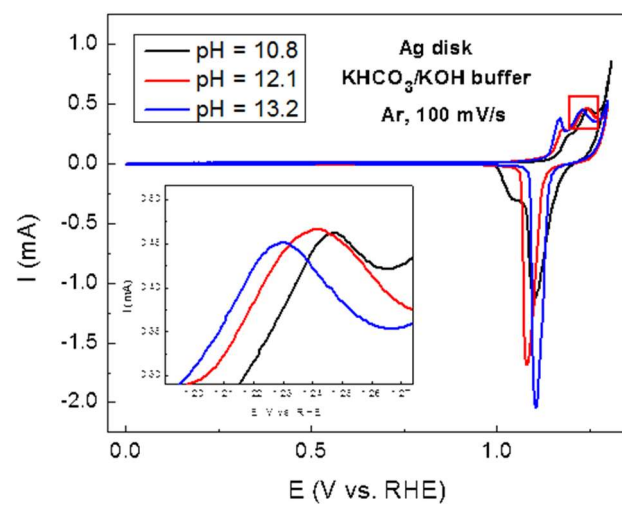
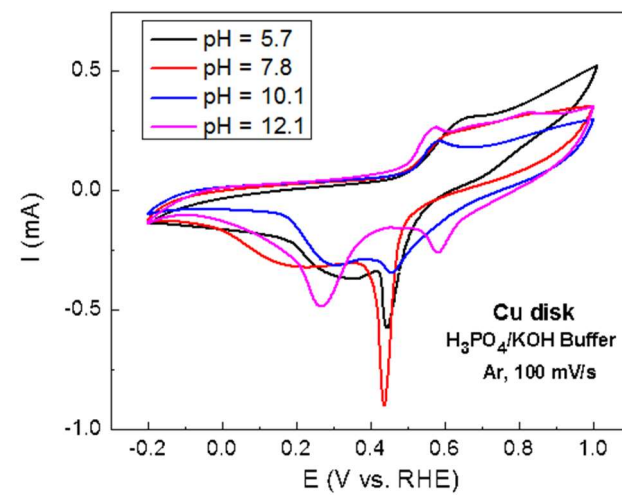
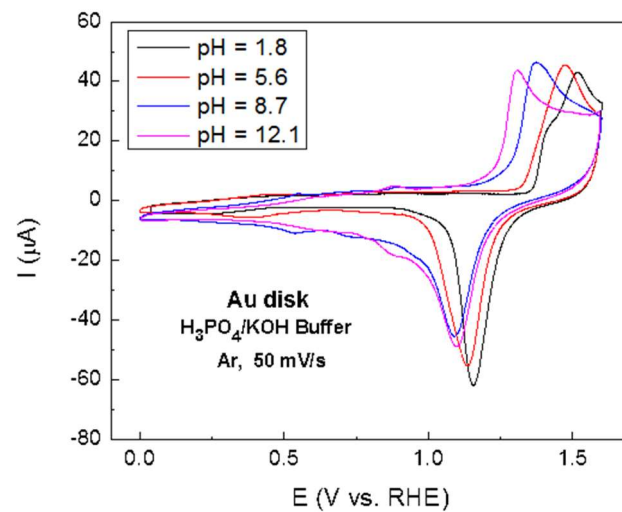


Figure D.7. Cyclic voltammograms of Au (a) and Cu (b) polycrystalline electrodes in an Ar-saturated phosphoric acid/phosphate buffer; (c) CVs of Ag electrode in Ar-saturated bicarbonate/carbonate buffer electrolytes, recorded at room temperature.

Pourbaix Diagrams with Hydroxyl Formation on PGMs

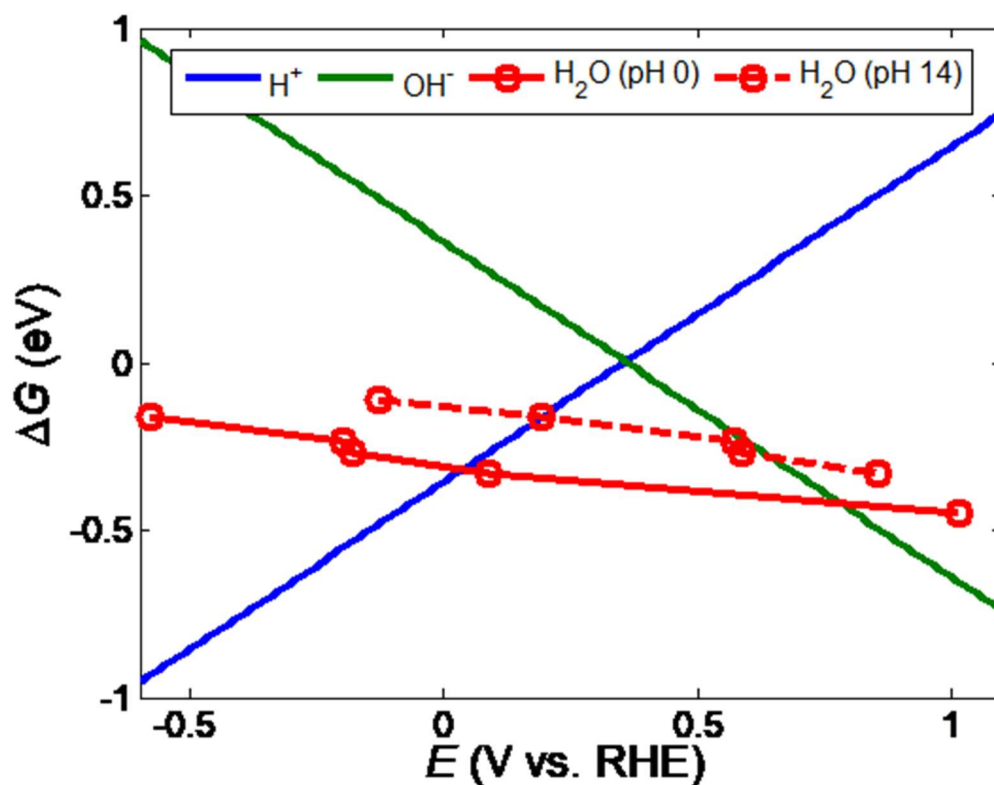


Figure D.8. Pourbaix diagram of Pt (110) depicting potential-dependent free energies of proton, hydroxide, and water adsorption.

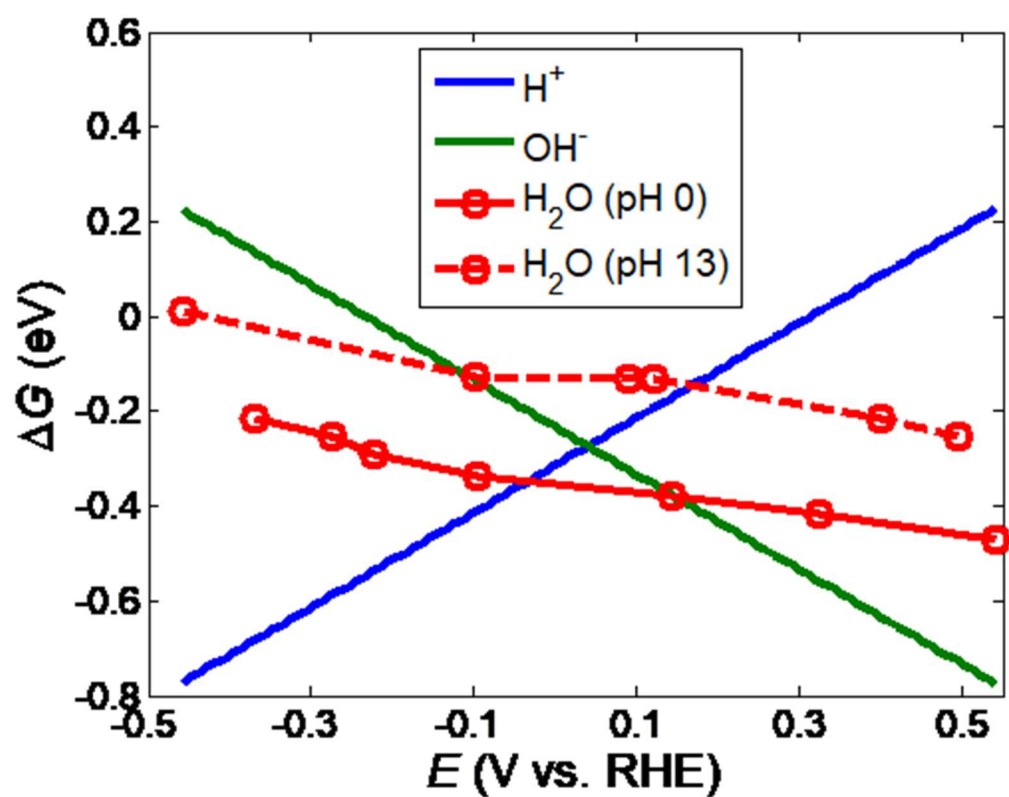


Figure D.9. Pourbaix diagram of Ir (110) depicting potential-dependent free energies of proton, hydroxide, and water adsorption.

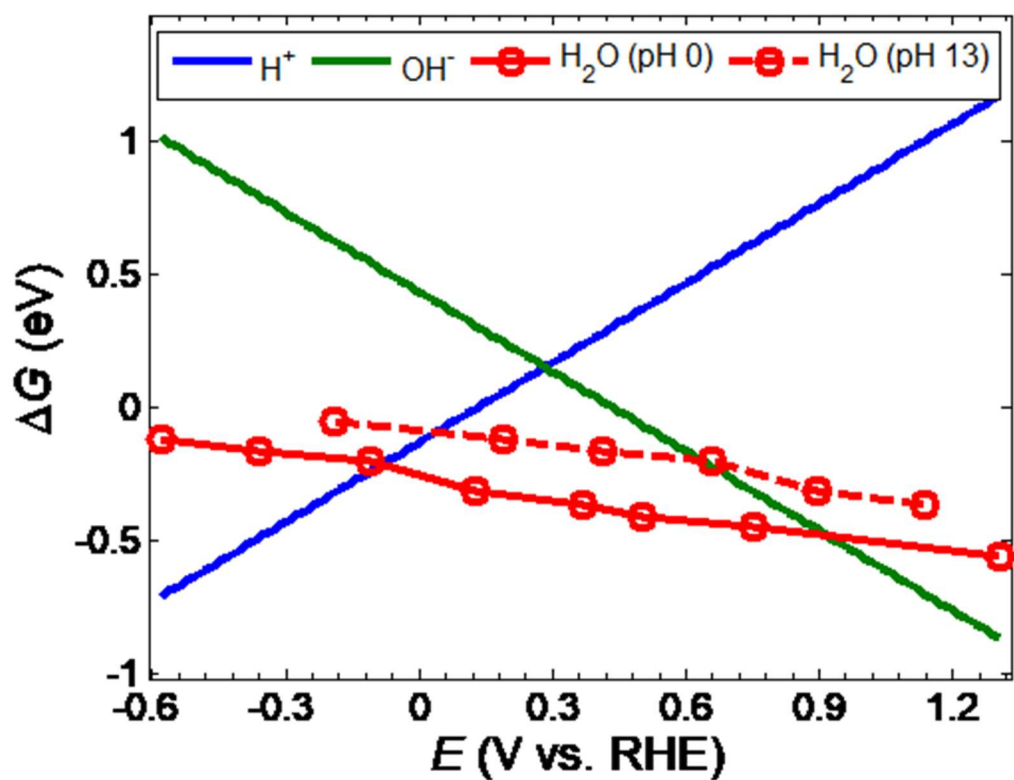


Figure D.10. Pourbaix diagram of Pd (110) depicting potential-dependent free energies of proton, hydroxide, and water adsorption.

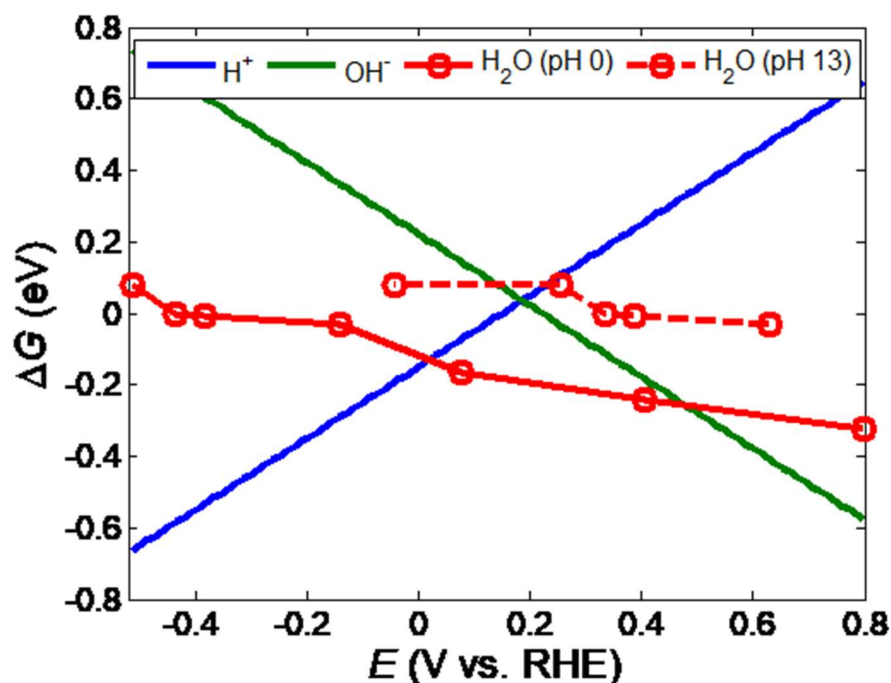


Figure D.11. Pourbaix diagram of Rh (110) depicting potential-dependent free energies of proton, hydroxide, and water adsorption.

HOR/HER Polarization Tests and Exchange Densities for Au, Cu, and Ag

The iR-corrected HER polarization curves for Au (Figure D.12a), Cu (Figure D.12b), and Ag (Figure D.12c) polycrystalline electrodes in H₂-saturated 0.2 M phosphoric acid/phosphate buffer electrolytes show increased overpotential (η) at a certain current density or decreased HER activity with increasing pH. The absence of the plateau regions in the HER polarization curves confirms the chosen buffer solution can sufficiently maintain the pH value at the electrode surface. The overpotentials (η) at a current density of 5 mA cm_{disk}⁻² increase as solution pH increases from ~1 to ~12 (Figure D.12d), indicating a decrease of HER activity as the pH increases. The obtained η values at pH = 1.8 and pH = 12.1 are in good agreement with literature data

measured in 0.1 M HClO₄ and 0.1 M KOH, respectively^{18,236}. However, the HER activities for the three metals decrease to different extents with pH. The largest η variation was observed in the case of gold polycrystalline electrode, increasing from 335 mV at pH = 1.8 to 603 mV at pH = 12.1. The polarization curves between $-0.5 \text{ mA cm}_{\text{disk}}^{-2}$ and $-4 \text{ mA cm}_{\text{disk}}^{-2}$ were used to calculate the geometric exchange current densities at the reversible potential by extrapolating the Tafel plots to 0 V vs. RHE (Figure D.13). The geometric exchange current densities were subsequently normalized to the corresponding roughness factor, defined as the ratio between surface area and the geometric disk area (0.196 cm^2), to obtain the intrinsic exchange current densities (i_0) (listed in Table D.2). The Tafel slopes and roughness factors (Table D.2) varied slightly at different solution pH, indicating the alkalinity and the phosphate anion had little influence on the whole reaction pathways as well as the electrode surface structure.

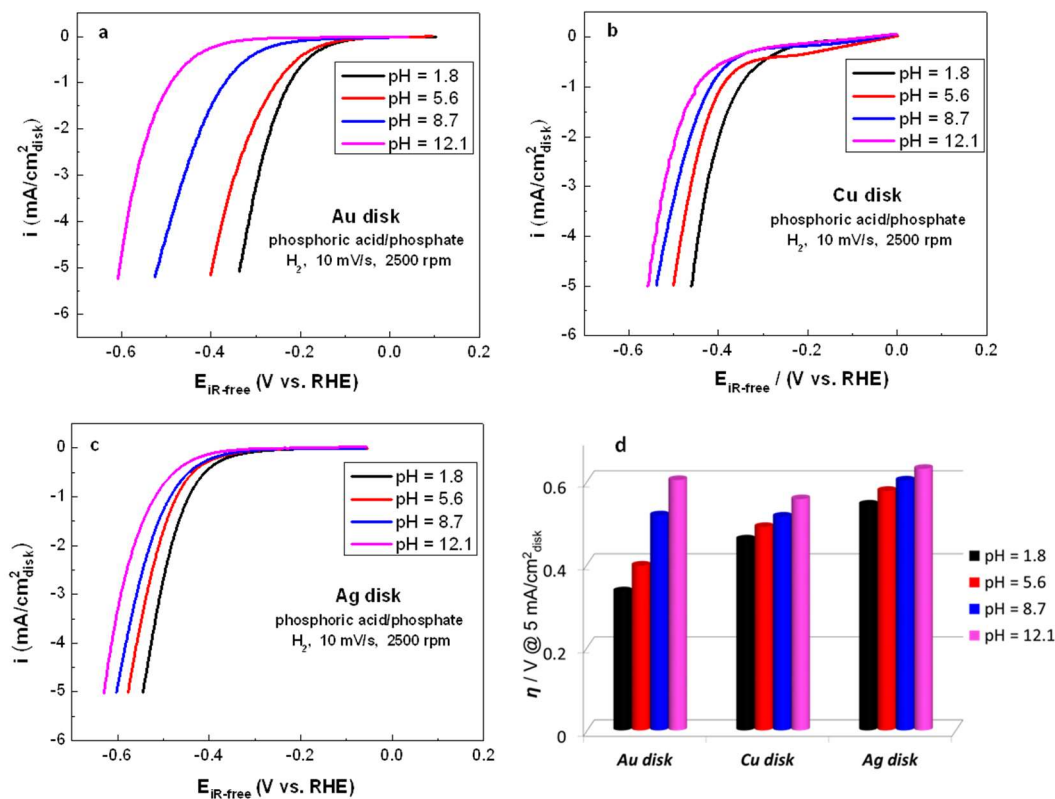


Figure D.12. IR-free polarization curves of Au (a), Cu (b) and Ag (c) polycrystalline disk in H₂-saturated 0.2 M phosphoric acid/phosphate buffer electrolytes at room temperature (scan rate: 10 mV s⁻¹; rotation speed: 2500 rpm); (d) Comparison of HER overpotentials (η) at 5 mA cm⁻²_{disk} for the three metal surfaces with solution pH ranging from 1 to 12.

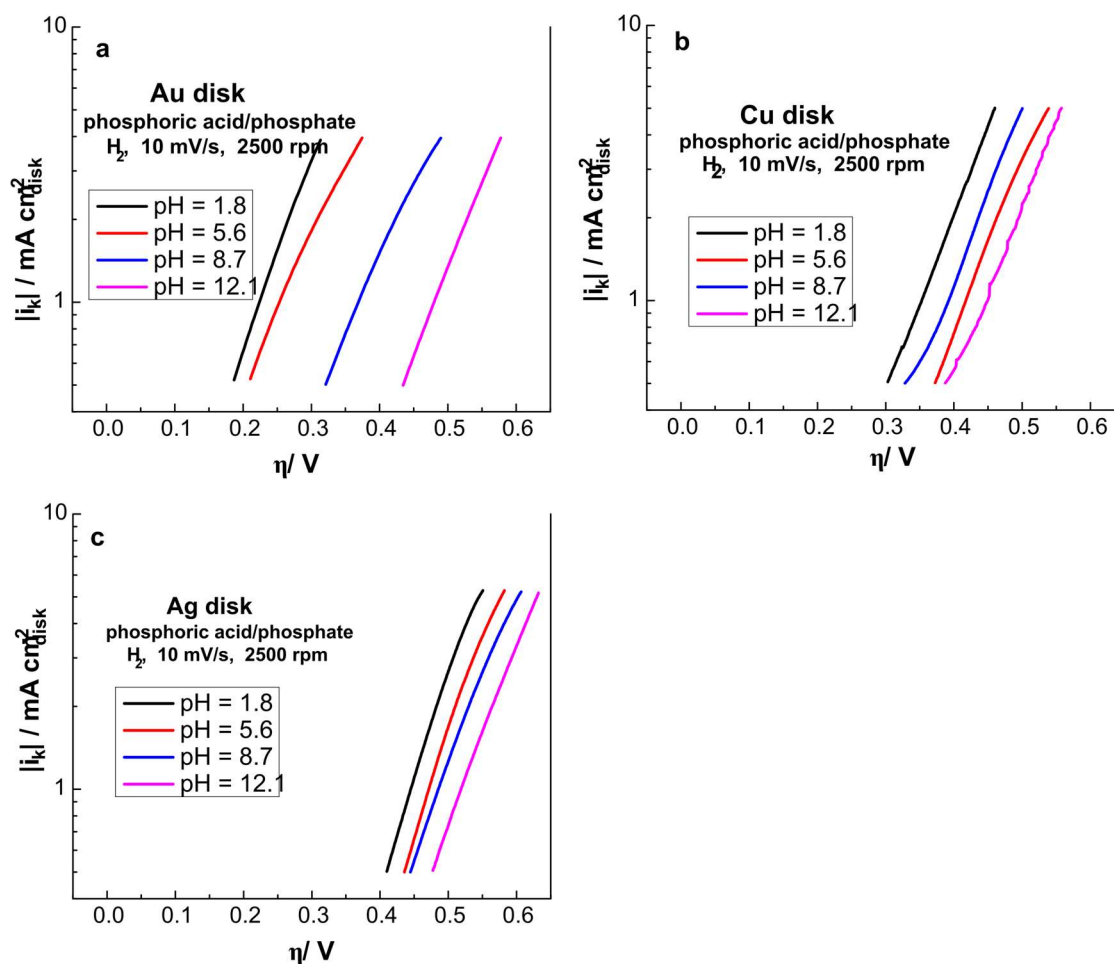


Figure D.13. Tafel plots of the HER on the Au (a), Cu (b) and Ag (c) polycrystalline electrodes in 0.2 M phosphoric acid/phosphate buffer electrolytes at room temperature.

Table D.2. Measured exchange current densities (i_0), roughness factors and Tafel slopes of Au, Ag and Cu polycrystalline electrodes in phosphoric acid/phosphate buffer electrolytes.

Electrode materials	Solution pH	Log (i_0 (A $\text{cm}_{\text{metal}}^{-2}$))	Roughness factor	Tafel slope (mV dec^{-1})
Au	1.8	-4.67 ± 0.5	2.10	158 ± 7
	5.6	-5.11 ± 0.31	2.04	145 ± 16
	8.7	-5.70 ± 0.18	1.85	159 ± 9
	12.1	-6.12 ± 0.25	1.92	165 ± 5

Cu	1.8	-5.55 ± 0.22	3.56	153 ± 10
	5.6	-5.75 ± 0.15	3.56	169 ± 18
	8.7	-5.80 ± 0.18	3.20	151 ± 15
	12.1	-5.93 ± 0.3	3.05	156 ± 13
Ag	1.8	-6.20 ± 0.16	1.55	143 ± 8
	5.6	-6.35 ± 0.13	1.55	153 ± 12
	8.7	-6.43 ± 0.24	1.55	164 ± 11
	12.1	-6.52 ± 0.21	1.55	158 ± 9

The HER exchange current densities decrease as the solution pH increases (Figure D.14a). The i_0 values of all three metals at pH = 12.1 are very close to the reported values measured in 0.1 M KOH electrolyte¹⁸, indicating that the existence of phosphate anion has negligible effect on the kinetics of HER on coinage metals. However, we notice that the i_0 of gold polycrystalline electrode at pH = 1.8 is more than one order of magnitude higher than some early literature data reported in 0.1 M HClO₄^{34,237}. This discrepancy is likely due to the different polarization curve region used to extract the i_0 . It is generally observed that the Au electrode exhibits two Tafel slopes in acid electrolytes: $\sim 60 \text{ mV dec}^{-1}$ at the low overpotential region and $\sim 120 \text{ mV dec}^{-1}$ at the high overpotential region (a typical CV, polarization curve and Tafel plot of Au electrode in 0.1 M HClO₄ is shown in Figure D.15). The 60 mV dec^{-1} region is also known as the barrierless discharge process as the charge transfer coefficient (α) is determined to be 1 according to an alternative form of Tafel equation^{238,239}, but the detailed kinetic behavior and mechanism of the barrierless discharge process have been under intense discussion. Besides, the low η region is not appropriate to obtain the i_0 by extrapolation of the Tafel plot because the Tafel equation is indeed a simplified form of the Butler-Volmer equation only when the overpotential is significantly large¹⁷. Moreover, the HER exchange current densities in

acid given in these articles is almost identical to the value measured in base, which is inconsistent with the fact that the η value increases by more than 200 mV from acid to base on Au electrode. Therefore, the i_0 value extracted from the higher Tafel slope region seems to be more reasonable. Consistent with the trend of activity expressed as η at a current density of $5 \text{ mA cm}_{\text{disk}}^{-2}$, the i_0 of all investigated monometallic electrodes decreased with the increasing media pH value. Among them, the Au disk shows that the largest activity decreases by about 1.5 orders of magnitude while the other two electrodes decrease by only several times. In order to rationalize the pH-dependent HER activities on the coinage metals, we further characterized the surface properties of these metals using cyclic voltammetries in identical Ar saturated buffer electrolytes.

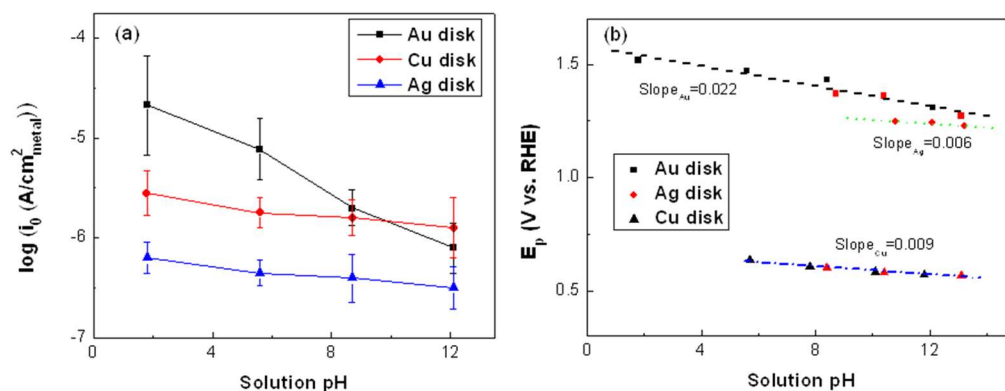


Figure D.14. (a) Measured exchange current densities, $\log(i_0)$, for HER on Au (black), Cu (red) and Ag (blue) polycrystalline electrodes plotted as a function of solution pH value. (b) The peak potential of the first oxidation peak from CVs measured in phosphate buffer (black) and carbonate buffer (red) plotted as a function of solution pH.

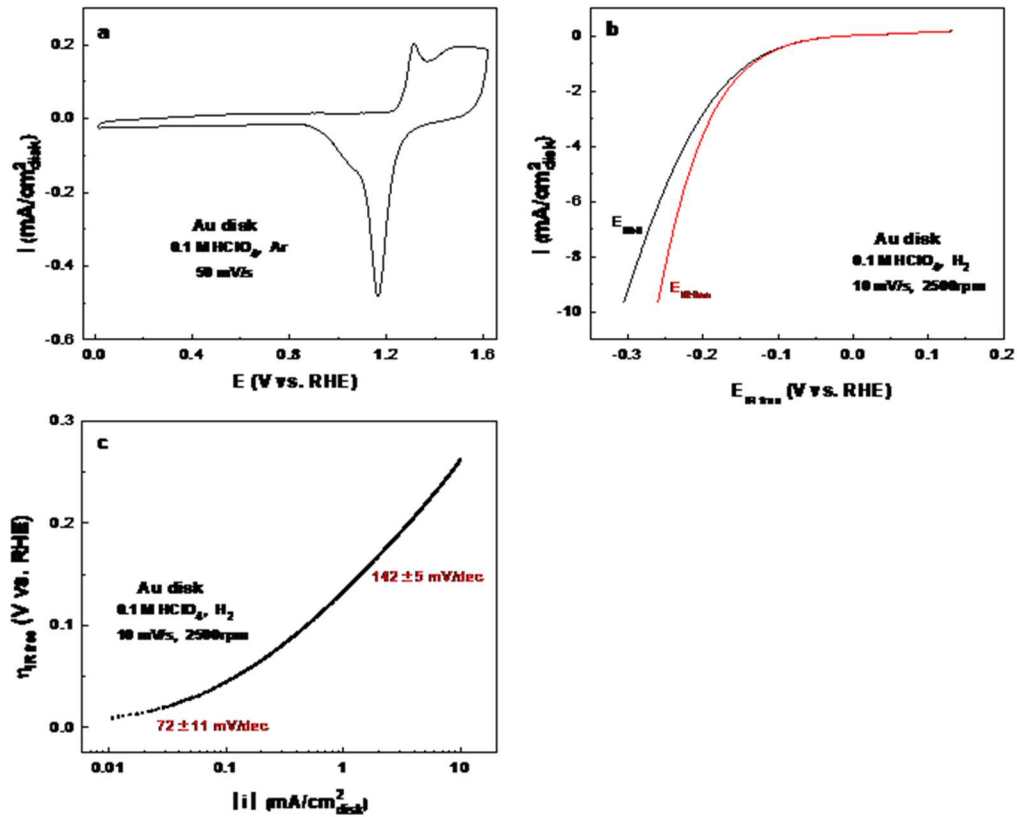
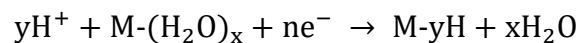


Figure D.15. Typical CV (a), polarization curves (b) and Tafel plots (c) of gold polycrystalline electrode in 0.1 M HClO₄ at room temperature.

Partial Oxidation/Reduction of H-up/H-down Water

An anomalous shift in the apparent hydrogen binding energy can be related to the number of electrons transferred during the HOR/HER process. As described by Schwarz *et al.*, when a catalyst is initially occupied by an adsorbed water molecule, the proton adsorption may be written as



where y is the number of hydrogen atoms per metal (M) site, and x is the number of displaced water molecules⁴². Moreover, from the Nernst equation, it can be deduced that the apparent hydrogen binding energy will shift according to the following equation,

$$\Delta\Delta G_{H, app} = \frac{59.2 \text{ mV/pH}}{n} - 59.2 \text{ mV/pH}$$

where n is the number of electrons transferred during either the adsorption or release of a proton. In the work of Schwarz *et al.*, y was found to equal 1.00 ± 0.04 irrespective of the catalyst surface. However, n was found to be greater than unity on stepped surfaces, indicating that water on stepped surfaces can become partially oxidized and that the apparent Gibbs free energy of hydrogen adsorption becomes more exergonic as the pH increases⁴². Herein, we observe the same behavior for the (110) surfaces of Pt, Pd, Ir, and Rh. Shown in Figure D.16 is the charge transfer and the optimized geometry for Pt (110) and Au (110). In all cases, the H-up water network is partially oxidized, whereas the H-down water network is partially reduced. Therefore, for the Pt, Pd, Ir, and Rh stepped surfaces, which have exergonic H-up water adsorption being preferred, n is greater than unity implies strengthening the apparent hydrogen adsorption on Pt, Pd, Ir, and Rh (where the H-up network is favored). However, since n is less than unity for Au(110), the apparent hydrogen adsorption weakens with increasing pH.

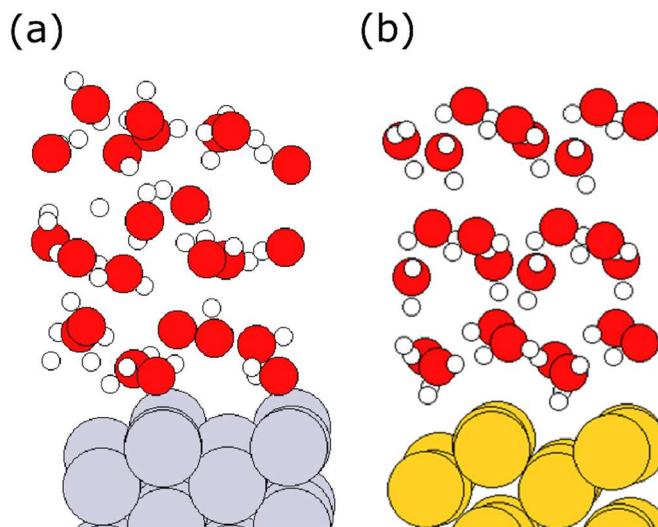


Figure D.16. (a) The H-up water network on Pt(110) at pH ~ 0 . The H-up oriented water at the Pt surface has a partial charge of $(+0.08 \pm 0.04) e^-$. (b) The H-up water network on Au(110) at pH ~ 0 . The H-down oriented water at the Au surface has a partial charge of $(-0.034 \pm 0.006) e^-$.

The partial oxidation (reduction) of H-up (H-down) water is a result of the electronic structure of the water molecule. The highest occupied molecular orbital (HOMO) of water is the $1b_1$ orbital, which is primarily localized around the oxygen atom and is associated with lone pair effects¹⁹⁴. The lowest unoccupied molecular orbital (LUMO) of water, however, is the $4a_1$ orbital and is localized along the O-H bond¹⁹⁴. Therefore, as the electrode surface becomes more electron-rich at negative electrode potentials (i.e., increasing pH), electron transfer from the metal into the LUMO of water becomes preferential.

Ab initio Molecular Dynamics on Au (110) with H-down Initial Configuration

To provide additional evidence for the presence of the H-down water configuration, we carried out *ab initio* molecular dynamics (AIMD). The resulting

distribution of H atoms along the z -direction is shown in Figure D.17. Comparison of the AIMD simulation to the static H-down structure optimized with DFT indicates good agreement in both the position and number of the hydrogen atoms most proximal to the electrode surface. Furthermore, the water molecules located further away from the electrode surface have a greater standard deviation in their position over time. This suggests that water further away from the surface (i.e., in approximately the third solvation shell) behaves in a more “bulk-like” fashion, whereas the water nearest the surface has a comparatively higher degree of order. The assertion that the electrode has a small effect on water outside of the third solvation shell is also supported by charge density differences from static DFT calculations. By comparing the resulting charge densities at different pH values, we observe most changes in the atomic charge densities occur in the first and second water layers, while the third water layer shows significantly less sensitivity, as shown in Figure D.1. Furthermore, the ordered nature of water at electrified interfaces has been a subject of numerous studies^{171,183,195,196}.

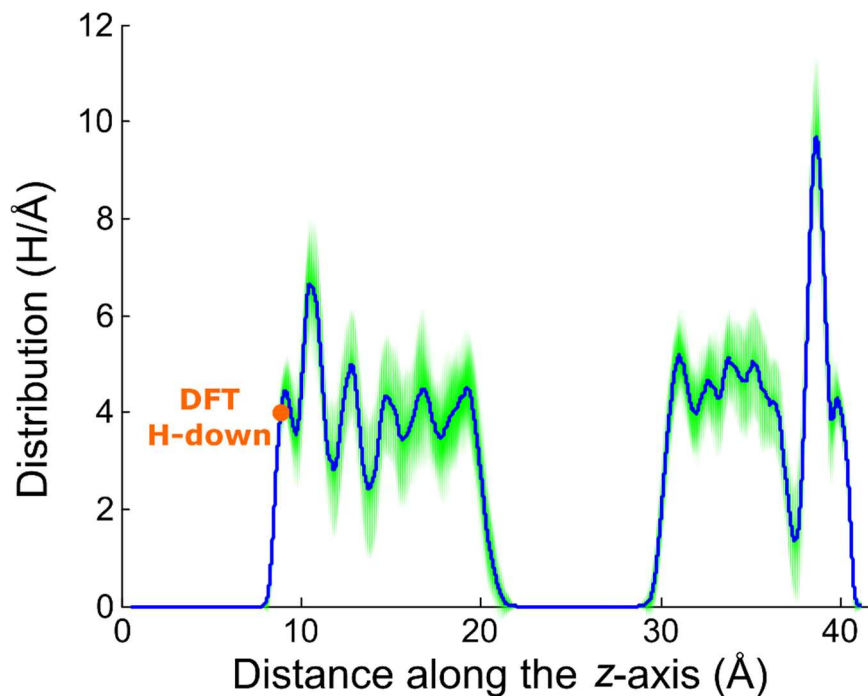


Figure D.17. Time-averaged distribution of hydrogen atoms along the z -direction from ab initio molecular dynamics (AIMD). The shaded green area represents the local standard deviation of the hydrogen distribution. The static DFT structure is depicted with the filled circle.

Ab initio Molecular Dynamics on Au (110) with H-up Initial Configuration

Furthermore, to provide evidence that the Au-H₂O system equilibrated sufficiently during the trajectory length of 10 ps, we performed an additional AIMD simulation on Au (110) with the H-up network as the initial geometry. Figure D.18 shows the distribution of oxygen atoms along the z -axis of the simulation cell. Apparent from Figure D.18 is that the Au-H₂O system, initialized here from the H-up geometry, develops a clear peak associated with the H-down network optimized through DFT. If a longer trajectory was used for the AIMD simulation, it is expected

that the peak associated with the H-down network would further grow relative to the peak corresponding to the H-up network.

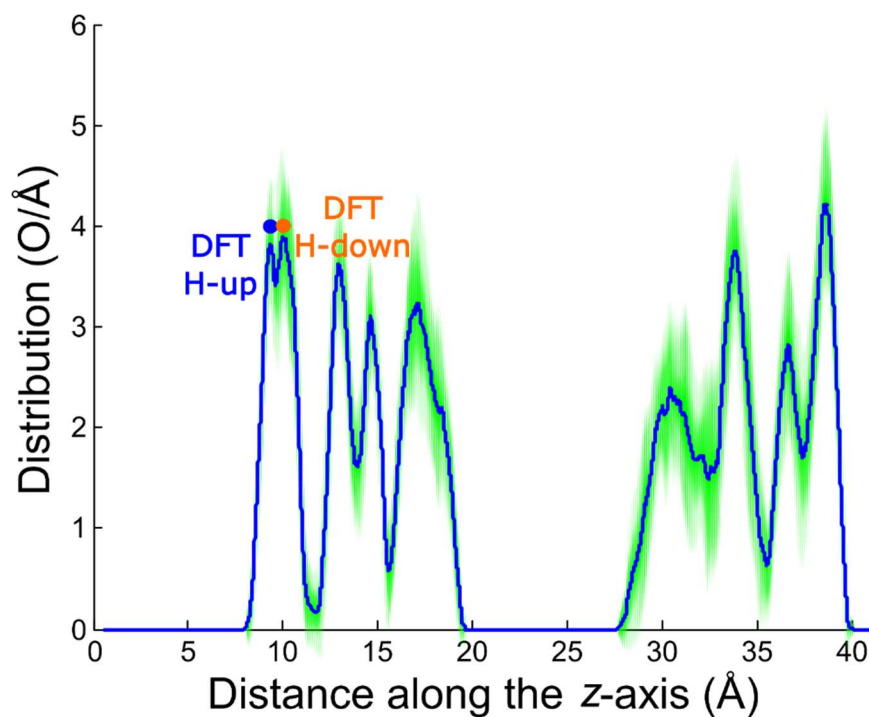


Figure D.18. Time-averaged distribution of oxygen atoms along the z-direction. The shaded green area represents the local standard deviation of the hydrogen distribution.

Appendix D

UNDERSTANDING THE pH DEPENDENCE OF THE MECHANISM AND ACTIVITY OF HYDROGEN OXIDATION/EVOLUTION REACTION ON A RU CATALYST

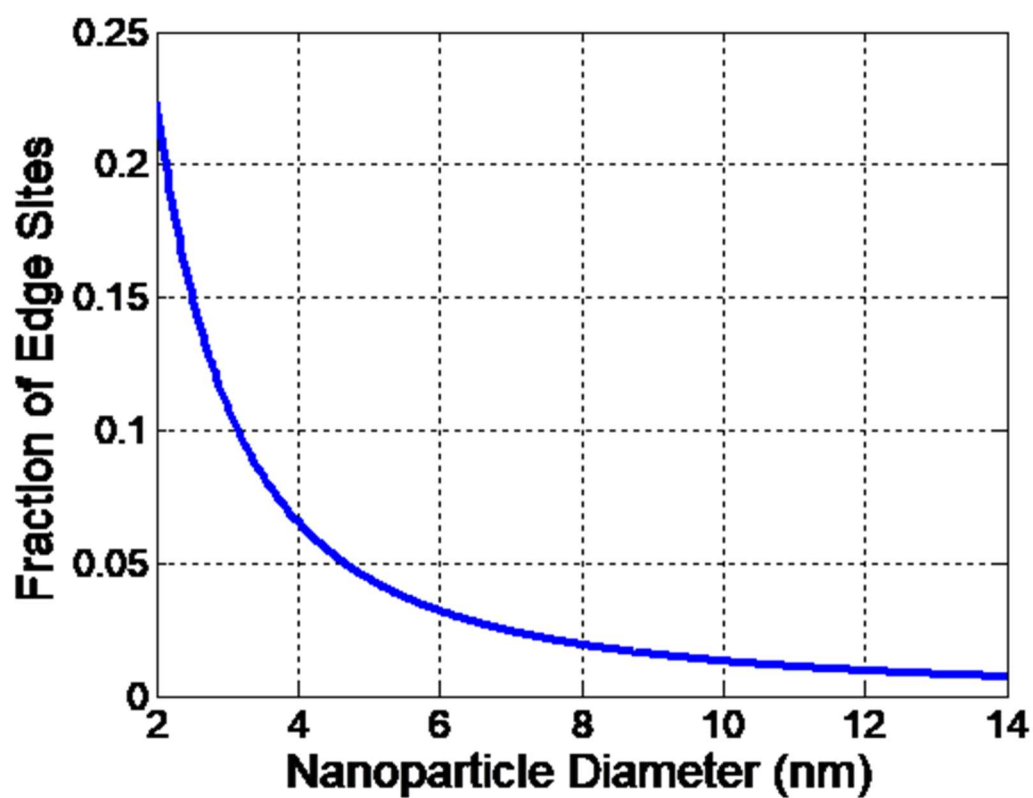


Figure E.1. Approximate fraction of edge sites on a Ru nanoparticle as a function of the nanoparticle diameter. Adapted from an empirical relationship developed for Au nanoparticles by Barmparis and Remediakis¹⁰⁵.

Herein, we have modeled both terrace and step sites of Ru. A key difference between Ru terraces and steps is that the Ru step was found to preferentially form adsorbed hydroxyl, leading to adsorption properties of hydrogen and water that are particularly suitable for fast HOR/HER. As a result, the relative abundance of edge sites in the experimental catalyst will have a large impact on the catalytic activity. To provide an estimate of the edge sites present, we show in Figure E.1 the empirical relationship between fraction of edge sites and nanoparticle diameter developed by Barmparis and Remediakis for Au nanoparticles¹⁰⁵. In our first-principles based modeling of Ru, a fraction of edge sites of 0.1 is observed to best reproduce the pH-dependent activity trend observed experimentally for Ru.

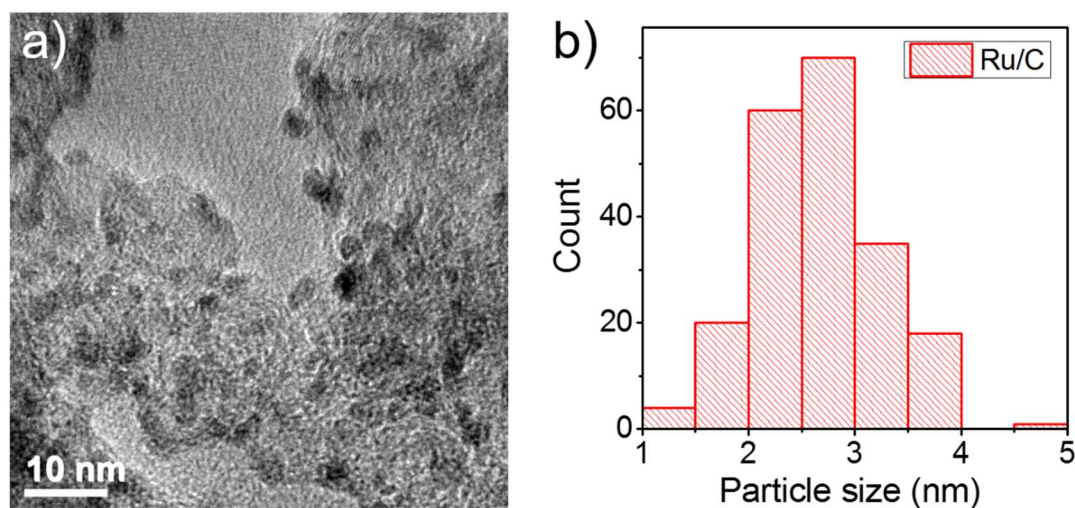


Figure E.2. (a) TEM image of Ru/C, (b) histogram of the particle size of Ru nanoparticles.

The particle size of Ru/C was characterized using the transmission electron microscope (TEM, JEOL, 2010F, 200 kV). The TEM sample was prepared by adding a drop of well-sonicated Ru/C suspension in water onto a Cu grid. The diameters of more than 200 Ru nanoparticles were measured from the TEM images and number-averaged size is about 2.6 ± 0.6 nm (Figure E.2). The size distribution of the experimental Ru nanoparticles is in close agreement with the assumed fraction of edge sites in the first-principles based activity model.

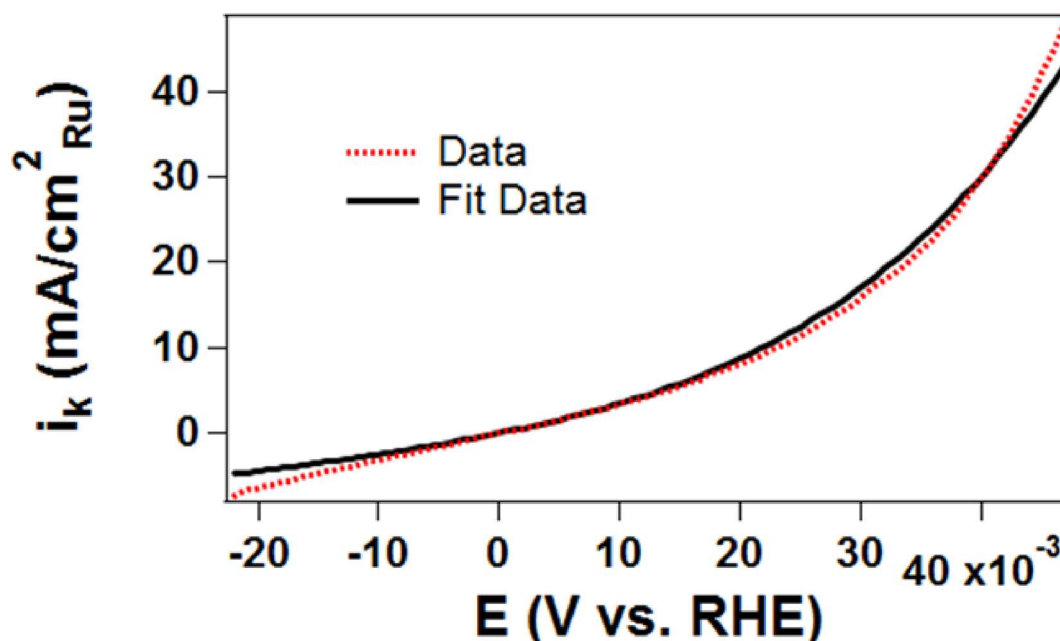


Figure E.3. Experimental and simulated HOR/HER kinetic polarization curve on Ru/C in selected acetate buffer at pH 4.3 with dual pathway kinetic model after correcting for mass transport.

In Figure E.3, an example of an experimental and simulated HOR/HER kinetic polarization curve is shown. The reaction barriers for the Tafel, Heyrovsky, and Volmer steps are used as adjustable parameters for the dual pathway kinetic model shown in Figure E.3. In Figure E.3, along with all other data presented herein, the current density has been normalized to the electrochemical surface area of Ru, thereby allowing for a fair comparison of reaction barriers across the entire pH range.

Figures E.4-E.6 show examples of a standard Butler-Volmer fitting of the HOR/HER polarization curves for three different electrolytes. In each case, the Butler-Volmer fitting was done allowing the anodic and cathodic transfer coefficients (α_a and α_c) to sum to either one or two. For all electrolytes, $\alpha_a + \alpha_c = 2$ was found to provide the best agreement with the experimental polarization curves.

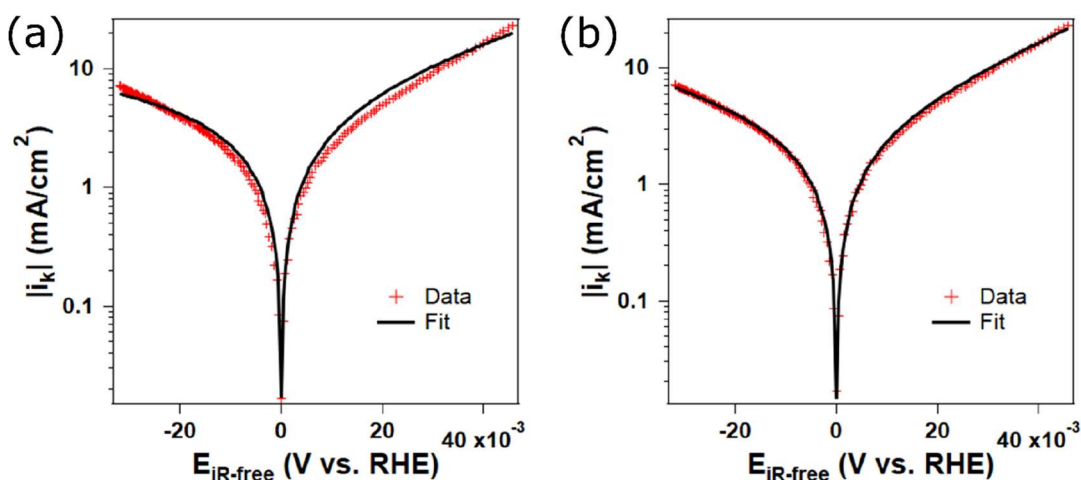


Figure E.4. HOR/HER polarization curves of Ru/C measured at a scanning rate of 10 mV/s and a rotation rate of 1600 rpm at 293 K. in H₂-saturated phosphoric acid at pH 2. Ru/C loading is 20 $\mu\text{g}_{\text{Ru}}/\text{cm}^2$. Butler-Volmer fitting of the polarization curves for the HOR polarization with (a) $\alpha_a + \alpha_c = 1$ and (b) $\alpha_a + \alpha_c = 2$.

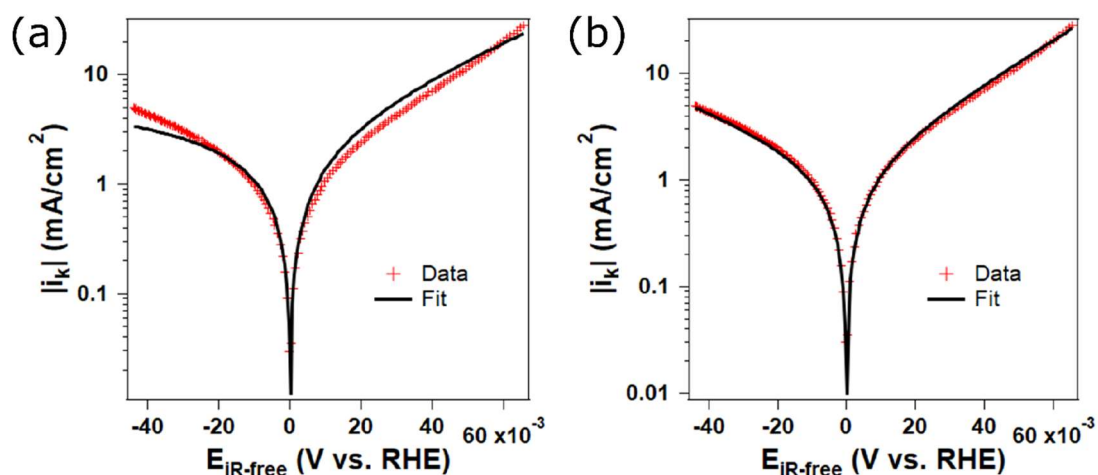


Figure E.5. HOR/HER polarization curves of Ru/C measured at a scanning rate of 10 mV/s and a rotation rate of 1600 rpm at 293 K. in H_2 -saturated phosphoric acid/phosphate buffer at pH 6.7. Ru/C loading is $20 \mu\text{g}_{\text{Ru}}/\text{cm}^2$. Butler-Volmer fitting of the polarization curves for the HOR polarization with (a) $\alpha_a + \alpha_c = 1$ and (b) $\alpha_a + \alpha_c = 2$.

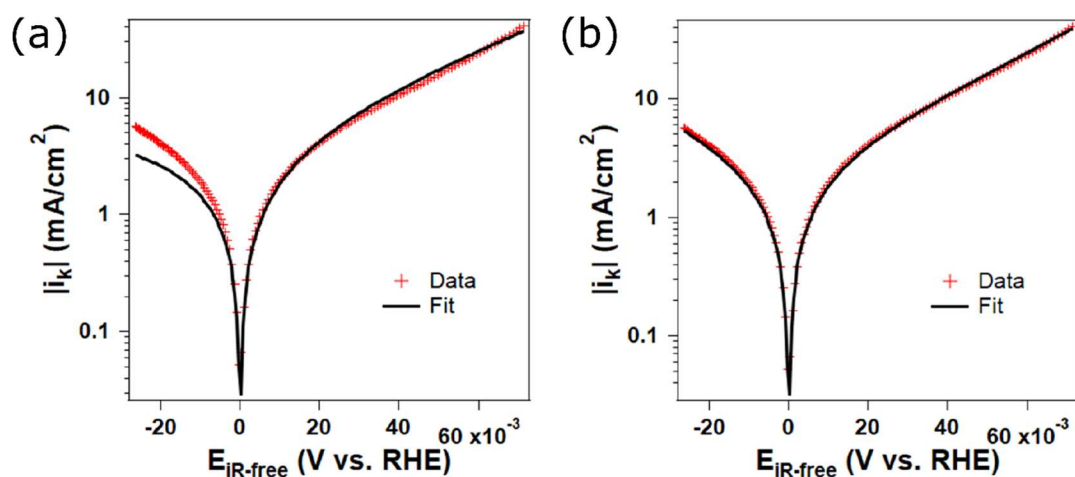


Figure E.6. HOR/HER polarization curves of Ru/C measured at a scanning rate of 10 mV/s and a rotation rate of 1600 rpm at 293 K. in H_2 -saturated 0.1 M KOH. Ru/C loading is $20 \mu\text{g}_{\text{Ru}}/\text{cm}^2$. Butler-Volmer fitting of the polarization curves for the HOR polarization with (a) $\alpha_a + \alpha_c = 1$ and (b) $\alpha_a + \alpha_c = 2$.

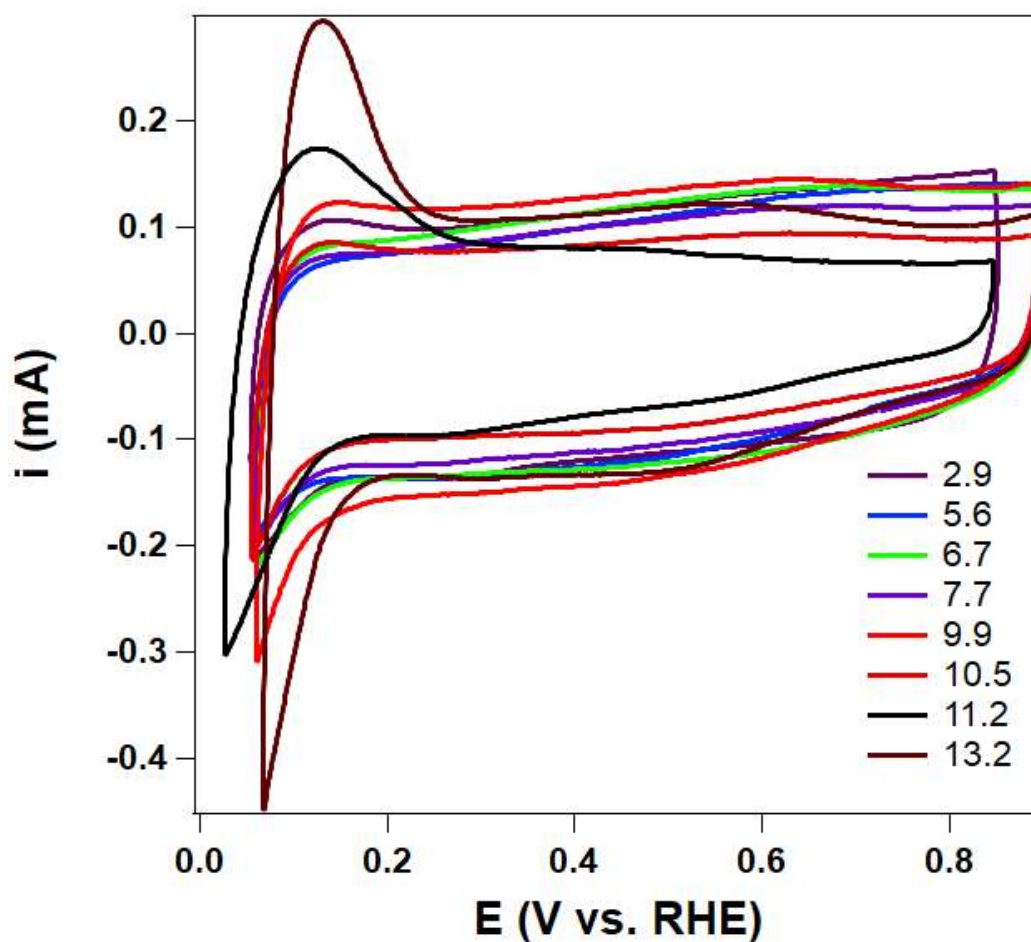


Figure E.7. CVs of Ru/C catalyst in Ar-saturated buffer solutions at different pH at a scanning rate of 50 mV/s and 293 K.

Figure E.7 shows the CV of Ru/C in a variety of Ar-saturated buffer solutions. The highest current is observed at pH 11.2 and 13.2 where the adsorbed hydroxyl on Ru edges leads to increased activity.

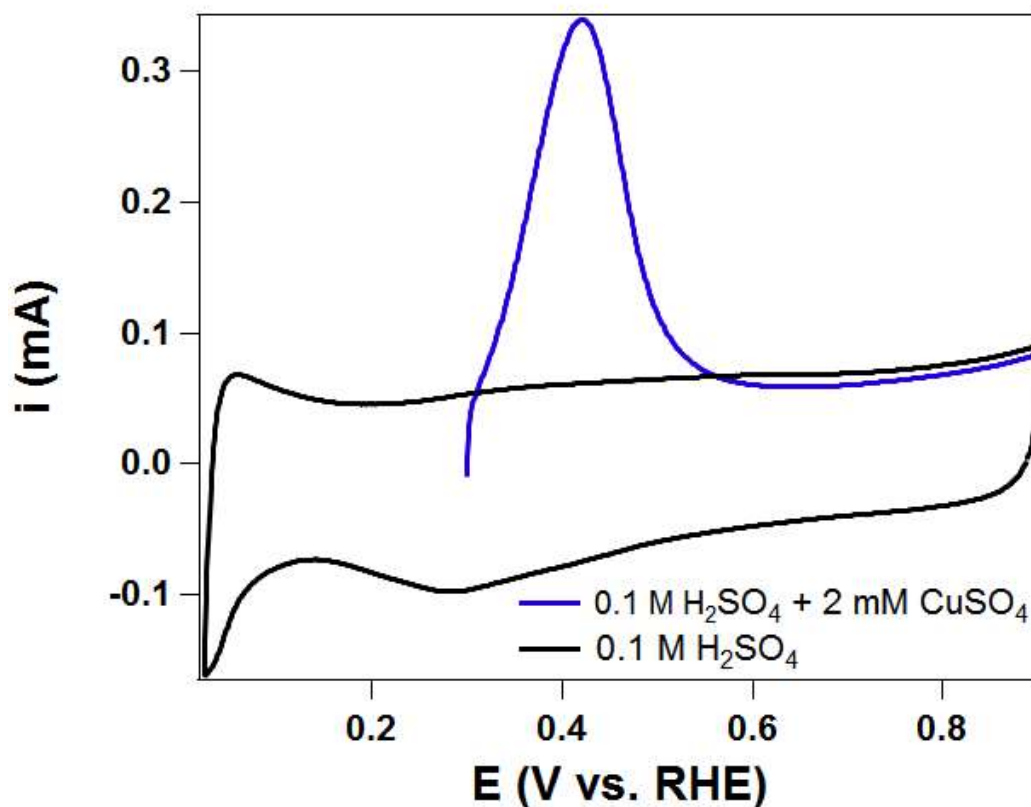


Figure E.8. Cu stripping voltammograms of Ru/C for determining the electrochemical surface area of Ru with a scanning rate of 20 mV/s and at 293 K.

Since the electrochemical surface area could not be obtained reliably from the CVs, Cu stripping was performed to determine the Ru surface area. An example of the Cu stripping voltammogram is shown in Figure E.8.

Appendix E

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Nickel supported on nitrogen-doped carbon nanotubes as hydrogen oxidation reaction catalyst in alkaline electrolyte

Zhongbin Zhuang, Stephen A. Giles, Jie Zhang, Glen R. Jensen, Stavros Caratzoulas, Dionisios G. Vlachos & Yushan Yan

Nature Communications 7, Article number: 10141 (2016) | [Download Citation >](#)

Abstract

The development of a low-cost, high-performance platinum-group-metal-free hydroxide exchange membrane fuel cell is hindered by the lack of a hydrogen oxidation reaction catalyst at the anode. Here we report that a composite catalyst, nickel nanoparticles supported on nitrogen-doped carbon nanotubes, has hydrogen oxidation activity similar to platinum-group metals in alkaline electrolyte. Although nitrogen-doped carbon nanotubes are a very poor hydrogen oxidation catalyst, as a support, it increases the catalytic performance of nickel nanoparticles by a factor of 33 (mass activity) or 21 (exchange current density) relative to unsupported nickel nanoparticles. Density functional theory calculations indicate that the nitrogen-doped support stabilizes the nanoparticle against reconstruction, while nitrogen located at the edge of the nanoparticle tunes local adsorption sites by affecting the d-orbitals of nickel. Owing to its high activity and low cost, our catalyst shows significant potential for use in low-cost, high-performance fuel cells.

About this article

Publication history

Received	Accepted	Published
12 July 2015	08 November 2015	14 January 2016

DOI

<https://doi.org/10.1038/ncomms10141>

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