Combined experimental and theoretical DFT studies on the decorated Pt@Au and Au@Pt electrocatalysts for formic acid oxidation

Yu, Yaolun

2011

Yu, Y. L. (2011). Combined experimental and theoretical DFT studies on the decorated Pt@Au and Au@Pt electrocatalysts for formic acid oxidation. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/46294>

<https://doi.org/10.32657/10356/46294>

Combined experimental and theoretical studies
on the decorated Pt@Au and Au@Pt catalysts
for formic acid oxidation

YU YAOLUN

School of Chemical and Biological Engineering

A thesis submitted to the Nanyang Technological University
in fulfillment of the requirement of the degree of
Doctor of Philosophy

2011

Acknowledgement

In his heart a man plans his course, in his mouth he says, "I will not fail."

My very first acknowledgement is dedicated to the LORD for his guidance through these 10 years as a student. His constant conservation, as well as his knowledge, will help me to finish what I have done today.

I need to express my most sincere gratitude to A.P. Wang for his enthusiasm and patience for the completion of his thesis. He always sent me a thread of light in my time of darkness and experience when I was lost in the darkness of research.

I also need to say a big thank you to Dr. Lai Kok Hwa for his kindness and his profound knowledge. He greatly helped me and is my actual mentor. Although he is my supervisor.

I would like to thank my research group members: Dr. N. Wang Shuangyin, Liu Yonghao, Li An, Nguyen Tien Hoa, Li Dingsheng, Wang Yi, Song Junling, Liu Jiehua, and Li Ming. Ms. Deng Xuan and Wei Xiangfeng sharing our happiness and achievements together. I need to thank Dr. Wen Shuhua, Yang Fan, Xi Hongyan, and Li Xianghui for their discussions and supports on the theoretical calculations and help me to give my

undergraduate students: Yan Yuhongda and Yeo Chengyao
hard workings during the final year projects.

I would like to take this opportunity to thank all my Agape SCBE and
deaf friends and NTU: Dr. Wang Bo, Wei Li, Li Shasha, Linmin,
Cunben, Chen Jiahao, Wang Yong, Zhang Wei, Gan Ye, Shi
Poernomo Gunawan, Zhang, Xiang, Qibao, Xiang, Yi, Yan Zhengha
Mr. Yu Jian for sharing the student journey with me.

Thanks to the Technical Executives at SCBE. They have helped me a lot during these years.

Besides those, I need to give thanks to pastors: Rev. Hui and Jian
Rev. Dr. Stephen Tong. Their sermons really inspired me
have set good examples for me. I thank the Agape and sisters in
Agape Reformed Evangelical Church for their supports in their pray
memorials. They are my family. I feel like I am with them though
I am thousands of miles away from my hometown.

At last, I need to thank my family and relatives for
continuous supports. Special thanks to my mother and wife
and hope along the way and nine years. Just as the
quod from the Holy Bible and wealth are inherited from
prudent wife is from the Lord. I hope to possess
your life through my life.

Table of contents

Table of contents	i
List of Figures	iii
List of Tables	vi
Abstracts	vii
Chapter 1 Introduction and scope of this thesis	1
1.1 Introduction	1
1.2 Scope of this thesis	2
Chapter 2 Literature review	4
2.1 Basis of Proton exchange membrane fuel cells (PEMFCs)	4
2.2 Electrochemical reactions and catalysts	7
2.2.1 Methanol oxidation reaction (MOR)	8
2.2.2 Formic acid oxidation reaction (FAO)	10
2.2.3 Oxygen reduction reaction (ORR)	15
2.2.4 Advantages in the preparation of electrocatalysts	17
2.3 Under potential deposition (UPD) technique	18
2.4 Density functional theory (DFT)	20
2.4.1 Basic theories of DFT	21
2.4.2 DFT Literature review	26
Chapter 3 Experimental methods and calculation details	31
3.1 Materials and equipment	31
3.2 Preparation of Au nanoparticle core	33
3.3 Preparation of Pt@Au electrocatalyst for electrochemical tests	34
3.4 Preparation of Pt@Au electrocatalyst by electrodeposition	34
3.5 Preparation of Au@Pt electrocatalyst by direct electrodeposition	35
3.6 FAO and CO stripping tests	36
3.7 Experimental research methodology	37

3.7 X-ray diffraction. (XRD).....	3.7.....
3.7.2 Transmission electron microscopy. (TEM).....	3.8.....
3.7.3 Voltammetric techniques.....	3.8.....
3.8 Calculation methods.....	4.1.....
Chapter 4 Decorated Pt based electrocatalysts for FAO:.....	4.1.....
4.1 Introduction: starting from pure Pt electrode.....	4.3.....
4.2 Pt@Au series.....	4.6.....
4.2.1 Validation and limitation of replacement technique.....	4.6.....
4.2.2 FAO tests.....	5.7.....
4.2.3 CO stripping tests.....	6.6.....
4.3 Au@Pt series.....	7.5.....
4.3.1 Limitations of replacement technique.....	7.6.....
4.3.2 Validation of direct electrodeposition method and s.....	7.9.....
4.4 Conclusions.....	8.4.....
Chapter 5 Decorated Pt based electrocatalysts for FAO: theoretical.....	8.6.....
5.1 Introduction.....	8.6.....
5.2 Pt@Au series.....	8.7.....
5.2.1 Slab models.....	8.7.....
5.2.2 Adsorption study.....	9.0.....
5.2.3 Reaction energies for the proposed reaction.....	10.6.....
5.2.4 Density of states study.....	10.9.....
5.3 Au@Pt series.....	11.8.....
5.4 Conclusions.....	12.7.....
Chapter 6 Conclusions and recommendations for future works.....	12.9.....
6.1 Conclusions.....	12.9.....
6.2 Limitations.....	13.0.....
6.3 Recommendations for future works.....	13.2.....
References.....	13.5.....

List of Figures

Figure 1. The schematic diagram of Pt@FeMoFCA. H.....	6
Figure 2. The reaction paths involved in the electrocatalytic oxidation of formic acid: (A) direct path (denoted as (A)), (B) indirect path through the formation of formate intermediate... (top) 1.1. [5.1]..	1.1
Figure 3. ORR Mechanism on Pt electrode. [7.1].....	1.5
Figure 4. Cyclic voltammetry curves of pure Pt electrode at scan rate of 10 mV/s in (a) 0.5 M H ₂ SO ₄ , 0 rpm; (b) 0.5 M HCOOH + 0.5 M H ₂ SO ₄ , 1000 rpm. 4.3.....	4.3
Figure 4. XRD patterns of Pt@FeMoFCA particles supported on carbon black V-72. 4.8.....	4.8
Figure 5. Cyclic voltammetry curves of Pt@FeMoFCA/C electrode in 0.5 M H ₂ SO ₄ at the sweep rate of 10 mV/s. Inset: a CV of 20 wt% Pt/C substrate in 0.5 M H ₂ SO ₄ electrolyte at the sweep rate of 100 mV/s. 4.9.....	4.9
Figure 6. (a) Current transient during the anode stripping process at sweep rate 400 mV/s. (b) The effect of sweep rate on the oxidation peak current under different deposition potentials. This is fixed at 180 s. The current at the end of the oxidation sweep process for the case of 0.10 V is shown as a horizontal line. (c) Oxidation charge of the Cu adlayer vs. deposition potentials.....	5.4
Figure 6. (a) CV curves for anode stripping process at different deposition potentials. (b) Oxidation charge of the Cu adlayer vs. deposition potential.....	5.6
Figure 7. CV curves of Pt@FeMoFCA/C with 34% surface coverage in 0.5 M HCOOH + 0.5 M H ₂ SO ₄ at sweep rate 100 mV/s, rotation speed 1000 rpm. The current density is normalized with the substrate electrode surface area.....	5.9
Figure 8. Voltammogram forward sweep of Pt@Au/C with different Pt coverage (20 and 40%) in 0.5 M HCOOH + 0.5 M H ₂ SO ₄ at sweep rate 100 mV/s, rotation speed 1000 rpm. The current density is normalized with the substrate surface area.....	6.2

surface area, respectively. In preparation of Pt@Au/C series in b	
0.5 M ₂ SO ₄	6.2.....
Figure 4.18 prolonged CV results of (a) 0.3 wt% Pt@Au/C in 0.5 M HCOOH +	
0.5 M ₂ SO ₄ , sweep rate 100 mV/s, rotation speed 1000 rpm.....	6.4.....
Figure 4.19 results of (a) 3% Pt@Au/C in 0.5 M HCOOH before and after	
prolonged CV test. Sweep rate 100 mV/s, rotation speed 1000 rpm.....	6.5.....
Figure 4.10 test of 3% Pt@Au/C in 0.5 M HCOOH with 5 M H	
the applied potential of 0.15 V, rotation speed 1000 rpm. The	
with the substrate electrode surface area, respectively....	6.6.....
Figure 4.11 enlarged CO stripping curves for the series of decorated	
50 wt% Pt/C in 0.5 M HCOOH sweep rate 20 mV/s. The current density is	
the substrate electrode surface area, respectively.....	6.9.....
Figure 4.12 schematic diagram on the morphologies of Pt@Au/C ele	
to the surface coverage of Pt on Au substrate (a) ideal mono	
coverage; (c) maximum coverage with 100% Pt on Au surface	
100%.....	7.4.....
Figure 4.13 amperogram of the commercial 50 wt% Pt/C electroc	
electrolyte (solid line), 0.5 M HCOOH (dash) and 0.5 M H	
Cu UPD redox replacement @ 0.10 V. Sweep rate 100 mV/s....	7.7.....
Figure 4.14 amperogram of the commercial 50 wt% Pt/C Au@Pt/C	
electrocatalyst - Au@Pt/C redox replacement @ 0.10 V. Electrolyte 0	
0.5 M ₂ SO ₄ , sweep rate 100 mV/s, rotation speed 1000 rpm. The	
normalized with the electrode surface area, respectively....	7.8.....
Figure 4.15 amperogram - prephase 27% Pt surface coverage of Au	
(A _u = 73%) and commercial Pt/C in 0.5 M HCOOH + 0.5 M H	
rotation speed 1000 rpm. The current density is normalized	
surface area, respectively.....	8.0.....
Figure 4.16 amperogram forward prepared Au@Pt/C with different	
coverages and the commercial Pt/C in 0.5 M HCOOH + 0.5 M H	

rotation speed 1000 rpm. The density is normalized with the substrate surface area, respectively. In preparation of Pt@Au/C the blank 0.5M H ₂ SO ₄	8.1.....
Figure 4.17 Cyclic voltammogram forward separated the Pt@Au (4%) (and Au@Pt/C (27%)) in 0.5M HCOOH, sweep rate 100 mV/s, rotation 1000 rpm. The current density is normalized with the three substrates, respectively.....	8.3.....
Figure 4.18 The reaction paths involved in F.A.O.....	8.6.....
Figure 5.1 2D layer (3x3) supercell 0.11 ML Pt@Au slab model.....	10.0.....
Figure 5.2 Types of Au atoms on the top layer of 0.11 ML Pt@Au surface.....	10.8.....
Figure 5.3 Side view of the most stable adsorption configurations of formate on Pt@Au and 0.11 ML Pt@Au (100) surfaces. Yellow sphere red O and white H. For clarity, only top layer metal atoms were shown.....	10.9.....
Figure 5.4 Tested structures for formate (HCOO ⁻) adsorption.....	11.0.....
Figure 5.5 Tested structures for formic acid (HCOOH) adsorption.....	11.3.....
Figure 5.6 Types of 0.50 ML Pt@Au surface.....	11.7.....
Figure 5.7 Side view of the most stable adsorption configurations of formate on Au@Pt and 0.88 ML Au@Pt (100) surfaces. For clarity, only top layer metal atoms were shown here.....	12.6.....

List Tables

Table 4.1	Normalized FAO peak current of Pt atoms under different	6.1
Table 4.2	stripping peak current potential.....	6.8
Table 6.1	Calculated BEs (eV) for the most stable complexes of ad hollow sites of Pt@Au (100) surfaces. For the adsorbates w COO, HCOO and HCOO, the adsorption site was referred to the central atom (u which is mainly interacting with the metal slab.....	9.1
Table 6.2	Calculated ΔG for the steps in the proposed FAO reaction netwo Pt@Au (100) slab surfaces.....	10.6
Table 6.3	Calculated bond center for the slab surface atoms of the sla of Pt adlayers on the Au (100) surfaces.....	11.2
Table 6.4	Calculated bond centers and CO binding energies for the se Pt@Au (100) surfaces with different Pt surface coverages	11.4
Table 6.5	Calculated ΔG for the steps in the proposed FAO reaction ne on Au@Pt (100) surfaces.....	12.3
Table 6.6	Calculated BEs (eV) for the most stable complexes of ad hollow sites of Au@Pt (100) surfaces. From the calculated adsorption site COO, HCOO and HCOO, the adsorption site was referred to the (underlined) which was mainly interacting with the metal slab.....	12.4
Table 6.7	Calculated bond centers and CO binding energies for the se (100) surfaces with different Au surface coverage and The dat center of the particles; the same meaning of the subscripts, e.g. were the same as discussed in Pt@Au series.....	12.5

Abstracts

Combined experimental and theoretical DFT studies

Pt@Au and Au@Pt electrocatalysts for formic acid oxidation

YU Yaolun

Nanyang Technological University

2011

Our aim of this thesis is to make more profound understanding of the amazing reactivity of Pt and Au decorated particles (Pt@Au and Au@Pt) in the formic acid oxidation reaction. Pt@Au with much lower Pt usage about 10% can achieve higher catalytic activity than Pt/C (50%) through the combination of experimental and theoretical density functional calculations (DFT).

First, the decorated Pt@Au electrocatalyst was synthesized by a new potential deposition (UPD) Pt redox replacement method instead of the conventional chemical reduction method. By studying the parameters and carefully calculating the oxidized UPD charge of the anode stripping method, we confirmed the successful synthesis of the decorated Pt@Au electrocatalyst.

Compared with the chemical method of electrodeposition, the UPD redox replacement technique has its unique advantages. The decorated Pt@Au alloyed with much more Pt can be prepared throughout the process. Pt surface coverage of Pt@Au

electrocatalysts reach extremely low turnover frequencies (TOFs) could be used as a model for more fundamental experiments and theoretical calculations.

Carbon monoxide poisoning has been considered as a major obstacle between experimental and theoretical calculations of the electrode surface adsorption properties.

On the other hand, a series of decorated Au@Pt nanoparticles were prepared through the direct electrodeposition method as a parallel approach with more detailed information.

Binding energies (E_b) of different intermediates on the series of decorated Pt@Au and Au@Pt surfaces were calculated using thermodynamic reaction energy pathways proposed for the FAO reaction network, as well as the coordination of metal surface atoms by using the Vienna-Abinitio Simulation Package (VASP) software under DFT basis.

By comparing the results both from experiments and theoretical calculations, the electrocatalytic activity of the decorated Pt@Au nanoparticles is discussed together with the effect of CO adsorption on the electrocatalytic activity. The experimental differences from the previous results should be well explained. The result shows that the ensemble effect, while the electronic effect has a minor effect on FAO. When considering the surface composition, the Pt atoms which also contained FAO on the surface, whether the Pt surface atom is isolated or surrounded by Pt atoms to form an ensemble is the key parameter. This phenomenon may also be the origin of the dramatic increase in the activity of the decorated Pt@Au nanoparticles towards FAO.

Chapter 1 Introduction and scope of this thesis

1.1 Introduction

Energy crisis is becoming more and more serious due to the emerging shortage of natural fossil resources compared with the demand for the sustainability and improvability of our human society.

The study on formic acid oxidation (FAO) has become a new research field since formic acid is a potential fuel cell alternative energy source. Although formic acid is one of the simplest molecules, the literatures have shown that FAO is actually very complicated.

In 2008, Noel Kristian from our research group found that conventional Pt catalysts introducing only a small amount of Au nanoparticle substrates, the FAO catalytic performance increased on the decorated Pt@Au nanocatalysts synthesized by the reduction method. He tried to prove that the reason for this increase was mainly caused from the ensemble effect on the decorated Pt@Au electrocatalyst, the likely species for formic acid dehydration pathway in FAO was proposed. This brilliant direct experiment evidence convinced researchers that they had a better understanding of the very nature of the catalyst. Although the common concept on fuel cell electrocatalysis at that time was: better active sites or more condensed active sites of the catalyst surface. Some papers have

been focused on synthesis of FAO electrocatalysts with core-shell structure by various metal couples and different

1. Scope of this thesis

Although Kristian Espinoza did work on electrocatalysis for the results were still not accurate enough to synthesize decorated Pt@Au electrocatalysts, and the proposed FAO was somewhat unclear due to the limitations of his experiments.

This research work here is focused on understanding the origin of increased reactivity of the decorated Pt@Au electrocatalysts toward experimental and computational approaches together.

The main work of this thesis is summarized as follows:

- 1) Validation of Cu UPD technique and synthesis of C
- 2) Synthesis and characterization of decorated Pt@Au electrocatalysts and CO stripping experiments
- 3) Synthesis and characterization of decorated Au@Pt via direct electrodeposition for FAO reaction
- 4) Theoretical calculations for decorated Pt@Au surface
- 5) Theoretical calculations for decorated Au@Pt surface

Since the entire work has been interconnected, experimental results and DFT calculations with DFT calculations and with DFT

calculative division of the results of this thesis into two parts: experimental and DFT calculations.

Following the description, Chapter 2 provides a review of literature introducing proton exchange membrane fuel cells (PEMFC) starting from the point of view of related chemical reactions and the state of the technology. Later are the introductions on UPD technique and the basic knowledge of DFT theory.

Chapter 3 presents the characterization experiments, as well as the methods used in DFT calculation.

Chapter 4 discusses a Pt-based electrocatalysis for FAO from the experiment point of view, while Chapter 5 is a discussion from the theoretical point of view.

Finally, Chapter 6 summarizes the conclusions, discusses the limitations of this research work and provides recommendations for the future work.

Chapter 2 Literature review

2.1 Basis of Proton exchange membrane fuel cells (PEMFC)

Fuel cells (FCs) are a type of galvanic cells which can directly convert the chemical energy of the reactant source fuel into electrical energy without the direct combustion of fuel and oxidant to produce thermal energy.

FCs generate electricity by allowing a chemical reaction between fuel and oxidant, triggered in the presence of an electrolyte. The reaction products flow out of it, while the electrolyte can operate continuously as long as the reactants are continuously supplied. In contrast with the conventional batteries which are chemically closed systems, FCs are thermodynamically open systems. In a thermodynamically open system, a reactant or a product must be replenished.

FCs have attracted much attention in the past few decades due to their many advantages; such as they are friendlier to the environment, have higher theoretical power densities compared to the conventional combustion engines and conventional electric cells [20, 21].

There are many possible combinations of fuels and oxidants. A typical hydrogen fuel cell uses hydrogen as its fuel and oxygen as its oxidant. Other fuels include hydrocarbons and alcohols, and other oxidants include chlorine and chlorine dioxide [22].

Proton exchange membrane fuel cells, also known as polymer electrolyte fuel cells (PEMFCs), are a type of FCs that use a proton-conducting polymer membrane as the electrolyte.

membrane fuel cells (PEMFC), showing a type of fuel cell that is well as for stationary and portable fuel cell applications.

Among the various only highlighted in FC family, molten carbonate fuel cells (MCFCs) and Solid Oxide Fuel Cells (SOFCs) are the most attractive candidate and are about to be commercialized for portable applications due to their distinguishing features and advantages, including lower temperature/pressure operation and the use of a solid electrolyte membrane [26, 25]. First, PEMFCs do not use hazardous materials towards the environment. Alkaline fuel cell (AFC) and phosphoric acid fuel cell (PAFC); instead, PEMFCs use a polymer electrolyte membrane (PEM), normally Nafion®, as the electrolyte which is friendlier to the environment. On the other hand, in engineering aspect, the use of solid electrolyte in PEMFCs system is much easier for miniaturization. The operating temperature of PEMFC is the lowest in FC family. As a result, PEMFCs are the safest to handle for individuals.

The anode reactions in PEMFCs are either hydrogen direct oxidation (H_2) or some other isomeric organic compounds, such as CO , $HCOOH$, $HCOONa$, CH_3OH , C_2H_5OH etc. The cathode reaction is oxygen reduction (O_2), in most cases, air from the atmosphere.

The heart of a PEMFC is the electrolyte membrane (MEA), which is normally composed of a PEM sandwiched between the anode and cathode catalyst layers, while each of the catalyst layers is

layer respectively. The anode and cathode catalyst layers are separated by a proton exchange membrane (PEM). The PEM is used to conduct protons generated at the anode and to prevent electrons from passing through it. The PEM also serves as an insulator between the anode and cathode.

Figure 2.1 The schematic diagram of a PEMFC

Take a typical PEMFC as the example, while its schematic principle drawing is shown in Figure 2.1. Hydrogen is delivered to the anode layer of the MEA and is catalytically oxidized to protons, represented by the oxidation reaction equation:

(*SHE: Standard Hydrogen Electrode, $E = 0.000 \text{ V}$)

The newly formed protons pass through the PEM to the cathode layer, while the electrons pass through the external load circuit to the cathode.

of MEA, creating the current output at the same time. M₂ is delivered to the cathode catalyst layer permeator through PEMs well as electrons through the external circuit to form water (H₂O). The cathodic reduction reaction is represented by the equation:

The overall reaction is represented by:

2. Electrochemical reactions and catalysts

The catalyst layers, which are mainly composed by electrode where electrochemical reactions take place. An electrode participates in electrochemical reactions. Different from normal catalyst materials, electrocatalysts are a specific form of catalysts that function may be the electrode surface. In PEMFC, researchers have developed heterogeneous electrocatalysts based on nanoparticles supported on carbon [28]. The electrocatalyst layer assists in the transfer of electrons between the electrode and reactants, and/or the chemical transformation described by the overall half

For the design and development of catalysts types for PEMFCs, a profound understanding of the catalysts is required to improve the performance of PEMFCs, a profound understanding

electrochemical reactions as well as heterogeneous chemical reactions are mainly concerned in our group at NTU. They are: In the following paragraphs will focus on their reaction mechanism and the current progress about which are used to catalyze these reactions.

2.2. Methanol oxidation reaction (MOR)

When methanol is pumped into the anode of a direct methanol fuel cell (DMFC), the complete anodic half-cell reaction in acidic media is represented by the following equation:

The overall cell reaction is represented by:

Although the final product of MOR is carbon dioxide, the oxidation process of methanol is a very complex process. It has been proven to be a very complex process with numerous intermediates, for example, the reaction of methanol on a platinum (Pt) catalyst. The reaction of methanol on a Pt catalyst has been proven to be a very complex process with numerous intermediates, for example, the reaction of methanol on a Pt catalyst.

The strongly adsorbed carbon species will (finally) react with adsorbed hydroxyl species to form CO_2 through a Langmuir-Hinshelwood mechanism under high potential. The reaction is represented by the equation below:

The main intermediate species would be $\text{Pt}-\text{C}$ as surface carbon poison the catalyst, and would finally lead to a permanent catalyst deactivation. To alleviate this problem, if $\text{Pt}-\text{C}$ species, it is vital to increase the concentration of OH species on the catalyst surface [32, 34].

However, it is difficult to increase the concentration of OH species on a Pt electrode with a small overpotential. To solve this problem, a strategy is to introduce another element which can adsorb OH species more easily on the new metal surface or tune the electronic structure of Pt to facilitate OH adsorption [33].

The bimetallic alloy catalyst PtRu was synthesized and a much increased MOR performance was observed. OH species can be formed more easily on Ru under a relatively low overpotential. The bifunctional mechanism proposed by Watanabe et al. and briefly shown [35, 36] was

As illustrated by this mechanism, Pt and Ru , respectively, would form separate active sites and continue to react to complete the reaction.

However, the difficulty to synthesize a bimetallic catalyst by a wet chemistry approach is obvious that the two elements

reduction potentials and different electrode materials. As a result, it is very difficult to control the surface atomic structure, therefore, activity performance varies from batch to batch.

2.2.2. Formic acid oxidation (FAO)

Formic acid is considered to be a potential candidate organic molecule which is in liquid phase at room temperature. Direct formic acid fuel cell (DFAFC) is formed when formic acid is used as a fuel. The advantages that formic acid possesses over methanol are: formic acid exhibits lower fuel crossover than methanol, efficiency of DFAFC is higher than that of DMFC. Second, methanol poisoning does not occur if it is ingested in case of leakage. The overall reaction is represented by the equation:

The overall reaction is represented by:

The electrocatalytic oxidation of formic acid has been the past decade result of its importance in the development of FAFCs [37]. There are a number of elegant studies for FAO on Pt

alloy surfaces that have been established the overall pathway provide insights in the mechanism [40, 43-50].

Three different paths for CO oxidation have been suggested in the literature [40, 43-50]. These three paths are illustrated

Figure 2. The reaction paths involved in the CO oxidation: (A) direct path ($\text{CO} + \text{O} \rightarrow \text{CO}_2$) (B) indirect path through C formate path through the formation of formate intermediate

The first path, which is known as the direct path, involves the adsorption of formic acid onto the metal followed by direct removal of protons to form CO. The direct path was clearly identified by studies in ^{13}C formic acid adsorbed onto Pt before ^{12}C formic acid. The resulting product was found to be unlabeled, indicating that CO was formed via a direct path from formic acid rather than via a formate intermediate [45]. The second path, which is known as the indirect path, involves the dehydration of formic acid to CO and the subsequent oxidation of CO to CO_2 .

formate pathH, the bond of formic acid is cleaved to form a (HCOO) intermediate which is then oxidized to CO₂ [38, 49]

During the process, several intermediates should be made are CO, COOH and COO.

The electrochemical oxidation of CO is mainly of interest and it is believed to be the main intermediate for the reaction. CO strongly adsorbs on the surface of electrocatalysts, such as Pt, and this is a major problem in contemporary fuel cell electrocatalysis. One of the main goals of contemporary fuel cell electrocatalysis is to develop new catalysts that are active at low overpotentials. The main problem is that only a small amount of CO is still capable of oxidizing the reaction. The current state of the art consists of Pt modified by second transition metals, such as Ru, for CO electrocatalysis. The electrochemical oxidation of CO on Pt (and other metals) has been studied over the past decades. The generally accepted mechanism proposed by [51] for CO electrooxidation on transition metal surfaces such as Pt, Rh, and Pd, assumes a Langmuir-Hinshelwood type reaction between CO and an oxygen-containing surface species. Despite the fact that the oxygen-containing species is not well defined, the authors write that the reaction is as follows:

The adsorbed CO acts as a poison on the pathway of FAO, as it blocks the active surface sites and is only removed at high overpotentials. The proposed direct

path plays an important role in the transition mechanism on Pt surfaces, gradually blocks surface sites for CO adsorption, while on Au, it even completely dominates the oxidation mechanism by suppressing the direct oxidation of CO.

Au is also known to be an excellent catalyst for electrochemical reactions, both in acidic and alkaline media. In the case of electrochemical CO oxidation, many studies have shown that Au is a very effective catalyst, and the need for a large overpotential is significantly reduced. The first systematic study of the electrochemical CO oxidation on Au was published by Weaver and Weaver in 1981. They suggested the following mechanism:

In contrast to CO oxidation on Pt, there is no competition between CO and H₂O for adsorption sites on Au, which is related to the low adsorption energy of CO on Au. The main difference between CO oxidation on Au and Pt, as far as the observation is concerned, is that CO oxidation on Au is catalyzed at potentials more negative than those corresponding to the initial formation of adsorbed CO. This observation suggests a stabilization of the surface adsorbed CO, or the direct oxidation of COOH species without the need for a large overpotential. Weaver and Weaver demonstrated a lack of CO poisoning during the electrochemical oxidation of CO on Au, which suggested an insignificant role for the adsorbed CO in the catalytic process.

In the oxidation process of formic acid, although the mechanism is well established, there is still some consensus in the literature concerning the adsorbed intermediate involved in the direct pathway. Most electrochemical papers consider adsorbed COOH as the intermediate according to the following equation:

However, the existence of this intermediate is still under debate. Recently, (UHV) experiments have shown that the main adsorbate resulting from the dehydrogenation of formic acid on many metals is H₂O. Also, recent surface-enhanced infrared spectroscopy experiments by Osawa et al. [53] have reported a band at 1715 cm⁻¹ during FAO at Pt, which should be ascribed to formate and suggests the reaction given by the following equation:

Although formic acid has been considered as an attractive fuel for small portable PEMFC applications, in contrast to the vast amount of scientific and engineering studies on FAO mainly focused from a fundamental perspective. As introduced in the early literature, the electrode is not a perfect catalyst for FAO due to the formation of surface adsorbed species described by the dehydration pathway. Just like other fuel cells, surface modifiers have been introduced to enhance the activity of the electrode. Elements such as Pt [54], Au [55], Ag [56], G [57], Sn [58], Ni [59], Pb [60], Bi [61], Cu [62], Zn [63], and Fe [64] have been studied.

Among the varieties of Pt/Pd alloys reported [67], an increase in Pt content resulted in a third boost in activity developed to explain the enhancement. Interestingly, base-free Pt catalysts give superior performances in DMFCs [68]. The power density under identical conditions, also reported to be almost 2 more active than Pt-based alloys catalysts. It is believed that for Pt-based catalysts, the direct pathway to yield CO than via the CO-poisoned with catalysts.

2.2.3 Oxygen reduction reaction (ORR)

For all types of PEMFCs, oxygen is the main oxidant takes place at cathode. Figure 2.3 shows the accepted ORR mechanism on surface of Pt [69].

Figure 2.3 ORR Mechanism on surface of Pt [69]

ORR can proceed through either a 4e⁻ or indirect 2e⁻ pathway after electron transfer followed by the O-O bond cleavage to form hydrogen peroxide (H₂O₂). In this 2e⁻ pathway, the reaction is terminated when H₂O₂ desorbs to the solution phase. Further transfer of two protons to H₂O₂ completes reduction to form the final product, water, however, these steps must involve the breaking of O-O bond and the formation of O-H bonds. The intermediate species are undesired since the strong O-H bond would slow down the whole ORR system in both scientific and engineering aspects. The ORR is generally believed to be the first step of adsorption with simultaneous charge and proton transfer to form Pt

By using a PdOx replacement technique, we have prepared Pt monolayer on Pd(111) surface (Pt@Pd(111)) and Pt nanoparticles (Pt@Pd/C) electrocatalysts. The kinetics of ORR studied in acidic electrolyte using a rotating disk electrode (RDE) setup. Pt@Pd(111) and Pt@Pd/C surfaces with Pt monolayer showed a significant activity enhancement compared to Pt catalyst even though these two novel catalysts contain very small Pt effects in the Pt monolayer and nanoparticles. Electrochemical characterization (XRD), adsorption-desorption fine structure spectroscopy data (EXAFS), appear to be the source of the

Later, the same group tried to synthesize Pt on a carbon support. The Pt@C catalyst showed better performance towards ORR in a cathode electrode.

2.2. Advantages in the preparation of electrocatalysts

In the catalyst, the precious metal Pt is the active site. Before PEMFCs get widely commercialized, the preliminary research goal is to decrease the usage of Pt while maintaining its catalytic activity towards the electrochemical reaction.

Since the electrochemical reactions take place only on the surface, in other words, only the surface catalyst atoms are potential active sites. In order to increase the ratio of the surface active atoms, the catalysts are synthesized with a small particle size. [7, 8] Another approach is to synthesize a core-shell structure [9, 10], where the active precious metal atoms stand on the outer surface of the catalyst and a cheap material is used as the core to support the catalyst.

The conventional method to synthesize catalysts is called the sol-gel reduction method, which was first introduced by Boudry in 1970 [11]. It was further developed by Schmidt [12] in 1990. It is a wet chemical method which fits for mass production. However, it is difficult to

shell precisely by varying the input ratio by electrodeposition et al.
 experiment conditions such as temperature, react time
 protecting agent et al.

2.3 Under potential deposition (UPD) technique

Electrodeposition has several tremendous advantages
 adlayer over the original metal substrate such as simpli
 low cost [84, 85] However, atomic level studies of the ep
 successive atomic layers of noble metals, e.g. Au and Pt
 electrodeposition kinetics and mechanism are still in progress
 atomic Au and Pt adlayers tend to result the formation of
 deposit [87] When direct electrodeposition method is appl
 precious metals, phosphate buffer is not used; but the current
 for the deposition is usually less than 100% utilization. As a
 result, the film thickness cannot be perfectly controlled

The UPD phenomenon has been discovered and studied
 foreign metal would under potentially deposit at a poten
 deposition potential, forming one monolayer or several
 substrate [90-93] The origin of UPD mainly comes from the
 between the foreign metal adatoms with the metal substr
 type surface [94-98] Such phenomenon allows the researchers to

of the foreign metal adatoms on the substrate precisely and the dependence between the catalytic activities and the surface composition. As a result, the UPD phenomenon is very important in the research field of surface chemistry and would make the current understandings on the initial electrodeposition process

In recent years, Byrnkovic [404] demonstrated a simple and reliable redox replacement process. After UPD, the authors used metal cations, Fe^{4+} , Fe^{2+} and Pt^{4+} to oxidize the UPD Cu adlayer; with noble metal cations, Au^{3+} , Ag^{+} and Pd^{2+} were reduced and deposited on the surface. By this redox replacement technique, they could control a series of morphology-controlled catalysts with ultrathin shell layers for various reactions [73, 75, 105, 109]. Since then, lots of researchers have used the UPD redox replacement technique and various catalysts have been characterized by different reactions [88, 110, 112].

Among the various electrocatalysts-redox replacement technique, the ultrathin shells catalysts are of particular interest as electrocatalysts for PEMFCs applications with the main advantage of low precious metal. On the other hand, the catalytic activities of the core-shell electrocatalysts towards different electrochemical reactions are determined by the core metal and the shell metal or electrocatalyst [74, 75, 113, 115].

Zhang et al.^[74] synthesized a catalyst with Pt deposited on the carbon-supported Pd nanoparticles for ORR. The results showed a significant activity enhancement for Pt@Pd/C catalyst in comparison with conventional Pt nanoparticles. Gao et al.^[75] synthesized a Pt overlayer/Au/graphite catalyst which showed high activity and stability for methanol oxidation. Li et al.^[76] synthesized Ru and Sn submonolayers decorated on Pt by UPD. Ru and Sn atoms were deposited, respectively. It showed that the submonolayered Sn/Pt electrode increased the ORR rate more several times as large as that on a pure Pt electrode. Li et al.^[77] prepared multiple Pt adlayers on Au substrate by a controlled replacement duty cycle. The electrocatalytic activity of the prepared Pt@Au electrocatalyst increased with ORR. Increasing the thickness of the shell.

2.4 Density functional theory (DFT)

Density functional theory (DFT) is a computational chemistry theory used by scientists to investigate electronic structure of many systems, e.g., atoms, molecules, and solids. In DFT, the properties of a many-electron system are determined by the electron density function, where the rate of change of the electron density is

Nowadays, with the greatly refined approximations used for exchange-correlation (XC) interactions, the results of DFT calculations for many systems could agree satisfactorily with experimental data. Due to the fast improvement of modern computer technology and the high performance of computers, the quantum computational cost is relatively low compared to the traditional methods based on the Hartree-Fock (HF) method. Some of the advantages of DFT computational experiments are listed in Table 1.1.

2.4. Basic theories of DFT

Schrödinger equation (SE) and wavefunction

DFT method has become the standard for physics calculations since the 1970s and for quantum chemistry calculations since the 1990s. The leading method for electronic structure calculations in both fields. The history of DFT development is actually a very long path. In the year 1926, the Austrian physicist Erwin Schrödinger published his famous Schrödinger equation, which is the center of quantum mechanics.

For a general quantum system, SE can be written as follows:

$$E\psi = H\psi \quad \text{or} \quad (2.1)$$

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V(\mathbf{r})\psi = E\psi$$

where E is the total energy, ψ is the wavefunction which is the amplitude for each specific systematic configuration and ∇^2 is the Laplacian operator, $\hbar$ is the reduced Planck constant and H is the Hamiltonian operator.

The wavefunction is called the quantum state or state vector, which provides a complete and profound description about a physical system from a quantum mechanical point of view. A wavefunction is a function (either of position or momentum, or possibly of both) that represents the probability amplitude of a particle. Mathematically speaking, the wavefunction considers the possible states of the system from a space of configurations. [123] The importance of the SE is that it describes how the quantum state of a system changes by time, or in other words, SE describes the evolution of a system over time. Therefore, the solutions of SE could be used to study the properties of a system, which is not only for atomic and subatomic systems but also for macroscopic systems as well.

However, the exact solution of SE as well as its consideration is impossible to be solved mathematically for most of the systems. Therefore, approximations have to be made and only numerical solutions are possible. The Hartree-Fock (HF) method is one of the most common numerical methods.

Shortly after the introduction of SE, the HF method was developed in order to determine the wavefunction of a system as a particular system. The HF method assumes that, depending on the system, the wavefunction can be approximated by a single Slater determinant.

systems, the exact system can be approximated by a single determinant using a single permanent orbital. By applying the variational principle, a set of equations about the coefficients of the spin orbitals can be solved, which would yield HF wave functions, which are approximations of the exact ones.

Actually, for molecules, HF method is the central starting point of quantum chemistry methods. However, the HF computation is based on the use of traditional wave functions directly from SE, which means that the electron behavior is described by wavefunctions. In other words, each electron is assumed to behave independently and is described by a particular orbital, and the total wavefunction is a product of all these orbitals. In the past, derivatives with more sophisticated HF methods have been developed and are categorized into two groups: post-HF methods, which more accurately describe the electron correlation, and density functional theory (DFT), which could be seen as a compromise between those so many methods. The expansion of the wavefunction to solve SE, the original HF method, is still the basis. However, the problem with HF methods is always the huge computational efforts, which make them impossible to be applied efficiently to complex systems.

Therefore, better approximations have to be made to improve the efficiency.

Thomas-Fermi (TF) model and Hohenberg-Kohn theorems

Another important contribution to the TF model, which was semiclassically developed to approximate the distribution of electrons in atoms [125]. Standing separately from the wavefunction theory, it was formulated in terms of the electron density $n(\mathbf{r})$ only. In this approximation, electrons are distributed uniformly in phase space. As a result, the TF model is the precursor of modern density functional theory.

However, using the approximation stated above for the electron density, the TF model gives very poor quantitative predictions. TF model even fails to capture the qualitative features of the density such as the atom shell structures. The TF model of an infinite charged system remains rather inaccurate for most applications due to the complete neglect of electron correlation.

Although TF model has established the fundamental concepts of density functional theory, the modern DFT was developed with the foundation of the Hohenberg-Kohn (HK) theorems [126].

The first HK theorem states that the ground state properties of a many-electron system are uniquely determined by the electron density $n(\mathbf{r})$ only on 3 spatial coordinates. Through the second HK theorem, the many-body problem of electrons with 3 spatial coordinates based on HF method to only 3 spatial coordinates. The second HK theorem greatly reduced the computational cost of DFT as compared to HF method.

The second HK theorem defines the energy functional $E[\rho]$ such that the energy functional would necessarily be the minimal energy for a given electron density ρ if the electron density is correct.

Kohn-Sham (KS) theorem and exchange-correlation (XC) approximation

To solve SE, in 1965, Walter Kohn and Lu Jeu Sham proposed a non-interacting particles system, called KS system, which could generate the same density as the interacting particle systems. In this system, fictitious local effective external potential v_{eff} is introduced to replace the moving properties of the original SE. Hence, the original SE could be simply transformed into a KS system [27]. According to HF theory for non-interacting fermions KS system, the KS wave function is a single Slater determinant and the lowest energy of the system can be calculated.

Within the context of the many-body system, the energy of the interacting electrons in a static external potential is related to the energy of non-interacting electrons defined by an effective potential v_{eff} . The KS include the external potential and a local effective interaction v_{xc} between the electrons, that is, the exchange-correlation (XC) interactions.

However, for KS, the XC potential and its corresponding energy expression are not known and have to be approximated. The treatment of XC interactions becomes the major problem

In physics, the most widely used approximation on local density approximation (LDA). According to LDA, the depends only on the value of the electronic density at the functional is evaluated. However, since LDA approximation density by the of a local constant electron density, it fails e.g. molecules where the electron density experiences rapid change.

Improvements on LDA have been made by considering electron density; and a generalized gradient approximation (GGA) method is constructed on the basis of LDA. GGA can results by approaching the correlated wavefunction with LDA.

There are several kinds of GGA based on different derivations. Some of them are based on experimental data while some are entirely the first principles conceptual. and most recent GGA methods are: PW functional (PW86 Perdew and [128], [129] PBE functional by Perdew, Burk and Ernzerhof [130]

2.4.2 Literature review

The efforts to understand catalytic and electrocatalytic computational approaches is not new. [131-133] and others.

pioneering empirical cluster calculations related to the fuel cell and Nørskov [134] have made an excellent review and analysis by using theoretical calculations and concepts.

Considering the main intermediate during FAO, through and work [135] found that the COOH has a significant binding (111) and Au (110), which suggests that it is stable on the other hand, CO is much more strongly adsorbed on Pt than on Au and OH on Pt (111) is associated with a barrier of about that COOH may be a key intermediate in CO oxidation formation mechanism on Pt.

On the other hand, the idea that CO oxidation and intermediate on Au (COOH) offer an attractive explanation activity of Au for CO oxidation.

Rodriguez and Gorte [136] have established a spectacular correlation spectroscopical data (surface electronic shifts) and energy of a series of metal surfaces. They found that the larger charge between different surface metals, the stronger cohesive energy.

Nørskov et al. [137] made an extensive ab initio DFT study of chemisorption energies and discussed the physics of CO on Pt (111), Ag (111), Pt (111), Pt (110), Pt (100), Au (111), Au (110), Au (100), Cu (111), Cu (110), Cu (100), and Cu (111) overlayer structures. They demonstrated that the trend is understood using a new method describing the CO spilling of

$2\text{\AA}^*$ states to the metal d valence states. The key surface strength of the bonding turns out to be the energy of the is called band center theory.

Since then, the linear relationship between Pt length and d center has been explored successfully for catalyst design.

Mavrikakis *et al.* [138] studied a metal [Ru(0001)] slab under or tensile stress and showed that both molecular CO adsorption energies as well as barriers for surface reactions (CO oxidation) on strained lattices. Their results showed that the surface lattice expansion, following a shift of the metal d states.

Xu *et al.* [139] studied the adsorption and dissociation of CO on the (111) facets of Co and FePt alloys and on monolayer Pt skins on these two alloys. They found that the reduced activity of Pt skins for oxygen can be rationalized as being due to increasingly away from the Fermi level that an alleviation by O and enhanced rates for reactions involving O may be. Pt skins are more active for ORR in PEMFC applications.

Stamenkovic and *et al.* [140] studied ORR by both experimental and theoretical approaches. They showed that Pt is more active for ORR than the corresponding Pt(111) surface and that the state of the Pt/C catalyst in PEMFCs. Pt(111) surface has an unique electronic structure (d-orbital position) and arrangement of surface

near surface region. As a result, the weak interaction between reactive oxygenated species and the number of active sites for

Shubina and Kostel^[140] studied the adsorption of CO and OH on Pt and PtSn alloys as well as the adsorption of CO on a Pt surface modified with a Pt overlayer.^[135] Furthermore, the authors studied the adsorption of CO, OH and COOH on Au (110) and Pt (111) surfaces using density functional theory, binding energy, and vibrational characteristics. The activation energy for COOH formation from CO and OH on both surfaces was computed and compared to resolve the seemingly disparate kinetics observed on these two surfaces.

Oana et al.^[142] recently used density functional theory to study the adsorption of CO on surface sites of Pt, PtBi and PtPb. They present a picture that CO is shifted in energy because of alloying. For p-metals and CO binds preferably on the bridge site between Pt atoms rather than on the Pt top site because of maximum orbital overlap. They found that the CO antibonding $2\sigma^*$ orbitals are almost filled and are easily broken.

Wang et al.^[143] used DFT calculations to study the electrocatalytic activity of intermetallic bimetallic PtPb and PtBi, a class of new anodes for PEMFCs, exhibiting an increased CO tolerance. They found that the CO tolerance of PtPb and PtBi compared to that of Pt is related to the adsorption of CO on (100) and (110) surfaces and the shift of

center to a lower energy as a result of an upward shift in the presence of sp electrons from Pb and Bi. In contrast, (100) is more strongly than Pt (111). The adsorption energy for H₂ dissociation on different materials and different surfaces all have their own characteristics, mainly because of relative electronegativity and the d-orbital filling.

Recently, Wieckowski et al. studied the reaction mechanism for FAO. They proposed that COOH intermediate (H-COO) would be formed during the reaction and calculated to be very stable, and thus acts as a poison. Their DFT calculations indicate that the direct path only requires a small surface area, whereas the indirect path requires a larger surface area. This suggests that alloys or decorated particles will not have a significant effect on FAO reaction.

Chapter 3 Experimental methods and calculation details

3.1 Materials and equipments

The used disposable chemicals are listed below:

Name	Formula	CAS	Grade	Producer
Tetrachloroauric(III)	HAuCl_4	27987-88-8	~50%	Aldrich
			Au basis	
Sodium borohydride	NaBH_4	16946-62-2	96%	Aldrich
Trisodium citrate (Na)	$\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$	61324-31-4	99%	Aldrich
Copper(II) sulfate pentahydrate	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	7758-98-9	99.995%	Aldrich
Potassium tetrachloroplatate	K_2PtCl_6	10029-97-7	99.99%	Aldrich
Sulfuric acid	H_2SO_4	7664-93-9	>98%	Merck
Hydrochloric acid	HCl	7647-10-0	36.5~38%	Merck
Formic acid	HCOOH	64186-01-5	>98%	Merck
Carbon black Vulcan C	C	133364-00-0	-----	GasHub
Ethanol	$\text{CH}_3\text{CH}_2\text{OH}$	64175-14-6	98%	Merck
Nafion® solution	-----	31172599-0	5wt% in isoprop	GasHub
Carbon supported Platinum nanoparticle	Pt/C	744064-00-0	50%	GasHub
			Pt basis	
Argon	Ar	744071-39-1	Ultrapur	SOXAL
Carbon monoxide	CO	63080-01-9	Ultrapur	SOXAL

The used main equipments are listed below:

Equipment	Abbrevia	CAS	Specific	Produce
		Number		Vendor
Glassy carbon rotating disk electrode	GCR DE	744040	5 mm dian	PINE, US
Silver/silver chloride reference electrode	Ag/AgCl	-----	-----	PINE, US
Pt foil electrode	Pt CE	744064	99.99%	PINE, US
Microsyringe	-----	-----	700 serie syringe	Hamilton USA
Ultra pure water	DDI ₂ ®	773285	~18.1 M	© Millipore

The used characterizing equipments are listed

Equipments	Abbrevia	Type	Locat	Producer
				Vendor
X-ray diffraction	XRD	D8	CBE	Bruker, USA
		ADVANCE		
Transmission electron microscopy	TEM	JEM 011	SPMS	JOEL, Japan
Galvanostat / Potentiostat	-----	Autolab	CBE	Eco Chemi
		PGSTAT		The Netherlands
Ring-disk electrode system		Model 6	CBE	Princeton,

3.2 Preparation of Au nanoparticle core

The method to prepare Au/C substrate is described briefly as follows. 1 mL of 1% aqueous HAuCl₄ solution was added to 10 mL DDW with vigorous stirring, followed by the addition of 1 mL 1% Na₂Citrate solution one minute later. After an additional one minute, 1 mL 1% Na₂Citrate solution was added. The solution was stirred for 5 minutes. The overall chemical reaction for the preparation of this Au hydrosol is

Na₂Citrate acts as a stabilizer where the acetate ions adsorb on the Au surface to prevent the continuous growth of Au. During the reaction, the solution changed quickly from bright yellow to dark brown. Na₂B₄H₈ solution, this indicates that Au³⁺ has been reduced by NaBH₄ at room temperature.

After Au hydrosol was prepared, 72 wt% aq. NaOH was added dropwise into the Au hydrosol flask without any surface modification. The Au nanoparticles were completed overnight with continuous stirring. Au/C nanoparticles were obtained after the filtration and further vacuum drying the filtration cake at 60°C overnight.

In this study, the metal loading of the Au/C substrate was 2.0 wt%.

3.3 Preparation of electrode for electrochemical tests

Glassy carbon (disc) electrode (GCE) (5 mm dia) on 1926 was used as the working electrode (WE); Ag/AgCl was used as the reference electrode (Rt) and Pt wire as the counter electrode (CE) respectively. All the electrochemical tests were conducted at 25 °C. Autolab PGSTAT30 Galvanostat/Potentiostat electrochemical software was used to conduct the experiment and for data collection. Potentials are reported against Ag/AgCl/Rt. This thesis

Porous film [145] was adopted to prepare the electrode. The film was prepared by supersonically dispersing 2.0 mg of catalyst into 0.5 mL of 0.05 M NaCl solution followed by the addition of 0.5 mL isopropanol with another 15 min supersonic irradiation. The homogenous suspension was then deposited onto the GC WE using a microsyringe. After drying in air, the electrode was immersed into the Ar deaerated electrolyte for electrochemical tests.

3.4 Preparation of Pt@Au electrocatalyst by PLRD method

UPD tests were conducted in 0.1 M HClO₄ electrolyte. A typical procedure of the anode stripping test was as follows: First, the electrode was held at 0.65 V for 20 seconds to ensure that there was no copper

potential was swept at 400mV/s to the desired UPD potential and then held for a certain holding time, the potential of the electrode was swept back to the initial potential at 400mV/s. There were various UPD potentials, deposition times and sweep rates to identify their effect on the results. The surface coverage of Cu adatoms was calculated based on the charges and discussed in detail in the next Chapter.

To finish the redox replacement reaction, after holding the potential in the UPD solution for 3 minutes, the electrode was quickly transferred to the UPD electrolyte under potential control (same as the UPD potential to avoid oxidation of the deposited Cu) and held for 10 to 15 minutes in the UPD solution for the replacement reaction. The redox replacement time was set for 10 minutes. The electrode was washed with ultrapure water for further tests after the redox replacement.

3.5 Preparation of Au@Pt electrocatalyst by direct electrodeposition method

UPD redox replacement technique is a facile and effective method to synthesize Au@Pt electrocatalysts. The synthesis of Au@Pt electrocatalysts by this method will be discussed in detail in the next Chapter.

The electrodeposition method is a facile and modified method to synthesize Au@Pt electrocatalysts. The electrodeposition of Pt/C was carried out in a 0.5M H₂SO₄ solution at a potential of 0.1V for 10 minutes.

electrode only. C WE was performed by several cycles the scan rate of 50 mV/s in a 0.15 M H_2SO_4 electrolyte to avoid hydrolysis. Au was dissolved in a small amount of H_2O_2 after that was transferred to the electrode [17].

The surface coverage of Au adatoms was controlled by and was calculated based on the rate of charging on 5 M H_2SO_4 electrolyte before and after deposition experiments.

3.6 FAO and CO stripping tests

FAO tests were conducted in Ar deaerated 0.5 M HCl electrolyte with 1000 rotation speed using Princeton RDE.

As for CO stripping experiments, pure CO was prepared by bubbling through 1 M HCl electrolyte for 20 minutes while the electrode potential at 0.2 V. After another 20 minutes to remove dissolved CO in the electrolyte, the adsorbed CO was oxidized at a scan rate of 20 mV/s, and the CO stripping curve was taken. Two scans were also recorded to verify the completeness of CO oxidation.

3. Experimental methodology

3.7. X-ray diffraction (XRD)

XRD is a technique used to characterize the crystallographic structure, phase, grain size (grain size), and preferred orientation of powdered samples. It is an electromagnetic radiation of wavelength comparable to the size of an atom. Powder diffraction is commonly used for identifying substances, by comparing diffraction data against a database maintained by the International Centre for Diffraction Data. It may also be used to identify heterogeneous mixtures to determine relative abundance of compounds. When it is coupled with lattice refinement techniques, it can provide structural information on unknown compounds. Powder diffraction is also a common method for determining grain sizes in crystalline materials. An effect of the finite crystallite sizes is seen as a broadening of the diffraction peaks, as is explained by the Scherrer equation (shown below). The equation can also be used to calculate the crystallite size.

$$L_{hkl} = K \lambda / \Delta 2\theta_{hkl} \cos \theta_{hkl} \quad (3.2)$$

where L_{hkl} is the crystallite length, λ is the wavelength of the incident X-ray, $\Delta 2\theta_{hkl}$ is the peak width at half maximum (FWHM) in radians, θ_{hkl} is the Bragg angle, and K is a shape factor that varies with the method of measurement (normally K is 0.89 to 1.49). In this study, the wavelength of incident X-ray is $1.5418 \text{ \AA}$, the angle of the

Cyclic voltammetry (CV)

CV is a type of potentiodynamic electrochemical measurement. In CV, the potential of the working electrode (WE) is ramped linearly versus time, and the resulting current is recorded. CV is similar to linear sweep voltammetry (LSV). CV takes the experimental parameters of LSV and adds a reverse scan. After the first scan, the potential of the WE is reversed and scanned back to the starting potential. This process is repeated multiple times during the experiment. The corresponding current of WE is plotted against the potential. The CV trace is a plot of current versus applied voltage to give the CV trace. CV is generally used to study the redox properties of an analyte in solution.

Chronoamperometry (CA)

CA is an electrochemical technique in which the potential of the WE is stepped to a constant value, and the resulting current from faradic processes occurring at the electrode surface is monitored as a function of time. Limiting current (the current that remains constant after the potential step) is monitored as a function of time. Limiting current is proportional to the concentration of the analyte. The ratio of the limiting current versus the peak reduction current. However, as CA generates high charging currents, the potential of the WE is stepped to a constant value, and the resulting current from faradic processes occurring at the electrode surface is monitored as a function of time. To measure the faradic current (the current that remains constant after the potential step), the current scan is integrated (when charging current has dissipated). The integrated current is proportional to the concentration of the analyte. CA gives a better signal in comparison to other amperometric techniques.

Steps & Sweep technique

As discussed above, like all the pulsed techniques, CA current, which would decay exponentially (shown below) is developed to describe the change in current with respect to electrode,

$$i = nFAc_0 D^{1/2} t^{-1/2} \quad (3.3)$$

where n is the number of electrons to reduce/oxidize, F is the Faraday constant, A is the area of the electrode, c_0 is the concentration of the redox species, D is the diffusion coefficient, while t is time.

In our UPD study, we cannot simply apply CA technique to measure the charge of the deposited Cu adlayer on Au surface by direct controlled potential because the charge of the UPD Cu adlayer is small, there is not enough time for the charging current to measure the faraday current precisely. As a result, the application of CA method fails to measure the charge of the deposited Cu adlayer on Au electrode surface.

Here, we adopted the Steps & Sweep technique to measure the charge of the deposited Cu adlayer on Au substrate. The Steps & Sweep technique makes an LSV between potential steps. Although the current is affected by the charging effect, by carefully selecting all the stripping process, e.g. potential, we can calculate the charge of the deposited Cu adlayer on Au electrode surface.

deposited Cu on a Au substrate. The detailed analysis will be presented in Chapter.

3. Calculation methods

All DFT calculations in this work were performed based with the VASP software [148], using the PBE functional with the GGA interaction between ions and electrons was described by the projector augmented wave (PAW) method [149]. The first Brillouin zone was sampled with the Monkhorst-Pack point method [150] for adsorption studies. The energy cutoff was used for DOS calculation throughout this study, of 400 eV. Coordinates of adsorbates and substrate atoms were relaxed until the force on each atom were less than 0.1 eV/nm.

The binding energy (BE) of an adsorbate to the metal surface is defined as follows:

$$BE = E_{\text{slab+ad}} - E_{\text{slab}} - E_{\text{ad}} \quad (3.4)$$

where $E_{\text{slab+ad}}$ is the total energy of the slab model covered with the adsorbate at the optimized geometry, E_{slab} and E_{ad} are the total energies of the adsorbate phase and of the clean substrate, respectively. From this equation, a positive BE implies favorable adsorption or release of energy, which is in line with the conventions adopted in thermodynamics.

The reaction energy of a step in the reaction path is following expression:

$$\Delta E_{\text{rxn}} = \Delta E_{\text{ads}} - \Delta E_{\text{gas}} \quad (3.5)$$

where ΔE_{ad} and ΔE_{ga} are the differences in total energies between adsorbate and reactants in the slab model and for the gas phase.

After the calculation of DOS, the density of states on the surface atoms level.

The slab model used in this work will be detailed in the related paragraphs.

Chapter 4 Decorated Pt based electrocatalysts for experimental studies

(Some parts of this chapter have been published in *Electrochimica Acta*, and the conclusion of the article is the same.)

4.1 Introduction starting from pure Pt electrode

This thesis is mainly focused on Pt based electrocatalysts (Pt and Au@Pt) for FAO applications. To understand the difference in results between the decorated Pt based catalysts, first a brief explanation on the results of pure Pt electrode is given.

Figure 4.1 shows the CV curves recorded in 0.5 M H_2SO_4 and in acidic formic acid electrolyte.

Figure 4.1 Cyclic voltammetry curves of pure Pt electrode in (a) 0.5 M H_2SO_4 , 0 rpm (b) 0.5 M HCOOH + 0.5 M H_2SO_4 , 100 rpm

As could be seen in Figure 4(a), the CV curve of Pt electrode in H_2SO_4 electrolyte could be divided into three parts (shown in the potential -0.05 to 0.16 V in the first region representing almost reversible behavior before the hydrogen evolution with the hydrogen adsorption process. This is a unique widely used to calculate the real active surface area for Pt in the second region where the corresponding currents are denoted as the double layer region, which is directly associated with the Pt electrode area. However, as shown in Figure 4(a), the double layer region in the positive sweep is relatively broad and in the reverse scan, it becomes difficult to determine the region overlapping with the hydrogen adsorption peak as well as the Pt oxidation peak. As the potential increases, the reversible region commences which is associated with the formation/reduction of Pt hydroxide (PtOH) at lower overpotential and Pt oxide (PtO) at higher overpotential.

Totally different CV results can be obtained in the H_2O electrolyte. As shown in Figure 4(b) in the positive scan, the oxidation commences at 1.1 V and reaches a plateau at 1.35 V. As the applied potential increases, the current ascends again at 1.5 V (peak I) and 1.7 V (peak II). During the reverse scan, the oxidation current ascends from 0.7 V and reaches 0.55 V which is much higher than the forward scan. After that, the peak III drops relatively

fast to the coverage of the surface. This process indicates the complex occurring on the Pt electrode surface.

At low overpotentials, HCOOH is able to be oxidized to CO₂ through the dehydrogenation pathway; however, this is not the only pathway. CO-like species form through an indirect dehydration pathway. The coverage of CO reduces the availability of Pt active surface for the oxidation pathway, and therefore, the corresponding oxidation current increase around 0.06 V. Subsequently, the oxidation current increase around 0.06 V is attributed to the oxidation of CO with the existence of the oxygen containing species on Pt. As more and more CO is formed, the HCOOH oxidation current increases again. When the Pt electrode is poisoned by CO, the FAO reaction is inhibited. During the reverse negative scan, the sharp reduction current coincides with the oxidation current. The reduction current is larger than that in the positive scan corresponds with the surface poisoning of Pt.

As discussed above, all the peaks during the FAO process on Pt electrode are influenced by the formation, oxidation or reduction of PtOH and PtO species within at least two consecutive cycles. The FAO mechanism shown in Figure 2.2, it is therefore very difficult to understand the FAO process by an electrochemical approach alone. More fundamental details are needed.

concept to get a full composition in a monolayer oxidation reaction.

4. Pt@Au serie

4.2. Validation and UPD replacement technique

The initial idea of adopting UPD replacement technique as an experimental procedure is to synthesize a catalyst with precise composition compared catalyst via electrochemical method.

Although ideally UPD can precisely control the amount of metal on the substrate, it is still something unclear about the form of the structure on crystalline nanoparticle substrate by UPD technique. First, it comes from the difficulty to control the UPD as well as the redox potential. Up to now, almost all the coupled researches with microscopy were on single monocrystalline surfaces [74, 93, 104, 106, 109] the potential and time which is selected to form a monolayer is arbitrary. Many researchers would select an empirical potential deposition commences and they claimed that they have a catalyst. Since UPD can occur in a wide potential range, it will have big effect on the resulting Cu adlayer coverage. To apply a potential in the region close to redox potential would grow

adlayer coverage, and no complete monolayer on nanoparticle before the overpotential deposition (OPD) occurs. Consequently, the structure and catalytic activity of the Pt adlayer result in the replacement. Therefore, the deposition potential and time are critical. However, to our knowledge, there are rarely published papers on the direct electrochemical method [160] and evidences

Here we focus on the behavior of Cu deposition on the polycrystalline Au/C substrate in sulfuric acid electrolyte. We study parameters affecting Cu UPD, including UPD potential, deposition time, and sweeping rate. We use anodic stripping voltammetry to study the oxidation associated with the UPD Cu. By comparing the UPD oxidation and reduction charge of the monolayer Au oxide of the Au/C substrate, we directly correlate the applied potential, Cu surface coverage, and the UPD charge with the ability to control the composition of the prepared Pt@Au/C electrocatalysts synthesized through the replacement experiments.

a

b

Figure 4.2 (a) TEM; (b) XRD configuration prepared with the nanoparticles supported on carbon black V-72 on XC

Figure 4.2(a) shows the TEM prepared Au nanoparticles supported on carbon black. After counting around 100 particles from the micrograph, the average diameter of these Au nanoparticles was calculated to be 4.0 ± 1.0 nm. The XRD pattern of Au/C nanoparticles is shown in Figure 4.2(b).

4.2(b). We used $\text{Au}(220)$ from 55° to 72° , to calculate the particle size by Scherrer equation. The calculated particle size was 3.7 ± 0.2 nm, which is in good agreement with the TEM result.

Figure 4.8 CV curve for UCD on Au/C substrate in 0.1 M H_2SO_4 electrolyte sweep rate of 10 mV/s. Inset: CV curve prepared on Au/C substrate in 0.5 M H_2SO_4 electrolyte sweep rate of 10 mV/s.

A typical CV curve for a pure Au could be clearly seen in Figure 4.8. When compared with the CV curve of the pure Pt in Figure 4.4(a), the biggest difference comes from the hydrogen adsorption butterfly region for the Au electrode. This is because of the adsorption of atomic hydrogen on Au electrode from the electrolyte environment. Another difference is that the Au electrode oxidizes at higher overpotentials (>1.1 V) compared with the Pt electrode. This is because the Au electrode has a higher overpotential for the oxidation of H_2O to O_2 compared with the Pt electrode.

elements is compared to Pt. Therefore, the corresponding double layer capacitance for the Au electrode is almost potential region (from 1.1 V). This uniformity is due to its inert nature of the noble Au element. As will be discussed, this causes the simplicity for the surface coverage calculation overlayer.

Burshtein method was adopted to calculate the surface area [162]. Normal potential range of 1.35 ~ 1.40 V was selected as a minimum potential for integrating the reduction of Au oxide (more exactly, from 1.5 V), the reduction charge of Au oxide monolayer was calculated. By using the capacitance of 400 $\mu\text{C}/\text{cm}^2$ from polycrystalline Au, the real electrode surface area can be calculated.

The cyclic voltammogram for Cu UPD (Figure 4.10) was similar to those in the literatures for Cu UPD on Au electrode [163]. The observed peak pairs A & B and C & D are the UPD and OPD main peak pair, respectively. The small peak pair probably due to the surface structure transferring process in sulfuric acid electrolyte [164].

Theoretically, Cu UPD process would not comply with Cu(0) surface with (1x1) structure on all the monocrystalline Au(hkl) surface [165]. Measuring the charge will give us a better understanding of the process. Most authors used potential step method to measure

transient of the electrode. The relative model to elucidate the current measured via chronoamperometry technique for two-dimensional instantaneous nucleation and growth model growth rate, which is accompanied by an adsorption (desorption) beginning potential step test; while the model for the three-dimensional nucleation process followed by growth with diffusion.

However, since Cu UPD is a surface reaction, no pure diffusion control current, Cottrell equation cannot be used to describe the transient current. Hwozke [164] added another term which explained by the adsorption of Cu adatom at defect sites, finally fitted the transient current very well. However, the model is complex with the nonlinear equations fitting of the experimental data simultaneously all the parameters.

Here, in this thesis, the Steps & Sweep technique and stripping method were used to study the Cu adlayer charge.

After the UPD process, anode stripping was realized by sweeping potential at constant rate to the terminal potential of 0.6 V. The result is shown in Figure 4.4(a). It can be seen that the transient current reaches a maximum at the very beginning of the oxidation process and then decreases to a plateau at the end of the sweeping process. At 0.65 V, the potential was high enough to ensure the electrode substrate was clean and free of Cu. It is reasonable to assume the pseudo double layer from

substrate the same throughout the sweeping process and the sweeping process would be the current from the pseudo only. The oxidation charge of Cu adlayer was then calculated after subtract the current from the double layer capacitance (Fig. 4(a)).

There is no doubt that the deposition potential and sweep rate are key factors for the UPD process, while the sweep rate would also affect the anode stripping charge. As shown in Fig. 4(b), the calculated oxidation charge from the deposition potential sweep rate at different deposition potentials in the potential region (e.g. 0.2 V) and the potential region (e.g. 0 V). It can be seen that the oxidation charge of Cu adlayer depends on the sweep rate. From the calculated charge was stable, while when the scan rate was too small, the calculated charge was smaller, especially when the scan rate was smaller than 100 mV/s. When the sweep rate was too slow, due to the proportion of oxidation charge could not be counted in with the current. On the contrary, if the sweep rate was too fast, the time for the transient current to decay to the real current from the layer capacitance might be too short. Both of the situations would affect the calculated charge.

In order to prove our assumption that the current at the potential region would be the current from the pseudo double layer capacitance,

current at the end of the potential sweeping process for also shown in Figure 4.4(b) as a dashed line. The sweep rate was a straight line with a linear regression coefficient of 0.99, indicating that the assumption was well applicable.

Figure 4.4(c) shows the effect of the deposition time on the oxidation peak potential. After about 60s when the UPD process was completed, there were no big differences in the oxidation charges and the deposition potential was within 0.05V region. However, the deposition time would affect the growth rate greatly in the OPD region because Cu OPD is a self-limiting process and allows multilayer growth. Both phenomena were in accordance with the literature that two-dimensional instantaneous nucleation and growth shows a linear growth rate, while one-dimensional nucleation process follows a square root growth rate, while three-dimensional nucleation process follows a cubic growth rate [63, 64].

Throughout this work, we took 400mV/s and 180s as sweep rate and deposition time.

Figure 4. (a) Current transient during the anode

potential 0.25 V, 4500 mV/s at (b). The effect of the scan rate on the charge of Cu adlayer under different deposition potentials is shown in Figure 4.5(b). The charge at the end of the oxidation scan at 0.10 V was also shown as the dashed line. (c) Oxidation time at different deposition potentials

The CV curves during the oxidation process are shown in Figure 4.5(a). Only one oxidation peak could be seen when the deposition potential was 0.25 V. There gradually formed a second shoulder peak when the deposition potential increased. At this potential, OPD could not occur yet; then the shoulder peak appeared. The structural change of the Cu UPD layer after further decreasing the potential, the UPD shoulder peak overlapped with the OPD peak. When the potential exceeded the main UPD peak (0.052 V in Figure 4.5(a)), the OPD region appeared.

Figure 4.5(b) showed the oxidation charge of Cu deposited at different potentials. The monotonic increase of the oxidation charge with the decrease of deposition potential indicated that there was no distinct point which separated the OPD region and the UPD region (from 0.005 V to 0.015 V). Even the UPD dominated region (below 0.02 V) (and the OPD dominant region above 0.02 V). We could also get the same conclusion from charge calculation. The reduction charge of Au surface oxide on the Au electrode was 4.718-4.77 C only about 70% surface coverage at this deposition potential.

(Theoretically, the charge of a Cu monolayer on Au electrode is equal to the reduction charge of Au surface oxide. Theoretically, if we assume that the monolayer is formed ideally two electron transfer reaction, then the charge of the monolayer should be twice the charge of the Au surface oxide. This means that no ideal monolayer can be formed on Au nanoparticle substrate by UPD only.

Figure 45. (a)-CV curves for anode stripping process at different deposition potentials. (b) Oxidation charge of the Cu adlayer versus deposition potentials.

There are several possible reasons for the partial coverage. The atomic size difference between Cu and Au may prevent the formation of a real monolayer. Dimitt et al. [160, 165] pointed out that it was theoretically possible to deposit a real monolayer of Cu per one binding site on Au. However, adsorbed ions from the supporting electrolyte or the contamination from the reference electrode might influence the UPD adlayer, because halogens adsorb on Au strongly and weaken the Cu-Au bonding [159]. Recently, Maizne et al. [163] reported that on iodine modified substrate, sulfuric acid electrolyte, a full monolayer could be deposited. The morphology of the porous Au/C substrate may play a role. According to the Au oxide adsorption value of 40 $\mu\text{mol}/\text{cm}^2$, the surface roughness factor of the electrode prepared by the porous film method was calculated at the range of 1.5-2.0. Au atoms on the rough surface may not be accessible.

4.2.2.2. A.C. test

From the discussions above, it is proved that the UPD cannot make a real monolayer. To fabricate a Cu@Au substrate, the porous Au/C does not possess the ideal structure, but the electrode structure. The advantage of the UPD is the calculated oxidation charge of UPD Cu is quite low. The anode stripping method is quite repeatable, and the

technique may precisely control the structure of the as prepared electrocatalyst.

Here we focused on the decorated Pt@Au/C catalyst for NO₃⁻ reduction. Kristian from our group decorated Au/C catalyst synthesis a two-step chemical approach had enhanced activity towards NO₃⁻ reduction. The enhanced activity is believed to result from the ensemble effect. The decorated catalyst would have much higher activity compared to the bulk Pt catalyst. In this work, we adopted the DP Displacement technique, to get the decorated catalysts with controlled Pt coverage and activities towards NO₃⁻ reduction. The catalysts were prepared by a two-step synthesis in ethylene glycol (EG) polyol method (particle size around 4 nm, the synthesis details are given elsewhere [46]).

After Cu was deposited on Au/C with certain surface coverage, the deposition potentials, the electrode was taken out of the solution under control and quickly soaked in a Cu²⁺ solution. Cu was redox replaced on the Au/C surface via the simple redox replacement reaction: $\text{Cu} + \text{Pt}^{2+} \rightarrow \text{Pt} + \text{Cu}^{2+}$. However, due to the remaining oxygen in the solution and the time span during the redox replacement process, the side competitive reaction of Cu²⁺ reduction could not be omitted; in other words, the efficiency of the redox replacement was lower. Pt²⁺ and Cu²⁺ could not be separated. Nevertheless, compared with the other chemical reduction methods, the DP Displacement technique gave more adaptability and accurate control of the structure of the synthesized

electrocatalysis, the nominal Pt coverage was calculated from the charge from UPD Cu adlayer oxidation and that of the hydrogen desorption peak, assuming that the efficiency of the redox replacement reaction was 100%. During these experiments, it could not be normalized by the hydrogen desorption peak, so it is not accurate anymore to calculate the electrode surface area of bimetallic catalysts. Instead, the density was normalized by the surface areas.

Figure 46. CV curves of the prepared 34% surface coverage Pt@Au/C and 20% Pt/C in 0.5M HCOOH at 0.5M pH rate 100mV/s, 500 rpm. The current density is normalized with the surface area of Pt/C respectively.

Figure 4.6 showed the CV curves prepared at decorated Pt@Au/C electrode with the Pt surface coverage of 34% and 20 wt%. Pt/C electrode by FAO reaction in same experiment condition could see, for this decorated 34% surface coverage Pt@Au/C, the peak I disappeared while peak I dominated at more positive scan rates. The intensity of peak I even exceeded peaks II and III. This means that the FAO reaction is almost totally suppressed and the FAO reaction shifted towards the dehydrogenation pathway to directly benefit this decorated Pt@Au/C electrode. Since there was no more information on the reactivity of the catalyst, and for the experiment, we mainly use the forward scan results to compare the electrocatalysts thereafter.

Figure 4.7 showed the forward voltammograms series of the FAO reaction on decorated Pt@Au/C with different surface coverages. Figure 4.8 showed the CV curves of this series of decorated Pt@Au/C. As the Pt surface area gradually decreased with the decrease of the nominal Pt amount, it was seen that the hydrogen adsorption/desorption area decreased, which is due to controlling the amount of Pt on Pt@Au/C replacement technique.

As could be seen in Figure 4.7, the second anodic dehydrogenation peak at 0.75V decreased with the lowering of total Pt amount, and the Pt surface coverage was below 34%. At this low Pt coverage, the dehydrogenation branch would be shifted to the dehydrogenation branch while the FAO reaction gradually

suppressed with the lowered Pt coverage. One thing should be noted is that even with the minimum coverage of Pt (3%) on Au in this study, the forward scan peak current density is 68% that of 75% coverage sample (the sample with the highest activity). This means that much higher Pt activity towards FAO could be achieved with only a little Pt amount. To further verify the specific activity of Pt towards FAO, the CV peak current at 0.3V was also normalized by the total number of Pt atoms (Au itself has negligible activity towards FAO) in Table 4. It was found that the specific activity with Pt atoms decreased as the Pt surface coverage decreased. The 3% coverage Pt@Au/C sample showed 23.9 folds more active towards FAO compared to the 100% Pt sample, respectively.

Table 4. Normalized FAO peak current density at different surface coverages

Nominal Pt cover	100	75	34	14	3
Peak current per Pt atom ¹⁸ (A/atom)	0.433	0.61	1.22	2.18	10.37

Figure 4.7. Voltammogram for Pt@Au/C catalysts prepared by electrodeposition with Pt coverage of 100%, 75%, 34%, 14%, 3% and Pt/C in 0.5 M HCOOH + 0.5 M H₂SO₄ at 100 mV/s, rotation speed 1000 rpm. The current density is normalized by the geometric area of the substrate electrode surface. The inset shows the CV curves for Pt@Au/C catalysts in 0.5 M HCOOH + 0.5 M H₂SO₄ at 100 mV/s, rotation speed 1000 rpm.

Since the decorated Pt@Au/C catalysts are more stable towards CO poisoning, it may have better stability during FAO life cycle. On the other hand, it is well known that Pt/Au system is strongly poisoned by Au, which may mark the end of the durability of the decorated catalyst depends on the amount of Pt. To get more information about the short-term stability of the catalyst towards FAO, a series of CV tests were performed.

First, a prolonged CV tests up to 2000 cycles were conducted. As shown in Figure 4.8, the activity towards FAO of Pt@Au/C catalysts decreased as the test continued; while for the 3% coverage Pt@Au/C sample, the activity

the activity did not change too much (it actually slightly increased). However, after 2000 cycles, the activity started to decrease with time. At the end of the test, the activity of 3% Pt@Au/C was 210 mA/g, which is higher than 20% Pt/C. The results in blank 0.5 M H₂SO₄ before and after the prolonged test are shown in Figure 4.9. The active surface area of both catalysts decreased after the test. The activity decline of the catalysts was mainly due to the loss of Pt. For the decorated catalyst, the activity didn't decrease as much, although the Pt surface area dropped significantly. As far as we know, this is probably due to the negligible hydrogen desorption area, most of the activity is contributed by Pt/Au surface. After 600 cycles, probably because of segregation of Pt/Au surface, the dissolution of Pt.

Chronoamperometric experiments were also conducted and the results were shown in Figure 4.10. The gradual current decay was due to the Pt surface area loss and CO poisoning effect. The activity loss is permanent and could not be resumed anymore. To avoid CO poisoning, an electrode cleaning protocol was introduced during chronoamperometric experiment, where the electrode was held at -0.2 V and 0.75 V for 1 s to clean the catalyst surface. After the cleaning, the electrode was held at the life test potential of 0.1 V for 15 s. The cleaning duty cycle was repeated twice to see whether the reactivity could be resumed after the cleaning effect on the catalysts. However,

3% coverage of Pt@Au/C sample had much lowered decline Pt/C catalyst. For Pt/C catalyst, it would suffer from the activity decline from the very beginning of decreased $\text{V}_{\text{Pt@Au/C}}$ sample, it had much less COs formed in the beginning accumulation of CO is also much slower. The much alleviation makes the decorated Pt@Au/C sample more capable to Pt/C catalyst.

Figure 4b. Prolonged CV results of (a) 2.3% Pt@Au/C and (b) Pt/C catalyst in $\text{HCOOH} + 0.5 \text{M H}_2\text{SO}_4$ at sweep rate 100 mV/s and 100 rpm.

Figure 4. CV results of (a) 3% Pt@Pn/C in 0.5M H₂SO₄ before and after prolonged CV test. Sweep rate 100mV/s

Figure 4.10 Life test of 3% Pt@Au on Pt/C in 0.5M HCOOH with the applied potential of 0.15V, rotation speed is 1600 rpm. The current density is normalized with the substrate electrode area.

4.2.3 CO stripping tests

Although all the synthesized decorated Pt@Au samples showed improved FAO reactivity compared to the pure Pt catalyst (Figure 4.7), the second anodic peak arising at 0.75V, which is the dehydration pathway to formate species, could be seen for the nominal 100% surface coverage samples. However, this dehydration peak disappeared when the surface coverage of Pt on Au is below 34%.

This phenomenon can be well explained by the bifunctional mechanism [167]. It has been shown that the formic acid adsorption on Pt is a site demanding reaction, where different Pt surface atoms are involved in the reaction. The Pt atoms with different coordination environments (e.g., Pt atoms on the surface of Pt nanoparticles and Pt atoms on the surface of Pt/C catalyst) show different activities for formic acid oxidation.

FAO reaction pathway is not finished, the dehydration pathway to form
poisonous $\text{Pt}^{\text{II}}\text{O}$ species is not continuous neighboring Pt atoms
need [51, 68, 144] contrast, the dehydrogenation pathway
product $\text{Pt}^{\text{II}}\text{O}$ not require such condition can be accomplished
single or isolated Pt atoms [51, 101, 158] surface

Considering -dimensional epitaxial growth mechanism
observed from the coupled in situ electrochemical scanning tunneling
(STM) measurement on spontaneous Pt/Au (111) facet, the most
stable structure is $(\sqrt{3}\sqrt{3})^{\text{R}}$ when the surface coverage is 34% [93] This
would further lead us to believe that Pt adatoms on Au
surface should be isolated when its surface coverage is low
34% [168] Therefore, the isolated Pt will decrease with
surface coverage increases (like the cases of 75% and 100%)
result, by continuously decreasing Pt surface coverage
decreasing the availability of Pt neighboring atoms is increasing
relative of isolated Pt adatoms, the dehydration pathway
hindered, while the dehydrogenation pathway can still occur

Therefore, it is reasonable to conclude that the inhibition
intermediates formation during FAO is mainly because
electrocatalytic sites are not suitable for Pt ensembles

Another consideration is that the results enable us to find that
for the de Pt/Au electrocatalytic system, the surface coverage

facilitating CO species removal from the catalyst surface, such as electronic defects in the neighboring slab, also affects the catalyst reactivity, and therefore, a synergistic effect together with the ensemble effect.

CO stripping tests have been conducted as tests unique to

It is reported that CO stripping is not intrinsically used to test the catalyst's behavior.^{12 or 1.69} Furthermore, on one hand, CO gas could be easily obtained and used in a more straightforward manner, and adsorption on the catalyst slab surfaces could be easily observed. There is a direct link between the experiment and DFT calculations, and the DFT calculations discussed in section

Table 2. CO stripping peak potential

Nominal Pt coverage	3%	14%	34%	70%	100%	Pt/C
Peak Potential (V)	0.60	0.64	0.65	0.68	0.67	0.66
Peak potential difference relative to Pt/C (V)	-0.06	-0.02	-0.01	0.01	0.01	0

Figure 4.1 Enlarged CO stripping curves for decorated and commercial Pt/C in 0.5 M OH⁻ sweep rate 20 mV/s. Current is normalized with the substrate electrodeless original stripping curves for decorated Pt@Au/C and Pt/C.

CO stripping experiments are shown in Figure 4.1. For clearness and simplicity, only the first stripping cycle is displayed in the inset of Figure 4.1. By knowing that Au atoms do not adsorb CO, all the CO oxidation peaks indicate the existence of Pt adatoms on the surface of Au electrode. commercial 50% Pt/C was also shown in Figure 4.1 as a reference. Same as Figure 4.2, the resulting current density for each Pt@Au electrode is normalized by their Au electrode specific surface area, and the current density for Pt/C is normalized by Pt electrode active surface area. By integrating the charge of the adsorbed CO on the electrode, the CO coverage (θ_{CO}) can be calculated by the following equation:

per hydrogen monolayer H_{up} in the range of 0.5–1.0 [27]. Besides, Table 2 shows the corresponding CO oxidation peak potentials relative to the $Ag/AgCl$ electrode.

As can be seen from Figure 4, there are two different theories decorated Pt@Au electrodes. stripping peak potentials 70% and nominal Pt surface coverage shift positively to higher potentials, indicating a s-CO bond strength compared to Pt/C. This can be seen to be rational and widely accepted and proposed by Nørskov [134, 174]. When monolayer deposited on Au, the slab band center shift up to maintain a constant d , which would lead to higher adsorption energy of adsorbed CO, and bonding in this case.

However, the d is not the same for 4% and 3.4% Pt@Au samples. For these three electrodes with low Pt surface coverage, stripping peak potentials shift to lower potentials compared to Pt/C, indicating a weaker C-O bond strength. This phenomenon is controversial with the previous [146, 175, 176] example, Kristina [144] through a step chemical synthesis [177] through the spontaneous electrodeposition method that the CO stripping potentials of all samples are higher than Pt/C, indicating a stronger C-O bond strength, in accordance with the d-band center theory. The data in Figure 4 shows that with the Pt

surface coverage of Pt on Au, the CO stripping peak potential shift more negative from 0.651 to 0.637 V (Fig. 2). Controversially, in Kristian and Du's experiment, the CO stripping peak potential would shift to higher potential with the surface coverage of Pt on Au decreasing, the CO stripping peak potential obtained by a single Pt adatom on Au surface model

However, our DFT calculation results (shown in the Table 1) are in good agreement with our experimental results. The strength of the CO stripping peak potential for a single Pt adatom is stronger than for a pair of neighboring Pt atoms as surrounded by other Pt atoms on the surface. As a result, the CO stripping peak potential for a single Pt adatom is more negative than for a pair of neighboring Pt atoms as surrounded by other Pt atoms on the surface.

There are some serious questions on the previous experimental results. Why the shifting of the CO stripping peak potential for these two categories with different Pt coverages (Pt coverage ranging from 70% ~ 100%)?

To answer this question, we have to think more about this particular situation. However, here, we will provide explanations for the DFT results on the CO stripping peak potential for different Pt coverages. The DFT results on the CO stripping peak potential for different Pt coverages will be further discussed in the next section.

As discussed in Chapter 2, deposition kinetics and high cohesive energy, epitaxial growth of noble metal Pt on the substrate is impossible when electrodeposition is applied. Results turned out that the Pt metal clusters were formed in the epitaxial adatom deposits on the surface. The situation is the same in chemical reduction method with fast kinetics.

However, this is not the case for Pt on Cu substrate. The difference between foreign metal Cu and Pt is due to the different crystal structure ($\sqrt{3} \times \sqrt{3}$)⁰ with a maximum theoretical coverage of 33% at the beginning stage of Cu UPD [93]. Therefore, Cu adatoms on the Au substrate surface are mainly isolated instead of between Cu and Au. As a result, a monolayer of Cu adatoms is formed by subsequent replacement within monolayer height at the external surface coverage.

The Cu UPD adlayer structure will change gradually ($\sqrt{3} \times \sqrt{3}$)⁰ with the increasing Cu surface coverage. During this process, although the adatoms are still below the monolayer height, the possibility of forming subsequent Pt neighbors becomes bigger. This is consistent with the theory and could be explained when the strength of the CO stripping peak is high, which is observed when Pt surface coverage is 30% to 70%. With increasing height range

The situations become complicated for 100% surface coverage Pt@Au sample. Since at its respective Cu UPD side reaction overlapped with OPD, as shown in Fig. 4.5. The three-dimensional nucleation process followed by a diffusion growth mechanism has to be considered [163, 164] and the subsequent Pt adatoms would not form a monolayer. Therefore, the observed nominal 100% Pt@Au/Cu did not possess a perfect ideal monolayer. The PAu substrate instead, it would only cover the Au electrode partially with coverage about 70-75% (based on Cu UPD study), while about 25% of the additional Pt adatoms on the Au layer, forming a island-like structure with lots of Pt ensembles on the Au substrate.

In this occasion, it is difficult to interpret experimental results of different effects both in the property of the CO stripping. On one hand, the more neighboring Pt ensembles on the Pt-Cu bond strength in accordance with the bond contraction. On the other hand, Pt adatoms in the surface and layers would be more likely to be the pure Pt electrode. It was found that for the nominal 100% sample, the CO stripping peak potential (0.676V) compared to that of the 70% surface coverage sample (0.652V), while the CO stripping peak potential is still more positive than that of Pt/Cu (0.605V), according to Kriswina and Du's results.

and we can now understand why the results from the inaccurate procedure could be ostensibly explained by the theory.

Therefore we can finally answer the long-deferred question about the discrepancy between the previous studies and current studies

Based on the previously discussed Au electrode structures, the subsequent Pt@Au electrocatalysts tested for H_2O_2 and CO stripping measurement, were made on a common support morphology of the synthesized Au/Pt electrodes with respect to the surface coverage of Pt atoms on Au, as illustrated schematically in Figure 4.2

Figure 4.2 Schematic diagram on the morphologies with respect to the surface coverage of Pt on Au: (a) extremely low surface coverage; (b) low surface coverage within a range of 10%; (c) maximum coverage within a range of 70%; (d) nominal 100%

Another proof is from the integrated CO stripping peak area, which is almost doubled when comparing 4% and 34% Pt@Au samples, the CO oxidation peak area of Pt@Au is almost equal with that of 70% surface coverage (see Figure 4.4). Since CO could only adsorb on the surface, the difference in stripping peak charge between the 70% and 100% Pt@Au samples indicates the Pt adatoms buried in the Au matrix for the 100% Pt@Au sample.

In conclusion, through CO stripping measurements, when the Pt surface coverage on Au substrate is below 34%, the Pt adatoms on Au surface are isolated and surrounded by the neighboring Au atoms. In these cases, the Pt adatoms on Au substrate can be isolated and surrounded by the neighboring Au atoms. This conclusion on the origin of the synergistic effect of the decorated Pt@Au electrodes by CO stripping experiments cannot rule out the electronic effect of the Pt adatoms on the neighboring Au atoms. Because when Pt surface coverage is synergistic for the electronic effect, it can be introduced into a quantum well.

4.3 Au@Pt series

Based on the Au@Pt deposition and CO stripping studies, it is difficult to separate the contributions of the ensemble

both are present on the decorated Pt@Au electrocatalysts. Pt surface coverage is low.

In order to distinguish effects from the Au@Pt reaction, we made a reversed experiment by investigating the Pt@Au electrode. Pt electrocatalyst decorated by Au@Pt to this (decreasing) to minimize the electrocatalytic effect on the electrode. Different from the decorated Pt@Au samples, it is favored since Pt adatoms are surrounded by the Au adatoms. Au@Pt electrodes are dominated by the Pt electronic states of which contact the Au adatoms on the electrode surface and adatoms.

4.3. Limitation of UPD redox replacement technique

To precisely control the surface composition of the surface, UPD redox replacement technique is not sufficient. The reason for this failure is discussed below.

By comparing the cyclic voltammograms of Pt/Cr catalyst in sulfuric acid and Pt/Cr catalyst in sulfuric acid, we found that the peak around 0.5 V just after the hydrogen adsorption (Fig. 4.3) is assigned to the oxidation of the deposited Cu. In accordance with [183, literature 184], in order to keep Cu-UPD, we added hydrogen adsorption first tried to keep the Cu-UPD. However,

obvious Au oxide reduction peak during the backward scan in Figure 4.4.3 after the entire duty cycle under the replacement experiment condition.

We further tested the FAO of the 50% Pt/C and the as-prepared Au@Pt/C electrocatalysts are shown in Figure 4.4.4. As could be seen, there is no difference between the two electrodes, the CV curve for the Au@Pt/C electrocatalyst by using replacement was almost the same as that of pure Pt/C catalyst, meaning that a little amount of Au deposited on the surface of the electrode after the redox replacement.

Figure 4.4.3 Voltammogram of the 50% Pt/C electrocatalyst in H_2SO_4 electrolyte (solid line), 0.1M CuSO_4 (dashed line) and H_2SO_4 after Cu-Au redox replacement (dotted line) at a sweep rate 100mV/s.

Figure 4-4 Voltammogram of the commercial Pt/C and synthesized Au@Pt/C electrocatalysts by Cu UPD @ 0.10 V in 0.5M HCOOH + 0.5M H₂SO₄ at sweep rate 100mV/s, rotation speed 500 rpm. The current density is normalized with the Pt electrocatalyst.

Since (Au) ions are certainly redox replaced on a surface higher to standard electrode potential, it is only possible that the Pt/C electrode is covered by Au atoms after the UPD experiment.

In order to generate more Au atoms deposited on Pt electrode surface, different approaches were used: (1) setting the deposition potential range < 0 V (2) making multiple Cu deposition redox replacement cycles (3) increasing the concentration of Cu ions in the acid electrolyte.

However, all of the efforts were unsuccessful for prepared Au@Pt/C electrodes to have a high current density after the UPD experiment. In H₂SO₄ electrolyte and subsequent FAD tests (results are not here).

All of these failures to believe that on Pt/C electrode, it is precisely the morphology of the Au@Pt/C electrocatalysts using Cu-Au UPD redox replacement technique. This is also the strategy of Cu UPD process as compared to the Au substrates were used.

By comparing CV curves of Pt/C (Fig. 4.1(a)) and Au/C (Fig. 4.1(b)) of electrodes in sulfuric acid, with the interested Cu UPD potential (0~0.6 V) on both of the electrodes, the unique character of the but hydrogen desorption but for Pt electrode is the key point. Mind that the hydrogen atom is much smaller than the Cu atom, the hydrogen adsorption/desorption process is fast enough to react with Pt electrode. Cu UPD is a slow process, so we get the conclusion for the failure of the Cu UPD technique due to the competitive hydrogen adsorption on Pt substrate accessibility. Cu UPD.

4.3.2 Validation of direct electrodeposition and FAO tests

We adopted direct electrodeposition to synthesize decorated Au@Pt/C electrodes as described in the experimental part, the deposition on Pt/C electrode was performed by increasing the Au (III) ion concentration to 0.05 M. The surface coverage controlled by the number of the cycles, and the integrated peak charge before and after deposition. The results are

normalized to current density with respect to the electrode surface area.

Although Au atoms do not adsorb any hydrogen, as discussed in the Pt@Au section, it is calculated by the electrode surface area of these decorated catalysts. Therefore, the calculated surface coverages of the Au@Pt/C series were not as accurate as the Pt@Au/C series. One thing needs to be stressed is that the direct electrochemical deposition of Au on Pt/C growth process. Therefore, the structures prepared Au@Pt/C electrodes are not simply monolayers but in the multilayer range.

Figure 4-5 Voltammogram of prepared Au@Pt/C (Pt surface coverage: 27%) and commercial Pt/C in 0.5M HCOOH₂SO₄ at 0.5M pH 100mV/s, rotation speed 1000 rpm. The current densities were normalized to the electrode surface area, respectively.

(27%) exposed on the electrode surface of the peak, which corresponds to the direct oxidation from HCOOH to CO higher than the peak of the bare Pt electrode. On backward scanning, the reverse current was much smaller compared to that of the forward scan, but the difference between the forward and backward was not as large as that of the Pt electrode, indicating a less poisoning on the former.

Figure 4.6 showed the forward scan of the Au@Pt/C electrodes prepared with different Pt surface coverages. As can be seen, the peak current density of HCOOH oxidation on bare Pt electrode was lower than that on Au@Pt/C electrodes, the peak current density of HCOOH oxidation on bare Pt electrode was higher than that on Au@Pt/C electrodes with high (72% sample), the peak current density of HCOOH oxidation on the Pt surface was lower than that on Au@Pt/C electrodes with low (8% and 10% samples), the peak current density decreased to the Pt active sites on the surface, while the peak current density reached a maximum with the medium Pt surface coverage.

On the descending part of the forward scan, the peak current density of HCOOH oxidation on Au@Pt/C samples appeared in the same potential region as that on the bare Pt electrode, indicating that a certain extent of CO poisoning was still present on the Au@Pt/C electrodes. The Au@Pt/C electrodes showed a higher peak current density than the bare Pt electrode, which was due to the use of Pt electrode as the substrate, and the Pt atom was exposed by covering the electrode surface with the Au adlayer.

All of the above facts suggest that the Pt active sites on Pt based electrocatalyst are less blocked by species produced in the CO oxidation reaction than the bare Pt electrode.

Therefore, it is reasonable to get the conclusion that the CO oxidation is the dominant effect which affects the electrocatalytic reaction taking place on Pt based electrocatalyst surfaces.

Figure 4-7 Voltammogram forward scan comparing Pt@Au (3.4%) and Au@Pt (2.7%) in 0.5M HCOOH, scan rate 5 mV/s, rotation speed 1000 rpm. The current densities are normalized by electrode surface area, respectively.

Since the ensemble effect is assumed to be the same for both electrodes, the similar Pt surface area we can further check the electronic effect by comparing the FAD_{CO}/A_{Pt} of Pt@Au (3.4%) and Au@Pt (2.7%) (minimal electronic effect Pt@Au/Claretronics effect).

shown in Figure 4.4.7, we could see that the electrocatalytic reaction starts slightly lower potential and the peak current potential is 0.04 V more than Au@Pt surface. It is compared to the much improved FAO (~0.15 V negatively shifted onset potential). The difference is very small and it concludes that the electron transfer is only the minor role though it can be completely fitted for the Pt@Au. More detailed results will be discussed in the next section.

4.4 Conclusions

The charge of the Cu adlayer prepared by electrochemical deposition on nanoparticles was calculated by using the results showed that under the current experiment condition, i.e., in sulfuric acid supported porous film electrode, we could not get an ideal fully covered underpotentially deposited particles. The OPD started

Various decorated Pt@Au/C catalysts with different surface coverage were synthesized by using the electrodeposition technique. The decorated catalysts show higher activity towards FAO than Pt/C catalyst. Particularly, the highest specific activity was obtained with the coverage of 43% in this study. Moreover, the decorated Pt@Au/C catalyst shows better stability than the Pt/C towards FAO due to the species adsorbed on the surface.

CO stripping experiments were conducted with the synthesized Pt@Au electrocatalysts. Comparing previous literature results, the peak potential negatively shifted when the Pt surface covered by Au; and, the CO stripping peak potential of Pt surface coverage was high. The surface morphology of Pt@Au/C electrodes with different Pt surface coverage was analyzed by DFT calculations.

Series of Au@Pt electrocatalysts were synthesized by electrodeposition. Results showed that the Au@Pt/C electrocatalysts possess much improved reactivity toward FAO reaction. By comparing the electrochemical results of Au@Pt series, we could get the conclusion that the enhancement for FAO reaction taking place on Pt based electrode from the Au atoms is only the minor effect.

Chapter 5 Decorated Pt based electrocatalysts for theoretical DFT calculations

(Some parts of this chapter have been submitted to the Journal of Electroanalytical Chemistry)

5.1 Introduction

In order to make a better understanding of the catalytic activity of the decorated Pt@Au catalyst, a computational study was carried out in this thesis.

As discussed in the literature, the oxidation of formic acid (FA) has been proposed to follow three main pathways: direct oxidation, dehydration pathway, and indirect pathway. For the direct oxidation, it is believed that the first step for HCOOH oxidation involves the adsorption of formic acid onto the metal surface as a formate species (COOH) as the main intermediate [51, 187]. Therefore, the reaction mechanism could be briefly defined as Fig. 5.1.

Fig. 5.1. The reaction pathways involved in the electrocatalytic oxidation of formic acid.

By carrying out DFT calculations on slab surfaces which analyze Pt@Au and Au@Pt systems, we first tried to look at the of formic acid, oxidized intermediates and products to qualify the reaction progress on paths as shown in Figure 5. Furthermore, a calculation of DOS for each slab surface for discussion and details would provide insight to the thermodynamic energetics of a different catalytic system.

5. Pt@Au series

5.2. Slab model

In this series (100) facet was chosen for simplicity in modeling the supercell was (3x3x3) except for DOS calculation. A supercell had been selected to present a low surface coverage of the coverage) in order to avoid additional effect that arises from the intermediate species when its surface coverage is too high periodically in the direction perpendicular to the surface than 10 Å to separate the neighboring slabs.

Four types of layered slab models were used in this series: pure Pt@Au; the ideal pseudomorphic monolayer on Au (denoted as 1ML Pt@Au); and Au slab with one of the surface Au atoms replaced by Pt atom (denoted as 0.11ML Pt@Au), hereafter referred to as Pt@Au surface.

low Pt surface coverage (3x3) supercell 0.11ML Pt@Au slab model (after optimization) is shown in Figure 52. Pedersen[191] had illustrated that at room temperature growth of Pt on Au (111) proceeded initially by isolated Pt atoms being alloyed in a concentration of around 3% of the monolayer. Therefore, the model decorated Pt@Au surface with this Pt@Au surface at the stage of deposition with Pt surface coverage. For the decoration of Pt@Au (100) surface, two types of surface Au atoms could be distinguished based on the distance between the central Pt atom on the top layer: the first type stands at Pt-nearest neighbor (nn) site, and the second type, denoted as Pt-2nd neighbor (2nn) site, is the Au atom which stands on the diagonal site of Pt.

Figure 52. Four-layer (3x3) supercell 0.11ML Pt@Au slab model

Figure 5. Types of Au atoms on the top layer of 0.11

By calculating the phase diagrams for surface Pt@Au [192], we had proposed an exchange mechanism representing the islands beneath the Pt adislands would be replaced by the Pt ad energy, leading to much more complicated surface model based on experimental results (shown Figure 4.40), our prepared decorated Pt@Au/C catalysts (especially 3% coverage surface) maintained the prolonged FAO life tests, indicating that the Pt adatoms on the substrate surface during the electrochemical tests. It seemed that the Pt adatoms might be kinetically hindered under our experimental conditions.

In short, we presented two realistic slab models (Pt@Au surface alloy model (0.11ML Pt@Au) representing the decorated surface and one idealized pseudomorphic overlayer model (1ML Pt@Au). In the optimization, the metal atoms in the bottom two layers were fixed at their high-symmetry position, while the metal atoms in the top two layers were allowed to be fully relaxed.

5.2. Adsorption study

Our calculated lattice constants for AuP(49) (3.89 Å) with the previous theoretical values of 3.94 Å with the PBE functional, respectively.

We studied the properties of formic acid and its intermediates, namely H, O, CO, OH, HCO, and CHCO, all of which were positioned on one side of the slab on all the high symmetry hollow). The calculated binding energies are listed in Table 5.1; while the most stable adsorption configurations on 1 Pt@Au surfaces are shown in Fig. 5.4. Detailed analysis will be discussed in the paragraphs below. The most stable adsorption complexes were confirmed by vibrational analysis to be the minima.

Table 5.1. Calculated BEs (eV) for the most stable complexes of adsorbates on atop, bridge and hollow sites. For adsorbates which have multiple C atoms, the C atom adsorption site is referred to the central C atom. For adsorbates which have multiple O atoms, the O atom adsorption site is referred to the central O atom. For adsorbates which have multiple H atoms, the H atom adsorption site is referred to the central H atom. The adsorbate complex is referred to the central atom mainly interacting with the metal slab.

Adsorbate	Pt (100)			Au (100)			1ML Pt@Au (100)			0.11ML Pt@Au (100)		
	Atop	Bridge	Hollow	Atop	Bridge	Hollow	Atop	Bridge	Hollow	Atop	Bridge	Hollow
H	-2.7	-2.90	-2.51	-1.9	-2.29	-1.94	-2.8	-3.15	-2.70	-2.6	-2.72	-a
O	-3.1	-4.30	-3.69	-1.9	-2.94	-3.04	-3.4	-4.69	-4.17	-3.2	-3.64	-3.57
_CO	-1.9	-2.10	-1.53	-0.5	-0.62	-0.20	-2.0	-2.54	-1.99	-1.8	-0.80	-0.21
_OH	-2.5	-3.05	-2.33	-1.9	-2.40	-2.20	-2.7	-3.47	-2.71	-2.5	-2.75	-2.19
_COOH	-2.7	-2.37	-a	-1.5	-a	-a	-3.0	-2.96	-a	-2.4	-a	-b
_COOH	-2.7	-2.43	-a	-1.6	-a	-a	-3.1	-a	-a	-2.5	-a	-b
HCOO	-2.6	-a	-b	-2.1	-a	-b	-2.7	-a	-b	-2.4	-a	-b

^a All the initial configurations are stable and change to other configurations after optimization

^b The adsorbate complex is not stable after optimization

Figure 54. Side view of the most stable adsorption configuration of formic acid on Pt@Au and 0.11ML Pt@AuY (100) surfaces. Blue-gray red and white. For clarity, only the top layers are shown at the bottom.

Atomic hydrogen (H)

Previous theoretical reports that the atomic H prefers coordination sites facet (111) [195, 197] & [195, 197]. Our current DFT calculations show of atomic H adsorbing surface at atop, bridge and hollow sites with binding energies of 2.72, 2.90 and 2.51 eV, respectively, with the bridge site as the most favorable. This is because open compared to the (111) surface and hence hollow sites with H adsorption on Pt and compared to (111) surface [198].

This preferential property for atomic H holds true for the three (100) surfaces studied, since the Au lattice constant hollow site even less favorable than that on Pt (100) surface.

Previous theoretical study reported that low Au (111) is the preferred site with 2.25 eV [199]. Our current values are 1.96 eV (atop), 2.29 eV (bridge) and 2.14 eV (hollow), the values are and reported previously by different models and GGA used.

H adsorption on 1ML Pt@Au (100) surface is that on Pt calculated BEs on 1ML Pt@Au at atop, bridge and hollow sites are 2.16, 2.63 and 2.70 eV, respectively. The higher binding energy leads anti-center shift of the Pt monolayer on Au substrate [173] as calculated. Detailed discussion and conclusion will be discussed in the later

On the 0.11 ML Pt@Au (100) surface, H prefers the bridge site with BE of 2.72 eV, as well as atop site on Pt with BE of 2.68 eV.

Atomic oxygen (O)

On Pt (100) surface, the calculated BEs for atomic O adsorption on atop, bridge and hollow sites are 3.14, 3.04 and 3.04 eV, respectively. The values agree with the previously reported results on Pt (100) surface using PBE functional and (2x2) supercell (3.79 eV for atop, bridge and hollow sites, respectively) [200]. Gey et al. [201] also theoretically studied the binding of atomic oxygen on Pt (100) surface and concluded that the bridge site possessed the strongest binding, followed by the hollow site, while the atop site was the least stable.

On Au (100) surface, the calculated BEs for atomic O adsorption on atop, bridge and hollow sites are 3.04, 2.94 and 2.94 eV, respectively. The difference between hollow and bridge sites is very small, which is in agreement with the previous work by Kopecký et al. [202]. Our calculations also found the hollow site to be the most stable configuration for atomic oxygen on Au (100) surface, which is in agreement with the values of 3.08 eV for atomic oxygen binding with the hollow site on (4x4) Au (111) facet using [203] PW91 functional.

The calculated BEs for O adsorption on atop, bridge and hollow sites on Pt@Au (100) surface are 3.48, 3.69 and 3.7 eV, respectively. Our calculations agree well with Jeliński et al. [204] for O adsorption on the hollow site of Pt@Au (100) surface.

in 1 ML Pt@Au (111). Our results show the bridge site is most favorable for O adsorption. This reminds us that the Pt@Au (100) behaves more like Pt (100) surface than pure Au (100). The electronic property of the surface layer is altered by the

Similar to the case of H adsorption, atomic O adsorbing on the (100) surface prefers the sites near the central Pt atom. The bridge site with Pt₁ and Au₁ and Au₂ fold hollow sites. The PtAu calculated BEEs at three most stable sites are 1.23, 1.64 and 0.57 eV, respectively. The small difference in energetic point of view related bridge and hollow sites, which is definitely not the case for 1 ML Pt@Au, indicates the decorated Pt@Au surface, the Pt atoms have a strong ligand effect on the central Pt atom, making it a high coordination site just as it is on Au (100) surface. The coordination around Pt changes its environment, and subsequently its catalytic activity. For the initial guesses, for which we did not know whether the atop, bridge or hollow sites were most favorable, we compared with the most favorable bridge site (the BEE difference is 0.57 eV).

Carbon monoxide

For all the four surfaces, the CO molecule is adsorbed with the C atom pointing away from the surface, forming a linear perpendicular

On Pt (100) surface, our calculated binding energies were 1.95, 2.10 and 1.53 eV, respectively, comparable to reported values of 1.79 (atop), 2.05 (bridge) and 1.48 (hollow) eV by Yue et al. [193]. The slightly more stable binding was believed to be resulted from the relaxation of the top two Pt layers.

Previous theoretical study reported that on (2x2) superlattice, the bridge site was slightly energetically preferred over atop site, while the energy difference was only 0.12 eV. Since the adsorption energy decreases with the increasing CO coverage, the current results for atop, bridge and hollow sites (0.54, 0.62 and 0.20 eV, respectively) well agree with the previously reported trend except for larger (3x3) supercell and different GGA used in our calculation.

On 1ML Pt@Au (100) surface, our calculated binding energies on atop, bridge and hollow sites are 1.20, 0.52, 1.54 and 1.09 eV, respectively. A stronger binding to this 1ML Pt@Au surface compared to the pseudomorphic monolayer of Pt@Au surface may be observed during FACS since all catalytic active sites are covered by the adsorbed CO.

However, on 0.11ML Pt@Au (100) surface, the optimized CO adsorption is still on Pt, with a binding energy of 1.1 eV. Actually, mainly due to the electronic effect, the CO molecule is quite rigid such that CO would not bind to Au site. When CO solely atop or bridge bound with

BE tend to be similar with those on pure Au surface. In turn, the BE of CO on Pt@Au is more than 1 eV compared with the most stable atop one Pt configuration on the other cases. Furthermore, for the other two initial configurations associated with the central Pt atom, the Pt@Au low coordination site, the final results also locate on Pt at the top position. Pt configuration is then the most favorable structure for CO adsorption on Pt@Au surface with a low Pt surface coverage.

Hydroxyl (OH)

Different from CO with a perpendicular orientation on the surface, the stable configurations on all the four surfaces for OH are parallel orientation to the surface with its O atom binding to the surface. The H atom slightly tilts through the middle bridge site. In this configuration, the tilted H atom interacts with the surface atoms to improve the perpendicular orientations towards the surface through its interaction. This is more favorable than this perpendicular configuration.

On the Pt(100) surface, the BE at the most stable parallel adsorption was calculated as -1.05 eV, which is in good agreement with the values by Norrby et al. [2001]. With the same BE, OH could also adsorb in the perpendicular orientation to the surface with its O atom binding to the surface. However, the H atom points to the diagonal direction. However, the parallel low sites were unstable and changed to the perpendicular configuration.

configurations after the optimization. Our calculated BEs for the perpendicular orientations towards the surface with Γ and bridge sites are 17.2 and 23.3 eV respectively.

On Au (100) surface, for the perpendicular orientations, the calculated BEs for the atop and bridge sites are 19.3 and 24.0 eV, respectively, which are in good agreement with the previously reported theoretical values of 19.3 eV for the atop site and 24.0 eV for the bridge site [135] despite the different surface models (1x1 and 1x2) and GGA (PBE and PW91) used. The BEs for the perpendicular orientations towards the surface with Γ and bridge sites are 13.2 and 21.9 eV, respectively.

On 1ML Pt@Au (100) surface, the BEs for the atop and bridge sites are 27.8 and 34.7 eV, respectively. While the calculated BEs for the atop, bridge and hollow sites are 19.3, 31.9 and 27.1 eV, respectively.

On 0.11ML Pt@Au (100) surface, for the perpendicular orientations towards the surface with Γ and bridge sites, the calculated BEs turn to be similar with those on pure Au surface, only the configurations which were reported here. The calculated BEs for the atop and bridge sites are 19.3 and 27.5 eV, for the hollow sites are 27.8 and 34.7 eV, respectively. However, the perpendicular orientations towards the surface with Γ and bridge sites are not stable. For the atop site on Pt, the BE was 0.0 eV after calculation, while for the bridge and hollow orientations changed to other configurations.

Carboxyl group (COOH)

Two types of COOH are studied in this study. One, is with the H atom tilted upward against the other is denoted as HCOO with the H atom tilted downward towards the surface. Similar to the case of the OH , the downward configuration allows attractive interaction between H and the surface metal slightly more stable (by ~ 0.1 eV) from the point of view. However, for the case of OH adsorption with its O to two metal atoms, for all the surfaces, the most stable COOH with its C atom bound atop the surface pointing towards the nearest metal atom.

On Pt (100) face, the calculated BEs for COOH and HCOO stable configurations are 2.70 and 2.79 eV, respectively, which are close to the previously reported the 2.44 eV value [169] considering the use of different surface ((100) vs. (111)). COOH and HCOO can also be stable with its C atom bridge bound to two Pt atoms towards the midfield axis of the bridge site. The binding configurations are calculated 2.37 and 2.43 eV for COOH and HCOO , respectively. However, the orientation is not stable in the hollow site.

On Au (100) surface, the atop configurations for COOH and HCOO are stable ones while neither the bridge configuration is stable. The

calculated BEs for the most stable configurations were 1.50 and 1.01 eV for COO_h and COOH respectively.

On 1ML Pt@Au (100) surface, COOH prefers atop configuration with BEs of -3.01 and 1 eV for COO_h and COOH respectively. On Pt@Au (100) surface, the bridge configuration (similar to the case of Pt(100)) was also considered for the case of COOH . It finally change to atop configuration after optimization.

On 0.11ML Au (100) surface, only atop configurations were considered while the bridge and hollow configurations were not optimized. The calculated BEs for atop were 2.14 and 2.01 eV, for COO_h and COOH respectively.

Formate group (HCOO)

For formate optimization, two shown in Figure 55, monodentate and bidentate were considered based on the theory of coordination [206]. On all the Pt@Au surfaces studied here (except the 0.11ML Pt@Au (100) surface, see the texts below), it was found that the only stable bidentate bridge configuration is through both of its oxygen atoms binding on the top of two equivalent manner. All the orientations with the monodentate binding were unstable and would either finally change to atop or bridge sites. The other starting bidentate configurations (bridge sites) were unstable and would either finally change to atop or bridge sites.

break up after the optimization. It fits with the previously calculated [106, 209] as well as the experimental results.

This rigid atop configuration would make it very difficult for HCOO to form the final products. According to [51] the dissociation of formic acid from this configuration requires bending out of the plane, and, alternatively, reorient the adsorbate to be bound by its oxygen atoms and the hydrogen atom. All of the processes cost over 1 eV in energy as the barrier on Pt (111) surface. Therefore, HCOO might just act as a spectator species rather than an intermediate [38, 196].

The calculated BEs for the only stable atop bidentate HCOO on 1 ML Pt@Au surface are 2.64, 2.12, 2.79 eV, respectively.

The case is a bit more complex on the 0.11 ML Pt@Au surface. The stable configuration is still the bidentate HCOO, but with one oxygen atom on the central Pt atom and the other oxygen atom on the Au atom with a BE of -2.40 eV. The bidentate HCOO is also stable when bind on the pure Au surface. The calculated BEs of bidentate HCOO on Au₁Au₁ and Au₂Au₂ sites were -2.05, -2.11 and -2.15 eV, respectively, which are slightly higher than the pure Au (111) surface.

Monodentate

Bidentate

Figure 5.5. Tested structures for HCOOH adsorption

Carbon dioxide (CO_2)

We have started to place the CO_2 molecule about 2.5 Å high above all the slab surfaces, using its central C atom binding to the surface. After geometry optimization, for all the CO_2 molecules studied, they retained its phase configuration standing parallel and 4 Å high above the slab surfaces with the calculated BEs essentially zero. This confirms previous reports that since CO_2 is a linear molecule, physisorption process would be dominant for CO_2 on metal surfaces [211, 212].

Formic acid (HCOOH)

Similar to HCOOH molecule is also fully coordinated physisorption process on the four slabs studied here. It is more strongly oriented on the surface than CO_2 due to the donation of lone pair electrons from the carbonyl oxygen atom.

Normally, HCOOH molecule possesses two gas phase transition states ($\text{HCOOH} \rightarrow \text{HCOOH}^\ddagger$ 29.89 eV) and ($\text{HCOOH} \rightarrow \text{HCOOH}^\ddagger$ 29.75 eV), defined by the rotation of the O-H group around the C=O bond. Since researchers had

of HCOOH was greatly influenced by the $\{213\}$ and $\{110\}$ binding sites on Pt (100) and Pt (111) surfaces. We tried to calculate all the possible configurations of HCOOH molecule with HCOOH molecule plane perpendicular to the slab surface on Pt (100) and Pt (111) surfaces.

trans-HCOOH

cis-HCOOH

Figure 5.6. Tested structures for formic acid (HCOOH) adsorption on Pt (100) and Pt (111) surfaces.

The lowest energy structure was found for the trans-HCOOH configuration whose carbon atom is bonded to Pt atom with its OH group pointing downward towards the Pt surface. This configuration is similar to the cases of CO adsorption, where the downward bending H atom towards the Pt surface provides additional stability.

This type of structure is also the most stable configuration studied. The calculated BEs for HCOOH adsorption on Pt@Au (100) were 0.19 eV and 0.31 eV, respectively, which are much lower than any other adsorption cases with the exception of C

Based on our periodic DFT slab models calculations, we find that the adsorption on (100) surface is a decisive high symmetry site. The two bridge site is preferred among the high symmetry sites for molecules having one adsorption site, e.g., H, O, CO and OH. Except for CO adsorption, the fourfold hollow site is normally unstable for most molecules.

Among the four surfaces, the (100) surface interacts most weakly with adsorbates, which indicates the inert behavior due to the high symmetry of the surface [197, 212-218].

There is a clear trend that all the adsorbates bind more strongly on the (111) surface compared to Pt, which is consistent with the previously reported results [204, 212-221]. This phenomenon has been well explained by the difference in the electronic structure of the Pt monolayer and the Au substrate, the strain effect is under primary consideration. As illustrated in Fig. 2.22, the lattice situation of the pseudomorphic Pt@Au surface. As illustrated in Ref.[137, 222, 223] interaction between the adsorbate states and the density of states is of importance for determining the binding energy. The d-band center of the metal slabs will be discussed below.

Although it does make significant BE differences from the (100) and (110) surfaces, based on our calculations, the strain effect of Pt@Au surface does not affect the favored adsorption sites [205].

The adsorption on 0.11ML Pt@Au surface are stronger than on pure Au surface, but weaker than Pt and 1ML Pt@Au surfaces. For the adsorbates bind on the pure Au surface, the most favorable adsorption site is still associated with the hollow site. For the Pt@Au surface, we have considered the influence of impure Pt atom to the Au environment and the effect of moving back to the central Pt atom on the adsorption behavior of the adsorbates.

For both H and O adsorption, the hollow site is the most stable configuration, while for CO adsorption, the initial guess converged to be atop on Pt site. On the other hand, for the atop adsorptions on the pure Au surface, the atop adsorption were unstable, and atop adsorptions on the decorated Au surface were stable. Moreover, the CO adsorption on the hollow site of pure Au bridge site is a local minimum based on the frequency analysis. The calculated adsorption energy is -0.80 eV on $1_{Au}1_{Au}$ bridge site, -0.67 eV on $1_{Au}2_{Au}$ bridge sites, respectively. Note that the bridge $1_{Au}1_{Au}$ and $2_{Au}1_{Au}$ sites are similar to the case of CO adsorption on Au (100) surface -0.62 eV site, while the BEA is bridge on Au a little bit larger than the Au surface. This means that the decorated Pt atom has a back-and-forth influence on the adsorption behavior of the adsorbates on the atoms could be neglected. As a result, we have to consider the atom group of the central Pt atom and its influence on the adsorption behavior on this decorated Pt@Au surface with low surface coverage.

5.2. Reaction energies for proposed reaction networks

In Table 52, we listed the reaction energies for the first steps in FAO process, illustrated in Figure 51.

Table 52. Calculated $\Delta D.E$ for the steps in the proposed reaction network on series Pt@ Au (100) surfaces

Reaction st	Pt	Au	1ML Pt@	0.11ML Pt
(1) $\text{HCOOH} \rightarrow \text{COOH} + \text{H}$	-0.32	0.52	-0.55	-0.10
(2) $\text{HCOOH} \rightarrow \text{COH} + \text{OH}$	-0.78	0.69	-1.18	-0.51
(3) $\text{HCOOH} \rightarrow \text{CO} + \text{H}_2\text{O}$	-0.32	-0.24	-0.41	-0.38
(4) $\text{COOH} \rightarrow \text{CO} + \text{H}$	0.14	-0.41	0.21	0.03
(5) $\text{COOH} \rightarrow \text{CO} + \text{OH}$	-0.35	0.60	-0.88	-0.04
(6) $\text{COOH} \rightarrow \text{CO} + \text{H}$	0.49	-1.01	1.10	0.08
(7) $\text{HCOOH} \rightarrow \text{CO} + \text{H}_2$	-0.64	0.28	-0.96	-0.48

From this table, we could see:

On Pt (100) surface, the highly favorable exothermic property of CO formation through COOH decomposition in step (5) and the highly property of CO formation through COOH decomposition (6) are due to the excessive strong adsorption of CO formed on Pt surface. CO is a poisonous species associated in the FAO process, its for-

step (5) and (6), are of primary consideration with this slab surface with the benchmark Pt (100) surface.

Opposite to the Pt (100) surface, the Au (100) surface formation in step (5) and exothermicity towards CO oxidation step (6) due to the adsorption of CO on the surface. CO can be removed and is not considered as a poisonous species for strong endothermic facts for step (1), (2), and (7) show intermediates (COOH and HCO) and the final products (overall reaction) are all highly unfavorable. This is in accordance with the theoretical studies that a volcano curve would be generated by binding energies of the adsorbates and the center of different surfaces. Too strong interaction (near the Fermi level) interaction (Fermi level) would be a catalyst poor [224, 225]. This is also in accordance with our previous experiments nanoparticles just have negative activity towards

The stronger exothermicity of step (5) and endothermicity much aggravated poisoning of the 1ML Pt@Au surface the much stronger CO bond strength has already been found that monolayer systems lattice constants are expanded, the step barriers are higher than those in the systems in which under compression [204]. As a result, 1ML Pt@Au surface shows activity towards F[403] reaction

The reaction energies on the 0.11 ML Pt@Au surface are lower than on pure Au. Take Pt as the reference, the reaction energies on the 0.11 ML Pt@Au surface are lower than on the ideal pseudomorphic monolayer of Pt@Au surface just like pure Pt. As illustrated above, since the 0.11 ML Pt@Au surface is not so different compared with the pure Pt surface, a reasonable deduction is that the 0.11 ML Pt@Au surface might be more active for FAO reaction. Indeed, the 0.11 ML Pt@Au surface not only facilitates FAO reaction, but also possesses good catalytic activity towards hydrogen evolution reaction (HER) reaction [120].

However, in the adsorption study section, we have shown that the adsorption of CO, HCOOH, and CH₃OH on 0.11 ML Pt@Au is quite rigid with the intermediates adsorbed on atop of the only surface Pt atoms. If these intermediates are formed during FAO efficiently, they would block the active sites and decrease the catalytic activity. However, this decorated Pt@Au possesses much improved FAO performance and prolonged durability than pure Pt nanoparticles. The explanation for this is that the spillover mechanism is inhibited by the Pt atoms. Similar to the case of atomic H adsorption, the catalytic activity of Pt@Au might be enhanced due to the spillover of H atoms from Pt to its neighboring Au atoms. From the energetic point of view, the spillover of H atoms with a high coverage of H atoms on Pt atoms would be possible [121]. As a result, the intermediates could be readily

removed from the central Pt atoms, and the high reactivity maintained for the decorated Pt@Au nanoparticle.

5.2. Density of states study

DOS is a function of energy describing the number of per each energy level which are available to be occupied, per unit volume of material.

In theoretical calculations, the adsorption properties explicitly depend on chemical composition of the surfaces, with the purpose to predict and design the novel catalysts reactivity towards certain reaction, for which a good parameter that may give the binding energies of various intermediates adsorbing on different metal surfaces.

Based on DFT calculations, the adsorption behavior on a metal surface can be calculated by the interaction of the relative adsorbate orbitals with the metal surface orbitals [163, Hammer and Nørskov, 1994]. They pointed out that the moment of the d-orbitals (and center) could be a universal parameter for the adsorption on metal surfaces. They have proposed a two level orbital mixing model to study the adsorbates and the transition metal surfaces. Adsorbate orbitals are first broadened by the interaction with the metal

surface and then are split by the band which represents the interaction [137]. However, the interactions of the adsorbates with the surface depend on the nature of the adsorbate and the surface metal. Therefore, the adsorption behavior of different adsorbates on various surfaces in different metals (or alloys) can be well predicted, with only a few exceptions [138].

There are two important factors which determine the structure of the bimetallic surface slab. First is called the strain effect. In different surface bond lengths between the adsorbates on the surface. Since the adsorbates are pseudomorphic adlayer on slab surface, the constant of the substrate, this effect is called the strain effect. When the metal slab through the overlapping of the orbitals is expanded parallel to the surface, when the surface is subjected to tensile strain, the overlap between the orbitals of the metal atoms is decreased, resulting in a narrower band of the metal d-orbitals. This causes the states move up in energy to keep the occupancy of the antibonding states created by adsorption would be lower, leading further to a stronger adsorption. Conversely, when the surface is subjected to compressive strain, the overlap between the orbitals of the metal atoms are increased, resulting in a broader band of the metal d-orbitals, leading to a weaker adsorption compared to those of the parent metal.

The second factor, termed as the ligand effect, comes from the two metal atoms. The presence of the other metal atoms around the Pt atom would change its electronic environment. The electronic structure of Pt would be modified accordingly. This could also be explained by the electronegativity difference between the elements. The Pauling electronegativity of Pt and Au are 2.28 and 2.54, respectively [22]. When Pt and Au combine to form Pt@Au, electrons would flow from Pt to Au until the chemical potentials become equal. Therefore, when Pt is adsorbed on Au, the Pt adatoms on the Au surface will make Pt adatoms in the decorated Pt@Au surface more difficult to be adsorbed. The surface energy of Pt@Au will be lower than that of pure Pt, so the Pt adatoms will be more stable on the Pt@Au surface than on the pure Pt surface. Therefore, the Pt adatoms will be more stable on the Pt@Au surface than on the pure Pt surface.

Here, in this thesis, we will use the DFT calculation to justify the binding properties of the decorated Pt@Au slabs calculated by the DFT study. This could further provide insight on our experimental results, especially CO stripping. The experimental results show that the CO stripping potential on the Pt@Au electrode is lower than that on the pure Pt electrode. This is related to the binding energy of CO on each electrode surface.

As discussed in the previous chapter, the CO adsorption on the decorated Pt@Au electrodes could be categorized by the Pt coverage on the substrate. There are two main factors affecting CO adsorption properties: whether the deposited Pt atoms are in monolayer or in multilayer atoms.

range(2) within monoatomic height range, whether or not isolated.

We first checked the center for the shell Pt@Au slab surface with different Pt overlayer thicknesses to accomplish this, a six (2x2) supercell Au (100) facet was used as a 1ML substrate. Pt@Au (100) models describe the adsorption section, the Au four layers in the slab were replaced by Pt atoms, while the Au atoms in the bottom two layers were kept unchanged. In this way, pseudomorphic inverse Au lattice constant. During geometry optimization, the bottom two Au layers fixed their positions in the top four layers were allowed to be fully relaxed. By doing so, core-shell Pt@Au surfaces with different Pt shell thicknesses (1-5 layers) modeled

The calculated d-band center results in Table 53, the results of pure and Au slabs with the same supercell comparison

Table 53. Calculated d-band center for the surface atoms of the slabs with different number of layers on the Au (100) surfaces

(100) slab	Pure	1ML Pt@	2ML	3ML	4ML	Pure
d-band cen	-2.36	-1.654	-2.17	-2.28	-2.24	-3.26

As could be seen, for the calculated Pt@Au samples, we subjected to tensile strain by adopting the lattice constant. The d-orbital overlap decreased, resulting in a band appearing at the center positively shifted in its average energy. Compared with this positive shift, the band for the monolayer Pt@Au slab becomes smaller when the number of layers increases. From the second adlayer, the Pt adatoms in the overlayer behave more like a monolayer on a Pt@Au substrate. This means that the strain effect increases with the number of adlayers, which is consistent with the previous DFT studies [179].

After that, we calculated for the decorated Pt@Au surface with varying the monolayer Pt surface coverage. Besides the previous four slab surfaces which described Pt@Au adsorption section, i.e., 1 ML Pt@Au and 0.11 ML Pt@Au, we used a (3×3) supercell size (100) face model, we also used a (2×2) supercell size (100) face model for 0.25 ML, 0.50 ML and 0.75 ML Pt@Au surface. In this way, we simulated different Pt surface coverage. Although it may not be appropriate to compare the calculated results with the experimental data, we have checked the calculated CO binding energies for the Pt@Au surface with different supercell size. Results showed negligible differences between the

found (not shown here). Therefore, we compared the results of the calculations on the (2x2) supercell models with confidence.

The calculated E_{ads} for the series of decorated Pt@Au surfaces are listed in Table 5.4. The binding energies for CO adsorption on the surface were also listed for comparison. Keep in mind that the calculation of DOS on the grid points (up to $12 \times 12 \times 12$) could be only accomplished on the model with smaller supercell sizes. The results listed in Table 5.4 were all based on the (2x2) supercell size model. The 0.11 ML Pt@Au model.

Table 5.4. Calculated and center CO binding energies of decorated Pt@Au (100) surfaces with different Pt surface coverages.

(100) slab	d-band center Single Pt atom	Two neighbor atoms ensem	CO BE (eV)
Pt	-2.387	-2.387	-2.10
1 ML Pt@Au	-1.650	-1.650	-2.54
0.75 ML Pt@Au	-1.614	-1.603	-2.45
0.50 ML Pt@Au	-1.687	-1.687	-2.44
0.50 ML Pt@Au	-1.674	-2.323	-1.96
0.25 ML Pt@Au	-1.839	-2.548	-1.87
0.11 ML Pt@Au	-1.764	-2.493	-1.87
Au	-3.289	-3.289	-0.62

Here in Table 5, we have listed the calculated different surface atom environments in the first type and the second type neighboring atoms of the binding sites referred to the most stable bounded surface atoms or contained at least one active atom where it was applicable.

As could be seen, for all the surfaces, i.e., Pt atom on the Pt@Au slab surface, the data computed were compared to the pure Pt slab; while on the other hand, the differences of Pt atom ensemble decorated Pt@Au with different surface coverages were relatively compared to the pure Pt slab. Therefore, the unique trends should be mainly assigned to the strain effect; while the differences between the decorated surfaces means that the different neighboring atom environment only plays a minor role in the electronic structure of the decorated Pt@Au surface.

The trend for the two ensembles was different from the single ensemble. The results showed that the atom ensemble were shifted with increasing Pt surface coverage.

Nørskov et al.^{22, 23} illustrated that when finding the binding site, the bond center should be calculated where the atom is studying adsorption. Since mainly adsorption on the (100) face of the surface in the bridging configuration with two neighboring

atoms, we therefore do not intend to further discuss the CO behaviors on the decorated Pt@Au surface.

As could be seen in Table 5, the band centers for the decorated slabs with low Pt surface coverage (0.41 ML and 0.25 ML) are more negative compared to the pure Pt slab, while for the slabs with surface coverage (0.75 ML and 1 ML) are positive than Pt. These results are consistent with our calculated CO adsorption results and the band center theory. This is in accordance with our experimental results: the CO bond strength becomes stronger when Pt surface coverage increases and the CO bond strength is weakened when Pt surface coverage is extremely low.

One special case is the 0.50 ML Au/Pt slab model, where two possible structures are shown in Fig. 5. For the slab with neighboring Pt atoms (denoted as, the gca) calculated values are similar to that of high surface coverage slabs, and the CO adsorption energy is weaker than the pure Pt slab. However, for the slab with diagonal Pt atoms (denoted as, the gcb) calculated values are similar to the low surface coverage slabs, while the CO adsorption energy is the same as that on the pure Pt slab with the same atop on Pt configuration.

neigh.

diag.

Figure 5. Two types of 0.50 ML Pt@Au surface

The above discussion indicates that whether the Pt atom may ensemble with its neighbor is critical when considering the properties on the decorated Pt@Au slab.

However, 0.50 ML Pt@Au is only the case of (100) facet surface. Considering the reality, there are hundred surface facets on a particle, where the thermodynamic possibility of various configurations exists. For neighboring atoms, the cohesive energy of Pt element is 4.23 eV. Therefore, the key parameter considers CO adsorption property on the decorated Pt@Au surface of the isolated atoms within Pt adatoms is possible to be affected the bond strength when the ratio of the number of Pt and Au atoms is

Now, we could finally answer the question from the CO stripping experiments and give the CO adsorption on the Pt@Au surfaces based on our DFT calculations.

For the series of Pt@Au samples, within the monolayer range, when the Pt surface coverage is extremely low, the

are mainly isolated. -CO bond strength is weaker than electrode consequently, CO oxidation peak potential is negative compared with Pt. With the increasing Pt surface coverage, the Pt adatoms decreases while the ones substituted by Pt neighboring atoms gradually increases and becomes the majority. -CO bond strength becomes stronger while the CO oxidation peak potential becomes more positive than the Pt electrode. As Pt coverage increases, Pt adatoms would deposit on the first Pt multilayer structure. The Pt adatoms in higher layers would behave more likely to be the pure Pt electrode. CO oxidation peak potential starts to approach the Pt electrode.

5.3 Au@Pt series

Three slab models of four-layer (3x3) supercell were used to simulate the Au@Pt surfaces. The first one is 1 ML Au@Pt (100) slab (Au surface) to simulate the decorated Au@Pt surfaces with extremely low Au surface coverage. The second one is the 0.88 ML Au@Pt slab (Au surface) to simulate high Au surface coverages to ensure the existence of the Pt surface. The third one is the 1 ML Au@Pt slab to simulate the situation with the entire electrode surface.

Since they just replicated the Au@Pt series, the trends between the Au@Pt slabs would only be discussed briefly instead of individually listed.

The calculated results (binding energy, desorption energy) are listed, with the most stable configuration of the slab shown in Figure 5.8.

Table 5.6 listed the calculated BEs of the most stable configuration of the adsorbates on different Au@Pt surfaces. The results of the 1ML slab were also listed as an indication. The calculated reaction free energy of the proposed reaction was also listed in Table 5.6.

As could be seen from both of the energy profiles, the reaction energy of 0.11ML Au@Pt is almost the same as pure Pt because this of the tested intermediates adsorbs with the most favorable bidentate PtPt bridge configurations under the current conditions, which indicates that the small amount of Au adatoms or isolated Au atoms do not change the FAO reaction adsorption properties of the Pt surface. This could be also partially seen from our experimental results, Figure 4.6. For the 48% and 72% Pt surface covered Au@Pt electrodes, the oxidation peaks II were almost the same as that of the Pt electrode, which means that small amount of Au impurities on Pt substrate do not change the situation of the intermediates that is required for the FAO reaction. The dehydrations could be accomplished without any suppression of the reaction.

Like the pure Au slab, all the intermediates adsorb on the Pt surface with relatively high binding energy. For intermediates O, OH and HCOO, the BEs on the 1ML Au@Pt would be weaker than those on Au slab,

This is because the Au adlayer is under compression due to the smaller lattice constant, and the relatively weaker interaction between the adlayer and the substrate can be explained by the center theory. However, on the other hand, for the interaction between the adlayer and the substrate, their calculated values are almost the same compared with the pure Au surface, which indicates that although the electronic properties are slightly different, the strain effect is not as pronounced as it is in the case of Pt adatom on Au substrate.

The calculated adsorption energies of the adsorbates on 0.88 ML Au@Pt surface are slightly weaker than those on pure Au surface, even when comparing the slabs with the same coverage on the surfaces, for the calculated adsorption energies of the adsorbates on 0.88 ML Au@Pt surface are slightly weaker than those on the 0.11 ML Pt@Au surface (Table 5.1). This could also be explained by the fact that the isolated Pt central atom is the active site for both of the two reactions in the interval, (the inner Au atoms in the 0.11 ML Pt@Au slab are not involved in the FAO reaction compared to pure Pt surface, it is reasonable to think that the 0.88 ML Au@Pt surface might be even better than the pure Au surface). We could also get the same deduction from the calculated reaction enthalpies from the thermodynamic point of view.

As shown in Fig. 5.5, the slightly endothermic property of step (1) for the reaction of the species HCOO is thermodynamically unfavorable on the 0.88 ML Au@Pt surface. Except for step (1), the other steps are all exothermic. Therefore, the proposed FAO reaction is overall exothermic. Especially for step (2), the reaction is highly exothermic.

CO is formed by the active intermediate COOH oxidation reaction, which is exothermic compared to the slightly endothermic reaction on the Pt@Au slab (Table 52). This results in exothermic COOH oxidation on the Pt@Au slab, which implies that the formation of COOH is favored by the active intermediate COOH oxidation process. This is also observed on the 0.11 ML Au@Pt slab. Indeed, during the FAO experiment, as shown in Figure 47, the current density for the Pt@Au electrode is higher than that of the Pt surface throughout the entire cyclic potential range.

The calculated center for the surface ensembles on the Pt@Au slab is shown in Table 57.

Different from the Pt@Au series, where the surface ensembles are notably shifted to the center compared to its parent Pt slab, in the Au@Pt series, the surface ensembles remain unchanged as its parent Au slab, which is related to the chemical inert property of the nobler Au. The Au orbitals hardly interact with Pt orbitals.

For the 0.11 ML, 0.25 ML and 0.50 ML (neighboring Pt atoms) Au@Pt slabs, the calculated center for the single Pt atom and the two Pt neighbors is also well as the CO adsorption energy is most unchanged compared to the pure Pt surface. This indicates that the Pt atoms on the Au surface can hardly modify the electronic structure of the Pt atoms. Our DFT results are also consistent with the experimental results.

no difference could be observed between Pt and the Au@Pt surface [Fig. 46]

For the 0.50 ML (diag.), 0.75 ML and 0.88 ML Au@Pt slabs, all isolated Pt atoms and surface Pt atoms are shifted compared to the pure Pt slab, due to the ligand Au atoms. However, the difference between the series with its parent ("Pt" or "Au") is much smaller than the differences of the single Pt surface Pt@Au series with Pt shown in Fig. 54). This again indicates that the strain effect in Pt atoms, while ligand effect [230] is not so pronounced

Same as Pt@Au for the 0.50 ML (diag.), 0.75 ML and 0.88 ML slabs, the band center for the bonding atoms is shifted due to the intimate contact of the neighboring Pt atom. All calculated BEs for these slabs are higher than the pure Pt slab. This indicates that whether the Pt is surrounded by another neighboring atom to form the surface ensemble is crucial when calculating and/or Feasibility of the surface.

Table 5. Calculated ΔG for the steps in the proposed network (Figure 4) on Au@Pt (100) surfaces

Reaction step	Pt	1ML Au@	0.11M	0.88M
(1) $\text{HCOOH} + \text{H} \rightarrow \text{HCOO} + \text{H}$	-0.31	0.68	-0.30	0.05
(2) $\text{HCOOH} + \text{H} \rightarrow \text{HCO} + \text{OH} + \text{H}$	-0.71	0.71	-0.76	-0.42
(3) $\text{HCOO} + \text{H} \rightarrow \text{HCO} + \text{OH} + \text{H}$	-0.31	-0.34	-0.35	-0.55
(4) $\text{COOH} + \text{H} \rightarrow \text{CO} + \text{OH} + \text{H}$	0.14	-0.38	0.10	-0.08
(5) $\text{COOH} + \text{OH} \rightarrow \text{CO} + \text{H}_2\text{O}$	-0.31	0.92	-0.34	-0.02
(6) $\text{COOH} + \text{H} \rightarrow \text{CO} + \text{OH} + \text{H}$	0.49	-1.29	0.45	-0.05
(7) $\text{HCOOH} + 2\text{H} \rightarrow \text{HCO} + \text{H}_2$	-0.64	0.34	-0.66	-0.49

Table 5.6. Calculated BEs (eV) for the most stable complexes of adsorbates on atop, bridge and hollow sites of Pt (100) and 1ML Au@Pt (100) and 0.11ML Au@Pt (100) and 0.88ML Au@Pt (100). Adsorbates which have multiple C atoms, HCOOCOOH adsorbs preferentially to the central atom (underlined C) as it was mainly interacting with the metal slab.

Adsorbate	Pt (100)			1ML Au@Pt (100)			0.11ML Au@Pt (100)			0.88ML Au@Pt (100)		
	Atop	Bridge	Hollow	Atop	Bridge	Hollow	Atop	Bridge	Hollow	Atop	Bridge	Hollow
H	-2.7	-2.90	-2.51	-2.0	-2.26	-1.99	-2.7	-2.90	-2.52	-2.6	-2.72	---
O	-3.1	-4.30	-3.69	-1.7	-2.66	-2.58	-3.1	-4.29	-3.70	-3.1	-3.48	-3.32
<u>C</u> O	-1.9	-2.10	-1.53	-0.5	-0.57	-0.27	-1.9	-2.08	-1.53	-1.8	-a	-a
<u>O</u> H	-2.5	-3.05	-2.33	-1.8	-2.15	-1.86	-2.5	-3.03	-a	-2.4	-2.53	-1.91
<u>C</u> O O H	-2.7	-2.37	-a	-1.5	-a	-b	-2.6	---	---	-2.3	-a	---
<u>C</u> O O H	-2.7	-2.43	-a	-1.6	-a	-b	-2.7	---	---	-2.3	-a	---
H <u>C</u> OO	-2.6	-a	-b	-1.9	---	---	-2.6	---	---	-2.2	---	---

^a All the initial configurations and other configurations after optimization were unstable.

^b The adsorbate complex after optimization.

Table 57. Calculated d-band center and CO binding energy series decorated Au@Pt (100) surfaces with different Au coverages. The data in bracket in the d-band center of the particles surfaces embel the meanings of subscript, i.e., Pt and Pt₂ were the same as discussed in Pt@Au series.

	d-band center (100) slab surf	Single atom Two neighb atom enser	CO BE (eV)
Pt	-2.387	-2.387	-2.10
0.11 ML Au@Pt	-2.344 (Pt) -2.38 (Pt ₂) -3.14 (Au)	-2.370 (Pt) -2.770 (Pt ₂)	-2.08
0.25 ML Au@Pt	-2.319 (Pt) -2.35 (Pt ₂) -3.15 (Au)	-2.337 (PtPt) -2.778 (PtAu)	-2.10
0.50 ML Au@Pt	-2.33 (Pt) -3.22 (Au)	-2.332 (PtPt) -2.804 (PtAu)	-2.11
0.50 ML Au@Pt	-2.25 (Pt) -3.06 (Au)	-2.696	-1.82
0.75 ML Au@Pt	-2.19 (Pt) -3.15 (Au) -3.29 (Au)	-2.710	-1.89
0.88 ML Au@Pt	-2.22 (Pt) -3.20 (Au) -3.28 (Au)	-2.750	-1.89
1 ML Au@Pt	-3.266	-3.266	-0.58
Au	-3.289	-3.289	-0.62

Figure 58. Side view of the most stable adsorption configurations of formic acid on Au@t and 1.1MLAu@t (100) surfaces. For clarity, only the HCOOH molecules are shown here.

5.4 Conclusions

In this work, we systematically studied the adsorption properties of formic acid and its possible intermediates on Pt@Au and the Au@Pt series, Pt@Au 1ML, Pt@Au 8ML, Au@Pt, 0.11ML Au@Pt, 1ML Au@Pt and Au slabs, under DFT basis.

For the Pt@Au series, Pt@Au surface can not possess better activity toward FAO. Activity could be expected for the Pt@Au (100) surface compared with the benchmark pure Pt (100) surface.

By DOS calculation, we can be well applied to the adsorption on these metal surfaces. By comparing results with Au@Pt series, we can conclude that the strain effect is of minor contribution while the ligand effect only has a minor influence on the electronic structures. With the help of DFT, the relationship between adsorption and the decorated surface structures is completely explained.

According to DFT results, we can interpret the oxidation and/or FAO reactivity of the Pt-based surfaces. The surface Pt atoms are the surrounding foreign metal atoms. The neighboring Pt atoms on the Pt surface are the key parameters. This is also a lateral proof of the effect of FAO reaction.

However, this part of DFT is a striking point; it is far not enough understood although the EAO reaction taking place on electrocatalytic surfaces need to be done.

Chapter 6 Conclusions, limitations and recommendations for future works

6.1 Conclusions

In this thesis, we tried to combine the experimental and DFT calculations together to get a profound understanding on the mechanism as well as the dramatic increased FAO reactivity of electrocatalysts with significant reduced Pt usages.

Through the anode stripping method, Pt nanosized core decorated Pt@Au electrocatalysts could be prepared by the replacement techniques as a facile synthesis.

The adsorption properties of possible intermediates on (100) of Pt@Au and Au@Pt have been systematically studied by DFT calculations.

Based on the results from thermodynamic point of view, the core-shell structured Pt@Au catalyst cannot possess inactivity compared to pure Pt electrode; while the decorated Pt@Au surface coverages are expected to have better reactivity.

Through DOS calculation, strain effect is of mainly concern on the electronic structures of these bimetallic surfaces; while the dominance for FAO reaction taking place on the Pt base

With the help of DFT calculations, the relationship between the properties of the decorated Pt@Au surface structure and the CO adsorption properties of the decorated Pt@Au surface structure is satisfactorily explained. Different CO stripping experiment results showed that the U-Redox replacement technique as the decorated Pt@Au electrode synthesis method.

Our results show that the Pt sites adsorb CO on the surface ensemble with high binding energy. This is a key parameter for CO oxidation, which is a lateral proof of the ensemble definition for CO oxidation. The activity of the Pt sites is also based on the activity of the Pt sites.

6.2 Limitations

The limitations of this work are very clear.

Experimentally, through the U-Redox replacement technique, although we can synthesize the decorated Pt@Au/C electrocatalysts with high Pt coverages on Au substrate, however, the calculation for the CO stripping method is limited to Au substrate only. This is due to the feature of Au element which has no characteristic adsorption potential, resulting in almost constant current in a broad potential region for Au substrate, which can be simply detected from the current.

As we have discussed in the Pt electrocatalysis section, the failure of UPD to replace the anode stripping method is just because of the interference of hydrogen adsorption on the same problem exists when Pd is used as a substrate for the anode stripping method applicable to calculate the coverage of Pd. Cyclic voltammetry on more complex surfaces [164] is not a fundamentally electrochemical approach. Rotating disk electrode (RDE) [232, 235] and/or electrochemical quartz microbalance (EQCM) [236, 237] techniques are needed for the calculation of UPD adlayer surface coverage for these

Although we can say that we have directly proved the FAO reaction mechanism, it is only a lateral proof of the current results. Based on the adsorption DOS calculations, we pointed out the relationship between the adsorption ensembles on the metal slabs. However, the specific reaction pathway is still under discussion. There are still many things unclear for FAO. For example, what is the direct H₂O oxidation pathway; what is the requirement of adsorption ensembles to complete the direct FAO pathway? for this direct oxidation pathway on the slabs with different adsorption ensembles? All of these questions cannot be answered by thermodynamic analysis results. Thermodynamic calculations

Another limitation for the current DFT analysis is the

We are actually not able to model electrochemical reactions which occur on the solid-liquid electrolyte interface due to the electric field intensities. However, the slab model is not affected much with any influence of electric field.

We have also tested the adsorption properties of the electrode under electric field (results shown in Table 1). The results show that the electric field has negligible influence on the adsorption properties consistent with previous literature [23]. However, this is not enough to simulate the real electrochemical experiment.

So far to our best knowledge, the literature which focuses on this topic, mainly due to the extreme difficulty to calculate the five electron decomposition reaction under the electrochemical conditions. One plausible work has been done by Neurock et al. in 2008 but with many statements in [5] which are further reports.

6. Recommendations for future works

Since we have shown that the current DFT is not a powerful and attractive approach for the fundamental analysis of the surface from DFT first.

Followed by limitations discussed, we have two important topics to be urgently continued to calculate the adsorption properties of metal slabs (primarily pure Pt) under the electrochemical condition. In the slab model under various electric fields, it is necessary to consider at least two model layers in the slab. Therefore, we calculate the transition state as well as the activation barrier for each slab surface through the nudged elastic band method (NEB). It is possible to find reaction steps in FAO and identify possible initial states. All of them completely may start from CO oxidation reaction.

Our ultimate objective is the combination of these two topics: transition state and the activation barrier for each reaction on metal slabs under electric field. Only the existence of H

Many researchers have illustrated that activity differs on different facets both experimentally and theoretically [23-24, 51]. Especially, the high-index facets always possess higher reactivity than the low-index facets [11, 22, 52]. Therefore, it would be very interesting to perform calculations, at least to the complex (111) facet.

Another important theoretical calculation is that it can point out the way which leads to the experimental synthesis of novel catalysts. In this case, we intend to calculate the activation barrier for adsorption and desorption of CO on different facets for the prediction

Since we have that Pd@Au possesses stronger adsorption properties compared with Pt the enlarged lattice constant mainly is not affected by the strain, as simple deduction from the atomic size of Au and Pd possess weaker adsorption properties when the strain is relieved. This is not only for the FAO or CO oxidation reaction applications, e.g., ORR and glucose oxidation has been pointed out by Nørskov et al. [134, 137] it has been applied in various electrocatalytic systems, Pt@Pd@Ni, Pt@Pd@Au@Ni, Pt@Pd@Co [74, 75, 107, 109, 140] and by ORR application beyond those, there are still other possible metal elements which have a lattice smaller. Therefore, of course we may synthesize the decorated bimetallic Pt@M or trimetallic Pt@M₁@M₂ (possibly Fe, Co, Ni, Cu, Zn, Mo, Ru, Rh, Pd, Pt, Os, and Ir) as catalysts with appropriate alloy composition, which may not be constrained by the electrodeposition technique. Instead, other methods or even physical methods, e.g., sputtering method, [253, 254] used

Alternatively, we may still synthesize the decorated Au (e.g., Pd@Au, Ag@Au and Ru@Au) with preselected surface coverages via electrodeposition technique under different conditions

References

1. Mohan, D., C.U. Pittman, Pandy P.S. *J. Electroanal. Chem.*, 1973, 20, p.688-698
2. Pimentel, D.F. *Oxidation and Reduction of Organic Compounds*, 1973. (18(24111)): p.444-43
3. Markovic, N.M. *ELECTROOXIDATION MECHANISMS OF METALS AND FORMETIC ACID ON METAL SURFACES*. *Chemica Acta*, 1999, 4(1): p.98-1
4. Rice, C., Direct formic acid fuel cell power sources (1992). p. 889.
5. Capon, A. and R. Oxidations of Alcohols at Metal Electrodes Part .3. Intermediates and Mechanisms. *Electroanalytical Chemistry*, 4(1973) p.-2315
6. Capon, A., and R. Oxidations of Alcohols at Metal Electrodes .2. Comparison of Behavior of Pure Elements and Alloys. *Electroanalytical Chemistry*, 1973(42): p.-2349
7. Capon, A. and R. Oxidations of Alcohols at Metal Electrodes .1. Review of Previous Work. *Electroanalytical Chemistry*, 1973(41) p.-2315
8. Capon, A. and R. Oxidations of Alcohols at Metal Electrodes .4. Platinum + Palladium Alloys. *Electroanalytical Chemistry*, 1973(45) p.-2305.
9. Kristian, N., Y.S. Yan High yield heterogeneous Au nanocatalysts for formic acid oxidation. *Communications*, 2008, 35355.
10. Kristian, N. Controlled synthesis of Pt nanostructure and its promoted activity toward formic acid oxidation. *Chemica Acta*, 2009, 54(21): p.-4492146
11. Tian, N., Synthesis of tetrahedral platinum nanocrystals with high electrocatalytic activity. *Science*, 2008, 321(5825): p.733-732
12. Gasteiger, H.A. *ELECTROOXIDATION OF CARBONACEOUS MATERIALS*. *Journal of Physical Chemistry*, 1994, 98(2): p.621-694.
13. Iwasita, T. Electrocatalysis of methanol oxidation. *Catalysis*, 2002, 47(223): p.-3654.
14. Wasmus, S. and M. Kärner, oxidation and direct methanol selective removal of Electroanalytical Chemistry, 1999, 46(12): p.1114, 1999.
15. Khosravi, M. and M. Karimipour, PdAu catalysts prepared by Cu underpotential-redox deposition and investigation of electrocatalytic activity for methanol oxidation and oxygen reduction. *International Journal of Hydrogen Energy*, 2011, 36(19): p.10523-10533.
16. Liu, Y., et al., Active Carbon Supported PdAu Catalyst for Methanol Electrooxidation and Study of Kinetics. *Physical Chemistry Chemical Physics*, 2011, 13(4): p. 2141-2142.

17. Yan, L.L., Electrochemical Oxidation of Formic Acid on Pt Nanosphere Modified Glassy Carbon Electrode. *Journal of Electroanalytical Chemistry* 425 (1997): p. 237-242.
18. Zhang, H.X., Carbon-Supported Pt Nanoalloy with Low Pt Content for Superior Catalysis for Formic Acid Oxidation. *Journal of Physical Chemistry C* 114 (2010): p. 6445-6451.
19. Zhang, S., Electrostatic Assembly of a Pt Nanocomposite with High Activity towards Formic Acid Oxidation. *International Journal of Electrochemistry* 4 (2012): p. 222-231.
20. U.S. Department of Energy, Fuel Cell Handbook, 7th ed. 2004.
21. Vielstich, W., A. Lamm, and H. A. Gasteiger, Fuel cells: fundamental technology, and applications. Wiley, 2003.
22. Meibuhr, R. Review of United States fuel cell technology. *Electrochimica Acta* 35 (1990): p. 163-168.
23. Costamagna, P. and S. J. V. S. in the PEMFC science and technology from the 1960s to the year 2000 Part I. *Journal of Power Sources* 102 (2001): p. 261-262.
24. Costamagna, P. and S. J. V. S. in the PEMFC science and technology from the 1960s to the year 2000 Part II. *Journal of Power Sources* 102 (2001): p. 263-269.
25. Prater, R. Bymer Electrochemical Fuel Cells. *Journal of Power Sources* 51 (1992): p. 119-124.
26. Parsons, R. and T. T. Van Der Vliet, A Survey of Recent Fuel Cell Research. *Journal of Electroanalytical Chemistry* 25 (1972): p. 45-59.
27. Litster, S. and B. E. M. Fuel cell electrocatalysis. *Power Sources* 13 (2002): p. 76-101.
28. Wang, C. N. T. tuned to provide electrocatalysis. *Journal of Power Sources* 102 (2001): p. 261-262.
29. McNicol, B.D., D.A.J. Rand, and K. R. Neill, Fuel cells for road transport. *Journal of Power Sources* 31 (1991): p. 319-329.
30. Hamnett, A. Mechanism and electrocatalysis in the direct oxidation of formic acid. *Catalysis Today* 34 (1997): p. 445-455.
31. Gilman, T. S., Mechanism of Electrochemical Oxidation of Carbon Monoxide on Platinum. II. The Role of Surface Adsorbed Methanol in the Electrochemical Oxidation of Carbon Monoxide. *Journal of Physical Chemistry* 66 (1962): p. 960-970.
32. Hable, C.T. and M. S. L. in the Electrochemical Oxidation of Methanol on a Comparison of Pt and Pt-Ru Catalysts. *Journal of Physical Chemistry* 101 (1997): p. 3322-3330.
33. Liu, H.S., A review of anode catalysis in the direct oxidation of methanol. *Power Sources* 15 (2000): p. 1-15.

34. Wang, K., On the reaction pathway for methanol and CO electrooxidation on Pt alloy versus alloy surface factors. *chimica Acta*, 1996, 116): p.-2259837.
35. Watanabe, M. and Chisimoto, M. Adsorbed CO on a polycrystalline platinum electrode. The effect of conditioning of the surface. *Journal of Electroanalytical Chemistry*, 2006, 121): p.12086.
36. Watanabe, M. and Chisimoto, M. Electrochemical oxidation of CO on Pt. Part III. Enhancement of the oxidation of carbon monoxide on a platinum electrode by oxygen. *Electroanalytical Chemistry*, 60(3):5p.-2375
37. Wieckowski, A., E.R. Savinova, and G. Wang. *Electrocatalysis by Nanoparticles*. 2003. CRC Press Taylor & Francis Group.
38. Chen, Y.X. Bridged formate: Active intermediate species in formic acid oxidation on a Pt electrode. *Journal of Electroanalytical Chemistry*, 2005, 1039:408.
39. Chen, Y.X. Kinetic isotope effects in complex reaction networks in electrocatalysis. *Chemphyschem*, 6(3):20073350
40. Chen, Y.X. Application of attenuated total reflection infrared spectroscopy for the understanding of complex kinetics: Formic acid oxidation on a Pt film electrode. *Journal of Physical Chemistry B*, 2005, 109:1344.
41. Gasteiger, H.A., Electrooxidation of Small Organic Molecules on Pt. *Characterization of Pt Electrodes*. *Electrochimica Acta*, 1994, 39:1825832.
42. Mukoyama, Y. Potential oscillations in galvanostatic electrooxidation of formic acid on platinum: A mathematical modeling. *Journal of Physical Chemistry B*, 2004, 108:1912.
43. Samjeske, G.M. Mechanistic study of electrocatalytic oxidation of formic acid on platinum in acidic solution by surface-enhanced infrared absorption spectroscopy. *Journal of Physical Chemistry B*, 2005, 109:120566.
44. Samjeske, G.P. Potential oscillations in galvanostatic electrooxidation of formic acid on platinum. *Surface-enhanced infrared absorption spectroscopy*. *Journal of Physical Chemistry B*, 2005, 109:3506.
45. Samjeske, G. and C. W. Constant oscillations during formic acid oxidation on a Pt electrode: Insights from in situ IR spectroscopy. *Chemical Communications*, 2005, 14:135): 200556984.
46. Tripkovic, A.V. Formic acid oxidation on Pt/Ru nanoparticles: effect of current. *Research in Advanced Materials*, 2005, 4:223P.
47. Capon, A. and R. H. The oxidation of formic acid at noble metals. Review of previous work. *Electroanalytical Chemistry*, 1977, 14:1).
48. Capon, A. and R. H. The oxidation of formic acid at noble metal electrodes. III. Intermediates and mechanism. *Journal of Electroanalytical Chemistry*, 1977, 41:27:3p.-2305

- [illegible]

- 139

81. Turkevich, J. and Palacki, R. Preparation and Catalytic Properties of Uniform Gold Nanoparticles of Uniform Size (Science 1957(93948): p.7973)
82. Schmid, G. Light-stabilized Bimetallic Colloids Identified by X-ray Photoelectron Spectroscopy. Angewandte International Edition in English 1991, 30(7): p.8764-8769.
83. Bonnemann, H. and Rindfleisch, R. Synthesis of Bimetallic Nanoparticles by Electrochemical Methods. Journal of Inorganic Chemistry 1991, 245(2): p.245-250.
84. Gregory, B.W. and Jelenko, J. Electrochemical Atomic Layer Epitaxy. Journal of Electroanalytical Chemistry 1991, 300(1-2): p.5-13.
85. Penner, R.M. Microscopic metal particles and wires by electrochemical deposition. Physical Chemistry 1991, 63(2): p.233-239.
86. Kim, Y.G., Park, J.H., and Lee, J.H. A study on the replacement of UPD copper by electrochemical deposition of copper. Physical Chemistry B 1998, 2(10): p.1899-1908.
87. Bauer, E. and J.H. Staudt. Growth of Crystalline Silver from Monolayer to Bulk. Surface Science 1981, 100(1-2): p.367-371.
88. Mrozek, M.F., Y. Xie, and S. M. Albrecht. Raman scattering of uniform platinum overlayers: Preparation by redox reaction under potential. Analytical Chemistry 1991, 63(12): p.5953-5960.
89. Kokkinidis, G. Underpotential Deposition and Electrodeposition. Electroanalytical Chemistry 1986, 20(12): p.2367-2376.
90. Engelsmann, K., W.J. Lorenz, and P. H. Schlemmer. Deposition of Lead on Polycrystalline Gold Surfaces. 1. The Kinetics. Journal of Electroanalytical Chemistry 1980, 110(1): p.1-10.
91. Engelsmann, K., W.J. Lorenz, and P. H. Schlemmer. Deposition of Lead on Polycrystalline Gold Surfaces. 2. The Kinetics. Journal of Electroanalytical Chemistry 1980, 110(2): p.21-30.
92. Kolb, D.M. Advances in Electrochemistry and Electrochemical Engineering. T.C.W. Gerisher H. Vol. 1. Interscience Wiley 1975, 1: p.1-10.
93. Magnussen, O.M. Atomic Structure of Ordered Copper Adlayers on Single Crystalline Gold Electrodes. Vacuum Science & Technology 1991, 9(2): p.97-109.
94. Scortichini, C.L. and S. C. N. R. Characterization of Pt Electrodeposited by Underpotential Deposition of Pt(II) on Au. Journal of Electroanalytical Chemistry 1992, 328(2): p.223-233.
95. Scortichini, C.L. and S. C. N. R. Characterization of Pt Electrodeposited by Underpotential Deposition of H and Cu. Journal of Electroanalytical Chemistry 1992, 328(2): p.234-247.
96. Scortichini, C.L. and S. C. N. R. Characterization of Pt Electrodeposited by Underpotential Deposition of H and Cu. 4. Surface Structure of the Nonequilibrium State of Hydrogen Adsorption. Journal of Electroanalytical Chemistry 1992, 328(2): p.248-255.

97. Scortichini, C.L. and S. R. Brankovic. Characterization of Pt Electrodes by Underpotential Deposition of H and Cu. *Journal of Electroanalytical Chemistry* 1977(11): p.1145.
98. Scortichini, C.L., F.E. Woodward, and C. N. Reilly. Underpotential Deposition of H and Cu on the Flame-annealed Pt(100) and Pt(111) Electrodes. *Journal of Electroanalytical Chemistry* 1978(23): p.275.
99. Herrero, E., L.J. Buller, and H. D. A. de Almeida. Underpotential deposition at single surfaces of Au, Pt, Ag and Cu. *Chemical Reviews* 1991(71): p.1897.
100. Brankovic, S.R., N. Dimitrov, and S. R. Brankovic. Underpotential deposition of Ag on Au(111). *Chemical and Solid State Letters* 1984(17): p.443.
101. Davidovic, D. and R. E. R. A. de Almeida. Underpotential deposition of Antimony Adsorbates on Deuterium-oxidized Gold. *Journal of Electroanalytical Chemistry* 1988(231): p.103.
102. McIntyre, J. and E. W. Fisher. Underpotential Deposition Effects Induced by Heavy Metal Ions. *Journal of the Electrochemical Society* 1976(123): p.1001.
103. Sieradzki, K., S.R. Brankovic, and D. R. U. de Almeida. Underpotential deposition of Au on Pt(111). *Surface Science* 1991(249): p.113.
104. Brankovic, S.R., J.X. Wang, and D. R. U. de Almeida. Underpotential deposition of Au on Pt(111). *Surface Science* 1991(249): p.113.
105. Sasaki, K. Pt monolayers on metal nanoparticles as catalysts for H₂ oxidation. *Electrochimica Acta* 2003(48): p.3843.
106. Vukmirovic, M. Pt monolayer electrocatalysts for oxygen reduction. *Electrochimica Acta* 2007(52): p.2253.
107. Zhang, J. Stabilization of platinum nanoparticles by electrocatalysts using clusters. *Science* 2009(326): p.2220.
108. Zhang, J.L. Mixed metal Pt monolayer electrocatalysts for oxygen reduction. *Journal of the American Chemical Society* 2006(128): p.12481.
109. Zhang, J.L., C. A. B. de Almeida, and J. L. Zhang. Catalytic activity of platinum electrocatalysts for oxygen reduction. *Journal of Electroanalytical Chemistry* 2004(564): p.211.
110. Jin, Y.D., Y. Shen, and E. S. J. de Almeida. Design of ultra-thin platinum-coated gold nanoparticle monolayer films as a new electrocatalyst for oxygen reduction. *Physical Chemistry B* 2006(110): p.8124.
111. Tang, H., C. A. B. de Almeida, and J. L. Zhang. Controlled synthesis of platinum catalysts on Au and their electrocatalytic property for oxygen reduction. *Applied Catalysis B* 2007(75): p.43.

112. Zhai, J.F., M.H. Huang and S. Dong, Designing of Au/Pt nanoparticles as nanostructured catalysts for oxygen reduction reaction. *Electrochimica Acta* 51(4): 2003-2006.
113. Tegou, A., Oxygen reduction and deposition of iron, cobalt, nickel and lead deposits on glassy carbon electrode. *Electrochimica Acta* 52(32): p. 1987.
114. Tegou, A., Oxygen reduction and deposition of copper deposits on glassy carbon substrate. *Electrochimica Acta* 50(8): 677.
115. Wei, Z.D., Electrooxidation of methanol on Pt and Pt modified Pt electrode. *Journal of Physical Chemistry B*, 2000, 104(15): 2606.
116. Dreizler, R. and E. S. Gyro. *Functional Density Theory*. Plenum Press.
117. Fiolhais, C., F. Nogueira, A. and M. Rei. *Functional Theory*. 2003: Springer.
118. Kohn, J. *Electronic Structure Calculations for Solids and Molecules*. Computational Methods. Cambridge University Press.
119. Sholl, D. and J. D. Steckel. *Functional Density Theory*. Introduction. 2009: Wiley.
120. Koch, W. and M.C. Alchamuste's, *Guide to Density Functional Theory*. 2 ed. 2002, Weinheim: Wiley.
121. Martin, R. *Electronic Structure: Basic Theory and Practical Aspects*. Cambridge University Press.
122. Schrödinger, E. *On the Theory of the Mechanics of Atoms*. *Physical Review* 2(6): 192. 61049.
123. Griffiths, D. *Introduction to Quantum Mechanics*. Prentice Hall.
124. Szabo, A. and N. S. Ostro. *Quantum Chemistry*. Dover Publishing.
125. Thomas, L. *The calculation of mathematical functions*. Proceedings of the Cambridge Philosophical Society. 21(55): 192. 54227.
126. Hohenberg, P. and W. Kohn. *Inhomogeneous Electron Gas*. *Physical Review*, 1964, 136(3B): p. B864.
127. Kohn, W. and L. J. Sham. *Self-Consistent Equations Including Exchange and Correlation Effects*. *Physical Review* 140(4): 1965. A1133.
128. Perdew, J.P. and A. Zunger. *Self-interaction correction to density functional approximation for atoms*. *Physical Review B* 23(1): 1992. 13244.
129. Perdew, J.P. *Atoms, molecules, solids, and surfaces: Application of the generalized gradient approximation for exchange and correlation*. *Physical Review B* 46(11): p. 6671.
130. Perdew, J.P., K. Burke, and M. Ernzerhof. *Generalized Gradient Approximation of the Density-Functional Theory of Atoms, Molecules, Solids, and Surfaces*. *Physical Review Letters*, 1996, 77(18): 3865.
131. Anderson, A.B., E. Grantscharova, and L. A. K. S. *Effect of Substitutional Sn Atoms on the Activity of Pt Anodes*. *Electrochimica Acta* 51(4): 2003-2006.
132. Anderson, A.B., E. Grantscharova, and L. A. K. S. *Effect of Substitutional Sn Atoms on the Activity of Pt Anodes*. *Electrochimica Acta* 51(4): 2003-2006.

- [illegible]

149. Kresse, G. and J. Furthmüller, Efficient iterative scheme for ab initio total energy calculations: application to silicon and germanium, *Physical Review B*, 61(19):12001-12005, 1999.
150. Perdew, J.P., K. Burke, and M. Ernzerhof, Generalized gradient approximation made simple, *Physical Review Letters*, 77(18):3865-3868, 1996.
151. Kresse, G. and D. Joubert, ultrasoft pseudopotentials to treat elements with valence d or f orbitals, *Physical Review B*, 59(10):1758-1775, 1999.
152. Monkhorst, H.J. and J.D. Pack, Efficient reduction of Brillouin zone integrations, *Physical Review B*, 13(12):5180-5181, 1976.
153. Yu, Y.L., et al., Study of Pt@Au electrocatalyst based on deposition and Pt redox electrodeposition, *Electrochimica Acta*, 111(1):309-317, 2013.
154. Perez, J., E.R. Gonzalez, and J.E. Barrios, A porous coating rotating platinum electrode for electrocatalysis, *Electrochimica Acta*, 33(1):132-139, 1988.
155. Fournier, J.H., et al., High performance, low Pt content catalysts for the oxygen reduction reaction in proton exchange membrane fuel cells, *Journal of Electrochemical Society*, 144(1):154-161, 1997.
156. Ciureanu, M. and E. Ruckenstein, Kinetic study of the oxygen reduction reaction on Pt-based diffusion electrodes, *Journal of Electrochemical Society*, 146(1):400-407, 1999.
157. Angerstein-Kozłowska, H., B.E. Conway, and R. Bockris, Electrochemical oxidation of platinum surfaces: Part I. Kinetics of the electrochemical oxidation of platinum, *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry*, 19(1):1-11, 1968.
158. Park, S., Y. Xie, and E. Ruckenstein, Kinetic study of the electrochemical oxidation of platinum nanoparticles: Comparison of the electrochemical oxidation of methanol, formic acid, and formaldehyde, *Journal of Electrochemical Society*, 155(1):1-11, 2008.
159. Manne, S., et al., Atomic Resolution Electrochemistry with the Atomic Force Microscope, *Science*, 259(5090):1868-1871, 1992.
160. Viñals, J., R. Vasilic, and E. Ruckenstein, Kinetic study of the electrochemical oxidation of Cu on Au and Ag(111) by surface limited electrodeposition, *Journal of Physical Chemistry*, 91(11):4400-4407, 1987.
161. Angerstein-Kozłowska, H., et al., Kinetic study of the electrochemical oxidation of Cu on Au(111) by surface limited electrodeposition, *Journal of Electroanalytical Chemistry*, 22(1):1-11, 1987.
162. Michri, A.A., A.G. Pshchinskii, and S. Ruckenstein, Kinetic study of the electrochemical oxidation of Cu on Au(111) by surface limited electrodeposition, *Journal of Electroanalytical Chemistry*, 22(1):1-11, 1987.
163. Martin, R., A. M. Pardo, and N. V. Bratkovskaya, Kinetic study of the electrochemical oxidation of copper on a modified Au(111) electrode, *Electrochimica Acta*, 53(15):2111-2120, 2008.

164. Holzle, M., Rettler, and D. The Kinetics of Stripping Cu Adlayers on Au(111). *Journal of Electroanalytical Chemistry*, 1999, 461(1): p. 109.
165. Vasilic, R., N. Vasiljevic, and N. Dimitrov. Stability of underpotential deposited monolayer on Cu(111). *Journal of Electroanalytical Chemistry*, 2003, 558(2): p. 223.
166. Zhou, Z.H., et al. Synthesis of highly active Pt/C cathode for direct methanol fuel cell. *Chemical Communications*, 2003(3): p. 394.
167. Casanova, E., et al. Electrochemical oxidation of formic acid on intermetallic Pt-Cu surface. *Electrochimica Acta*, 2003, 48(2): p. 319.
168. Kim, J., et al. Electrochemical oxidation of formic acid and methanol on Au(111). *Journal of Electroanalytical Chemistry*, 2007, 618(1): p. 103.
169. Schmidt, T.J.C., et al. Characterization of high area electrocatalysts on rotating disk electrodes. *Journal of Electroanalytical Chemistry*, 2003, 558(2): p. 235.
170. Wieckowski, A., and B. The World global climate change: a coordinated response by electrochemistry and solid state chemistry. *Proceedings of the first international symposium on electrochemistry*, 2001: p. 10.
171. Greeley, J., J.K. Norskov, et al. The structure and catalytic activity of metal surfaces. *Annual Review of Physical Chemistry*, 2002, 53: p. 199.
172. Demirci, U. Theoretical means for searching bimetallic electrocatalysts for fuel cells. *Journal of Power Sources*, 2003, 127(1): p. 18.
173. Ruban, A., et al. Surface electronic structure and reactivity of metal surfaces. *Journal of Molecular Catalysis*, 1997, 131(1): p. 42.
174. Hammer, B., and J. Kleinschmitt. Factors determining the reactivity of metal surfaces. *Surface Science*, 2001, 463(1): p. 52.
175. Park, S.I., et al. Surface Structure of Pt-Au Nanoparticles and its Effect on Electrocatalytic Activity in Formic Acid Oxidation. *Journal of Physical Chemistry C*, 2007, 111(20): p. 1126.
176. Kumar, S., and S. Zou. Oxidation of carbon monoxide and ethanol on platinum-coated gold nanoparticles: Effect of surface composition. *Journal of Electroanalytical Chemistry*, 2002, 531(1): p. 73.
177. Du, B.C., and Y. Yang. Temperature dependent study of Pt spontaneous deposition onto Au and Ru surfaces: Direct experimental evidence for methanol oxidation. *Journal of Physical Chemistry B*, 2005, 109(15): p. 7780.
178. Hachiya, T., H. Honbuchi, and K. Ueda. Potential deposition of gold(III) in aqueous solution. *Journal of Electroanalytical Chemistry*, 1991, 301(1): p. 29.
179. Meier, J.J., et al. Nanoscale effects in electrochemistry. *Physics Letters*, 2003, 319(46): p. 440.

180. Smith, S.P.E. and St. Ducaubraun effects on the oxidation of bismuth modified Pt(111) electrodes without (111) monat Electroanalytical Chemistry, 4(112) p. 499.
181. Smith, S.P.E., D.K.F. and H.D.S. A structural effects on the oxidation of HCOOH by bismuth modified Pt(111) electrodes with (100) monat Langmuir, 15(29) p. 7733.
182. Schmidt, T.J. Formic acid oxidation on modified Pt(111): Temperature dependence, 15(20) p. 881.
183. Jimkna, D. Nucleation and growth of Cu onto polycrystalline Cu from acidic CuSO₄ solution in the presence of H₂SeO₃ and SeO₂, Surface Science Letters, 107(2) p. 447.
184. Danilov, A.I. The influence of intermediate particles on copper on polycrystalline Pt, Electrochimica Acta, 37(7) p. 973.
185. Slater, A.C. MIC RADII IN CRYSTALS of Chemical Physics, 4(10) p. 81.
186. Huheey, J.E., E.A. Keiter, and R.L. Keiter, Principles of Inorganic Chemistry, 4th ed., 1993, New York: HarperCollins.
187. Zhan, D., J. Velmurugan, and M. Von Dröge, Adsorption of Hydrogen on Nanoelectrodes: Evidence of Surface Diffusion, Surface Science, 200(1) p. 147.
188. Macdonald, D. Recent techniques in Electrochemistry, Plenum Press.
189. Minevski, L.V. and R. Radovic, A High Surface Area Platinum Supported Platinum Modified by Iron, Journal of Applied Electrochemistry, 10(2) p. 82.
190. Hu, Q.M., K. Reuter, and W. Schaffner, A direct treatment of excitation correlation in materials: Application to the "CO adsorption" Physical Reviews, 92(1077).
191. Pedersen, M. How a gold substrate can increase the reactivity of overlayers, Surface Science, 142(3) p. 99.
192. Christensen, A. Phase diagrams for Pt-H₂, Physica Scripta, 1993, 5(10) p. 583.
193. Yue, C. and K. Hsiao, Adsorption of Formic Acid and its Decomposition on (100) Surfaces of Pt and Pd: A Density Functional Theory Study, Journal of Physical Chemistry, 102(12) p. 2226.
194. Yourdshahyan, Y. and S. A. Rapp, Kinetics of alkanethiol adsorption on the Au(111) surface, Journal of Chemical Physics, 117(2) p. 825.
195. Ford, D.C., Y. Xu, and M. Mavinkand, Molecular adsorption on Pt(111) Surface Science, 587(2) p. 51.
196. Grabow, L.C. Mechanism of the water gas shift reaction on Pt: experiments, and microkinetic modeling, Physical Chemistry Chemical Physics, 11(21) p. 4661.
197. Kandoi, S. Why Al, and Cu are more active than Pt for the oxidation of CO at low temperatures, Catalysis Letters, 3(2) p. 100.

198. Li, X., M. Wong, and K. P. Liem, Adsorption of tetralin and hydrogenated and products on the (100) surfaces of Ir₂Te₃ and Pd: a Chemistry Accounts: Theory, Computation, and Modeling (2010).
199. Greeley, J. and M. SMAfarckle and subsurface hydrogen: properties on transitions metal alloys and of Chemistry B, 2006(98): p. -3460.
200. Novelléruth, G., J.M. Ricard-Rand, and P. J. (1990) Catalyzed ammonia oxidation studied by DFT: Mechanism and of Polymeric Chemistry C1,1(2008).p. -13552.
201. Ge, .Q et al. Site symmetry dependence of repulsive interaction of chemisorbed oxygen atoms on Pt(100) Chemical Physics, 10(63): p. -1215.
202. Vassilev, P. and M. Elmroth, Chemical reduction of oxygen surfaces: A density functional theory study of intermediate Journal of Physical Chemistry C 11(16): p. 6207.
203. Baker, T.A., C.M. Friend, and E. Okun, Adsorption on A Surfaces with DFT of Physical Chemistry C 3(38): p. 22309.
204. Jelic, J. and R. J. D. M. E. Study of pseudomorphic monolayer catalysts for NOx storage reduction Catalysis Today 162(6): p. 763.
205. Hyman, M. R. and M. E. Effects of electronic structure modification on adsorption of oxygen reduction reaction intermediates surface Journal of Physical Chemistry C, 11(145): p. 12700672.
206. Kitchen, J. R. M. Modification of the surface electronic and chemical Pt(111) by subsurface 3d Journal of Chemical Physics, 12(121): p. -10246.
207. Mehmood, F. Comparative study of CO adsorption on flat, stepped and Au surfaces using density functional theory Physical Review B 79(12): p. 121405.
208. Zeinali-Yazdi, C. D. and A. M. P. Effects of adsorbed-Pt on the Mechanism of Gas-Surface Reaction Journal of Physical Chemistry C 11(248): p. -19039.
209. Beltramo, G. L., T. E. Shubina, and A. M. T. M. of Koper, acid and carbon monoxide on gold electrodes studied by surface enhanced Raman spectroscopy and DFT J. Phys. Chem. C 11(12): p. 2260967.
210. Avery, N. A. Adsorption of a Formic Acid on Clean and Oxygen Covered Pt Applied Surface Science 12(12): p. 1987273.4
211. Freund, H. J. and M. S. W. Surface Chemistry of Carbonaceous Solids Reports, 21(1996).p. -2725
212. Solymos, T. E. Bonding, and Reductions of CO₂ Adsorbed on Promoted-Surfaces Journal of Molecular Catalysis 153(1): p. 337991.

213. Wang, H.F. and Zrnic, L. Acid Oxidation at Pt/H₂O Interface: DFT Calculations Integrated with Ab Initio Molecular Dynamics. *Physical Chemistry C*, 11(2008): p. -17508.
214. Hartnig, C., J. Grimming and J. Schmitz. Adsorption of formic acid on Pt(111) in the presence of water. *Journal of Electroanalytical Chemistry*, 60(2007): p. 113.
215. Bako, I. and G.V. Parthasarathy. Partitions of small molecules on Pt(111) surface. *Science*, 62(2008): p. -3381049.
216. Carabineiro, S.A.C. and B.A. N. P. Adsorption of small molecules on single crystal gold surfaces. *Surface Science*, 474(2001): p. -3288.
217. Bond, G.C. and D.T. Calhoun. Adsorption of small molecules on Pt(111) surface. *Surface Science*, 474(2001): p. -3288.
218. Meyer, R. Surface chemistry of catalytic materials. *Surface Science*, 57(2004): p. 7-2.
219. Song, C.R., Q.F. Ge, and D.T. Calhoun. Adsorption of Pt/Au bimetallic clusters on their interactions with the CO molecule. *Physical Chemistry B*, 10(2007): p. -22350.
220. Sadek, M.M. and E. C. Wang. Adsorption and dissociation of CO on Pt/Au bimetallic clusters on the CO frequency: A density functional theory study. *Physical Chemistry B*, 10(2007): p. -22350.
221. Chen, J.G., C.A. Menning, and M. Mayer. Bimetallic surface catalysis: Experimental and theoretical studies of trends in electronic and structural properties. *Surface Science Reports*, 65(2008): p. -22350.
222. Greeley, J. and J.A. Kitchin. A scheme for the estimation of energies on binary transition metal surfaces. *Surface Science*, 592(2005): p. 104-111.
223. Hammer, B. Special sites at noble and late transition metal surfaces. *Catalysis*, 3(2006): p. 163.
224. Shao, M.H. Origin of enhanced activity in palladium alloy catalysts for oxygen reduction reaction. *Journal of Physical Chemistry B*, 11(2007): p. 6772-775.
225. Lima, F.H.B. Catalytic activity-center correlation for the O₂ reaction on platinum in a bimetallic alloy. *Physical Chemistry C*, 11(2008): p. -4404.
226. Wolfschmidt, H., R. Bussar, and G. Stams. Reactions on nanostructured Au(111) surfaces: influence of the surface electrocatalytic activity. *Electrochimica Acta*, 53(2008): p. 2037-2008.
227. Eikerling, M., J. Meier, and H. G. Stams. Hydrogen evolution at a single nanoparticle: A kinetic study. *Zeitschrift für Physikalische Chemie*, 117(2003): p. 394-414.
228. Stamenkovic, V. et al. The activity of electrocatalysts for oxygen reduction by tuning the surface electronic structure. *Angewandte Chemie International Edition*, 47(2008): p. -2280917.

229. Dean, J.L. *Lang's Handbook of Chemistry*. 1985, New McGraw-Hill Book Company.
230. Liu, P. and J.K. Li. *Non-Faradaic ensemble effects in adsorption* Physical Chemistry Chemical Physics 3(17): 3381-3384, 2001.
231. Voorhees, P.W. *Wald Ripening Phase Transition: A Review of Materials Science* 22(4): 19-21, 1957.
232. Chierchie, T. and V. C. T. *TAMMETRIC STUDY OF THE UNDERPOTENTIAL DEPOSITION OF COPPER ON POLYCRYSTALLINE PALLADIUM SURFACES* *Chimica Acta* 3(13): p933-941.
233. Grgur, B.N., N.M. Markovic. *Underpotential Deposition of Pt(111) in perchloric acid solution: Raman Spectroscopy* *J. Electroanal. Chem.* 132(4): p. 663-674.
234. Markovic, N.M., H.A. Gasteiger. *COPPER ELECTRODEPOSITION ON PT(111) IN THE PRESENCE OF CHLORIDE AND ROTATING PT(111) DISK ELECTRODE* *J. Electroanal. Chem.* 404/405: p. 409-418.
235. Omar, I.H., H.J. Pauling. *UNDERPOTENTIAL DEPOSITION OF COPPER ON AU(111) SURFACES: TAMMETRIC AND ROTATING DISK ELECTRODE STUDY* *J. Electrochem. Soc.* 140(8): p. 2187.
236. Miwa, D.W., M.C. Santos, and A. S. G. *Simultaneous adsorption of anions and copper on polycrystalline Au(111) surface* *J. Electrochem. Soc.* 153(12): p. 2006.
237. Wunsche, M., H. Meyer, and R. M. *FORMATION AND PROPERTIES OF COPPER DEPOSITS ON POLYCRYSTALLINE ELECTRODES* *Electrochimica Acta* 40(5): p963-969.
238. Norskov, J.K. *Origin of the overpotential for oxygen reduction on Pt(111)* *J. Phys. Chem. B* 104(46): p. 11708-11716.
239. Moller, F., O.M. Magnusson. *CULYDIA FORMATION AND CL INDUCED SURFACE ALLOYING: STM STUDY ON CU UNDERPOTENTIAL DEPOSITION ON AU(110) ELECTRODES* *Electrochimica Acta* 40(12): p951-959.
240. Angers-Kozlowska, H. *Elementary Steps of Electrochemical Sing Crystal Planes of Au .1. Chemical Basis of Processes of Anions and the Electrode Surface* *Chimica Acta* 3(18): p981-991.
241. Adzic, R.R.V., Tripkovic, and V. *STRUCTURAL EFFECTS IN ELECTROCATALYTIC OXIDATION OF FORMIC ACID AND HYDROGEN ADSORPTION ON PLATINUM SINGLE-CRYSTAL SURFACES* *J. Electroanal. Chem.* 204(1-2): p. 349-366.
242. Markovic, N.M. *STRUCTURAL EFFECTS IN ELECTROCATALYTIC OXYGEN REDUCTION ON PLATINUM SINGLE-CRYSTAL SURFACES IN PERCHLORIC ACID SOLUTIONS* *J. Electroanal. Chem.* 371(1-2): p. 25-49.

243. Adzic, R.R., A.V. Tripkovic, and S. Trasatti, *STRUCTURAL EFFECTS IN ELECTROCATALYTIC OXIDATION OF FORMIC ACID AND OXYGEN REDUCTION ON CRYSTALLINE ELECTRODES AND THE EFFECT OF FOREIGN METAL ADATOMS*, *Journal of Electroanalytical Chemistry*, 15(12): p.889.
244. Adzic, R.R., Tripkovic, and W. Strasser, *STRUCTURAL EFFECTS IN ELECTROCATALYSIS*, *Journal of Electroanalytical Chemistry*, 29(52.53): p.3837.
245. Markovic, N.M. and S. Trasatti, *Science studies of model electrocatalysis*, *Science*, 254(5046): p.2229.
246. Chen, Z.X., *Effect of steps on the decomposition of CH₃OH on a Pt surface*, *Journal of Physical Chemistry B*, 4(1998): p.4570.
247. Lim, K.H., *Adsorption of acrolein on surfaces of silver: Density functional calculations*, *Chemical Physics Letters*, 42(1998): p.2006.
248. Lim, K.H., *Mechanism of Selective Hydrogenation of Aldehydes on Silver Catalysts: A Density Functional Calculation*, *Chemistry Letters*, 13(2009): p.13240.
249. Liu, Z.P. and G. Henkel, *rules for predicting where a catalytic reaction occur on metal surfaces: A density functional theory study of CO breaking/making on flat, stepped, and kinked metal surfaces*, *Chemical Society Reviews*, 37(2008): p.1958.
250. Wang, Z.L., T.S. Ahmad, and M. Alekseyev, *Effect of kinks on the activity of platinum nanoparticles in CO oxidation*, *Journal of Physical Chemistry C*, 10(2006): p.30210.
251. Somorjai, G.A., R. McCrea, and D. Zlot, *Insights in heterogeneous catalysis: development of molecular concepts and future challenges*, *Journal of Catalysis*, 18(34): p.1166.
252. Vedrine, J.C., J.M.M. Millet, and J. Guzman, *Development of active sites for oxidation reactions: A density functional theory study*, *Catalysis Today*, 13(1994): p.11215.
253. Strasser, P., *High throughput experimental and theoretical study of materials: comparative strategies for new fuel cell catalysts*, *Journal of Physical Chemistry B*, 10(2006): p.12100.
254. Wee, J.H., K.Y. Lee, and B. Schumm, *A method for identifying electrocatalysts in proton exchange membrane fuel cells*, *Journal of Electroanalytical Chemistry*, 15(2007): p.6677.