

Electrocatalytic and Fundamental Properties of Nanoscale Materials and
Development of New Nanoscale Electrochemical Methods

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Abstract

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This dissertation mainly discusses the fundamental properties and electrocatalytic activity of single, isolated nanomaterial structures, such as nanowires, nanoparticles and graphene. It also discusses the development of new nanoscale electrochemical techniques to investigate various aspects of heterogeneous catalysis and single cell analysis. There is a brief introduction about the nature of electrochemistry and electrochemical catalysts as well as some various nanomaterials and voltammetric techniques involved in this work.

The fabrication and of new ultralong metal nanowires made from platinum or gold through a laser assisted mechanical pulling procedure is discussed in chapter 2. Single platinum nanowires of this type are then used to study the Oxygen Reduction Reaction (ORR) on nanowires with various diameters in Chapter 3. The catalytic activities of several different nanoparticles are studied in Chapters 4 and 5 using the technique of Fast Scan Cyclic Voltammetry (FSCV), where detailed chemical information can be obtained from nanoparticle collision events by recording single nanoparticle Cyclic Voltammograms (CVs) for the oxidation of hydrazine. Combined with numerical simulations, the single nanoparticle CVs allow for the determination of the electron transfer kinetics and the Gibbs free energy of activation for

hydrazine oxidation. These combined methods can be a powerful tool in many aspects of fundamental catalytic research.

Chapter 6 details the phenomena of fast formation and growth of platinum oxide at low anodic potentials using platinum nanoelectrodes as model nanoparticle electrocatalysts. Chapter 7 discusses the technique of Fluorescence Enabled Electrochemical Microscopy (FEEM) and its application towards heterogeneous electrocatalyst screening, where a fluorogenic reaction is monitored at one side of an array of closed bipolar electrodes, which is coupled to a reaction occurring at the same region on the other side of the array. Chapter 8 is a study of the electrocatalytic activity of single graphene sheets with different numbers of layers for the ORR. The testing of recessed ring disk electrodes for the purpose of molecular scavenging during single cell exocytosis experiments is presented in Chapter 9 and chapter 10 describes the design and fabrication of two different Transmission Electron Microscopy (TEM) chip based electrodes for the goal of in-situ TEM experiments.

Table of Contents

Table of Contents	i
List of Figures	vi
List of Tables	x
Glossary.....	xi
Acknowledgements.....	xiii
Chapter 1 Introduction	1
1.1 Electrochemistry.....	1
1.2 Heterogeneous Electrochemical Catalysis	2
1.3 Nanoscale Structures.....	4
1.4 Electrochemical Techniques.....	6
1.5 Electrochemical Sensing and Imaging	8
1.6 References	10
Chapter 2 Laser-Pulled Ultralong Platinum and Gold Nanowires	14
2.1 Introduction.....	14
2.2 Experimental	15
2.2.1 Chemicals and Materials.....	15
2.2.2 Physical Vapor Deposition	16
2.2.3 Electrical Measurements	16
2.2.4 Electron Microscopy and Energy Dispersive X-ray Spectroscopy	16
2.2.5 Atomic Force Microscopy	16
2.2.6 X-ray Diffraction.....	16
2.3 Results and Discussion.....	17
2.3.1 Fabrication of Nanowires.....	17
2.3.2 Characterization of Laser-Pulled Nanowires.....	18
2.3.3 Nanowire Device Patterns	20
2.3.4 Electrical Measurement.....	20
2.4 Conclusions.....	24
2.5 Tables and Figures	25
2.6 References	37
Chapter 3 Electrocatalytic Reduction of Oxygen at Single Platinum Nanowires	40

3.1 Introduction	40
3.2 Experimental Section	41
3.2.1 Chemicals and Materials	41
3.2.2 Physical Vapor Deposition	42
3.2.3 Cyclic Voltammetry	42
3.2.4 Scanning Electron Microscopy	42
3.3 Results and Discussion	42
3.3.1 Fabrication of Single Pt Nanowire Electrodes	42
3.3.2 SEM and Electrochemical Characterization	43
3.3.3 Oxygen Reduction Reaction	45
3.4 Conclusion	50
3.5 Figures	52
3.6 References	63
Chapter 4 Chemically Resolved Transient Collision Events of Single Electrocatalytic Nanoparticles	66
4.1 Introduction	66
4.2 Experimental	67
4.2.1 Chemicals and Materials	67
4.2.2 Synthesis of 12 nm Au Nanoparticles	68
4.2.3 Synthesis of 4 nm Pt Nanoparticles	68
4.2.4 Preparation of Carbon Fiber Electrodes	68
4.2.5 Electrochemical Measurements	69
4.2.6 Electron Microscopy	69
4.3 Results and Discussion	69
4.3.1 Analysis of Platinum Nanoparticles	69
4.3.2 Analysis of Gold Nanoparticles	71
4.3.3 Chemical Resolution of Gold and Platinum Nanoparticle Mixtures	72
4.4 Conclusion	73
4.5 Figures	74
4.6 Supplemental Information: Estimate of the Collision Frequency from Diffusive Flux and the Diffusion Layer Thickness Using the Einstein Equation	82
4.6.1 Estimate of the Collision Frequency from Diffusive Flux	82
4.6.2 Estimate of the Diffusion Layer Thickness Using the Einstein Equation	82
4.7 References	83
Chapter 5 Heterogeneous Electron-Transfer Kinetics and Electrocatalytic Activity at Single Metal Nanoparticles	85

5.1 Introduction.....	85
5.2 Experimental	86
5.2.1 Chemicals and Materials.....	86
5.2.2 Synthesis of 12 nm and 50 nm Au Nanoparticles	87
5.2.3 Synthesis of 5 nm Au Nanoparticles	87
5.2.4 Synthesis of 4 nm Pt Nanoparticles	87
5.2.5 Synthesis of 10 nm Cubic Pt Nanoparticles	88
5.2.6 Preparation of Carbon Fiber Electrodes	88
5.2.7 Electrochemical Measurements	89
5.2.8 Transmission Electron Microscopy	89
5.2.9 Electron Transfer Simulation	89
5.3 Results and Discussion.....	90
5.3.1 Hydrazine Oxidation and Nanoparticle Collision FSCV	90
5.3.2 Electron Transfer Simulation Model	95
5.3.3 Thermodynamic Analysis	100
5.4 Conclusions.....	102
5.5 Tables and Figures	103
5.6 References	120
Chapter 6 A Study of the Formation and Quick Growth of Thick Oxide Films Using Platinum Nanoelectrodes as a Model Electrocatalyst	124
6.1 Introduction.....	124
6.2 Experimental	125
6.2.1 Chemicals and Materials.....	125
6.2.2 Electrochemical Measurements	126
6.2.3 Scanning Electron Microscopy and Energy Dispersive X-ray Spectroscopy.....	126
6.3 Results and Discussion.....	126
6.3.1 Fabrication and Characterization of Pt Nanoelectrodes.....	126
6.3.2 Potential Step Experiments	129
6.3.3 Prolonged Anodic Polarization.....	130
6.3.4 Protruding Oxide Reduction	131
6.4 Conclusions.....	133
6.5 Figures	134
6.6 References	142
Chapter 7 Fluorescence Coupling for Direct Imaging of Electrocatalytic Heterogeneity.....	145
7.1 Introduction.....	145
7.2 Experimental	147

7.2.1 Chemicals and Materials	147
7.2.2 Fabrication of Bipolar CF Electrode Arrays and Pt Deposition	148
7.2.3 FEEM Apparatus Setup.....	148
7.2.4 Video Acquisition and Processing	149
7.2.5 Scanning Electron Microscopy	149
7.3 Results and Discussion	149
7.3.1 Fluorescence Coupling on a Closed Bipolar Electrode	149
7.3.2 Fluorescence-Enable Electrochemical Imaging.....	151
7.3.3 Electrochemical Imaging of Electrocatalytic Heterogeneity	153
7.4 Conclusions	154
7.5 Figures	155
7.6 Supplemental Information: Derivation of the relationship between the Faradaic current on a closed bipolar electrode and the time derivative of the fluorescence intensity.....	165
7.6 References	167
Chapter 8 The Oxygen Reduction Reaction at Graphene Edges with Various Layer Numbers	169
8.1 Introduction	169
8.2 Experimental	170
8.2.1 Chemicals and Materials	170
8.2.2 Physical Vapor Deposition	170
8.2.3 Cyclic Voltammetry	171
8.2.4 Atomic Force Microscopy	171
8.2.5 Raman Spectroscopy.....	171
8.2.6 Scanning Electron Microscopy	171
8.3 Results and Discussion	172
8.3.1 Fabrication of Single Sheet Graphene Electrodes.....	172
8.3.2 Electrochemical Characterization	173
8.3.3 The Oxygen Reduction Reaction	174
8.4 Conclusions	176
8.5 Figures	177
8.6 References	183
Chapter 9 An On-Chip Recessed Ring-Disk Ultramicroelectrode with a 200 nm Ring-Disk Gap Used for Scavenging of Redox Molecules.....	185
9.1 Introduction	185
9.2 Experimental	186
9.2.1 Chemicals and Materials	186

9.2.2 Physical Vapor Deposition	187
9.2.3 Plasma Enhanced Chemical Vapor Deposition	187
9.2.4 Reactive Ion Etching.....	187
9.2.5 Electrochemical Data and Finite Element Numerical Simulations.....	187
9.2.6 Scanning Electron Microscopy and Atomic Force Microscopy	188
9.2.7 Cell Culturing.....	188
9.2.8 Single Cell Experimental Setup	189
9.3 Results and Discussion.....	189
9.3.1 Electrode Fabrication and Characterization	189
9.3.2 Numerical Simulation	192
9.3.3 Redox Scavenging	195
9.3.4 Single Cell Exocytosis	197
9.4 Conclusion	198
9.5 Tables and Figures	199
9.6 References	210
Chapter 10 Gold Nanowire and Carbon Film TEM Chip Electrodes	212
10.1 Introduction.....	212
10.2 Experimental	213
10.2.1 Chemicals and Materials.....	213
10.2.2 Low Pressure Chemical Vapor Deposition and Carbon Thin Film Deposition.....	213
10.2.3 UV Photolithography and Reactive Ion Etching.....	214
10.2.4 Electron Microscopy and Focused Ion Beam Milling	214
10.2.5 Synthesis of Decahedra Gold Nanoparticles.....	214
10.2.6 Electrochemical Measurements	215
10.3 Results and Discussion.....	215
10.3.1 Silicon Wafer Anisotropic Wet Etching	215
10.3.2 Fabrication of Gold Nanowire TEM Chip Electrodes.....	216
10.3.3 Selective Patterning of Carbon TEM Chip Electrodes	219
10.4 Conclusion	221
10.5 Figures	222
10.6 References	227
Bibliography	229
Vitae	244

List of Figures

Figure 2.1 Laser-Pulled Ultralong Nanowires	27
Figure 2.2 Nanowire SEM Images	28
Figure 2.3 Ultralong Nanowire XRD Reflections	29
Figure 2.4 Microwire XRD Reflections	30
Figure 2.5 High Resolution Nanowire TEM Imaging	31
Figure 2.6 Arranged Nanowire Patterns	32
Figure 2.7 Single Nanowire Electrical Measurements	33
Figure 2.8 Nanowire Breakage Points.....	34
Figure 2.9 Single Nanowire Conductivities	35
Figure 2.10 Non-Linear Current Behavior from Ohmic Heating	36
Figure 3.1 Single Platinum Nanowire Isolation	52
Figure 3.2 Nanowire Hemi-Cylinder Redox Diffusion	53
Figure 3.3 Single Isolated Platinum Nanowire SEM.....	54
Figure 3.4 Single Platinum Nanowire Redox CVs.....	55
Figure 3.5 Copper Under Potential Deposition.....	56
Figure 3.6 Nanowire Oxygen Reduction Reaction	57
Figure 3.7 Voltage Cycled Sulfuric Acid Etched Nanowire	58
Figure 3.8 Onset Potential vs Wire Radius.....	59
Figure 3.9 Current Density and Mass Activity.....	60
Figure 3.10 Deviation of Experimental ORR Current	61
Figure 3.11 Platinum ORR Tafel Plots	62
Figure 4.1 Fast Scan Cyclic Voltammetry of Nanoparticle Collision.....	74
Figure 4.2 FSCV Single Collisional Events of Platinum Nanoparticles on Carbon	75

Figure 4.3 Amperometric Detection of Platinum Nanoparticles.....	76
Figure 4.4 FSCV and Amperometry Peak Current Comparison	77
Figure 4.5 Gold Single Nanoparticle Collisions.....	78
Figure 4.6 Gold Single Nanoparticle CV.....	79
Figure 4.7 FSCV Scan Rate Dependence	80
Figure 4.8 Chemically Resolving Single Nanoparticles	81
Figure 5.1 Nanoparticle Collision Electrocatalytic Amplification	106
Figure 5.2 Gold Nanoparticle TEM Analysis	107
Figure 5.3 Platinum Nanoparticle TEM Analysis	108
Figure 5.4 Nanoparticle Collision FSCV Analysis.....	109
Figure 5.5 Single Nanoparticle Collision Events	110
Figure 5.6 Nanoparticle Hydrazine Oxidation Activity Histograms	111
Figure 5.7 Averaged Nanoparticle Hydrazine Oxidation Activities	112
Figure 5.8 Platinum Nanoelectrode Hydrazine Oxidation Activity.....	113
Figure 5.9 Single Nanoparticle Simulation Environment.....	114
Figure 5.10 Single Nanoparticle Simulated CVs.....	115
Figure 5.11 Platinum Nanoelectrode Simulated CVs	116
Figure 5.12 Rotating Disk Electrode Plots	117
Figure 5.13 Platinum Surface Interaction with Hydrogen Ions	118
Figure 5.14 Gibbs-Free Energy Change	119
Figure 6.1 Platinum Nanoelectrode SEM Images.....	134
Figure 6.2 Electrochemical Characterization.....	135
Figure 6.3 Potential Step Current Response	136
Figure 6.4 Surface Growth After Potential Step Experiments.....	137
Figure 6.5 Protruding Oxide Growth with Schematic.....	138

Figure 6.6 Oxide Growth EDS Analysis.....	139
Figure 6.7 Protruding Oxide Electro-Reduction.....	140
Figure 6.8 Recessed Nanoelectrode Oxide Growth.....	141
Figure 7.1 Fluorescence Enabled Electrochemical Microscopy.....	155
Figure 7.2 Bipolar UME Setup.....	156
Figure 7.3 FEEM UME Voltammetric Response.....	157
Figure 7.4 FEEM Fluorescence Concentration Response.....	158
Figure 7.5 Analyte Mass Transport FEEM Imaging.....	159
Figure 7.6 Carbon Fiber Bipolar Array SEM Image.....	160
Figure 7.7 Fluorescence Intensity at Different Positions on The Array.....	161
Figure 7.8 FEEM Imaging of Patterned Array.....	162
Figure 7.9 Imaging of Electrocatalytic Heterogeneity.....	163
Figure 7.10 Fluorescence Derivative Plots.....	164
Figure 8.1 Graphene Electrode Fabrication Schematic.....	177
Figure 8.2 Single Graphene Sheet Characterization.....	178
Figure 8.3 Raman Spectroscopy Graphene Peak G/2D Ratio Change.....	179
Figure 8.4 Electrochemical Response of Graphene Electrodes.....	180
Figure 8.5 Graphene Oxygen Reduction Reaction.....	181
Figure 8.6 Sheet Layer ORR Activity Dependence.....	182
Figure 9.1 Recessed Ring-Disc Redox Scavenger Schematic.....	200
Figure 9.2 Schematic of Fabrication Steps.....	201
Figure 9.3 Electrode SEM and AFM Characterization.....	202
Figure 9.4 Recessed Ring Disc Electrochemical Response.....	203
Figure 9.5 Simulated Potential Wave and Concentration Curve.....	204
Figure 9.6 Simulation Geometry and Simulated CVs.....	205

Figure 9.7 Ring Disk Simulated Current Comparison	206
Figure 9.8 Redox Scavenging Simulated and Experimental CVs.....	207
Figure 9.9 Single Cell Exocytotic Event Detection	208
Figure 9.10 Vesicle Dopamine Content	209
Figure 10.1 Silicon Wafer Patterning and Anisotropic Wet Etching.....	222
Figure 10.2 Gold Nanowire TEM Chip Electrode	223
Figure 10.3 Gold Nanowire Nanoparticle Attachment and TEM Imaging.....	224
Figure 10.4 Carbon TEM Chip Electrode Selective Patterning and Characterization.....	225
Figure 10.5 Carbon TEM Chip Voltammetric Response and Nanoparticle Detection	226

List of Tables

Table 2.1 Nanowire Crystal Grain Diameters.....	25
Table 2.2 Microwire Crystal Grain Diameters.....	26
Table 5.1 Nanoparticle Size TEM Analysis	103
Table 5.2 Physical Constant used in Nanoparticle Simulations	104
Table 5.3 Single Nanoparticle Kinetics Summary.....	105
Table 9.1 Redox Molecule Scavenging Summary	199

Glossary

AFM – Atomic Force Microscopy

C_b – Concentration of reactant in the bulk solution (mol cm^{-3})

CV – Cyclic Voltammogram or Cyclic Voltammetry

D – Diffusion Coefficient of a reactant molecule ($\text{m}^2 \text{s}^{-1}$ or $\text{cm}^2 \text{s}^{-1}$)

EDS – Energy Dispersive X-ray Spectroscopy

$E_{1/2}$ – Half wave Potential (V)

E° - Formal Potential (V)

FcMeOH – Ferrocene Methanol

FCC – Face Centered Cubic

FEEM – Fluorescence Enable Electrochemical Microscopy

FFT – Fast Fourier Transform

FIB – Focused Ion Beam

FSCV – Fast Scan Cyclic Voltammetry

LPCVD – Low Pressure Chemical Vapor Deposition

NP – Nanoparticle

ORR – Oxygen Reduction Reaction

PECVD – Plasma Enhanced Chemical Vapor Deposition

PVP – Physical Vapor Deposition

r – Radius

RIE – Reactive Ion Etching

SEM – Scanning Electron Microscopy

TEM – Transmission Electron Microscopy

UME – Ultra-Micro Electrode

UPD – Under Potential Deposition

XRD – X-ray Diffraction

k_b – Boltzmann Constant ($1.3806488 \times 10^{-23} \text{ J K}^{-1} [\text{m}^2 \text{ kg s}^{-2} \text{ K}^{-1}]$)

i_{ss} – Steady State Current (nA)

k_a – Anodic Rate Constant (cm s^{-1})

k_c – Cathodic Rate Constant (cm s^{-1})

α – Charge Transfer Coefficient (unit less)

k_o – Standard Heterogeneous Electron Transfer Rate Constant (cm s^{-1})

F – Faraday Constant (96485 C mol^{-1})

R – Universal Gas Constant ($8.31446 \text{ J K}^{-1} \text{ mol}^{-1}$)

n – Number of electrons

T – Absolute Temperature (K)

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*“Every day I remind myself that my inner and outer life
are based on the labors of other men, living and dead,
and that I must exert myself in order to give in the same measure
as I have received and am still receiving.”*

- Albert Einstein

Chapter 1 Introduction

1.1 Electrochemistry

Electrochemistry is a widely diverse, multidisciplinary field with many useful applications ranging from heterogeneous catalysis and chemical analysis to sensing and imaging.¹ Electrochemical techniques allow for the determination of numerous properties from an electroactive molecular species including: identity of the chemical species, thermodynamic properties, concentration of analyte, reaction kinetics and mobility of a molecule in solution.¹⁻³ The majority of these processes are studied at the interface of an electrode (electronic conductor) and an electrolyte (ionic conductor) where an applied electrical potential will, if large enough, result in the transfer of electrons (or holes) to the lower potential region.¹ There have been numerous great contributions to the study of electrochemical processes and the behavior of charged interfaces.

When a solid surface (the electrode) is placed in an electrolyte solution, a physical structure called the electrical double layer is spontaneously formed at the electrode/solution interface and can affect many physical aspects of electrochemistry.^{4,5} The electrical double layer comprises an inner layer, called the Stern layer, consisting of solvent molecules and ions adsorbed onto the surface of the electrode.⁴ Beyond the Stern layer, is the diffuse layer which extends into the bulk solution and is made up of solvated ions that are only weakly interacting with the electrode surface through long range electrostatic forces. Formation of the electrical double layer on a charged electrode gives rise to the capacitance at the electrode surface.⁵ The resulting capacitance is dependent on the electrode structure and composition as well as the type and concentration of the electrolyte in solution and can be exploited for use in electrochemical supercapacitors.^{5,6} The electrical double layer can also affect reactions at the electrode where the electrolyte species adsorbed on to the surface of the electrode may block active surface sites, thus changing the reaction rate.

The nature of an electrochemical reaction (whether it is considered a catalytic process or a simple electron transfer redox process) has to do with the physical location within the double layer where the reaction can occur. An outer sphere electrode reaction will approach the electrode surface in the diffuse layer and will undergo the electron transfer process without breaking the solvent coordination sphere.^{1,5} In contrast, an inner sphere electrode reaction requires that the

reacting molecule strongly interacts or absorbs with the surface of the electrode, possibly forming chemical bonds with the electrode, where it undergoes the subsequent reaction steps.¹ This is true for most catalytic reactions with a few prominent examples being hydrogen and hydrazine oxidation or oxygen reduction. Furthermore, the structure or material of the electrode surface can affect the catalytic reaction changing either the products, energy/potential required to drive the reaction or the reaction rate.⁷⁻⁹ The difference between the thermodynamically determined reduction potential and the experimentally observed reduction potential for a catalytic reaction is called its overpotential.¹ Finding new or improving upon existing catalysts that have lower overpotentials and higher current densities is one very important aspect of electrochemistry in addition to chemical sensing and analysis.

1.2 Heterogeneous Electrochemical Catalysis

Many energy technologies depend on heterogeneous electrocatalysts to produce or store and release energy in the form of electricity, including; metal-air batteries,¹⁰ photoelectrocatalysts,¹¹ proton exchange membrane fuel cells¹² and solid oxide fuel cells.¹³ Heterogeneous catalysts are in a different phase than the reactant, such as a solid surface with a gaseous atmosphere or a solution containing a reactant. Therefore, heterogeneous catalysis includes aqueous and organic phase electrochemical reactions and high temperature gas phase reactions. In both of these types, the solid phase acts as the catalyst causing the reactant to undergo the desired reaction yielding a product that wouldn't normally or easily form without the catalyst present. Some forms of heterogeneous catalysis are used to synthesize a desired product, such as alkene hydrogenation, while others are optimized to harness the energy of the catalytic process. Catalysts can act as electron transfer mediators, lowering the energy barrier involved in the reaction pathway or increasing the rate of a given reaction. Most of the catalytic studies in this work were done with the goal of increasing the fundamental understanding of the catalyst behavior towards associated reactions that could be used to harness energy in fuel cell applications.

A fuel cell is a type of electrochemical cell where electrical energy is produced from the indirect reaction between the fuel and an oxidant.¹⁴ Fuel cells oxidize a fuel on a catalyst covering the anode electrode to free the electrons from the reactant. The electrons then travel through the circuit to the cathodic side of the fuel cell where the oxidant, typically oxygen, is reduced on a catalyst covering the cathode electrode generating an electrical current.¹⁴ Both the anodic and

cathodic reactions are catalytic in nature and require very active catalysts to facilitate the reactions efficiently. In both acidic and alkaline fuel cells the Oxygen Reduction Reaction (ORR) is a very important reaction as oxygen is the most widely used oxidant in fuel cells and its kinetics can be sluggish requiring large overpotentials, even on the best catalysts.^{14,15}

The reactant to be oxidized in a fuel cell can be a simple hydrocarbon or a carbon neutral reactant, but the choice of fuel will affect the current density and the voltage obtained from the cell. Molecular hydrogen is a carbon neutral reactant that when combined with oxygen in a fuel cell reacts to produce pure water as the only product, but has a limiting theoretical cell potential of 1.23 V.¹⁴ To achieve higher voltage, fuel cells can be connected in series forming fuel cell stacks or by using a different fuel source. A different carbon neutral fuel that has received a lot of attention and may be a viable alternative to hydrogen is hydrazine (N_2H_4). Hydrazine has a higher theoretical voltage of 1.56 V when combined with oxygen as the oxidant and the only reaction products are water and nitrogen.¹⁶ The ORR and hydrazine oxidation are the two main reactions studied in the following work using various nanomaterials.

Modern day electrocatalysts are typically nanoparticles or nanowires that are immobilized onto an inert support on an electrode.¹⁴ Typically, the catalysts of choice are noble metals such as platinum, palladium or iridium. Constructing a catalyst electrode from bulk noble metals would be prohibitively expensive in order to make the finished product cost effective for wide-scale use. Therefore, reducing the amount of raw materials used can be achieved by reducing the dimensions of the materials to the nanoscale and dispersing the resulting nanomaterials over a large area. Additionally, the available electroactive surface area is greatly increased allowing more of the reactant to be catalyzed and this maximization of available surface area for the reaction will also help to minimize the activation overpotential.¹⁴ This approach is widely used to not only increase activity and reduce the cost but commonly new and interesting properties are revealed in nanomaterials that are not observed in the bulk. However, with so many ways to make these nanostructures, the resulting activity is not easily predictable facilitating the synthesis and subsequent investigation of many types of nanomaterials, from different sizes and shapes to different compositions.

1.3 Nanoscale Structures

There are many types of functional nanostructures that have been fabricated and characterized.¹⁷ Methods to create nanostructures can be divided into two main classes, top-down and bottom-up.¹⁷ Top-down fabrication involves taking a macroscale amount of material from which the nanostructures are directly formed, while bottom-up fabrication is where the nanostructures are made starting from molecular reagents. The materials that these nanostructures are made from tend to exhibit drastically different properties in the nanoscale than compared to the bulk.¹⁸ For example, noble metals that are very poor catalysts can become great catalysts at the nanoscale and metals that are great conductors, when small enough, will become semiconductors or even insulators.¹⁸ The most common forms of nanostructures are typically formed from metals or metal oxides and include nanoparticles, nanowires and recently 2-dimensional nanosheets of carbon or semiconducting materials.

Metal nanoparticles have become universally used in everything from medicine to energy technologies and are a very common catalyst for both the anodic and cathodic reactions in fuel cells. Nanoparticles are typically made from bottom up approaches where molecular precursors are combined to form the nanoparticles in solution. Solvated metal nanoparticles are coated with a layer of stabilizers which can be charged ions, surfactants or capping ligands.¹⁹ These stabilizers repel the nanoparticles from one another preventing them from agglomerating and can be used to control the nanoparticles size and shape when the nanoparticle is formed. However, the catalytic behavior of the nanoparticles can change depending on size and shape. By changing the shape of the nanoparticle, different crystal faces are exposed and the catalytic activity can be strongly affected by the exposed crystal face.^{7,20} Changing the nanoparticle size will lead to changing thermodynamics of the small metal clusters which could affect the subsequent activity either positively or negatively.²¹

Considered to be 1-dimensional nanostructures, conductive metal nanowires can be used as catalysts and can additionally be used in sensors, photonic waveguides and photovoltaics or as electrical connections in nanodevices.²²⁻²⁴ They offer the advantage of increased conductivity for high current applications and can be made with bare surfaces without the use of stabilizing ligands and can be either single crystalline or polycrystalline. Most metal nanowires are made by a bottom-up process where the wires are grown in a rigid template such as a porous membrane through

electrodeposition or chemical reduction of the metal precursor. Template grown nanowires can be difficult to isolate and test or used to construct functional devices. As such, methods that are top-down processes are often also used that produce single nanowires that are easily isolatable. The ability to isolate and test single nanowires is highly desirable and allows single nanostructures to be investigated and characterized to great detail.

One of the most studied and promising materials in recent times is graphene which, due to its remarkable properties, has potential applications in a wide range of applications such as electronics, optical devices, catalyst supports, sensing and energy generation or storage.²⁵⁻²⁷ Graphene is composed entirely of sp^2 hybridized carbon and it is the first 2-dimensional material to be isolated and its physical properties extensively examined. One remarkable aspect of graphene is it is the first material isolated that is a zero band gap semiconductor, meaning that its electronic conduction band overlaps with the valence band at the point where its Fermi energy level is located thus it will easily conduct electrons and holes at very fast rates.²⁸ Graphene was isolated in a top-down method from bulk graphite by an exfoliation process, but since its discovery it is more commonly made through a bottom-up Chemical Vapor Deposition (CVD) process. Various forms of graphene sheets have been investigated for their use as catalysts and catalyst supports.²⁹ The discovery of graphene led to an explosion of research and now many more 2 dimensional materials are being created and tested with many exhibiting amazing properties.

With a myriad of known nanostructures and new types being created at a fast pace they must be tested to determine their activity for possible catalytic reactions. A catalyst's activity can be affected by many things; including the substrate³⁰ it is deposited onto, the size and shape³¹ or the composition³² of the nanostructure. The capping agent used to synthesize the nanoparticle can have differing effects on the activity as well, because the capping agent can obscure the reactive sites on a catalyst surface or can change the local electronic environment (depending on the nature of the reaction and electronic effect, this can be a positive or negative effect).³³ Because of the different effects that can change a nanoparticle's activity, discerning the effect that the catalyst structure has on the activity can be very difficult.

The vast majority of investigations have been conducted using relatively large quantities of the nanomaterials immobilized on a macro-scale electrode or built into the working fuel cell. As a result the evaluated performance of such nanomaterials is an average of the ensemble. The

averaged response from all the immobilized particles will be due to the presence of many different sizes and shapes and furthermore the response can be affected due to the close proximity to neighboring particles.^{34,35} To obtain more detailed information on how the activities and kinetics change with the material's size, composition, and shape, detailed studies on single nanostructures are required. These structure and function effects are, in particular, why single nanostructure experiments are important and will help illuminate the optimal catalyst compositions. In previous investigations, little has been done with respect to the direct electrical contact of the nanostructure being evaluated. Some studies have investigated single nanoparticles where single gold nanoparticles were physically attached to nanometer sized electrodes³⁶ and single platinum nanoparticles were electrochemically grown on a nanometer sized carbon electrode.³⁷ The ability to directly measure the voltammetric responses from single nanostructures is an essential step in evaluating the true activity of a nanoscale catalyst and discerning ways to improve upon them.

1.4 Electrochemical Techniques

The modern study of electrochemical phenomena is done in an electrochemical cell, where there is an electrolyte solution where the working electrode, reference electrode and, if needed, a counter electrode are placed (in systems with low currents the reference and counter electrodes are the same).^{1,2} The working electrode is the electrode where the reaction of interest is occurring and the reference electrode defines the relative magnitude of the applied potential. Voltammetry is an electrochemical technique where a potential is applied to the working electrode in an analyte solution of interest and the current is measured. The ability to precisely control the potential at the working electrode has led to much advancement in the various electrochemical techniques.³⁸ Previously, very little control over the electrode potential was possible without changing electrode materials, temperature, current density, solution electrolyte species or concentration.³⁸ A few of the techniques that are widely used include cyclic voltammetry, chronoamperometry, polarography, and Scanning Electrochemical Microscopy (SECM).¹

In the technique of cyclic voltammetry the potential applied to the working electrode is swept linearly to a maximum and then back to the initial potential starting point, which is typically shaped as a triangle wave.^{1,2} While this potential is cycled the current at the working electrode is recorded for each value of the potential sweep creating a voltammogram. The individual Cyclic Voltammograms (CV) collected from an electrode allow the determination of: the surface area of an

electrode, the catalytic activity of a material and reveals any surface processes taking place.¹ One powerful variant of the CV technique is Fast Scan Cyclic Voltammetry (FSCV) which is similar to cyclic voltammetry but is much more detailed.³⁹ FSCV cycles the potential very fast with high frequency while the current is recorded. These successive CVs are plotted together vs time into a color plot where each CV is a single line in the y-axis and the color represents the magnitude of the current response. This is a very useful technique because not only do the individual CVs provide very useful data, but it also mimics another widely used technique, chronoamperometry (commonly simplified as amperometry). Amperometry is where the current at the working electrode is monitored over time at a fixed potential, and can be used to monitor the change in concentration of an analyte or the change in catalytic activity.

Recently, working electrodes with very small dimensions, called Ultra-Micro Electrodes (UMEs) and nanoelectrodes, have become widely useful tools that are allowing more detailed analysis of electrochemical reactions.^{40,41} Any electrodes with at least one dimension in the nanoscale regime are termed nanoelectrodes and have increased sensitivity and signal to noise ratio. Additionally, the mass transport to these electrodes is higher than larger macro-scale electrodes. This is due to a radial diffusion profile of analyte in solution for the nanoelectrodes as opposed to a linear diffusion profile for the macroelectrodes. This type of diffusion profile is important for interpretation of redox molecule CVs from a UME or nanoelectrode where the current will attain a maximum limit of current that is proportional to the electrodes size (for a given electrode geometry).⁴² Another unique aspect of nanoelectrodes is their use as model nanocatalysts where a single nanoelectrode is analogous to a single nanoparticle. They have the advantage of being easily characterizable electrochemically and can be easily observed through electron microscopy. Their use as model electrocatalysts has allowed the investigation of various phenomena that real electrocatalysts experience and has led to the discovery of new processes that could adversely affect the catalysts activity if not controlled, such as platinum dissolution during the ORR.⁴³

The diffusion limited steady state current from a CV can be used to determine one of a number of variables in a given system, so long as the rest of the variables are known beforehand. These variables include the concentration of analyte, the number of electrons passed in a reaction, the analytes' diffusion coefficient and the radius of the electrode. However, electrodes that possess

the same radius but different geometric surfaces (disk vs sphere) will have different steady state limiting currents and hence different forms of steady state current equations.⁴⁴ These equations can be very useful to determine the size of an electrode or the predicted flux of reactant to an electrode, both of which may be necessary when evaluating the activity of an electrocatalyst.

There are many methods used to measure the activity of a catalyst, however the most common method for measuring an electrocatalyst's activity is by taking CVs for the reaction of interest where the electrode is stationary or where there is forced convection of solution, such as with a Rotating Disk Electrode (RDE). From the voltammograms, the activity is measured by the current density which is a measurement of the amount of current (equivalent to the reaction taking place) per unit area of catalyst. Another method is by looking at the potential that has to be applied to the catalyst to reach either 50% of the max current or a smaller value (typically 10% or 20%) which is termed the $E_{1/2}$ or the onset potential respectively.

1.5 Electrochemical Sensing and Imaging

Electrochemical techniques and analyte sensitive electrodes are very useful when applied to sensing or imaging applications. These electrochemical sensing electrode methods include the use of gas sensing electrodes, enzyme coupled devices and ion selective electrodes.¹ A very common type of ion selective electrode, widely used scientifically, is a pH sensing electrode.⁴⁵ Glucose test strips that are used to measure blood glucose levels in diabetic patients are an example of enzyme coupled electrochemical devices.⁴⁶ These are just two common applications of sensing electrodes but there are many more applications ranging from molecular oxygen sensors, DNA sensing and environmental pollutant monitoring.^{47,48}

Another important application of electrochemical sensing is the detection of neurotransmitter release from neuronal cells, both *in vivo* and *in vitro*.^{49,50} This application has been used extensively to study the process of dopamine exocytosis in model neuronal cells and has led to the further understanding of the nature of cellular processes.⁵¹ In these experiments the amount of dopamine released from a cellular vesicle is quantified by the charge passed in order to oxidize it and the event duration is determined by the vesicle fusion kinetics. These experiments typically use an electrode that has a diameter on the order of the size of the cell being studied and are physically placed above the cell. This method gives detailed temporal information but very little spatial

information about where the neurotransmitter release is occurring. Some studies have been done to gain more spatial resolution where multiple, individually addressable carbon fibers have been incorporated into a single electrode and the dopamine release monitored at a single cell.⁵² However, there is some question about whether the bottom of the cell is releasing dopamine similarly to the top side of the cell and whether some observed small events are due to an incomplete dopamine release event or by freely diffusing dopamine released farther away from the electrode. For this reason chip based electrochemical dopamine sensors that are fabricated on the bottom of a glass or silicon chip are important for studying the release of neurotransmitters from single cells.⁵³

Electrochemical imaging is a relatively new aspect of electrochemistry and involves using adapted methods for the detailed investigation of surfaces or to visually monitor an electrochemical reaction. The most widely used electrochemical imaging technique is Scanning Electrochemical Microscopy (SECM)⁵⁴, which is a form of scanning probe microscopy. In the SECM method a micro- or nanoscale electrode is scanned across a surface in a redox molecule containing solution and the resulting electrochemical current recorded over the scanned area. The response of the current at the electrode tip changes based on the distance the electrode is to the surface of the substrate and by maintaining a constant current over the course of a scan (hence a constant distance from the tip to the substrate) a topographical image can be created. SECM can also determine the electrochemical activity of electrocatalysts based on the generation of a redox active product from a reaction at the catalysts surface that is collected by the scanning electrode. A major issue with SECM is the fact that the probe must be scanned over the area in order to generate an image, which can be time consuming or just too slow to monitor active processes.

Another type of sensing and imaging electrochemical method is bipolar electrochemistry, which doesn't involve scanning a sample and can be used to actively monitor a large area simultaneously. Bipolar electrochemistry has been shown in the past as a useful tool in the construction of Janus particles.^{55,56} Bipolar electrochemistry is a method where a conductive material (the bipolar electrode) is not physically connected to the source of an applied potential in either a closed or open bipolar cell. When a voltage potential is applied to the cell from the external source, a potential is formed between the two ends of the bipolar electrode that is proportional to the externally applied voltage. The bipolar electrode will then oxidize molecules at one end,

conducting the electrons to the other end where another species of redox molecules is reduced. An array of bipolar electrodes can be easily combined with a fluorogenic or electrochemiluminescent reaction to monitor the production or release and diffusion of electrochemical species at the opposite end of the electrode. This monitoring can be used to actively investigate the diffusion layer of a chemical species or dopamine exocytosis from a neuronal network after an applied stimulation or can be used to image the activity differences between different electrocatalysts. Bipolar electrochemical methods have recently been shown to be advantageous as an electrocatalyst screening method⁵⁷ and as a way to directly visualize the activity of electrocatalysts.⁵⁸

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Chapter 2 Laser-Pulled Ultralong Platinum and Gold Nanowires*

2.1 Introduction

Metal nanowires are a widely varied group of nanomaterials finding useful applications in increasingly diverse areas.^{1,2} Single, long, metal nanowires are of great interest in the study of the quasi one-dimensional properties of the metal nanowires and are being widely studied for their optical^{3,4} and electronic properties.^{1,5,6} A number of bottom-up and top-down processes have been developed to produce such nanowires. Examples of popular bottom up processes include solution phase synthesis,^{7,8} template-based electrodeposition using anodic aluminum oxide (AAO)⁹⁻¹¹ or track-etched polycarbonate membranes,¹¹⁻¹⁴ photolithography patterned electrochemical deposition^{1,15} or electron-beam lithography (EBL) patterned electrochemical deposition¹⁶ or physical vapor deposition¹⁷ as well as Focused Ion Beam (FIB) fabrication.¹⁸ Solution-based synthesis methods can produce a large quantity of single crystalline nanowires with smooth surfaces, although they are typically of submicron lengths. Additionally, these methods produce nanoparticle by-products and single nanowires can be difficult to isolate from a bulk solution. Lithography-based electrochemical deposition methods can produce single nanowires or their arrays that typically have rectangular cross sections.^{1,15} These nanowires can be of significant length, but typically are highly polycrystalline with a large number of non-uniform grain boundaries and rough surfaces.^{1,15}

The unconventional method of mechanical production of nanowires has not been widely investigated, but has advantages of relatively simple production steps, reduced waste of noble metals and production of easily isolated single nanowires. One such mechanical method involves inserting a larger diameter wire into a metal holder and drawing the holder through dies of decreasing size, ultimately forming encased nanowires.¹⁹ This method can produce a single platinum nanowire with a diameter as small as 8 nm, but is a time consuming process and produces unwanted structural disorder of the resulting nanowires due to the low temperature drawing which can severely affect their functionality.²⁰

Another important mechanical pulling method, called the “Taylor process”, involves sealing a metal wire into a glass holder and pulling the holder down to smaller dimensions while being

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heated.²¹ This method has been used to create Bi nanowires²² as small as 220 nm and Au wires²³ as small as 260 nm. Through an extension of this process semiconducting nanowires encased in polymer can be made as small as 5 nm.²⁴

Here, we report a top-down method similar to the Taylor process, for the easy and reproducible fabrication of mm-long single platinum and gold nanowires. These nanowires are made by sealing a small piece of microwire in quartz and pulling the quartz/metal ensemble using a laser micropipette puller. This method has the added advantage that commercially available equipment is used, avoiding a large thermal drawing setup and is available to a larger scientific community. The nanowires are completely sealed in quartz and can be easily released by HF acid etching. This method not only reduces amounts of materials used but also produces wires having a low degree of structural disorder due to the elevated temperatures used in the pulling procedure and is demonstrated by this investigation. Using both Transmission Electron Microscopy (TEM) and X-ray Diffraction (XRD) we show that these nanowires are highly crystalline and well ordered. Electrical measurements demonstrate that such nanowires possess resistivity comparable to the bulk metals with high current densities before failure. The quartz encasement offers added mechanical stability enabling easy manipulation of mm-long nanowires. This is demonstrated by arranging single nanowires into desired patterns on silicon substrates. This unique nanowire platform can be useful for a variety of increasingly complex applications, including new chemical sensors,²⁵ surface enhanced Raman spectroscopy (SERS),⁹ and nanowire catalysis research.¹²

2.2 Experimental

2.2.1 Chemicals and Materials

All chemicals and materials were used as received from the manufacturers. Deionized water (>18 MΩ cm, Barnstead Nanopure Systems), acetone (Mallinckrodt Baker), isopropyl alcohol (IPA, Mallinckrodt Baker), 25 μm platinum wire (99.95%, Alfa Aesar), gold wire (99.99%, Kurt J. Lesker), hydrofluoric acid (HF, 48 wt% conc. Sigma Aldrich), double side polished silicon wafers (Silicon Quest International Inc.), polished quartz wafers (UniversityWafer.com), carbon coated Formvar copper TEM grids (Ted Pella).

2.2.2 Physical Vapor Deposition

Physical Vapor Deposition (PVD) was performed using Gold pellets (99.999%, Kurt J. Lesker) placed in tungsten metal evaporation boats along with chromium coated tungsten rods (99.999%, Kurt J. Lesker) for deposition of electrical contacts using an in-house two source PVD system.

2.2.3 Electrical Measurements

Linear sweep current-voltage response was recorded using an EG&G 175 voltage programmer and an EG&G 173 potentiostat. The current-voltage data was recorded using an in-house LabVIEW 8.5 program on a desktop PC equipped with a PCI-6251 (National Instruments) card.

2.2.4 Electron Microscopy and Energy Dispersive X-ray Spectroscopy

Scanning Electron Microscope (SEM) images were obtained using a field-emission SEM (FEI Sirion). Only wires used to obtain electrical measurements were sputter coated with a ~2 nm of Gold/Palladium alloy or carbon for SEM imaging. Energy Dispersive X-ray Spectroscopy (EDS) data was obtained using an Oxford X-max 80 mm² Silicon Drift Detector equipped on the SEM. Transmission Electron Microscopy imaging was performed on a FEI Tecnai G2 F20 S-Twin operating at 200 kV using a single tilt sample holder.

2.2.5 Atomic Force Microscopy

Atomic Force Microscopy (AFM) was performed using a Veeco Dimension 3100 AFM in tapping mode using OTESPA cantilever tips. The microscope was placed within a noise and vibration isolation table and images have been flattened to remove the background curvature of the substrate surface, but are otherwise free of modification.

2.2.6 X-ray Diffraction

X-ray Diffraction was performed using a Bruker D8 Discover system using Copper K α X-rays. Bare nanowires were etched out of the quartz on a small silicon chip. Upwards of 80 nanowires of both platinum and gold were used to collect the XRD information.

2.3 Results and Discussion

2.3.1 Fabrication of Nanowires

As illustrated in Figure 2.1, the platinum and gold nanowires were mechanically pulled using a laser puller (P-2000, Sutter Instrument Co.). A similar pulling procedure can also be used to make platinum nanoelectrodes.²⁶⁻²⁸ Briefly, a 25 μm platinum wire was placed in a quartz capillary (Outer Diameter: 1 mm, Inner Diameter: 0.3 mm) and one end sealed closed using an oxygen/hydrogen flame. The platinum microwire was sealed in quartz with laser heating under vacuum. The Pt/quartz ensemble was then pulled (Heat = 750, Filament = 2, Velocity = 60, Delay = 140, Pull = 250) resulting in two sharp quartz tips with the platinum nanowires sealed inside. Changing the pulling parameters may give smaller or more uniform diameters in the nanowires but may also lead to an increased incidence of breaks in the nanowire.

The gold nanowires required a slightly modified procedure because of its lower melting point, 1064 °C compared to 1768 °C for platinum. The high temperatures needed to melt the quartz (1670 °C) in order to seal the wire would inevitably melt the gold forming discrete beads to minimize its surface tension²⁹ resulting in discontinuous sections. A piece of gold microwire preform already sealed in quartz would be made using a hand pulling method.^{21,30,31} A 1 cm long piece was placed in a quartz capillary and pulled with laser. This method, not requiring the initial laser sealing step, utilizes slightly different parameters (Heat = 725 Filament = 3, Velocity = 100, Delay = 110, Pull = 225).

The tips were then broken off and placed on a silicon chip. Silicon was chosen for its resistance to HF etching and for easiness in SEM analysis, allowing the imaging without metal sputter coating, but other materials such as polyimide could also be used. The nanowire tips were then chemically etched with HF resulting in a single, ultralong (typically 4-5 mm) nanowire. (CAUTION: HF acid is hazardous. Use appropriate safety equipment.) The nanowires were either left on the silicon for the XRD and SEM studies or transferred to different substrates using a “wedging” technique.³²

2.3.2 Characterization of Laser-Pulled Nanowires

This method allows for easy and consistent preparation of continuous nanowires over their entire length. Figure 2.2 shows typical examples of laser-pulled single nanowires. Due to the nature of the pulling process, these wires are tapered and the diameter will vary over the length of the wire. For example, the platinum wire shown in Figure 2.2A and 2.2B is ~ 10 nm diameter at the narrow tip, and ~ 860 nm at the opposite end. This change in diameter over the length of the wire shown, ~ 3 mm, means the wire decreases in diameter by ~ 2.8 Å/ μm . Figure 2.2C and Figure 2.2D show the length and diameter for a gold nanowire where the length is ~ 2.7 mm and the tip diameter is ~ 40 nm and ~ 3 μm at the opposite end. The diameter at the tip of the gold nanowire is typically larger than the platinum wire due to the lower melting temperature of gold.

XRD was utilized to determine the crystal faces present in these nanowires. To perform XRD, upwards of 80 nanowires, for each gold and platinum, were placed in a semi-random orientation on silicon chips. While not quite the same as powder diffraction XRD experiments it is very similar, and the resulting diffraction peaks will be from the numerous randomly arranged crystal orientations parallel to the Si substrate (crystal face axis oriented normal to the nanowire lengths). Figure 2.3 shows the XRD results for laser-pulled nanowires and delineates several characteristic diffraction peaks and their corresponding Miller indices. It is clear that the {111} crystal face is the most abundant crystal face perpendicular to the nanowire lengths. Also shown, directly below the XRD spectra, are the expected diffraction peak intensities for the respective crystal faces from a bulk platinum or gold sample. Interestingly, the {200} peak is nearly absent from the diffraction spectra for both the metal nanowires. When compared to XRD scans of commercially available 25 μm diameter Au and Pt wires (Figure 2.4), which are used to make the nanowires, there is a clear reduction of the {200} peak in going from the micro wire to the nanowires. Both metals have the Face Center Cubic (FCC) crystal structure where the {111} crystal face has the lowest surface energy relative to any of the other faces.^{33,34} The FCC {200}, being equivalent to the FCC {100} crystal face, is known to pose the lowest strain energy of the crystal faces.³⁵ The large {111} peak and the limited faceting of the {200} crystal face with respect to the axis normal to the nanowire length, show that during the high temperature pulling process the metal nanowire will prefer to minimize its surface energy with respect to the quartz interface while strain energy is not minimized.

From the X-ray diffraction data an estimate of the average crystallite size was calculated for both the Au and Pt nanowires using the Scherrer equation and assuming a spherical geometry for the crystallite shapes.^{36,37}

$$d = \frac{K\lambda_{diff}}{\omega \cos \theta} \quad (1)$$

where d is the average crystallite size, K is a constant (0.94 used for spherical crystallites of FCC crystal structure), λ_{diff} is the wavelength of the X-rays (Copper $K\alpha = 1.5418 \text{ \AA}$) used for diffraction, θ is the diffraction angle, in radians. The peak line width of the X-ray diffraction peak, ω , is measured in radians at the FWHM of the diffraction peak and will increase in width as the thickness of the crystallites decreases. The average crystallite size obtained for the two most prominent diffraction peaks are summarized in Table 2.1.

For both types of metal nanowires the average grain size is approximately 62 nm which is larger than the grain sizes for the precursor 25 μm diameter wires (Table 2.2). This increase in crystallite size is due to the high temperatures used in the pulling step which anneals the wires leading to the increase in grain size. There is evidence, from the TEM images, that the crystallite's length is not dependent on the diameter of the nanowire. A representative TEM image of the end of a platinum nanowire, Figure 2.5A, shows that even as the nanowire diameter decreases below the average crystallite size the lengths of the crystallites don't shorten as the wire diameter decreases. When the nanowire diameter is below the average crystallite size, it appears that the nanowire can be thought of as a chain of single crystal domains linked end to end.

To further investigate the structural characteristics of the nanowires and to confirm the {111} crystal face is dominant in the axis perpendicular to the wire length, TEM was used to identify and measure the atomic lattice spacing of the respective metal wires. Figure 2.5B and Figure 2.5C show the TEM images of the sides of a platinum and gold nanowire, respectively, where the {111} crystal lattice was observed at the edges of both metal wires. The lattice spacing was determined from the reduced Fast Fourier Transform (FFT) images and the reduced FFT for the gold nanowire is shown in Figure 2.5D which corresponds to the [01-1] zone axis. For the {111} crystal face a spacing of 2.355 $\text{\AA}$ is expected for gold³⁸ and 2.26 $\text{\AA}$ for platinum.³⁹ The experimental value of the lattice spacing closely matched the literature values and further demonstrates that the atomic lattices of the nanowires are not significantly strained from the pulling process. Both the XRD and TEM data

show the {111} face is the dominant face normal to the length of the wire suggesting that the {200} crystal face is more abundant in the direction parallel to the length of the wire, which could explain why the {200} XRD reflections are much weaker than expected.

2.3.3 Nanowire Device Patterns

A unique aspect of laser-pulled metal nanowires is that they can be easily handled and manipulated to form patterns and designs of increasing complexity. This is demonstrated in Figure 2.6, which shows how the nanowires can be placed on top of each other to form electrical connections. A crossing point made out of two gold wires can be seen in Figure 2.6A, and designs with three and four crossing gold wires are shown in Figure 2.6B and Figure 2.6C respectively. These configurations, while being relatively simple, demonstrate the versatility of these nanowires and one could imagine insulating some wires, patterning and exposing specific portions of the wires, and placing the connecting wires on top of the exposed contacts thereby forming basic circuits. Also illustrated in Figure 2.6 are EDS images of different combinations of nanowires on silicon. Figure 2.6D shows a contact point between two platinum nanowires to create a single junction. Alternatively, the wires could be gold or a combination of metal nanowires as shown in Figure 2.6E and Figure 2.6F, respectively. Specific combinations of metal nanowires could be placed into desired positions to achieve a type of hybrid chemical sensor where a specific combination of metal nanowires may be more sensitive for a specific analyte than a single metal alone.

2.3.4 Electrical Measurement

The evaluation of the electrical properties of these nanowires is very important if they are to be used in any sort of electronic device or sensor. Therefore, representative single nanowires for both metals were transferred onto gold contact pads separated by $\sim 500\ \mu\text{m}$ distance and the I-V curves measured for each metal nanowire. The $\sim 500\ \mu\text{m}$ spacing between contacts was chosen because it was desirable to show the electrical properties of these nanowires measured over long lengths, which resulted in the use of relatively larger diameter nanowires. Due to the wedging transfer process it was difficult to transfer smaller diameter nanowires onto the contact pads that were unbroken over the $500\ \mu\text{m}$ lengths. Figure 2.7A shows a single Au nanowire spanning the $500\ \mu\text{m}$ length between the contacts and Figure 2.7B is an SEM image of the same nanowire after measurements were performed showing that the wire is now broken.

The I-V curve for the platinum nanowire is shown in Figure 2.7D, where the current is seen to suddenly drop, quickly followed by a total current loss, indicating a break occurred in the nanowire. Interestingly, the nanowire broke on the reverse potential scan (after the voltage, and hence the current) had surpassed the value where it ended up failing. The sudden breakage of the wire could be due to electromigration or may indicate the presence of defects in the nanowire where a build-up of thermal energy generated by resistive heating may have caused the wire to slightly crack followed by an arcing of the current past the crack, thus completely severing the wire. Evidence for the dramatic breakdown can be seen in Figure 2.7B which shows that the gold nanowire has dramatically moved relative to its initial position and the broken end of the wire is seen to have experienced significant melting (magnified image in Figure 2.8). Both ends of the broken Pt wire can be seen in Figure 2.7C and shows that substantial melting of the nanowire occurred indicating a dramatic localized resistive heating or electrical arcing just after the breakage. Evidence that electromigration also played a role in the severing of the wires is seen where a thinning of the wire is observed in the magnified SEM images of the platinum wire (shown in the Figure 2.8). The wire is seen to have regions of alternating thickness indicating the migration of the platinum atoms leading to the thinning and eventual breakage of the wire.

The nanowire dimensions were measured from the SEM images where the radius was determined as the average of multiple measurements taken along the measured length between contacts. Assuming a cylindrical shape with circular cross sectional area, the resistivities and current density for the gold (~487 μm length and ~342 nm radius) and platinum (~484 μm length and ~406 nm radius) nanowires was calculated. From the largest observed currents for each nanowire, the current densities observed were $2.24 \times 10^{10} \text{ A/m}^2$ for the gold nanowire and $3.25 \times 10^9 \text{ A/m}^2$ for the platinum.

Figure 2.9 shows the linear portions of the I-V curves from a single platinum and gold nanowire (same wires as in Figure 2.6) from which the resistances of the single nanowires was determined from the slopes of the lines. The platinum nanowire showed a total resistance of 119 Ω whereas the gold wire had a resistance of 74 Ω . The resistivity of each nanowire was then determined using equation 2 below,

$$R = \frac{\rho L}{A} \quad (2)$$

where R is the electrical resistance of the measured nanowire, ρ is the resistivity, L is the length of the measured nanowire between the electrical contacts and A is the cross sectional area. Assuming a circular cross sectional area, the resistivity of the Au nanowire was $5.59 \times 10^{-8} \Omega \text{ m}$ and $1.27 \times 10^{-7} \Omega \text{ m}$ for the Pt nanowire. These values are close to the bulk resistivity values of the metals at room temperature being $2.255 \times 10^{-8} \Omega \text{ m}$ for Au and $1.06 \times 10^{-7} \Omega \text{ m}$ for Pt.⁴⁰

Metal nanowires are expected to have higher resistivities than bulk metals, which can be attributed to scattering of the conduction electrons from the surfaces⁷ and grain boundaries,⁴¹ as well as the normal scattering due to lattice vibrations and impurity sites. Conduction electrons can scatter elastically from the surface where there will be no loss of momentum, termed specular reflection, and has been described by Fuchs⁴² and Sondheimer.⁴³

The contribution of surface scattering of conduction electrons to the total resistivity increases as the wire diameter decreases due to an increase in the surface/volume ratio. Thus, the larger diameter of these nanowires means that the largest contribution to the resistivity due to electron scattering comes from the scattering at crystal grain boundaries in the nanowires and can be calculated using the Mayadas and Shatzkes model.^{44,45} The Mayadas and Shatzkes model of grain boundary scattering has been extended by Steinhögl and coworkers^{46,47} to include the surface scattering contributions from Fuchs and Sondheimer theory.

$$\rho = \rho_o \left(\frac{1/3}{\left[\frac{1}{3} - \frac{\alpha}{2} + \alpha^2 - \alpha^3 \ln \left(1 + \frac{1}{\alpha} \right) \right]} + C(1-p) \left(\frac{U}{S} \right) \lambda \right) \quad (3)$$

where $\alpha = \left(\frac{\lambda}{d} \right) \left(\frac{R_{GB}}{1 - R_{GB}} \right)$, ρ is the measured resistivity, ρ_o is the bulk metal resistivity, C is a constant (3/16 in the case for a circular wire cross section⁴⁸), d is the crystal grain diameter, λ is the electron mean free path length (23 nm for Pt⁴⁹ and 41 nm for Au⁵⁰), p is the probability of elastic surface scattering ($p = 1$ is totally specular scattering and $p = 0$ is totally diffuse), and U and S are the circumference and cross sectional area of the nanowire respectively. R_{GB} is the reflection coefficient for electrons to scatter at the grain boundaries in the metal nanowire which for these wires will contribute most to the resistivity. The surface scattering will be small as compared to the grain boundary scattering, for these diameter wires, so taking a value of p that is similar to that reported previously will allow an approximate calculation of R_{GB} . Taking $p = 0.5$, which has been reported

previously by Durkan and coworkers,⁴¹ and solving for the grain boundary reflectance coefficient is an appropriate assumption where specular surface scattering has been reported as high as ~0.85 for Au {111} surface.⁵¹ The resistivities of these nanowires, being close to that of the bulk metals, could mean that a majority of the electrons flowing through the wire are scattered elastically from the surface and that there is a low probability of being diffusely reflected from a grain boundary. Using these simple assumptions grain boundary reflection coefficients of 0.616 and a low 0.259 have been calculated for the gold and platinum wire respectively. The Pt reflection coefficient is quite low indicating a low probability of grain boundary reflection and in fact is not far from previous reports of 0.35 for Pt thin films.⁴⁹

Interestingly, the gold nanowire I-V curve, seen in Figure 2.10A, began to show nonlinearity at higher bias voltages and the nonlinear current-voltage behavior becomes more pronounced at higher potentials. This behavior may be due to a temperature increase resulting from Ohmic heating leading to a resistance increase.¹⁶ Assuming a linear relationship, the increase in resistivity as the temperature of the nanowire increases can be expressed as the simple relation known as Mattheisen's rule.

$$\rho = \rho_o[1 + \alpha_{TCR}(T - T_o)] \quad (4)$$

where ρ_o is the wire resistivity at a reference temperature, T_o (25 °C in this case), T is the temperature of the metal nanowire, and α_{TCR} is the temperature coefficient of resistivity for the given material being $3.715 \times 10^{-3} \text{ } ^\circ\text{C}^{-1}$ for Au.^{15,40} By using this simple assumption, the changing resistivity can be used to calculate the temperature of the wire. Figure 2.10B shows the inferred temperature for the gold wire as a function of the voltage biased across the wire. As the bias potential is scanned from -1 to 0 Volts, the nanowire temperature decreases to a minimum (the room temperature value ~25 °C), and the nanowire resistivity decreases to its room temperature value. Scanning from 0 up to +1 Volts, the resistivity again begins to increase and this resistivity change corresponds to an inferred temperature of over 850 °C without the nanowire breaking. SEM images of the broken ends of the gold nanowire, seen in the supporting information, do show evidence of substantial heating where the wire has melted and resulted in failure of the wire.

2.4 Conclusions

Millimeter-long single metal nanowires have been prepared using a laser pulling method. These laser pulled nanowires have unsurpassed aspect ratios and are highly crystalline with low structural disorder. Additionally, the process used to make these nanowires appears to produce wires that favor low surface energy crystal faces normal to the length of the wire as exemplified by the {111} crystal face for gold and platinum, which are both FCC crystals. XRD data confirms that the wires are polycrystalline with crystal grains of approximately 62 nm in diameter, on average. TEM analysis allowed the atomic lattice spacing to be measured and verifies that the atomic lattice is not highly strained from the pulling procedure. These nanowires can be easily manipulated to make increasingly complex patterns that can be incorporated into functional nano-devices utilizing combinations of the metal nanowires. The nanowires exhibit a very low resistivity approaching that of the bulk metals and also showed fairly high current densities before wire failure. At higher voltages the gold wire displayed a nonlinear current response that may be explained as an increasing resistance due to Ohmic heating. The reflection coefficient for the nanowires was calculated to be 0.616 for gold and a remarkably low 0.259 for platinum.

This nanowire preparation method is simple and highly reproducible. Single metal nanowires fabricated with this method have very high aspect ratios and can be easily manipulated and incorporated into nano-devices. These metal nanowires can be used as a unique platform for nanowire-based chemical and biological sensors or for studying catalytic reactions on single nanowires. Both gold and platinum nanowires have been made although other metals may also be used with this procedure. Future studies will be done to investigate the conductance of smaller diameter nanowires as well as two crossed nanowires to investigate the nature of the conductance of the point where the wires touch, as it may form an atomic scale conductor.

2.5 Tables and Figures

Table 2.1 Nanowire Crystal Grain Diameters

Average crystal grain diameter sizes for laser-pulled nanowires obtained using the Scherrer equation and the two most prominent XRD peaks.

<i>XRD Reflections</i>	<i>Grain size (nm)</i> <i>Gold</i>	<i>Grain size (nm)</i> <i>Platinum</i>
{111}	62.8	63.1
{220}	61.4	62.4
Average	62.1	62.7

Table 2.2 Microwire Crystal Grain Diameters

Average crystal grain diameters for the 25 μm gold and platinum wires obtained from the XRD data using the Scherrer equation.

<i>XRD Reflections</i>	<i>Grain size (nm)</i>	
	<i>25 μm Gold</i>	<i>25 μm Platinum</i>
{111}	43.96	51.95
{200}	64.09	64.5
{220}	46.08	49.9
{311}	46.36	45.6
Average	50.3	53.9

Figure 2.1 Laser-Pulled Ultralong Nanowires

Scheme illustrating the Fabrication of (A) platinum nanowires and (B) gold nanowires by a laser assisted mechanical pulling method.

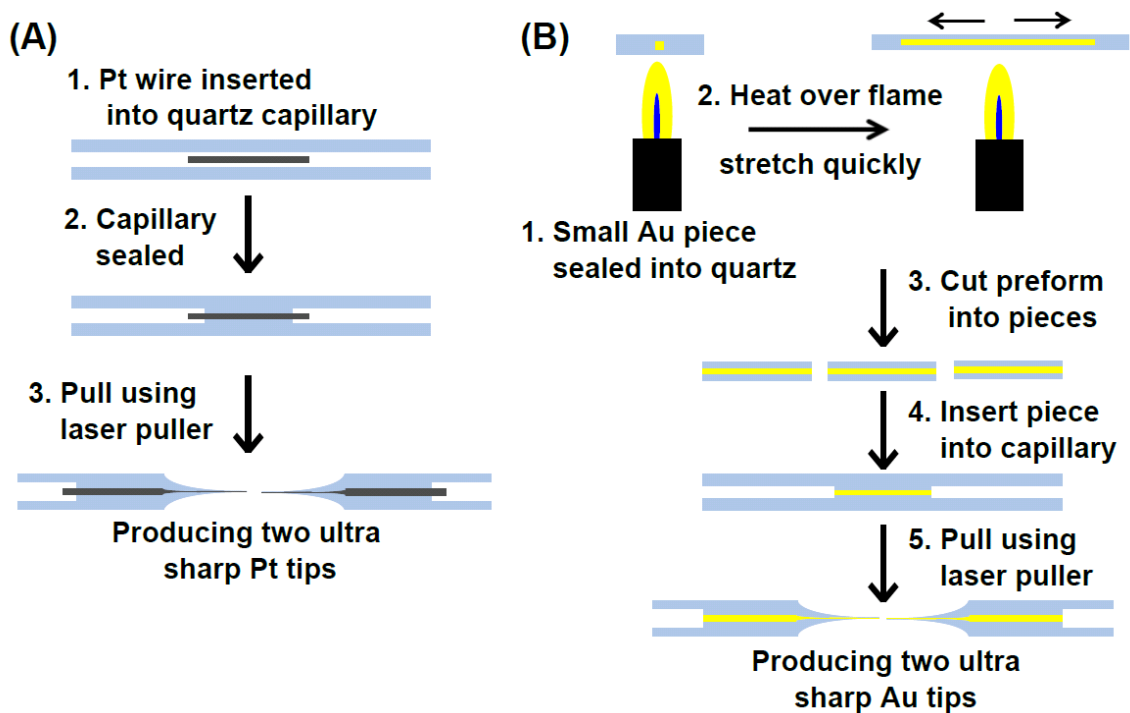


Figure 2.2 Nanowire SEM Images

SEM images showing (A) a 3 mm long platinum nanowire and (B) the ~ 10 nm tip of the same wire located at the arrow in (A). SEM images showing a 2.7 mm long gold nanowire (C) and (D) the ~ 40 nm tip located at the arrow shown in (C).

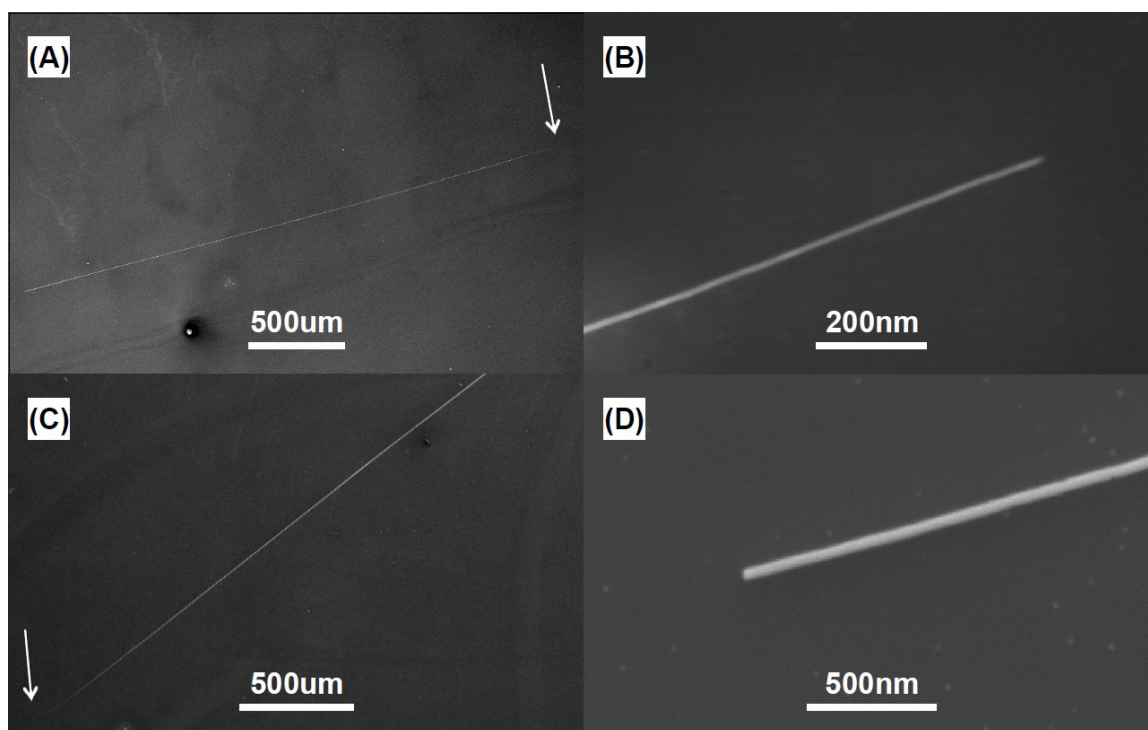


Figure 2.3 Ultralong Nanowire XRD Reflections

XRD data from both platinum and gold nanowires; included is a schematic illustrating the semi random nanowire distribution on the silicon chips. The expected intensities of each crystal reflection are shown below the nanowire XRD data for comparison.

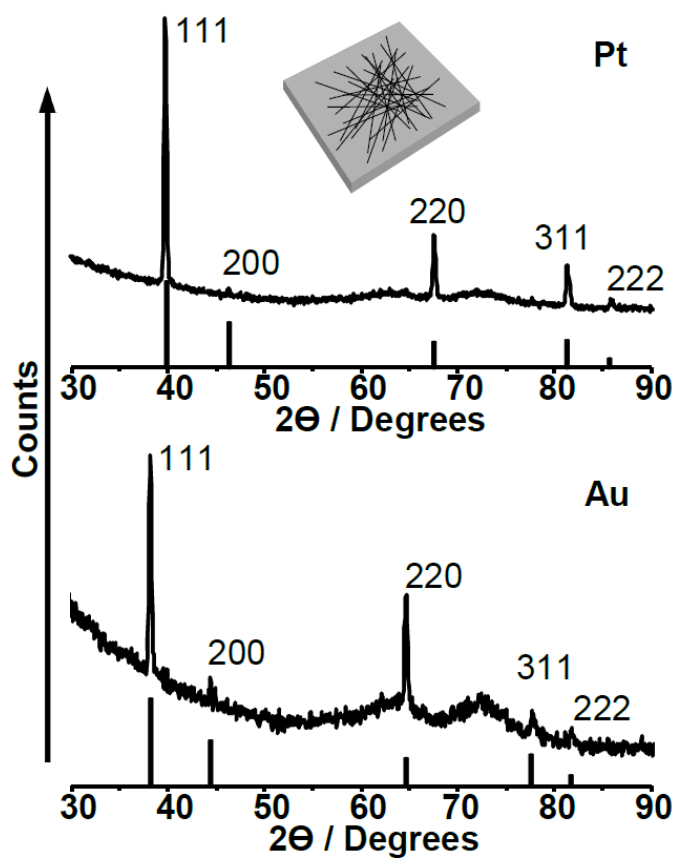


Figure 2.4 Microwire XRD Reflections

XRD reflection data for both the 25 μm platinum and gold wires used to make the nanowires.

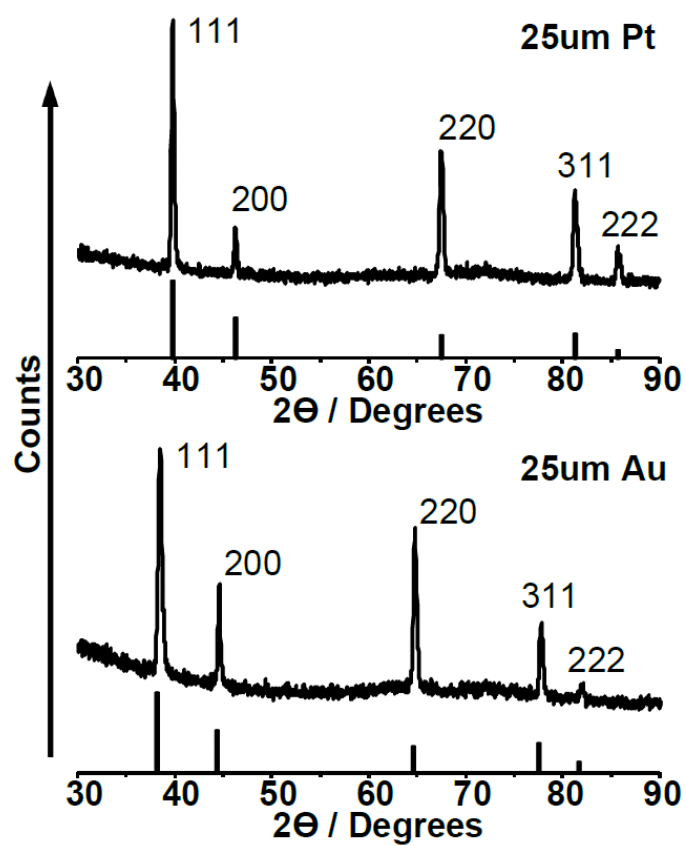


Figure 2.5 High Resolution Nanowire TEM Imaging

(A) TEM image of a laser-pulled 40 nm diameter platinum nanowire tip where the width is seen to be comprised of single crystal domains with crystallites on either side. (B) and (C) TEM images of nanowires showing the atomic lattice spacing of the {111} crystal planes for (B) platinum and (C) gold. (D) FFT of the gold wire TEM image in (C) showing the reciprocal space of the [01-1] zone axis with the spatial frequencies corresponding to the (111), (1-1-1) and the (200) reflections circled. Note: the scale bar in (B) is larger than the scale bar in (C) despite both representing a 2 nm length and is the reason the spacing for the gold atomic lattice appears closer than the platinum lattice.

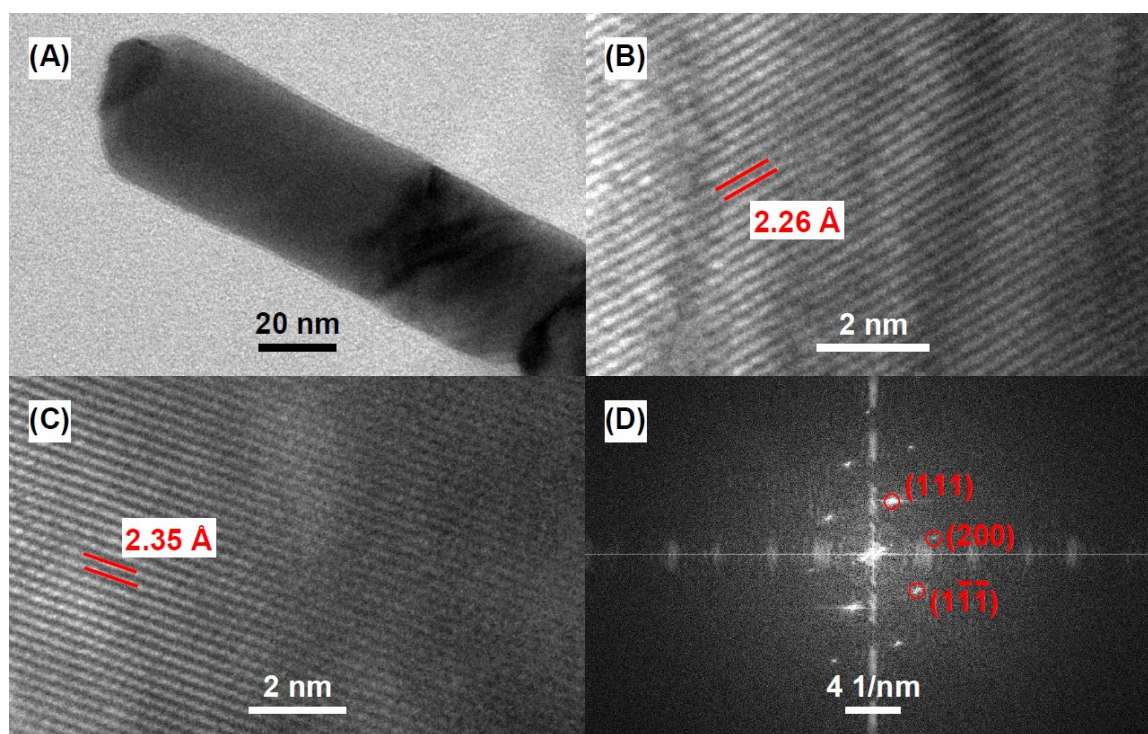


Figure 2.6 Arranged Nanowire Patterns

SEM images of gold nanowires arranged in more complex patterns. (A) A cross made from two gold wires forming a single contact point. (B) A triangle made from three gold nanowires forming three contact points. (C) A “pound sign” made from four gold nanowires forming four contact points between them. EDS color plots of platinum and gold nanowires contacting each other showing the versatility of the wires; (D) Pt-Pt, (E) Au-Au, and (F) Pt-Au contact points. The “shadow” seen in A and B is due to the EDS detector offset from the electron beam.

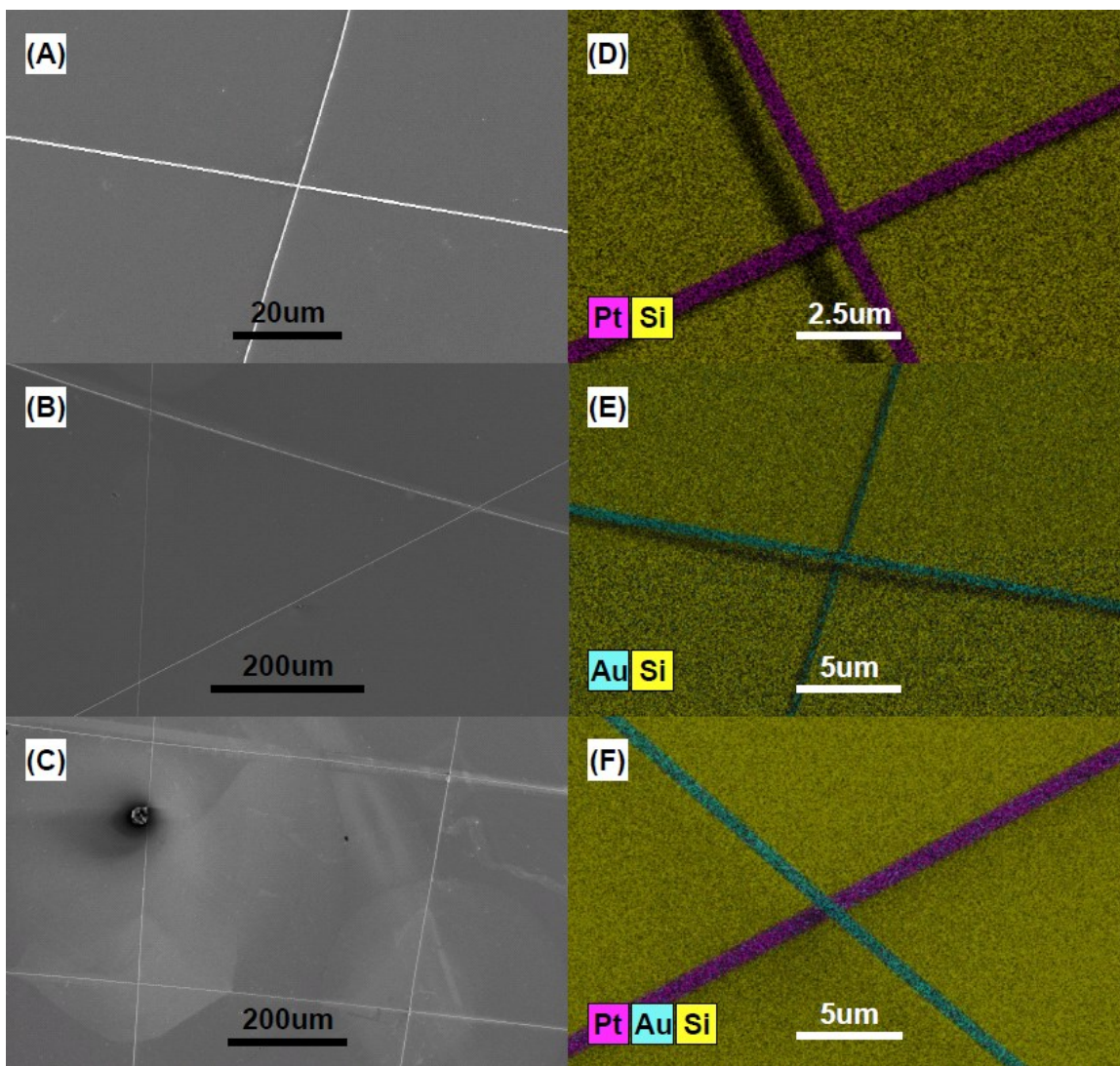


Figure 2.7 Single Nanowire Electrical Measurements

(A) Optical microscope image of a single gold nanowire extending across the gap between two electrical contacts, the arrow indicates the approximate point where the wire broke during electrical measurements as seen from the SEM image of the same wire in (B). (C) SEM image of a platinum nanowire after breakage occurred showing the wire had melted and possibly arced from the current. (D) I-V curve for the platinum wire where after scanning the potential up to 0.2 V and reversing scan direction the wire experienced a partial breakage at approximately 0.148 V followed by complete breakage at 0.127 V, arrows denote scan direction.

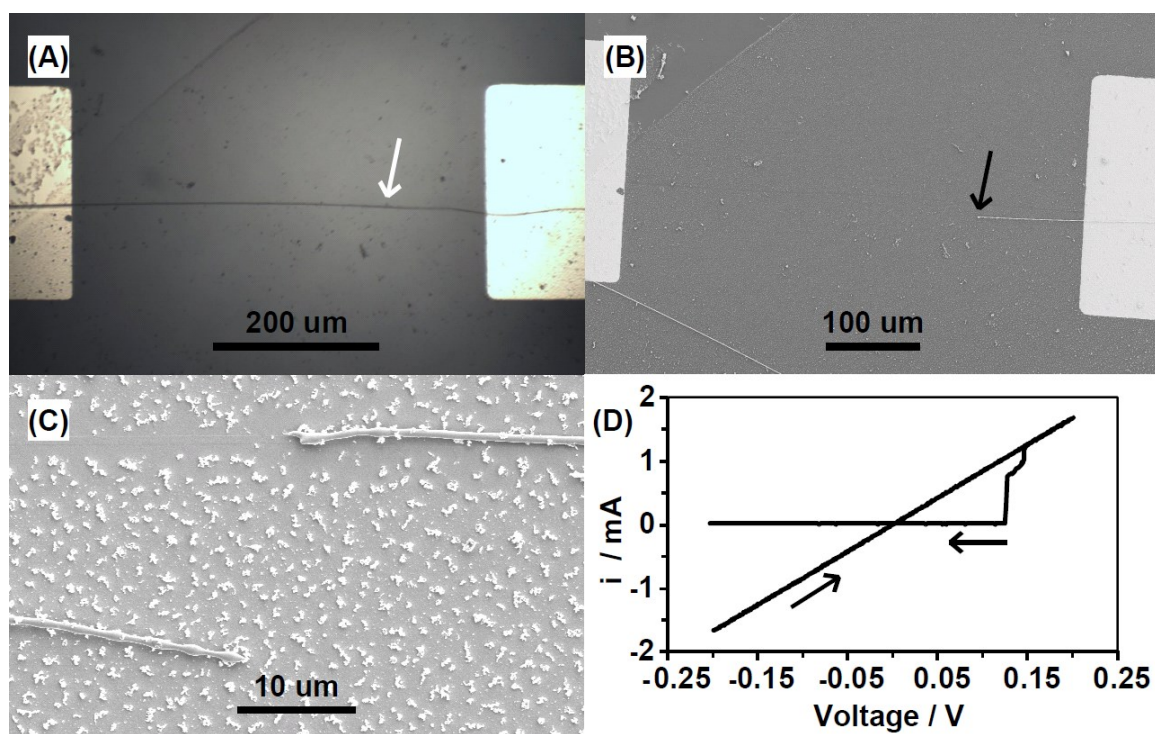


Figure 2.8 Nanowire Breakage Points

SEM images of the nanowires after measuring the current showing either side of the breakage points associated for the gold nanowire, (A) and (B), and the platinum nanowire, (C) and (D). Both show evidence of substantial heating and melting indicating the increased temperature of the wire upon failure.

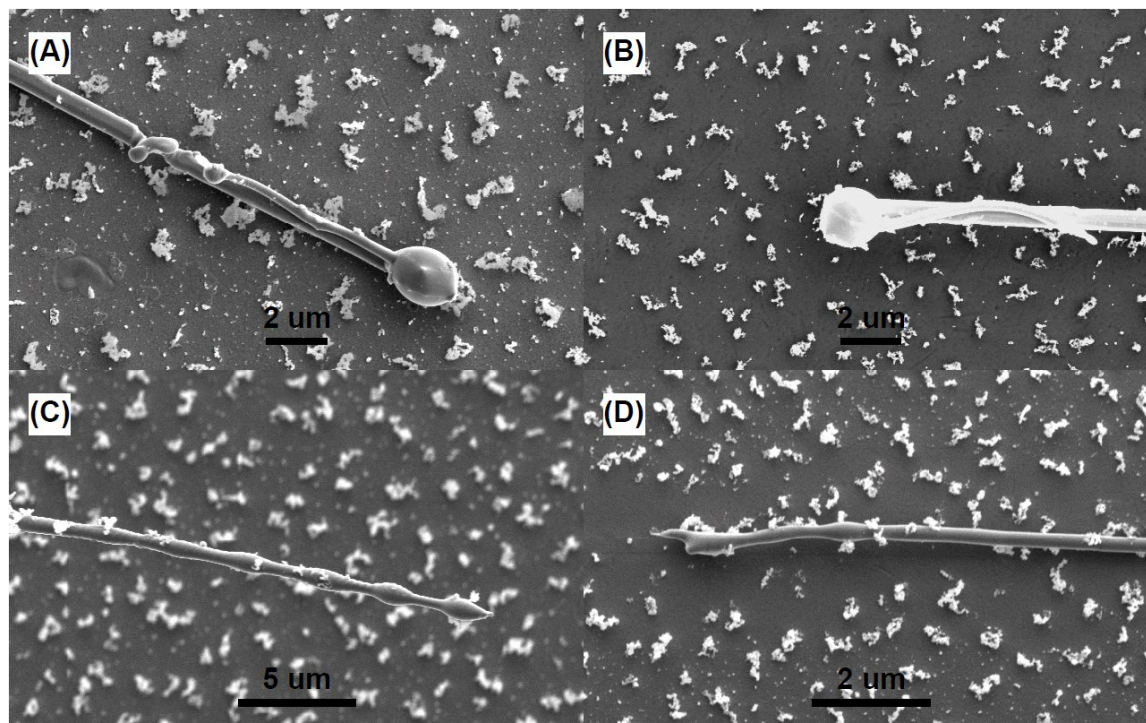


Figure 2.9 Single Nanowire Conductivities

Linear portion of the I-V curves from -0.2 to 0.2 V for both the platinum and gold wires which were used to evaluate the electrical properties of the nanowires.

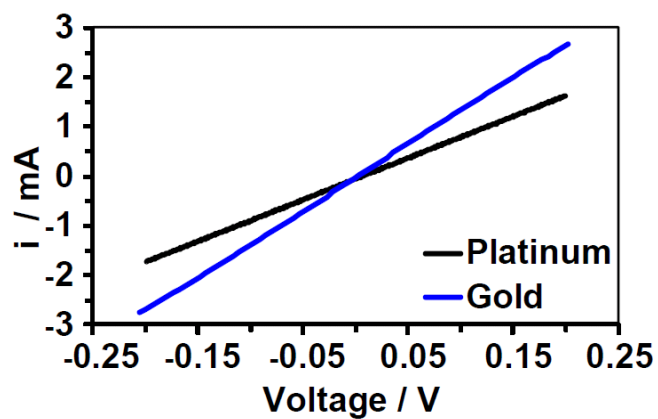
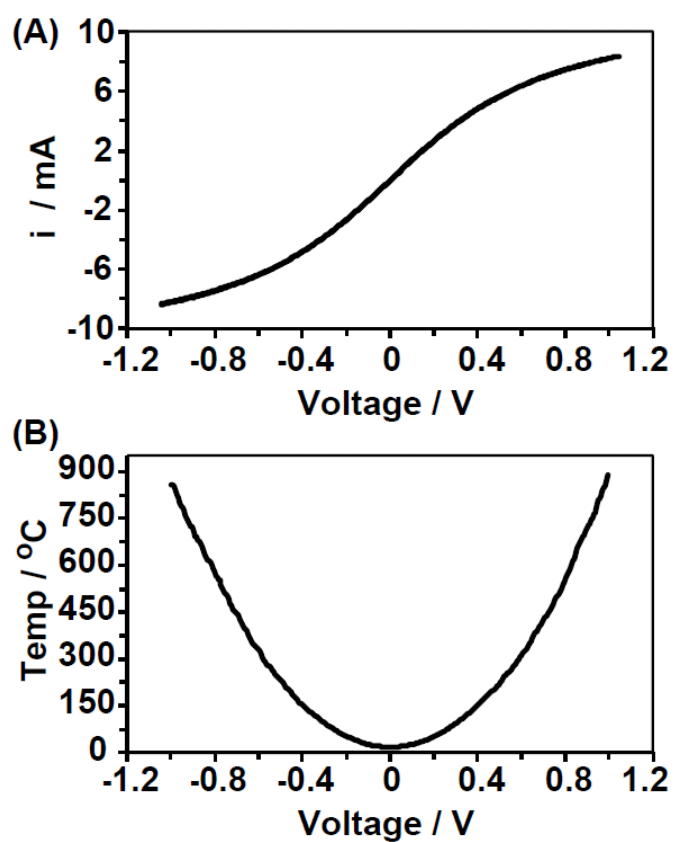


Figure 2.10 Non-Linear Current Behavior from Ohmic Heating

(A) I-V curve for a gold nanowire showing the current non-linearity at higher potentials, and (B) the inferred temperature of the gold nanowire as a function of voltage due to Ohmic heating, taken from the resistance change seen in (A).



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Chapter 3 Electrocatalytic Reduction of Oxygen at Single Platinum Nanowires[†]

3.1 Introduction

Platinum nanomaterials are widely used electrocatalysts in polymer electrolyte membrane (PEM) fuel cells for the anodic oxidation of a fuel source, such as molecular hydrogen, and are also the catalyst of choice for the cathodic oxygen reduction reaction (ORR).¹ It is well known that in an acidic electrolyte, oxygen can be reduced directly to H₂O through a one-step 4-e⁻ process or alternatively, by a two-step 2-e⁻ step process, with H₂O₂ as an intermediate product.²⁻⁴ By reducing the critical dimensions of the electrocatalyst from bulk to nanoscale, the available electrocatalytic surface area per unit mass is greatly increased allowing more of the reactant to be catalyzed and decreasing the amount of catalytic material.⁵

The majority of previous investigations have utilized large amounts of nanomaterials immobilized on a macroscopic electrode or built into a working fuel cell. As a result, the evaluated performance of such nanomaterial electrocatalysts represents an average of the ensemble.⁶ However, the ensemble properties can depend on the spatial organization and particle density of the nanomaterials to one another, affecting the mass transport of reactant and skewing the recorded activities of the nanomaterial.⁷ Previous reports speculate the decreasing Specific Activity (SA) of Pt nanomaterials results from either competition of neighboring catalyst particles for reactant⁷ or an increase in adsorption energy for oxygenated chemical species,⁸ which slows the ORR kinetics.

To obtain a more complete picture of how the activity and kinetics change with the materials size or composition, studies on single nanowires and nanoparticles become increasingly important. Recently, major advancement has been made using surface plasmon resonance (SPR) to indirectly monitor the reactivity of single Pt nanoparticles.⁹ However, minimal investigation has been done in the single nanoparticle or nanowire area where a direct electrical contact is made to the specific nanostructure in question. Recent studies have examined single gold nanoparticles

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attached to nanoelectrodes⁶ or a carbon film¹⁰ and single nanoparticles electrochemically grown on a nanoelectrode.^{4,11,12} In addition, nanoelectrodes have been made using single carbon nanotubes^{13,14} and lithographically patterned, electrochemically grown gold nanowires have been used to study electrooxidation at the single nanowire level.¹⁵

Here we report the fabrication and electrocatalytic study of single Pt nanowire electrodes with radii from 25 to 130 nm towards the ORR. To the best of our knowledge this is the first reported system where single Pt nanowire electrodes of systematically varying radii have been used to examine an electrocatalytic reaction, such as the ORR. The Pt nanowires were fabricated by mechanically pulling a 25 μm Pt microwire, reducing it to nanoscale and patterning individual nanowires using both photolithography and non-lithographic techniques resulting in a small section of the wire exposed for testing. These nanowire electrodes were characterized using Cyclic Voltammetry (CV), copper under potential deposition (UPD), as well as scanning electron microscopy (SEM). The UPD of copper was used to determine the roughness factor for the Pt wires, which can be relevant to the SA for the ORR on the wires. We found that as the wire radius decreases the onset potential shifts negatively and the Mass Activity (MA) increases while the current density decreases. In addition, we conclude that as the radius of the wire decreases the surface adsorption energy of oxygenated species increases, leading to a decrease in the ORR kinetics at the single Pt nanowires.

3.2 Experimental Section

3.2.1 Chemicals and Materials

All aqueous solutions were prepared using deionized water (>18 M Ω cm) prepared on a Barnstead Nanopure water purification system. Ferrocene methanol (FcMeOH, Aldrich 97%), sodium sulfate anhydrous (Na_2SO_4 , J. T. Baker), potassium chloride (KCl, Mallinckrodt Baker), Potassium Ferricyanide ($\text{K}_3\text{Fe}(\text{CN})_6$, Sigma-Aldrich 99%), Potassium Ferrocyanide ($\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ Fluka 99.5%), sulfuric acid (H_2SO_4 , Fisher), photoresist AZ1512 with AZ351 developer (AZ Corporation, developer diluted 1:5 developer:DI H_2O), hydrofluoric acid (HF, 48 wt% conc. Sigma Aldrich), sodium fluoride (NaF, J. T. Baker), nitrogen (N_2 , >99% Praxair), oxygen (O_2 , >99% Praxair), Pt microwire (99.95%, Alfa Aesar, 25 μm diameter) were all used as received from the manufacturers.

3.2.2 Physical Vapor Deposition

Physical Vapor Deposition (PVD) was performed using Au pellets (99.999% high purity, Kurt J. Lesker) placed in tungsten metal evaporation boats along with chromium-coated tungsten rods (99.999% high purity, Kurt J. Lesker) for deposition of Au/Cr electrodes using an in-house two source PVD system.

3.2.3 Cyclic Voltammetry

Steady-state voltammograms were recorded using a computer-controlled Dagan Chem-Clamp voltammeter/amperometer and data was recorded using an in-house virtual instrumentation program written in LabVIEW (National instruments) on a desktop PC equipped with a PCI-6251(National Instruments) data acquisition card. A commercially available Ag/AgCl reference electrode (Bioanalytical Sciences, Inc.) or a Hg/Hg₂SO₄ reference electrode (CH Instruments, Inc.) was used as reference electrode for all CVs and data was manually baseline corrected and slope corrected. Redox CVs that used KCl salt as the supporting electrolyte were recorded after the ORR experiments in order to prevent contamination from the chloride ion on the Pt surface as it is known to hinder the ORR.¹⁶ The Hg/Hg₂SO₄ reference electrode was used for all ORR studies to prevent chloride contamination to the solution and all potentials presented are referenced to a Hg/Hg₂SO₄ reference electrode unless otherwise noted. Solutions used for ORR were bubbled with oxygen or nitrogen for >20 minutes prior to use to ensure the solution was saturated with the desired gas.

3.2.4 Scanning Electron Microscopy

Scanning Electron Microscope (SEM) images obtained using a field-emission microscope (FEI Sirion) equipped with a through lens secondary electron detector with a resolution of 1 to 3 nm at the Nanotech User Facility located at the University of Washington. All samples were sputter coated with a 2-3 nm thin conducting layer of Au/Pd prior to SEM imaging.

3.3 Results and Discussion

3.3.1 Fabrication of Single Pt Nanowire Electrodes

The platinum microwires were first mechanically pulled using a CO₂ laser puller according to a method described in detail elsewhere.¹⁷⁻¹⁹ Briefly, a 25 μm-diameter platinum microwire was placed in a quartz capillary tube (OD: 1 mm ID: 0.4 mm, Sutter Instrument Co.) and one end sealed

closed in a hydrogen/oxygen flame. The quartz capillary was then placed in a P-2000 laser puller (Pull parameters: Heat = 750 Fil = 2, Vel = 60, Del = 140, Pul = 250, Sutter Instrument Co.) and vacuum applied to the unsealed end of the capillary. The laser was first used to heat the quartz around the platinum without pulling the capillary to obtain a tight seal between the quartz and the Pt wire. Once the wire was sealed in the quartz it was pulled, resulting in two ultrasharp quartz tips with the platinum nanowires sealed inside. This laser method can produce Pt nanowires with radii as small as 1 nm.

The Pt/quartz tips were broken off and placed on a small square of Kapton (polyimide) film as shown in the fabrication scheme in Figure 3.1, then chemically etched using concentrated HF resulting in a single long (typically >5 mm) tapered nanowire sitting on the Kapton sheet. Gold contact pads (100-nm-thick gold film) were thermally evaporated onto the large back end of the nanowire using a simple shadow mask to ensure the gold coated only the desired area. Photoresist (AZ1512) was spin coated onto the wires and patterned using a chromium-on-glass UV mask to open a small rectangular window ($10 \times 100 \mu\text{m}$) where only the side of the wire would be exposed. This resulted in a hemi-cylindrical section of the side of the nanowire being exposed from the photoresist, as shown in the scheme in Figure 3.2, due to the presence of photoresist beneath the wire as a result of the wire “shadowing” it during the UV exposure step which then doesn’t dissolve during the development step. Resulting lengths of the exposed wires were dependent on whether or not the wire crossed the open window in a straight line perpendicular to the $100 \mu\text{m}$ edge and deviation from this ideal configuration resulted in a longer section of exposed wire. Attempts were made to keep the wire lengths equal but some variability occurred.

3.3.2 SEM and Electrochemical Characterization

The platinum nanowire electrodes were characterized using basic electrochemical methods including cyclic voltammetry with various redox molecules, copper UPD, and SEM. An SEM image of a typical nanowire electrode is shown in Figure 3.3. The wire is on the Kapton surface and spans the width of the trench. It is important to note that the exposed short nanowire segment in the trench can essentially be viewed as a cylindrical nanowire electrode. Using the SEM images, accurate measurements of the wire dimensions could be made. The radius of a given wire was taken as the average of multiple measurements along the exposed segment of the wire within the trench.

The platinum nanowire electrodes were characterized in various redox solutions including

FcMeOH, $\text{K}_3\text{Fe}(\text{CN})_6$, and $\text{K}_4\text{Fe}(\text{CN})_6$. Figure 3.4 shows some characteristic CVs for two nanowire electrodes. Figure 3.4A and Figure 3.4B show the CVs for the oxidation of 2 mM FcMeOH on a 19.84 μm long, 40.5 nm radius nanowire and a 20.35 μm long, 116 nm radius nanowire, respectively. The steady-state diffusion-limited current, from these graphs, for the 40.5 nm radius electrode is 1.23 nA and 1.45 nA for the 116 nm radius electrode, both current values taken at 450 mV in the anodic scan direction. More CVs from the same 116 nm radius electrode are shown in Figure 3.4C for the reduction of 5 mM $\text{K}_3\text{Fe}(\text{CN})_6$ and in Figure 3.4D for the oxidation of 5 mM $\text{K}_4\text{Fe}(\text{CN})_6$. The currents obtained from these CV graphs are 4.43 nA (at -100 mV in the cathodic scan direction) for $\text{K}_3\text{Fe}(\text{CN})_6$ and 3.41 nA (at 600 mV in the anodic scan direction) for $\text{K}_4\text{Fe}(\text{CN})_6$.

The steady-state limiting current for a single nanowire can be approximated using the quasi steady-state current equation for a cylindrical shaped ultramicroelectrode,^{20,21}

$$i_{qss} = \frac{2nFADC_b}{r \ln(\tau)} \quad (1)$$

using $\frac{1}{2}$ of the area of the cylinder, approximating the wire as a psuedo-hemicylinder, as discussed previously, where $A = 2\pi rh$ with r as the radius and h as the length of the cylinder, the i_{qss} effectively becomes equivalent to equation 2 which is that of a hemicylinder,²¹⁻²³

$$i_{qss} = \frac{2\pi nFhDC_b}{\ln(\tau)} \quad (2)$$

where n is the number of transferred electrons per redox molecule, F is Faradays constant, D and C_b are the diffusion coefficient of the redox molecule and its bulk concentration, respectively. A good approximation can be made for τ , being $\tau = (4Dt/r^2)^{22,24}$ and the time component, t , can be approximated as $t = (RT/Fv)^{25}$ where v is the potential scan rate. The approximation shown above gives current predictions that are close to the observed experimental values on the nanowire electrodes.

Using the diffusion coefficient of FcMeOH ($6.7 \times 10^{-6} \text{ cm}^2/\text{s}$)²⁶ at 0.050 V/s scan rate with the length and radius for the wire shown in Figure 3.4A (19.84 μm length and 40.5 nm radius), the limiting current calculated, based on equation 2, is 1.18 nA. This matches very well with the measured limiting current of 1.23 nA. For the wire dimensions used to obtain the CVs in Figure 3.4B (20.35 μm length with 116 nm radius) the estimated limiting current is 1.44 nA in FcMeOH at 0.050

V/s, which is in excellent agreement with the experimental value of 1.45 nA. To further validate this approximation, the limiting currents were calculated for the electrode in Figure 3.4B using 5 mM $\text{K}_3\text{Fe}(\text{CN})_6$ ($D = 7.6 \times 10^{-6} \text{ cm}^2/\text{s}$)²⁷ and 5 mM $\text{K}_4\text{Fe}(\text{CN})_6$ ($D = 6.3 \times 10^{-6} \text{ cm}^2/\text{s}$)²⁷ which gave currents of 4.02 and 3.39 nA respectively. These values again are in close agreement with the measured values of 4.43 nA and 3.41 nA. These results show that the approximations used to calculate the quasi steady-state limiting currents can be used to understand the electrochemical response of these nanowire electrodes.

To further characterize these Pt nanowire electrodes, the surface roughness was determined using copper UPD.²⁸ Surface roughness is related to the geometric surface area, A_g , by a ratio termed the roughness factor, ρ , where $\rho = A_m/A_g$, and A_m is the microscopic, or actual surface area. The actual surface area is always larger than the geometric surface area due to crystal grain step edges and microscopic surface texture. To determine the roughness factor, the wires were held for various times at a potential that is more positive than the reversible Nernstian potential for bulk copper deposition so that a monolayer of copper adatoms would be adsorbed onto the Pt surface.^{29,30} Once a full monolayer of copper adatoms has formed, no more atoms will deposit onto the surface; the charge obtained from stripping them off is used to calculate the surface area.³¹

Figure 3.5A shows the linear sweep voltammograms from a wire with a length of 21.94 μm and a radius of 49 nm for each different holding time. The potential was held at 0.0 V (vs. Ag/AgCl) in a solution containing 10 mM CuSO_4 and 0.5 M H_2SO_4 then scanned up to 600 mV to strip off the adsorbed copper and the area under the peak integrated to yield the charge. Figure 3.5B shows the charge graphed as a function of the holding time and shows the amount of charge begins to quickly plateau. By 120 seconds of holding time the charge changes little with increased holding times. Using the charge of stripping a monolayer of copper off of polycrystalline Pt ($410 \mu\text{C}/\text{cm}^2$)³² with an average value of 55.9 pC for the copper stripping charge, a surface roughness of 4.03 was obtained (using the area for the half cylinder). This value is greater than the usual roughness factors reported in the literature, which is likely due to partial exposure of the bottom half Pt surfaces.

3.3.3 Oxygen Reduction Reaction

The main goal of this work was to study electrocatalytic ORR on single Pt nanowires of varying radii. Figure 3.6A shows a typical CV from a single 116 nm-radius Pt nanowire in N_2 saturated and O_2 saturated 0.5 M H_2SO_4 . Figure 3.6A displays a clear difference in the current

responses confirming that the reduction wave in the oxygenated solution is due to reduction of oxygen. Interestingly, the O_2 saturated CV on the nanowire electrode shows a clear hysteresis in the return scan which is significantly greater than that of the Pt disk microelectrode, shown in Figure 3.6B. This large hysteresis may be an indication that adsorbed fluoride ions on these nanowires interacts somewhat differently (more strongly) with hydrogen, making it more inhibiting for the ORR. The peak current obtained from this wire segment for the ORR is 3.31 nA with an onset potential of 101 ± 51 mV. All the onset potentials were taken as 5% of the maximum current observed from the ORR CVs and are the average of the ORR CVs from a single nanowire with the error representing one standard deviation of the average. Conversely, Figure 3.6B displays the ORR response of a glass-sealed 12.5 μm -radius Pt disk electrode in oxygenated 0.5 M H_2SO_4 solution before and after treating in a NaF solution. Here, the NaF treating was used to approximate the nanowire's exposure to HF during fabrication. The Pt disk electrode reveals a nice sigmoidal shape voltammetric response, characteristic of enhanced radial-type mass transport at micro and nanostructures. The reduction of oxygen on the Pt disk happens at an onset potential of 140 ± 8 mV vs Hg/Hg_2SO_4 indicating higher electrocatalytic activity than that demonstrated by the nanowires. The decrease of the reduction current at approximately -0.6 V is due to hydrogen adsorption on Pt, which decreases the electrocatalytic activity of the electrode, followed by a sharp increase in current due to proton reduction.

Compared to the inlaid disk, the Pt nanowire electrode shows lower electrocatalytic activity with a negative shift in the onset potential of nearly 39 ± 52 mV for the nanowire with the largest radius. Additionally, starting at around -0.4V and proceeding until the H^+ reduction potential²⁰, the hydrogen adsorption region begins to interfere with the ORR due to adsorbed H^+ ions competing with O_2 for surface sites, leading to a decrease in the reduction current. The decrease in the electrocatalytic activity and the increased competition from the hydrogen region contribute to a somewhat peak-shaped reduction wave as seen in the Figure 3.6A. These two effects are believed to be due to the contamination of F^- on the Pt surface, and are also seen when the potential is started below -0.6V and scanned positively, (not shown). The increased competition from adsorbed hydrogen seen on the fluoride contaminated electrode might be due to a large number of platinum surface sites being already blocked by the F^- ions leading to a decrease in available sites for hydrogen adsorption. As a consequence, the overall current is seen to start decreasing at a more positive potential, ~200mV, relative to the uncontaminated electrode. The adsorption of F^- is an

unexpected consequence of the fabrication process used to etch and release the nanowires from quartz using HF acid. It is well known that halides such as chloride¹⁶ and bromide³³ are inhibitors of the ORR on Pt by strong surface adsorption and blocking the active catalytic sites and recently fluoride has also been implicated in the poisoning of ORR catalytic sites.³⁴ However, the platinum disk microelectrode was freshly polished and washed prior to ORR testing to ensure a clean contaminant-free platinum surface.

In order to confirm the inhibiting effect of the F^- , the disk microelectrode was immersed in a 200 mM NaF solution for 20 minutes then washed with DI water before ORR testing. A drastic change in the voltammetric behavior of the disk microelectrode before and after NaF soaking is clearly seen in Figure 3.6B. The CV response of NaF-soaked Pt now becomes more peak shaped much like it is with the nanowire ORR CVs. Additionally, the onset potential is shifted negatively and in fact, is in the range of measured onset potential for the nanowires. On average, the onset potential for the ORR on the NaF-soaked Pt disk is 73 ± 28 mV as compared to 140 ± 8 mV for the cleanly polished Pt disk electrode. The adsorbed fluoride ion clearly depresses the ORR on the Pt disk and results in an average loss of peak current of ~ 8 nA and a negative shift for the onset potential of 67 ± 29 mV. Electrochemical cycling in sulfuric acid (-0.63 to $+0.9$ V vs Hg/HgSO₄) was used to attempt to clean the Pt nanowire electrodes, as it was found to be able to eventually clean and restore the behavior of the Pt disk microelectrode. We believe the sulfuric acid cycling started to cause dissolution of the nanowires and evidence can be seen in SEM images, seen in Figure 3.7. Despite this, the nanowires were cycled for a limited time to clean them, but cycling was kept to a minimum so as not to significantly etch the nanowire.

The results of all the ORR testing on nanowires with various radii are presented in Figure 3.8 which shows the onset potential as a function of the wire radius. As seen from this graph, as the radius of the wire decreases, the onset potential shifts slightly to more negative potentials indicating relatively lower catalytic activity. The onset potential for the nanowires is lower than that of the Pt microelectrode, being at ~ 140 mV, however, it does come close for the largest nanowire with an onset potential of ~ 101 mV as discussed previously. The slight negative shift of the onset potential with decreasing nanowire size shows a weak dependence in the activation energy barrier for the ORR on the nanowires radius. It is likely that the more negative onset potentials on single nanowires compared to the large Pt disk is mainly due to F^- adsorption. This may also partially

account for the loss in electrocatalytic activity of conventional fuel cell electrode catalysts. During regular operation in a fuel cell, especially at higher temperatures and/or for periods of extended operation, the catalyst layer may be exposed to fluoride ions due to partial decomposition of fluorinated proton exchange membranes (such as Nafion®),⁵ in the presence of un-reacted hydrogen peroxide³⁵ or at elevated operating temperatures.³⁶

As the electrodes decrease in dimension, the current density is expected to increase due to increased mass transport rates.^{4,37} When comparing the Pt nanowires to the Pt disk microelectrode the current density is larger for FcMeOH on all of the wires. An increase in current density for FcMeOH was observed as the wire radius decreased and exhibited a maximum current density on the 26 nm radius wire as shown in Figure 3.9A. This wire had a limiting current of 0.524 nA yielding a current density of 60.2 mA/cm². The limiting current for FcMeOH predicted using equation 2 is 0.596 nA giving a calculated current density of 68.4 mA/cm² which is in fair agreement to the experimental values. Interestingly, the current density for ORR decreased as the radius decreased also shown in Figure 3.9A. The current density for the Pt disk was found to be 4.55 mA/cm² for the ORR corresponding to the dashed line in Figure 3.9A and 1.41 mA/cm² for FcMeOH (not shown). All of the nanowires had a higher ORR current density than the Pt disk electrode, despite decreasing as the radius decreased. Figure 3.9B shows the mass activity for the nanowires increases as the nanowire radius decreases contrary to the current density trend and can be attributed to the increased surface/volume ratio. A similar effect of a decreasing current density and increasing mass activity has been observed before for decreasing Pt particle size.^{8,38} This observation was thought to be a result of competition effects for reactant through overlapping spherical diffusion layers between closely spaced nanoparticles.⁷ The fact that these are single nanowires further validates reports^{8,38} that the decrease in current density is not due to competition between nanoparticle ensembles, although very high nanoparticle loadings can certainly lead to competition.

To further investigate the decreasing current density with wire radius the predicted currents for the single nanowires, using equation 2, were calculated with the assumption that the number of electrons involved is $n = 4$ for a complete reduction of oxygen using the O₂ diffusion coefficient, $D = 1.4 \times 10^{-5}$ cm²/s, and bulk concentration, $C_b = 1.10 \times 10^{-6}$ mol/cm³, of oxygen saturated in 0.5 M H₂SO₄ at 25 °C.³⁹ When the current is calculated for the Pt disk using the equation for a disk microelectrode,²⁰ a calculated current of 40.2 nA is obtained in excellent agreement to its measured

value of 40.9 nA, validating our assumptions for calculating the ORR currents for the single nanowires. Figure 3.10 shows the percent difference between the experimentally obtained current and the predicted current, for both FcMeOH and ORR. Some difference between currents were expected because FcMeOH is a simple outer-sphere 1-e^- redox species and its CV is essentially diffusion limited while the oxygen is an inner-sphere species and its reduction involves diffusion, adsorption, catalytic reduction and desorption of the products. The percent difference for FcMeOH is, at most, $\sim 12\%$ different from experimental results and for the majority of the wires tested it is below 5% difference. However, for the ORR the percent difference is dramatically intensified to upwards of 91.7% for the smallest radius wire, yet just 49.5 % for the largest, where the experimental currents obtained were all below the predicted ORR current. This result indicates that the reaction of oxygen on Pt nanowires is far from diffusion limitation.

Chen and Kucernik⁴ found that on single electrodeposited Pt nanoparticles, as the size decreases the effective electron number used in the ORR also decreases, meaning more hydrogen peroxide is formed that would otherwise have been reduced to water. Additionally, on nanoparticles smaller than 50 nm, about 75% of the oxygen is reduced to water and 25% is reduced to hydrogen peroxide.⁴ Another factor in the discrepancy between the predicted and experimental ORR currents can be partially explained by the contamination of the fluoride ion. When comparing the calculated 40.2 nA current to the experimental 32.7 nA for the NaF exposed Pt disk electrode there is a 18.7% difference. The fluoride contamination could be contributing to the decrease in observed current by shifting the reaction mechanism from the 4 e^- reduction more to the 2 e^- reduction, which could be analogous to how adsorbed copper atoms block catalytic sites forcing the oxygen to adsorb in an end-on configuration.³² The percent difference of the ORR using the assumption $n = 2\text{ e}^-$ for the H_2O_2 pathway can be seen in Figure 3.10B. Even with this extreme assumption, upwards of 83% of the predicted ORR current is still not observed for the smallest wire. This indicates the observed experimental current on the nanowires is limited by the kinetics of the ORR and not the diffusion of the molecules to the surface and that more importantly the kinetics slow down as the wire radius decreases. The decrease in current density has been seen in Pt nanoparticle ensembles that vary in diameter and is proposed to be a result of the increasing adsorption energy of oxygenated species.^{8,40}

Tafel plots from the ORR for a 26 nm radius wire and the Pt disk microelectrode are shown

in Figure 3.11 and display the characteristic change in Tafel slopes indicating a change in adsorption from Tempkin isotherm to Langmuir isotherm.^{38,41} The high overpotential (low current density) region has a Tafel slope of around 60 mV/decade corresponding to an oxide covered Pt surface. The low overpotential (high current density) region has a slope of ~120 mV/decade corresponding to an oxide free Pt surface.^{41,42} Additionally, the change in the slope on the 26 nm wire occurs at around 0.8 V (vs. RHE), whereas the change occurs at 0.9 V (vs. RHE) on the polycrystalline Pt disk. The lower potential necessary for the slope change on the nanowire indicates higher adsorption energy for oxygenated species.^{8,38,40} Oxygenated species, such as OH⁻ or HO₂⁻, are more strongly adsorbed to the Pt surface hindering the ORR kinetics leading to a decrease in the catalytic activity of the Pt wires for the ORR.⁴⁰

3.4 Conclusion

In conclusion, electrodes were made from single platinum nanowires that were mechanically prepared with a laser pulling method in order to study the catalytic ORR on single platinum nanowires of decreasing radii. The electrocatalytic activity has been found to be dependent on the nanowire size revealed from a change of the onset potential. A clear increase in the mass activity is observed as the wire radius is decreased. It was found that the nanowires were contaminated with fluoride ions that inhibit the ORR, possibly resulting in a decreasing density of catalytic sites as the wire narrows, which may help account for the notable decrease in ORR current density of the nanowires. The Tafel plots indicate increased adsorption energy of oxygenated species to the Pt nanowire surface due to the switching of the Tafel slopes at a lower potential for the wires than for the polycrystalline platinum. This increase in the adsorption strength slows the ORR kinetics and lowers the observed current density. The decreases in the ORR experimental current, with respect to the calculated current, is seen to be a combination of both fluoride anion adsorption to catalytic sites blocking the ORR and a decrease in the ORR kinetics from the higher adsorption energy of oxygenated species.

Future nanowires used for catalytic reaction studies will be etched out of the quartz coating using hydroxide which will eliminate the contamination from the fluoride ions and allow a more detailed understanding of these platinum nanowires. Additionally, catalytic studies using single nanowires in organic, alkaline, as well as acidic solutions, is possible using a photo-definable polyimide that once patterned and cross linked will be able to withstand harsh chemical

environments. Despite the hurdles these wires hold a unique opportunity to study a range of phenomena where single nanowires offer a versatile platform to more fully understand the changing properties of bulk materials at nanoscale dimensions.

3.5 Figures

Figure 3.1 Single Platinum Nanowire Isolation

Schematic depicting the fabrication steps used to contact and expose the sides of single Pt nanowires for the study of the ORR.

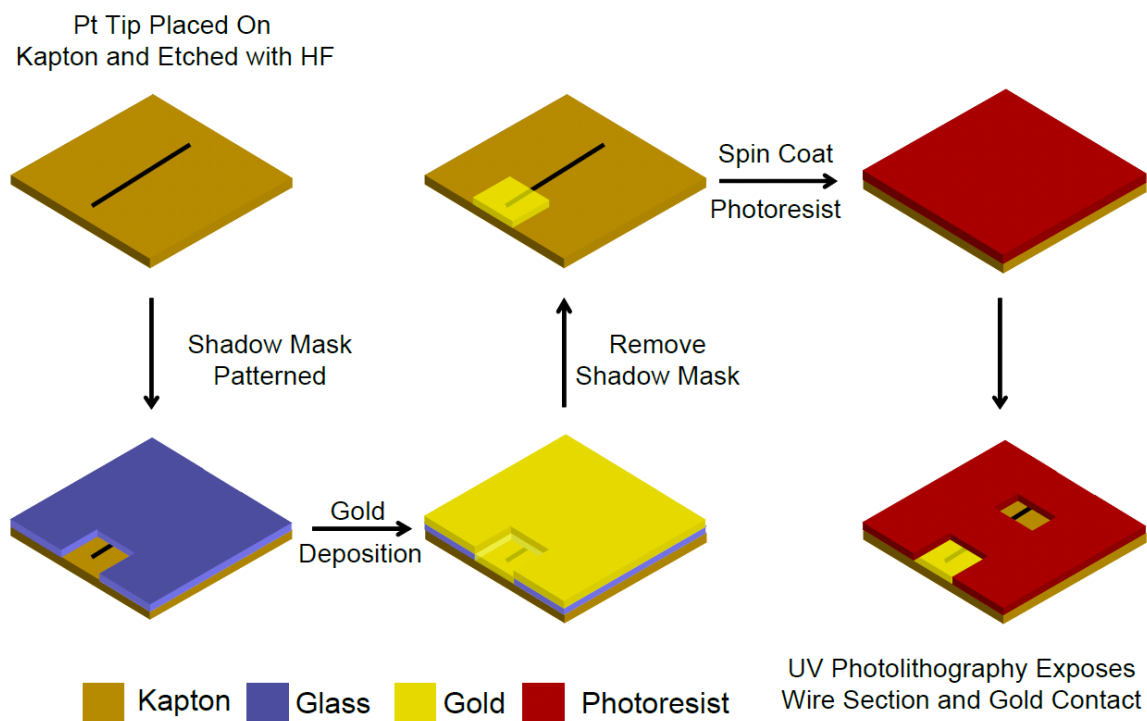


Figure 3.2 Nanowire Hemi-Cylinder Redox Diffusion

Schematic showing how the platinum wire is thought to shadow the photoresist beneath it, resulting in blockage of the diffusing redox molecules to the bottom half of the nanowire in solution.

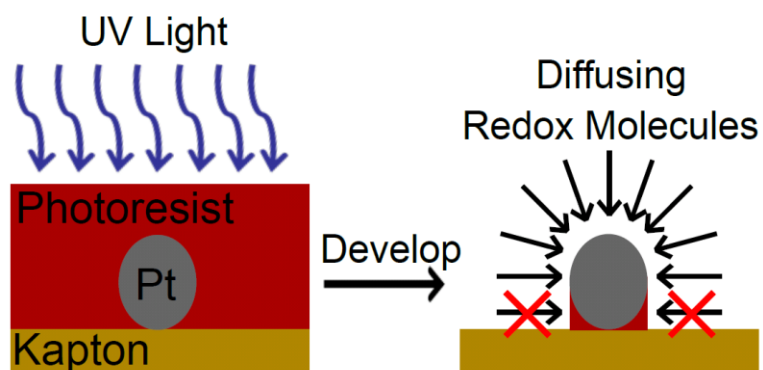


Figure 3.3 Single Isolated Platinum Nanowire SEM

SEM images of a platinum nanowire electrode showing the photoresist trench and a 13.32 μm length of a 92.5 nm radius wire. Inset shows a magnified image of the same nanowire segment.

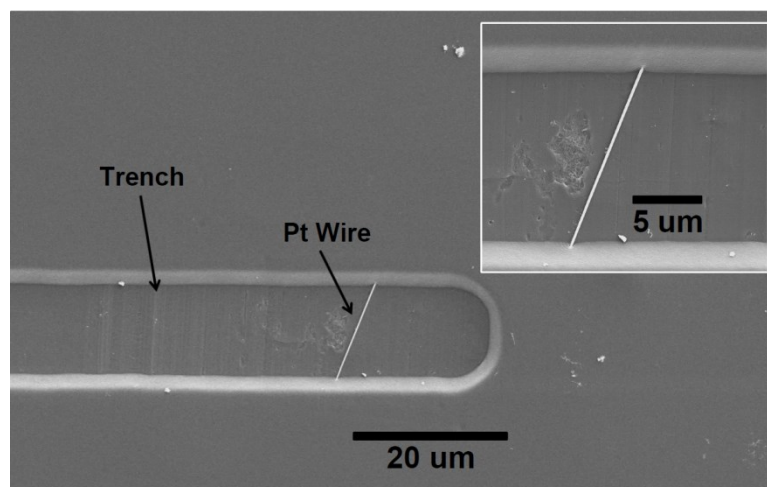


Figure 3.4 Single Platinum Nanowire Redox CVs

CVs in 2 mM FcMeOH in 100mM KCl from A) of a 40.5-nm-radius 19.84 μm long Pt nanowire and B) of a 116 nm-radius 20.35 μm long Pt nanowire. C) and D) show the CVs from the same wire segment in B), using C) 5 mM $\text{K}_3\text{Fe}(\text{CN})_6$ with 1.5 M KCl and D) 5 mM $\text{K}_4\text{Fe}(\text{CN})_6$ with 1.5 M KCl. All scan rates were 50 mV/s.

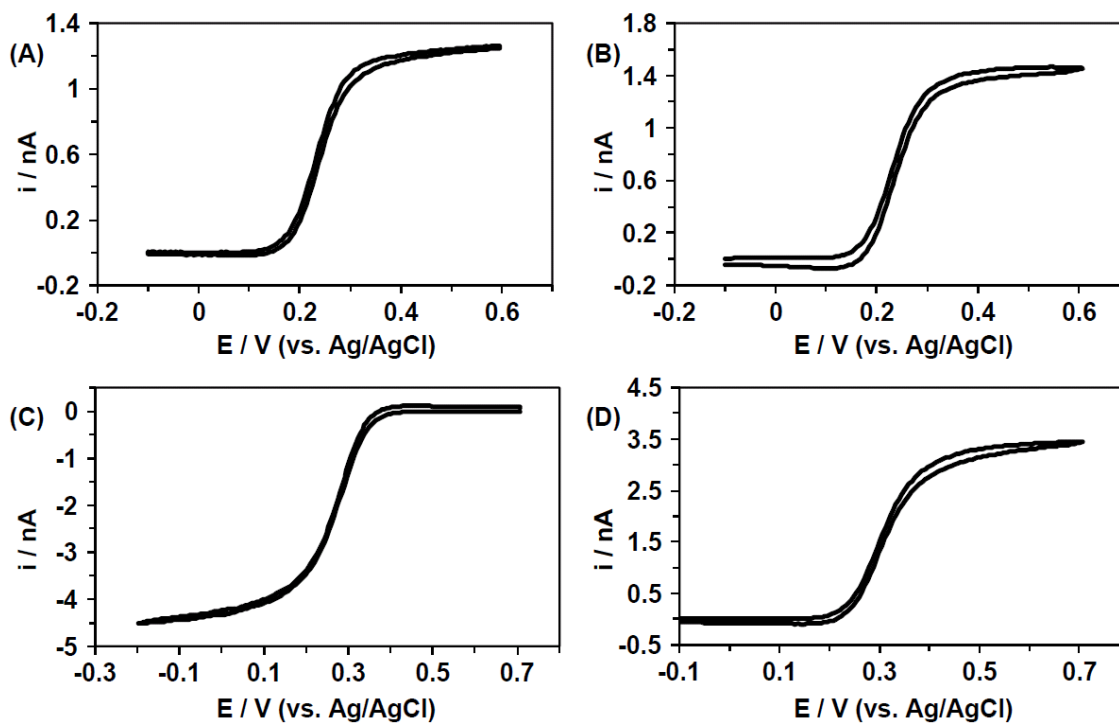


Figure 3.5 Copper Under Potential Deposition

A) Linear sweep voltammetric responses of a 49 nm radius 21.94 μm long Pt nanowire after copper UPD for different amount of time. The wire was held at 0 V (vs. Ag/AgCl) for the amount of time indicated above each trace before initiating the linear sweep, scale bar is 50 pA. B) Total charge obtained by integrating the area under the copper stripping peaks shown in (A). The Scan rate was 100 mV/s.

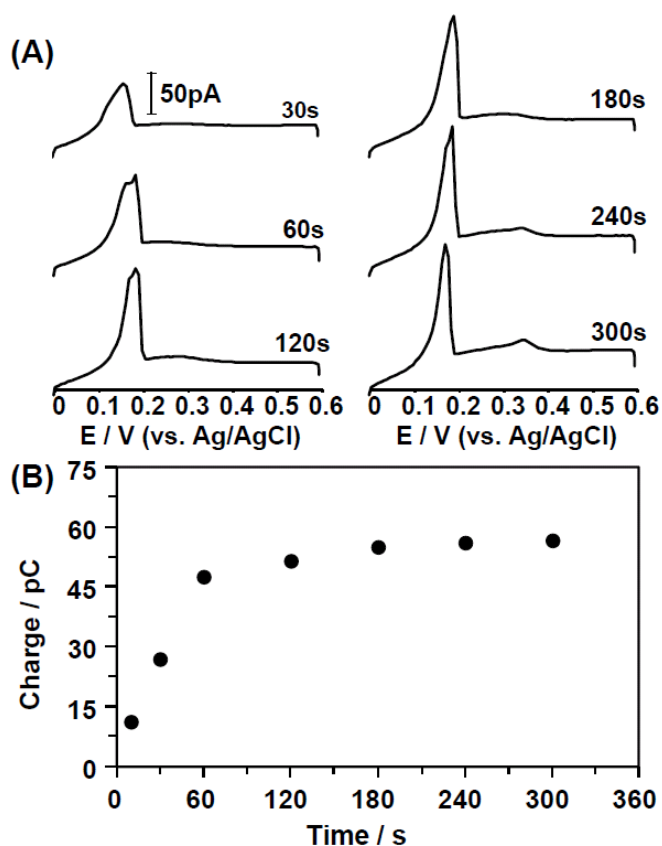


Figure 3.6 Nanowire Oxygen Reduction Reaction

A) CVs of a 116 nm radius 20.35 μm long Pt nanowire electrode in O_2 bubbled or N_2 bubbled 0.5 M H_2SO_4 and B) a 12.5 μm radius Pt disk microelectrode in 0.5 M H_2SO_4 bubbled with O_2 showing the effects of a 20 minute soak in 200 mM NaF solution on the ORR. All scan rates were 100 mV/s.

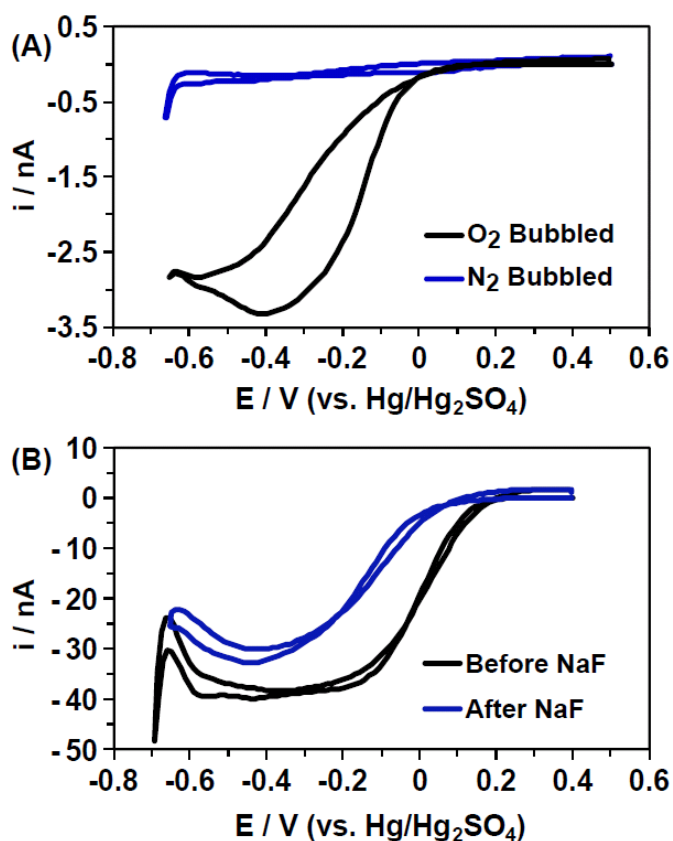


Figure 3.7 Voltage Cycled Sulfuric Acid Etched Nanowire

SEM image of a Platinum nanowire after potential cycling in 0.5M H_2SO_4 showing the preferential etching of the wire at the farthest exposed end from the Au contact. After the nanowire has been etched away the previously shadowed photoresist can also be seen in the SEM image.

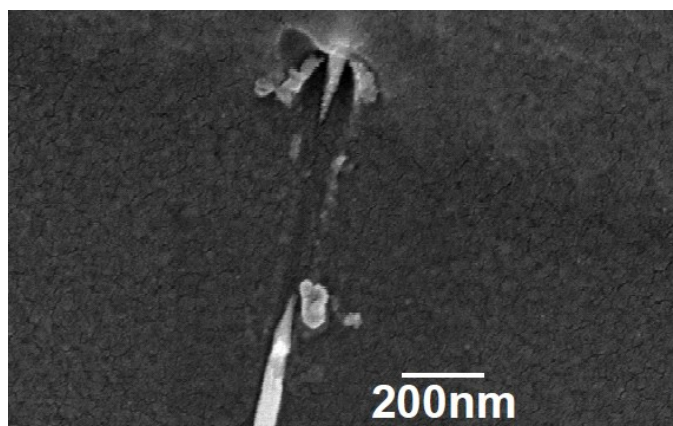


Figure 3.8 Onset Potential vs Wire Radius

Relationship between the onset potential and the wire radius for the ORR for each nanowire, taken as 5% of the maximum current observed for each CV. Error bars indicate one standard deviation from the mean onset potential for each individual nanowire.

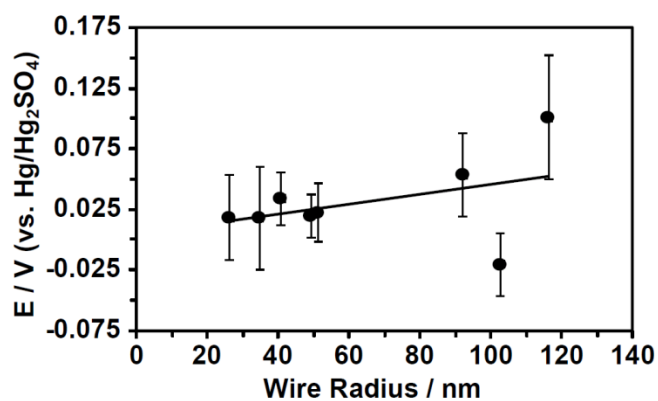


Figure 3.9 Current Density and Mass Activity

A) Current density vs. wire radius for the 2 mM FcMeOH with the theoretical current density of 2 mM FcMeOH calculated from equation 2 and the current density for the ORR using the geometric surface area, dashed line at $\sim 4 \text{ mA/cm}^2$ represents the Pt disk ORR current density. B) Mass activity for the wires as a function of the wire radius.

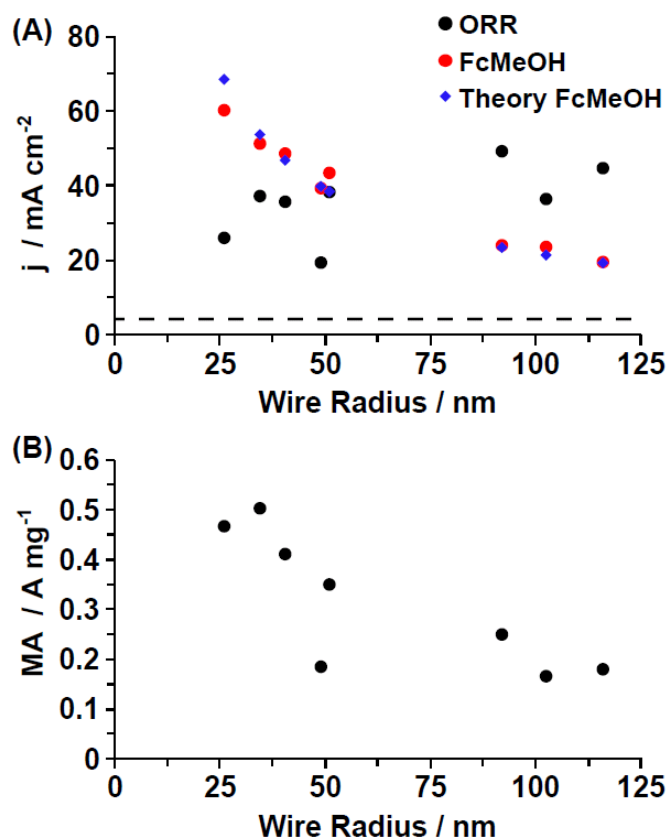


Figure 3.10 Deviation of Experimental ORR Current

A) Percent difference between experimental and calculated peak currents for FcMeOH and ORR assuming $n = 4 e^-$ and B) ORR percent difference assuming $n = 2 e^-$. i_{exp} is the experimentally obtained current and i_{pred} is the calculated current from equation 2 using $\frac{1}{2}$ the area of the cylinder for each wire segment.

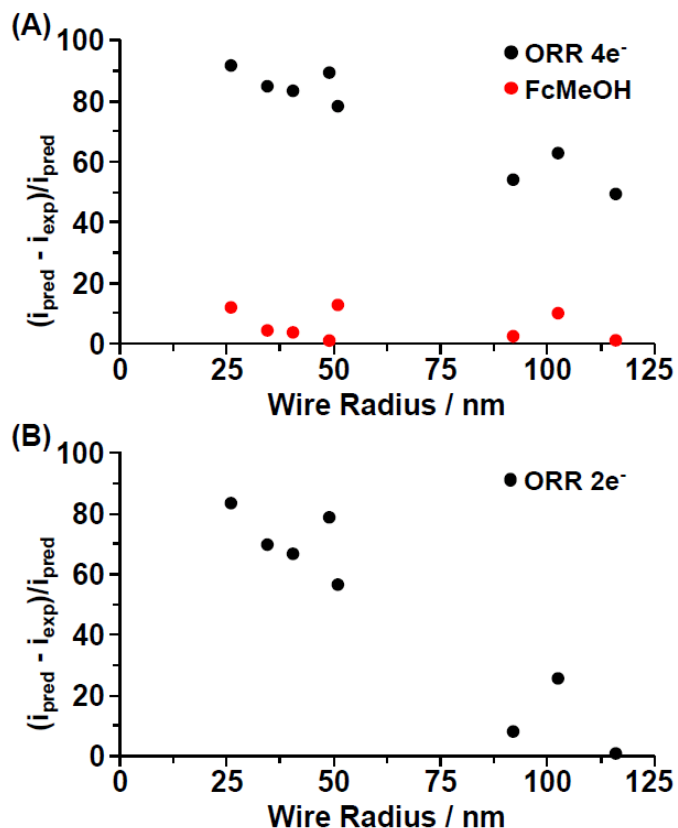
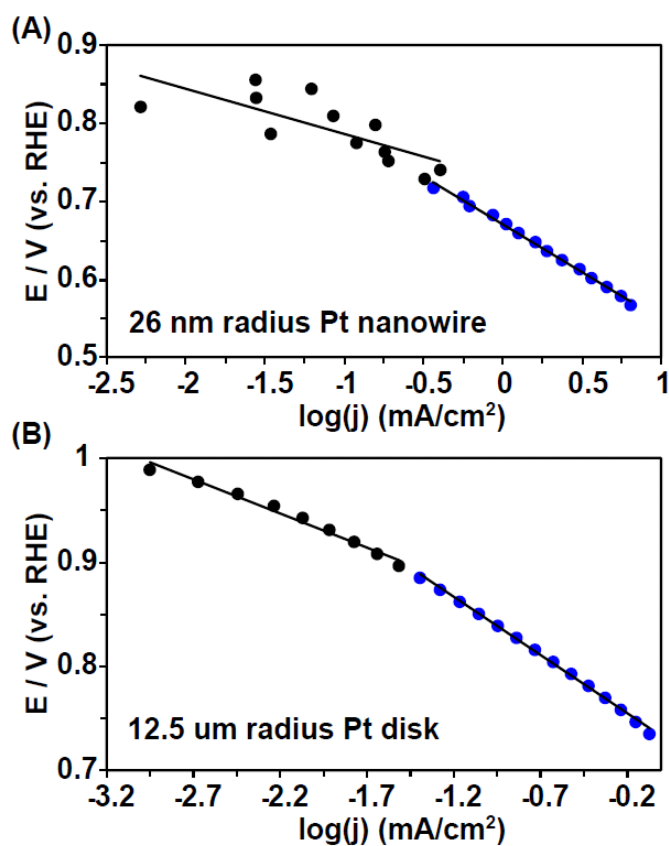


Figure 3.11 Platinum ORR Tafel Plots

Tafel plots for a 26 nm radius Pt nanowire (A) and a Pt disk microelectrode (B) with 100 mV/s scan rates. The shift between slopes for the nanowire is seen to happen at a lower potential than the Pt disk.



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Chapter 4 Chemically Resolved Transient Collision Events of Single Electrocatalytic Nanoparticles[‡]

4.1 Introduction

Metal nanoparticles (NPs) find wide application in studies including biotechnology^{1,2} and sensing^{3,4} and are the materials of choice in numerous electrocatalytic processes.⁵⁻⁷ This is at least partially due to their unique size and shape tunable electronic, optical, and catalytic properties.⁸⁻¹¹ Previous research in the area of NP electrochemistry and electrocatalysis has mainly studied the structure–function relationships of NP ensembles.^{10,12} This, however, is challenging due to ensemble averaging and possible overlap in the diffusion field in closely spaced NPs.¹³ The ability to directly analyze structurally well-characterized single particles opens up new avenues in this area.

A number of excellent single-particle experiments have recently been published. These include experiments utilizing transient particle-electrode collision¹⁴ and catalytic amplification,¹⁵⁻¹⁸ single-molecule fluorescence,¹⁹ and surface plasmon spectroscopy.²⁰ Fluorescence and surface plasmon based methods allow a single-NP response to be optically addressed from an ensemble allowing many particles to be studied simultaneously.²¹ Direct electrical measurements generally require isolation of individual particles from the bulk. There are three major ways to isolate single NPs: particle–electrode collision,¹⁵⁻¹⁸ single-particle immobilization on a nanoelectrode,^{22,23} and methods based on the use of a scanning probe.²⁴ We, along with others,²⁵ have used nanoelectrodes to isolate, immobilize, and characterize single metal NPs.

Single-particle collision has become a particularly useful approach because of its simplicity, speed, and power allowing for quick analysis of hundreds of NPs in minutes. Previous particle collision experiments involve holding a constant potential on a probe ultra-microelectrode (UME) and recording its time-dependent faradaic response as single particles interact with the electrode. Each NP collision event results in a transient current fluctuation due to catalytic current amplification¹⁶ or current blockage.²⁶ A limitation of this approach, however, is the lack of chemical

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resolution. As such, its application has been primarily limited to the study of highly pure NPs at a fixed potential where no additional information is gained beyond the transient current response.

We have been working on a new approach to extend the single particle collision concept to better understand the transient interfacial kinetics of NPs. Our approach is based on the use of a fast and repetitive voltage perturbation on an inert electrode to obtain a transient electrocatalytic response during collision events of single NPs. Our goal is to gain necessary chemical information on single NPs undergoing quick collisions. This study will likely extend the use of the powerful particle-electrode collision approach to uncovering some of the hidden details of the electrocatalytic process.

Our approach involves the use of Fast-Scan Cyclic Voltammetry (FSCV) and is illustrated in Figure 4.1. In this work, a popular electrocatalytic amplification scheme has been adopted, which consists of a 5 μm diameter carbon-fiber UME as the probe electrode, 15 mM hydrazine (N_2H_4) as the redox indicator, and platinum and gold NPs. Here, a triangular voltage waveform is continuously scanned on the probe UME and the background subtracted faradaic response is monitored. The voltage on the UME is scanned in a range typically between -0.4 and $+0.4$ V vs a Ag/AgCl electrode where oxidation of hydrazine is kinetically slow on carbon but can be catalytically enhanced on platinum or gold. When a platinum (or gold) NP approaches and attaches on the carbon UME, hydrazine oxidation can quickly proceed on the NP resulting in a sudden, drastic increase in the faradaic signal.^{16,17} It is important to note that FSCV is a popular electroanalytical technique pioneered by Wightman and coworkers^{27,28} and is particularly useful in the study of fast neurochemical events in the brain.

4.2 Experimental

4.2.1 Chemicals and Materials

All chemicals and materials were used as received from the manufacturers. Deionized water (>18 M Ω cm, Barnstead Nanopure Systems), methanol (Sigma Aldrich), potassium chloride (KCl, Fisher Scientific), Ferrocene methanol (FcMeOH, Aldrich 97%), ferricyanide ($\text{K}_3\text{Fe}(\text{CN})_6$, Sigma-Aldrich 99%), ferrocyanide ($\text{K}_4\text{Fe}(\text{CN})_6$, Fluka 99.5%), hydrazine (anhydrous 98%, Sigma Aldrich), monobasic potassium phosphate (KH_2PO_4 , J. T. Baker), dibasic potassium phosphate (K_2HPO_4 , J. T. Baker), Gold Chloride trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, Sigma Aldrich), Chloroplatinic acid hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$,

Sigma Aldrich), sodium citrate dihydrate (J. T. Baker), citric acid (Fisher Scientific), Sodium Borohydride (Sigma Aldrich), 2-allylphenol (Sigma Aldrich), ammonium hydroxide (Fisher Scientific), 30 nm Pt nanoparticles (nanoComposix, Inc. San Diego, CA), were all used as received from the manufacturer.

4.2.2 Synthesis of 12 nm Au Nanoparticles

Gold nanoparticles were synthesized by the reduction of HAuCl_4 with sodium citrate. All glassware was thoroughly cleaned with fresh piranha solution prior to use and rinsed thoroughly before use. 50 ml of 0.01% m/v of HAuCl_4 was refluxed while stirring and 1.8 ml of sodium citrate solution (1% m/v) was then rapidly injected into the flask. The solution was allowed to reflux for 15 minutes and then allowed to cool to room temperature.

4.2.3 Synthesis of 4 nm Pt Nanoparticles

Platinum nanoparticles were synthesized using thoroughly cleaned glassware (as described previously), where 36 ml of a 0.2% chloroplatinic acid hexahydrate was added to 464 ml of DI water. The solution was brought to a boil and 11 ml of 1% sodium citrate and 0.05% citric acid was added. After a half of a minute, 5.5 ml of freshly prepared 0.08% sodium borohydride with 1% sodium citrate and 0.05% citric acid was very quickly injected into the boiling solution and allowed to boil while stirring under reflux. After 10 min the product was cooled to room temperature.

4.2.4 Preparation of Carbon Fiber Electrodes

To prepare the carbon fiber electrodes, 5 μm carbon fibers were sealed in borosilicate capillaries (Outer diameter: 1.2 mm, inner diameter 0.69 mm) by thermal pulling on a micropipette puller (Sutter instruments P-97). Electrical contact was then made using silver conductive paste (Dupont) and tungsten wires. The carbon fibers lengths would extend out of the borosilicate capillary after the pulling procedure and would need to be insulated. To insulate the carbon fibers the electrodeposition and cross linking of 2-allylphenol copolymer was used. Electrodeposition of the 2-allylphenol was done using a 0.90 mM 2-allylphenol in a 1:1 H_2O :methanol solution where the pH was adjusted to 9.0-9.2 using ammonium hydroxide. The electrodes were submerged in the 2-allylphenol solution and the copolymer was deposited by electrooxidation where positive 4 volts was applied to the carbon fiber vs. a platinum wire counter electrode for ~10 minutes. The electrodes were then heated to 150 $^\circ\text{C}$ for 30 minutes in an oven to cure the copolymer coating.

4.2.5 Electrochemical Measurements

Steady-state voltammograms were recorded using a computer-controlled Dagan Chem-Clamp voltammeter/amperometer and data was recorded using an in-house virtual instrumentation program written in LabVIEW (National Instruments) on a desktop PC equipped with a PCI-6251 (National Instruments) data acquisition card. A commercially available Ag/AgCl reference electrode (Bioanalytical Sciences, Inc.) was used as reference electrode for all electrochemical data. Fast-Scan Cyclic Voltammetry (FSCV) data was obtained using a home-built breakout box (UNC Chemistry Electronics Design Facility) equipped with a low noise current amplifier (Electro Optical Components, Inc. model: LCA-10K-500M) running the FSCV software developed by the Wightman's group at the University of North Carolina.²⁹

4.2.6 Electron Microscopy

Scanning Electron Microscope (SEM) images were obtained using a field-emission SEM (FEI Sirion). Samples were sputter coated with a 2-3 nm thick layer of Au/Pd prior to SEM imaging. Transmission Electron Microscope (TEM) imaging was performed on a FEI Tecnai G2 F20 S-Twin operating at 200 kV using a single tilt sample holder and carbon coated Formvar copper TEM grids (Ted Pella).

4.3 Results and Discussion

4.3.1 Analysis of Platinum Nanoparticles

Figure 4.2a displays a characteristic 60 s FSCV trace recorded on a 5 μm diameter carbon UME in a solution containing 15 mM N_2H_4 , 5 mM phosphate at pH 7.4, and 0.5 nM 4 nm platinum NPs. Here, a color plot is employed to present 6000 continuously recorded, background-subtracted CVs together in one figure. The current is color-coded, and the electrode potential is plotted on the y-axis. Additional details about FSCV and the use of color plots can be found in a recent article by Wightman and co-workers.²⁹ A NP collision event in Figure 4.2a is represented by a quick color (current) change. Here, five discrete collision events, at approximately 2.5, 7.5, 17, 33, and 51 s, respectively, are clearly resolved. Each event shows distinct voltammetric characteristics indicating that they are from different particles and not the same particle bouncing back and forth on the electrode. Here, the rate at which Pt particles are detected is smaller than that predicted from

diffusion flux (Supplemental Information) indicating that only a small number of particles reaching the electrode result in effective detection.

The faradaic current at a certain applied potential from each individual CV can be easily extracted out of the color plot to generate a current–time response similar to that recorded in conventional amperometry. Figure 4.2b is the current–time trace at 0.1 V obtained from Figure 4.2a where Figure 4.2b has kept some of the essential characteristics of single NP collision events of Pt in hydrazine. Each particle collision event can be seen as a quick increase in the faradaic current originating from the electrocatalytic amplification of platinum on carbon. The drop in current is believed to be largely due to particle deactivation although the exact mechanism is unclear. A similar response has been observed in constant-potential amperometry, as shown in Figure 4.3.

Figure 4.2c shows a background-subtracted CV response recorded at 7.7 s, which corresponds to immediately after collision and immobilization of a second Pt NP in this 60 s trace. The current–voltage response at 7.5, right before the sharp current increase, was used as the background. The collision event results in a sigmoidal shape CV response which is due to the electrocatalytic oxidation of hydrazine on the Pt. Interestingly, even at a scan rate of $v = 400$ V/s, the voltammetric response still displays steady-state behavior. This is due to fast and radial-type diffusion of hydrazine and kinetic limitation. First, a quick estimate (see Supplemental Information below) using the Einstein relation,³⁰ $d = (2Dt)^{1/2}$, gives a diffusion layer thickness d of 422 nm.³¹ Here, $D = 1.39 \times 10^{-5}$ cm²/s is the diffusion coefficient of hydrazine,³² $t = RT/Fv$ is the experimental time duration, R is the gas constant, T is the temperature, and F is the Faraday constant. This is more than 2 orders of magnitude greater than the radius of the NP. This gives rise to a radial type diffusion and sigmoidal shape voltammogram.³¹ Second, the peak current in Figure 4.2b or the plateau current in Figure 4.2c is smaller than the theoretical prediction based on the diffusion limitation (see below), indicating that the hydrazine oxidation on Pt is kinetically limited due to the presence of citrate ligand molecules.

We have compared the faradaic responses recorded using both FSCV and amperometry in order to further validate the use of FSCV to study single particle collisions, and the results are shown in Figure 4.4. Here, a 5 μ m carbon UME, 15 mM N₂H₄, and 0.5 nM 4 nm Pt particles were used. The hydrazine oxidation peak currents were recorded at the same voltage, +0.1 V vs Ag/AgCl. The FSCV histogram closely matches that of amperometry and the Gaussian fitting gives an average peak

current of ~ 36 pA in both cases, indicating that FSCV gives comparable electrocatalytic results in particle collisions. More importantly, FSCV also offers additional chemical resolution, which is otherwise difficult to obtain with amperometry. This is further demonstrated in the following section.

We note that the average peak current is a bit smaller than the theoretical prediction (~ 140 pA) based on the diffusion limitation,¹⁶

$$i_{ss} = 4\pi \ln(2)nFDC_b r \quad (1)$$

where i_{ss} is the diffusion limited hydrazine current, $n = 4$ is the number of electrons transferred per molecule, C_b is the bulk concentration, and r is the NP radius. There are three possible reasons leading to this smaller peak current. First, hydrazine is an inner-sphere redox molecule, and its oxidation on Pt surface may be strongly hindered by the presence of the ligand molecules on the NP.³³ Therefore, not all the surface area is available for hydrazine oxidation. Second, the measurement of the peak current may be affected by a quick deactivation of the Pt surface, as the NP is in close contact with the UME surface. Third, the high mass transfer on the NP could lead to partial decomposition of hydrazine and some of the reaction intermediates can be carried away by quick diffusion leading to a smaller apparent number of transferred electrons, n . Similar effects have been discussed in the literature for the reduction of oxygen on nanometer-scale electrodes.²⁵

4.3.2 Analysis of Gold Nanoparticles

As expected, the use of FSCV is not restricted to the study of platinum NPs. Single-particle collisions can also be probed for gold particles on carbon UMEs with FSCV. The gold particles used in this work are citrate-stabilized, 12 nm spherical particles. Figure 4.5a shows an FSCV color plot collected on a 5 μ m carbon UME in a 15 mM N_2H_4 solution containing 0.1 nM 12 nm gold particles. Five collision events have been detected and are resolved on the color plot. Figure 4.6 shows a characteristic CV recorded from a 12 nm gold particle taken from the FSCV color plot. The current-time trace taken from the FSCV color plot at 0.2 V vs Ag/AgCl (not shown) has five discrete collision events. This is similar to an amperometric trace taken in the same conditions (not shown) where discrete particle collisions have been clearly seen in both methods. Figure 4.5b is a comparison of peak current collected using both methods, and the results again show a good agreement between two detection methods in the distribution of event characteristics. Both

methods have similar peak current distributions with the Gaussians centered at ~ 80 pA. This peak current is also smaller than the theoretical prediction (~ 420 pA) based on eq 1 and the particle size measured in TEM, and we hypothesize that this is due to the same possible factors: hindrance from ligands, particle deactivation, and high mass-transport rate.

The voltage scan rate, v , is an important parameter in FSCV and should be carefully selected in a particular collision experiment. The scan rate can have several key effects. First, it is directly related to the temporal resolution, and therefore, a high v is preferred because it allows for a higher repetition rate, i.e. number of CVs per unit time, and thus increased temporal resolution. Second, one would think that it may affect the faradaic current collected on the NP. Our results have shown (Figure 4.7) that the faradaic response recorded with FSCV is essentially independent of scan rate due to the extremely small size of NPs and high mass transfer rate. We normally use scan rates in the range of 50–500 V/s, and the characteristic radial-type diffusion is expected to be maintained. Third, the voltage scan rate cannot be too high because the double layer charging current increases linearly with scan rate. Therefore, depending on the size of the probe UME, it may cause extra noise or even current overload of the detection equipment.

4.3.3 Chemical Resolution of Gold and Platinum Nanoparticle Mixtures

One of the most significant features of FSCV is its excellent chemical resolution in addition to high temporal resolution. Wightman and co-workers have reported that it is possible to identify up to 9 different redox species in a 2 volt CV scan window.³⁴ Here, chemical resolution is also demonstrated in this study using a mixed solution containing platinum and gold NPs. We note that a mixed solution of Pt and Au particles is not chemically stable and one can often see quick color changes indicating particle aggregation upon mixing. Figure 4.8a is an FSCV color plot recorded on a 5 μm carbon electrode in a 5 mM phosphate buffer containing 15 mM N_2H_4 , 0.1 nM 12 nm gold NPs, and 0.1 nM 30 nm platinum NPs. There are 11 collision events detected in this 60 s detection period. Each NP collision event can be individually examined to extract its CVs prior to and after particle immobilization. A careful analysis of their voltammetric responses reveals that both platinum and gold NPs were detected: events 2, 3, 8, 9, and 10 are likely due to platinum NPs with a representative CV shown in Figure 4.8b (blue CV curve); events 4 and 5 are likely due to gold NPs, Figure 4.8b (black CV curve). Interestingly, a few events exhibited characteristics of both metals, likely due to the collision of gold–platinum dual particles, where Pt NPs may have adsorbed onto the

Au NPs before collision. These include events 1, 6, 7, and 11. There are two consecutive oxidation waves seen in the CV as shown in the red CV curve in Figure 4.8b. The first wave at ~ -0.2 V is likely due to platinum, and the second wave at $+0.2$ V is likely due to the presence of gold.

4.4 Conclusion

In conclusion, we have presented the use of fast-scan cyclic voltammetry to study single-nanoparticle collisions and immobilization on an inert ultramicroelectrode. This method uses a scanning potential on an inert UME at high scan and repetition rates and records its faradaic response as single electrocatalytic electrode surface. The use of FSCV has enabled us to obtain chemically resolved information about transient particle-electrode interactions which is otherwise difficult to obtain with previous constant-potential techniques. Voltammetric responses can be obtained at single colliding NPs with millisecond time resolution prior to and after particle collision and immobilization. Such information can be particularly valuable for future mechanistic studies for electrocatalytic NPs such as particle-electrode interaction, particle activation and deactivation, and heterogeneous electron-transfer kinetics. These are among the subjects of our ongoing studies.

4.5 Figures

Figure 4.1 Fast Scan Cyclic Voltammetry of Nanoparticle Collision

A scheme depicting the electrocatalytic amplification of a metal nanoparticle colliding with an inert UME which will then catalyze the hydrazine oxidation reaction. During the FSCV scans a fast, successive potential scan is applied to the electrode and before the nanoparticle collision there is no catalytic current response but after collision the nanoparticle CV is observed.

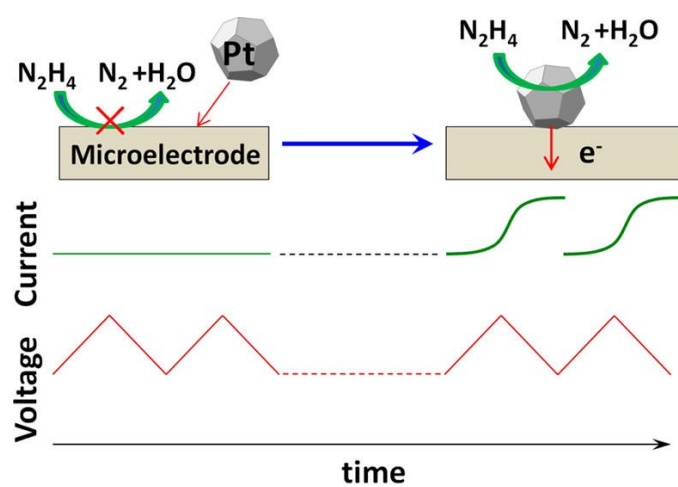


Figure 4.2 FSCV Single Collisional Events of Platinum Nanoparticles on Carbon

(a) A 60 s FSCV recording at $v = 400$ V/s showing detection of 5 Pt NPs on a $5\ \mu\text{m}$ carbon UME in a 15 mM hydrazine solution. (b) The current-time trace taken from (a) at $+0.1$ V vs Ag/AgCl showing single-particle current peaks similar to that recorded with conventional amperometry. (c) Background-subtracted CV recorded at 7.7 s in (a) showing faradaic response of an ~ 4 nm Pt particle.

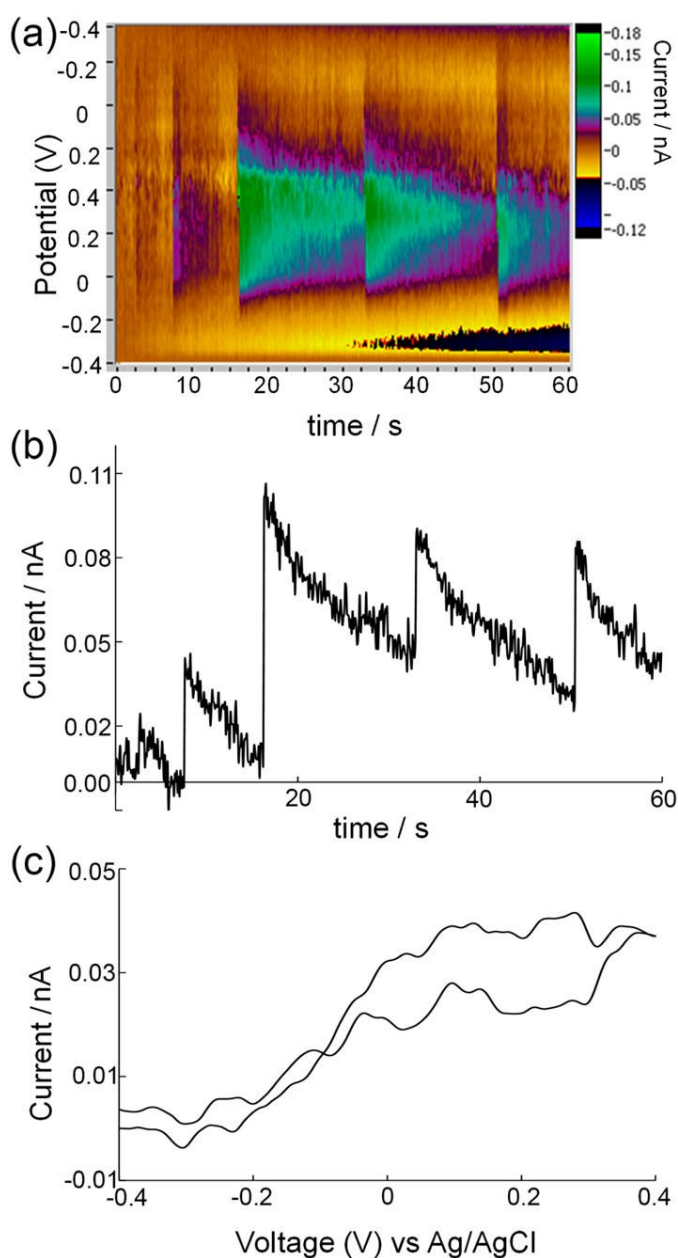


Figure 4.3 Amperometric Detection of Platinum Nanoparticles

A typical current-time trace from a 5 μm carbon fiber with 0.1 nM 4 nm Pt nanoparticles in 15 mM hydrazine, 5 mM phosphate at pH 7.4 with the potential fixed at 0.1 V vs Ag/AgCl.

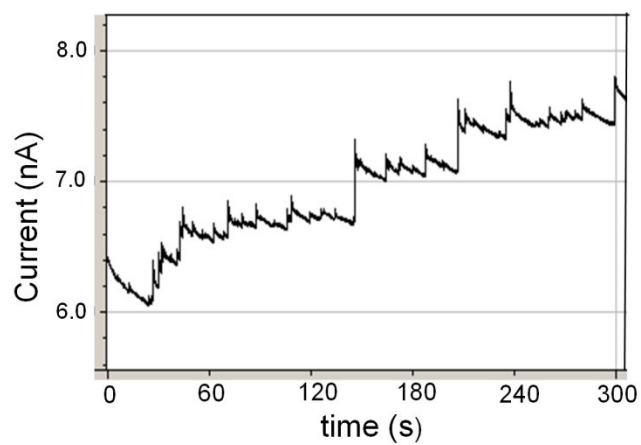


Figure 4.4 FSCV and Amperometry Peak Current Comparison

A comparison of peak current recorded in amperometry and FSCV for single-particle collision experiments. Here, all currents were recorded at +0.1 V vs Ag/AgCl on a 5 μm carbon UME. Both experiments used a 15 mM hydrazine solution and 0.5 nM 4 nm Pt NPs.

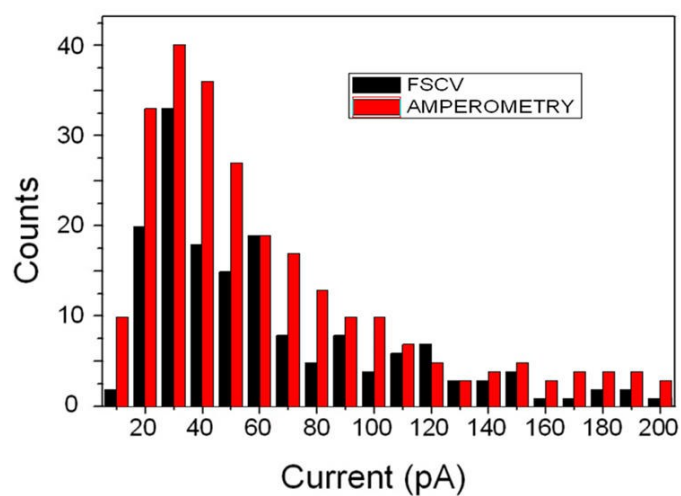


Figure 4.5 Gold Single Nanoparticle Collisions

Single collisional events of 12 nm gold particles on carbon in a 15 mM hydrazine solution. (a) A 60 s FSCV color plot showing detection of gold particles on a 5 μm carbon UME. (b) A histogram of peak current detected with FSCV (black) and amperometry (red) for the same 12 nm gold particles in 15 mM hydrazine. The current was recorded at 0.2 V in both experiments.

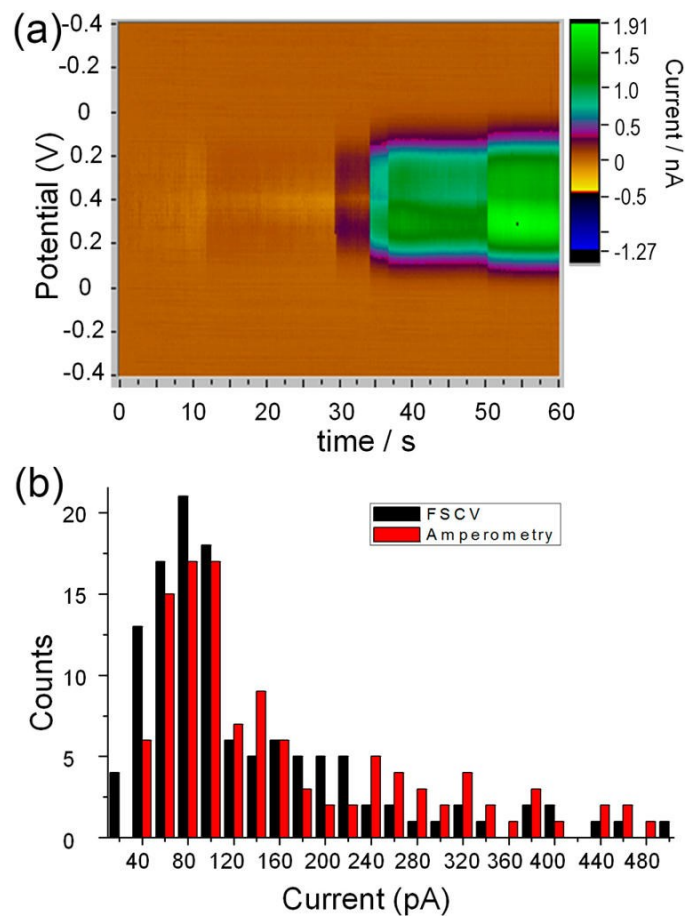


Figure 4.6 Gold Single Nanoparticle CV

CV from a 12nm Au nanoparticle taken from the FSCV trace shown in Figure 4.5 text at 13 s in 15 mM hydrazine in 5 mM phosphate at pH 7.4.

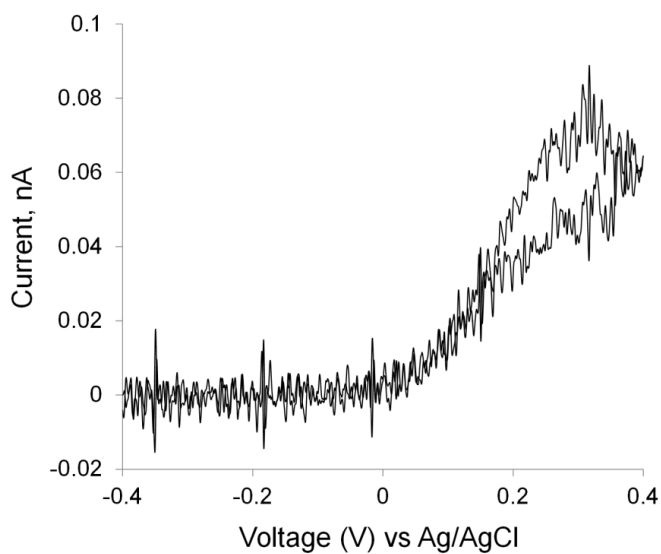


Figure 4.7 FSCV Scan Rate Dependence

Histogram showing the current step distributions for 4 nm Pt nanoparticles using FSCV at two different scan rates using a 5 μm carbon fiber UME in 15 mM hydrazine with 5 mM phosphate at pH 7.4.

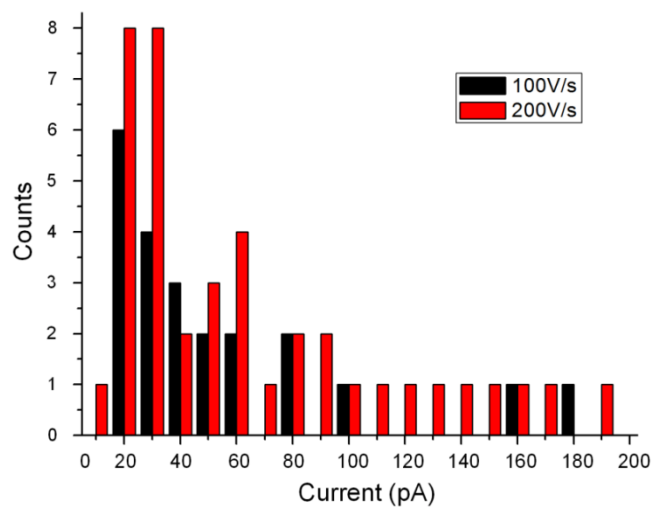
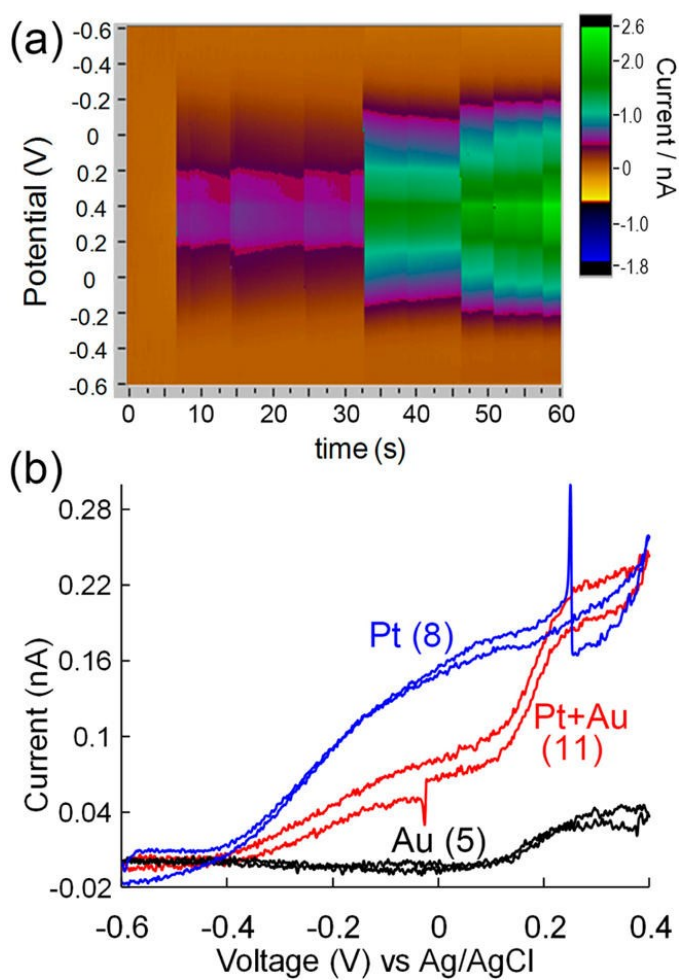


Figure 4.8 Chemically Resolving Single Nanoparticles

(a) A 60 s FSCV color plot showing detection of 11 single collision events on a 5 μm carbon UME in a 15 mM hydrazine solution. (b) Typical single-particle CVs recorded with FSCV. The blue, red, and black CVs are extracted from particles 8, 11, and 5 respectively.



4.6 Supplemental Information: Estimate of the Collision Frequency from Diffusive Flux and the Diffusion Layer Thickness Using the Einstein Equation

4.6.1 Estimate of the Collision Frequency from Diffusive Flux

For the 4 nm Pt nanoparticle, collision frequency on the 5 μm carbon electrode can be estimated by calculating the diffusion flux:³⁵

$$f = 4DC_b r$$

$$f = 4(1.1 \times 10^{-6} \text{ cm}^2/\text{s}) [(500 \times 10^{-15} \text{ mol}/\text{cm}^3)(6.02 \times 10^{23} \text{ particles}/\text{mol})] (2.5 \times 10^{-4} \text{ cm})$$

$$= 331 \text{ particles}/\text{s}$$

Here, f (*particles/s*) is the estimated frequency of particles reaching the electrode surface, D (cm^2/s) is the diffusion coefficient of the nanoparticles, C_b (*particles/cm³*) is the bulk concentration of particles, r (*cm*) is the radius of the electrode.

The diffusion coefficient is calculated from Stokes-Einstein equation,

$$D = \frac{kT}{6\pi\eta r}$$

This is much greater than the measured frequency of nanoparticle collision indicating that only a small fraction of nanoparticles colliding on the electrode are measured.

4.6.2 Estimate of the Diffusion Layer Thickness Using the Einstein Equation

$$d = \sqrt{2Dt}$$

$$d = \sqrt{2 * (1.39 \times 10^{-5} \text{ cm}^2/\text{s}) * (6.42 \times 10^{-5} \text{ s})} = 4.22 \times 10^{-5} \text{ cm or } 422 \text{ nm}$$

Where, $D = 1.39 \times 10^{-5} \text{ cm}^2/\text{s}$ and

$$t = \frac{RT}{Fv} = \frac{(8.314 \text{ VC K}^{-1} \text{ mol}^{-1})(298 \text{ K})}{(96485 \text{ C mol}^{-1})(400 \text{ V s}^{-1})} = 6.42 \times 10^{-5} \text{ seconds}$$

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Chapter 5 Heterogeneous Electron-Transfer Kinetics and Electrocatalytic Activity at Single Metal Nanoparticles[§]

5.1 Introduction

Metal nanoparticles are widely used in numerous applications including biotechnology,^{1,2} sensing,^{3,4} and catalysis.⁵⁻⁷ Their catalyst activity often varies drastically based on a number of factors including size,^{6,8-10} shape,^{7,11,12} capping agents,¹³ and composition.^{5,14} As such, it is a challenge to develop a detailed understanding of how each factor contributes to their catalytic activity, due to the presence of large variations on typical nanoparticles. Moreover, it can be particularly difficult to examine the true activity of nanoparticles from typically used ensemble experiments due to large variation in particle spacing, overlapping diffusion fields of closely-spaced particles, and the ensemble averaging.¹⁵ The ability to examine single nanoparticles will help illuminate some of the mysterious factors governing their catalytic activity and may lead to cleaner, more efficient energy technologies. Several single-particle experiments have been reported and they range from surface plasmon resonance¹⁶ and single fluorescent molecule analysis^{17,18} and direct electrical characterization using nanoelectrodes,¹⁹⁻²² to scanning electrochemical microscopy (SECM)²³ and nanoparticle collision.²⁴⁻³³ Despite these exciting studies with the varied and detailed information obtained from them, many key questions remain.

The concept of electrocatalytic amplification through nanoparticle collisions has been pioneered by Bard and coworkers.²⁴⁻²⁶ This technique allows the study of single nanoparticles in a quick and easy manner, where many nanoparticles can be detected in minutes. Metal nanoparticles are allowed to freely diffuse in an electrolyte solution where they collide and stick to a catalytically inert ultramicroelectrode (UME) generating a detectable signal. Figure 5.1A gives a general scheme of a collision experiment where in situation (I) there is little or no oxidation of hydrazine occurring on an inert UME. In situation (II), however, the metal nanoparticle collides and subsequently sticks to the electrode surface leading to a sudden increase in the faradaic response, due to the catalytic enhancement on the nanoparticle.

[§] This chapter is adapted with permission from Percival, S. J.; Zhang, B. "Heterogeneous Electron-Transfer Kinetics and Electrocatalytic Activity at Single Metal Nanoparticles" *To Be Submitted*.

Our research in this area has been directed on the use of cyclic voltammetry to examine dynamic single-particle collision events to collect some of the critical information which has been unable to obtain in previous constant-potential experiments. Toward this goal, we have recently incorporated the FSCV technique (originally developed by Wightman and coworkers^{34,35} for use in studying neurotransmitters and the brain activity). The use of FSCV enables one to record transient voltammetric responses during single nanoparticle collision events.³⁶

In this work we further demonstrate the unique power of FSCV in the study of single nanoparticle collision and show how one can perform detailed analysis of single-particle voltammetry to understand electrocatalytic activity of single gold and platinum nanoparticles. Furthermore, we show one can combine single-particle voltammetry with numerical simulation to extract useful kinetics information, such as electron-transfer rate constant and charge transfer coefficient, for the oxidation of hydrazine. We compare gold and platinum nanoparticles of different size and shape to discuss how their electrocatalytic performance changes with particle size. The Gibbs free energy of activation, ΔG , for different nanoparticles was also calculated from their electron-transfer rate constant and is found to be smaller than bulk metals and decreases with decreasing nanoparticle size.

5.2 Experimental

5.2.1 Chemicals and Materials

All chemicals and materials were used as received from the manufacturers. Deionized water (>18 M Ω cm, Barnstead Nanopure Systems), methanol (Sigma Aldrich), potassium chloride (KCl, Fisher Scientific), ferrocene methanol (FcMeOH, Aldrich 97%), hydrazine (anhydrous 98%, Sigma Aldrich), monobasic potassium phosphate (KH₂PO₄, J. T. Baker), dibasic potassium phosphate (K₂HPO₄, J. T. Baker), gold chloride trihydrate (HAuCl₄·3H₂O, Sigma Aldrich 99.9%), chloroplatinic acid hexahydrate (H₂PtCl₆·6H₂O, Sigma Aldrich), potassium tetrachloroplatinate (K₂PtCl₄, Sigma-Aldrich), sodium citrate dihydrate (J. T. Baker), citric acid (Fisher Scientific), sodium borohydride (Sigma Aldrich), 2-allylphenol (Sigma Aldrich), ammonium hydroxide (Fisher Scientific), hydrogen peroxide (J. T. Baker 30%), Sulfuric Acid (H₂SO₄, J. T. Baker), hydrochloric acid (HCl, EMD Millipore), nitric acid (HNO₃, Mallinckrodt Baker), hydrogen gas (H₂, Praxair), argon (Ar, Praxair), sodium polyacrylate (PA, Aldrich Average MW = 2100 g/mol), copper sulfate pentahydrate (CuSO₄·5H₂O,

Mallinckrodt), 30 nm diameter platinum nanoparticles (sodium citrate capped, dispersed in 2 mM citrate, NanoComposix, Inc. San Diego, CA).

5.2.2 Synthesis of 12 nm and 50 nm Au Nanoparticles

The 12 and 50 nm diameter gold nanoparticles were synthesized by the reduction of HAuCl_4 with sodium citrate.^{37,38} All glassware was thoroughly cleaned prior to use with fresh piranha solution, rinsed and then cleaned with Aqua Regia and rinsed thoroughly with DI water. 50 ml of 0.01% m/v of HAuCl_4 was refluxed while stirring using a magnetic stirrer and 1.0 ml of sodium citrate solution (3% m/v) was then rapidly injected into the flask to synthesize the 12 nm Au NPs. The solution turned a ruby red color and was allowed to reflux for 15 minutes and then allowed to cool to room temperature. Alternatively, to synthesize the 50 nm gold nanoparticles the same procedure was used except the amount of sodium citrate was lowered while the volume of solution injected kept consistent at 1.0 ml of sodium citrate solution (1% m/v). The 50 nm Au NPs solution was a darker red color as compared to the 12 nm Au NP solution and was again allowed to reflux for 15 minutes and cooled to room temperature.

5.2.3 Synthesis of 5 nm Au Nanoparticles

Small diameter gold nanoparticles were synthesized by the reduction of HAuCl_4 with sodium borohydride.³⁹ All glassware was cleaned in the manner discussed previously. 0.5 ml of HAuCl_4 (1 wt%) solution was added to 45 ml of DI water then 1 ml of sodium citrate (3% m/v) was added and the solution was stirred for 2 minutes using a magnetic stirrer. Then 0.5 ml of a solution consisting of 0.075 wt% NaBH_4 with 1 wt% sodium citrate was quickly injected into the stirring solution. The solution turned a dark red color immediately after the addition and was allowed to stir for 15 minutes.

5.2.4 Synthesis of 4 nm Pt Nanoparticles

Platinum nanoparticles were synthesized according to a previous report.⁴⁰ Using thoroughly cleaned glassware (as described previously), 3.88 ml of a 0.2% chloroplatinic acid hexahydrate was added to 50 ml of DI water. The solution was brought to a boil and 1.185 ml of 1% sodium citrate and 0.05% citric acid was added. After a half of a minute, 0.59 ml of freshly prepared 0.08% sodium borohydride with 1% sodium citrate and 0.05% citric acid was very quickly injected into the solution

and allowed to boil while stirring under reflux. After 15 min the product was cooled to room temperature.

5.2.5 Synthesis of 10 nm Cubic Pt Nanoparticles

The 10 nm cubic platinum nanoparticles were synthesized according to the previously reported procedure using sodium polyacrylate (PA) as the capping agent.^{41,42} Using thoroughly cleaned glassware (as described previously) a solution of K_2PtCl_4 was dissolved in DI water and was aged for 3 days in darkness to allow for partial ligand exchange. After the ageing of the K_2PtCl_4 solution a final solution (250 ml) with a concentration of 0.1 mM K_2PtCl_4 dissolved in DI was prepared with 0.5 mM PA giving a Pt:PA mole ratio of 1:5. The pH was then adjusted to 7.5 and argon bubbled through the solution for 30 minutes to purge the solution of oxygen. The solution was then vigorously bubbled with H_2 for 20 minutes and then sealed very tightly and placed in a dark cabinet for 24 hours for the reaction to be completed. The solution turned a light yellowish color indicating the formation of a colloidal platinum nanoparticle solution.

5.2.6 Preparation of Carbon Fiber Electrodes

The preparation of the carbon fiber electrodes was described in detail elsewhere⁴³ but briefly, 5 μm carbon fibers were sealed in borosilicate capillaries (Outer diameter: 1.2 mm, inner diameter 0.69 mm) by thermal pulling on a micropipette puller (Sutter instruments P-97). Electrical contact was then made using Silver conductive paste (Dupont) and tungsten wires. The carbon fibers lengths would extend out of the borosilicate capillary after the pulling procedure and would need to be insulated. To insulate the carbon fibers the electrodeposition and cross linking of 2-allylphenol copolymer was used. Electrodeposition of the 2-allylphenol was done using a 0.90 mM 2-allylphenol in a 1:1 H_2O :methanol solution where the pH was adjusted to 9.0-9.2 using ammonium hydroxide. The electrodes were submerged in the 2-allylphenol solution and the copolymer was deposited by electrooxidation, where, positive 4 volts was applied to the carbon fiber vs. a platinum wire counter electrode for ~10 minutes. The electrodes were then heated to 150 °C for 30 minutes in an oven to cure the copolymer coating.

5.2.7 Electrochemical Measurements

Steady-state voltammograms were recorded using a computer-controlled Dagan Chem-Clamp voltammeter/amperometer and data was recorded using an in-house virtual instrumentation program written in LabVIEW (National Instruments) on a desktop PC equipped with a PCI-6251 (National Instruments) data acquisition card. A commercially available Ag/AgCl reference electrode (Bioanalytical Sciences, Inc.) was used as reference electrode for all electrochemical data. Fast-Scan Cyclic Voltammetry (FSCV) data was obtained using a home-built breakout box (UNC Chemistry Electronics Design Facility) equipped with a low noise current amplifier (Electro Optical Components, Inc. model: LCA-10K-500M) running the FSCV software developed by the Wightman group at the University of North Carolina.⁴⁴ The extracted CVs were the averaged result of five sequential CVs taken from the program with a background subtraction where the background was the averaged result of 10 sequential CVs at a point designated before the nanoparticle collision event. Rotating Disk Electrode (RDE) measurements were made using a Pine (Grove City, PA) Modulated Speed Rotator (MSR) with E3 series 5 mm diameter glassy carbon RDE tips. The RDE electrochemical measurements were made using a Pine model AFCBP1 Bipotentiostat. The tips were thoroughly polished with 1 μm and 0.05 μm alumina powder to a mirror finish before drop casting the nanoparticle solutions onto the glassy carbon electrode and the nanoparticles mass loadings were kept consistent between the different nanoparticle solutions.

5.2.8 Transmission Electron Microscopy

Transmission Electron Microscopy (TEM) imaging was performed on a FEI Tecnai G2 F20 S-Twin operating at 200 kV using a single tilt sample holder and carbon coated Formvar copper TEM grids (Ted Pella). Nanoparticle sizes were measured from the TEM images using the analysis program ImageJ⁴⁵ and were measured across the longest edge observed.

5.2.9 Electron Transfer Simulation

All simulations were done using COMSOL® Multiphysics software (version 4.3a, COMSOL Inc., Burlington, MA) using 2D axial symmetry with the transport of dilute species module. To simulate the electrochemical oxidation of hydrazine on individual nanoparticles we assumed the nanoparticle geometry was spherical and placed a single semicircle (boundary representing the nanoparticle) at the origin of the simulation geometry where the axis of symmetry was located. A

simple triangle waveform was used as the simulated potential sweep, with a sweep rate of 25 V/s for the simulations. The equation used to control the simulated flux was derived from the Butler-Volmer equation and is discussed in detail below.

5.3 Results and Discussion

5.3.1 Hydrazine Oxidation and Nanoparticle Collision FSCV

The oxidation of hydrazine is of great interest to fuel cells but the reaction occurs at high overpotentials even on good catalysts.⁴⁶ It is thus important to study what structural effects of a nanoparticle are favorable for the increased activity of hydrazine oxidation on nanoparticles. The overall electrochemical oxidation of hydrazine in basic solution is a 4-electron process and can be expressed as following,⁴⁷



The standard oxidation potential, E° , is -0.33 V vs RHE⁴⁷ or -0.56 V vs Ag/AgCl. In Figure 5.1A the selection of the inert electrode is obvious when different materials are compared in a simple CV experiment, as shown in Figure 5.1B. Bulk platinum is the most active material followed by gold and finally carbon being the material of choice for the inert electrode. The use of carbon ensures very little hydrazine oxidation will occur at the potentials used in the study of gold and platinum nanoparticles.

Three different types of nanoparticles are studied using FSCV for both gold and platinum (six types in total). The sizes of the nanoparticles were determined with TEM and the reported diameter is the average size from each separate group, summarized in Table 5.1. The gold nanoparticles were all citrate capped and included 5, 12 and 50 nm diameter nanoparticles. The platinum nanoparticles included 4, and 30 nm citrate capped nanoparticles as well as 10 nm particles that were capped with polyacrylate ligands which displayed a higher degree of crystallinity and had more cubic shaped particles. TEM images and the measured nanoparticle size histograms for each set can be seen in Figure 5.2 and Figure 5.3 for the gold and platinum nanoparticles respectively.

FSCV recording of single particle collision involves continuous scanning of the potential on the carbon UME and recording its current voltage response. A CV repetition rate in the range of 10-100 Hz is normally used, which yields recording of hundreds to thousands of CVs in a 60 second

period. Depending on particle concentration and collision frequency, this allows one to obtain several tens of CVs on each particle prior to and following its collision with the UME. The CVs are displayed in a unique color plot where each CV is one vertical line in the y-axis and the color change reflects different current magnitude.⁴⁸ Figure 5.4A is a representative FSCV recording, which shows the collision of five Au nanoparticles (12 nm). The current increases in a stair step manner due to the oxidation of hydrazine on gold nanoparticles. The current increases can be more easily observed by a current-time trace, as shown in Figure 5.4B taken from the color plot at 0.465 V indicated by the black line in the forward sweep direction. In the trace it is clear that there were five distinct nanoparticle collision events, apparent by the sudden increase in the current. Four of the five collision events were labeled and their representative CVs plotted in Figure 5.4C. Events 1, 2, and 3 are seen to display CVs that show the characteristic diffusion-limited sigmoidal shape for electrodes of this size. Alternatively, event 4 does not seem to reach the diffusion limitation in this potential range and thus the oxidation of hydrazine is likely under kinetic control: the rate of oxidation at each potential is smaller than the maximum diffusion rate and increasing the potential will increase the reaction rate. Further increasing the potential sufficiently high would cause event 4 to reach a diffusion limited state. However, this would lead to a large background current due to increased hydrazine oxidation on the carbon UME. The fifth event at approximately 17 s (unlabeled in the plots) has a large current step indicating it is due to a particle aggregate. Events that are large like this are thrown out and only events that show a peak current below a threshold current, which is the predicted current of a particle that has a radius of three standard deviations from the average nanoparticle size from a given batch, are kept. The diffusion limited current is estimated using the equation for a spherical particle on a planar surface,²⁵

$$i_{ss} = 4 \ln(2) \pi n F D C_b r \quad (2)$$

where n is the number of electrons transferred per redox molecule ($n = 4$ for hydrazine), F is the Faraday constant, $D = 1.39 \times 10^{-5} \text{ cm}^2/\text{s}$ is the diffusion coefficient of hydrazine,⁴⁹ C_b is the bulk concentration, and r is the particle radius. This equation was also used to estimate the size of the nanoparticles from the sample events that were simulated, discussed in detail below.

The CVs of single nanoparticles were analyzed by examining and plotting the half-wave potential, $E_{1/2}$, and the onset potential, E_{onset} (defined as 20% of the peak current) versus the observed peak current for each nanoparticle collision event, presented in Figure 5.5. Figure 5.5A

and Figure 5.5B are scatter plots for $E_{1/2}$ and E_{onset} for gold nanoparticles and Figure 5.5C and Figure 5.5D are the corresponding scatter plots for platinum. A closer inspection of these results reveals several distinct features in the distributions of the scattered points. First, the platinum nanoparticles display higher catalytic activities than the gold ones with more negative onset and half-wave potentials. Second, the smaller nanoparticles are found to group around a more positive potential than the larger particles which are spread out more. Additionally, there are some events that lie at more positive potentials (higher overpotential) in relation to the grouping. These events are generally collected from particles that display sluggish kinetics and are kinetically limited.

Interestingly, the 50 nm Au particles show catalytic activity that is much more scattered than the other sizes. Some events are detected at low peak currents and higher potentials while others are seen at higher peak currents and lower potentials. This is significantly distinct from the 30 nm Pt particles which display more uniform catalytic activities possibly due to the high degree of polycrystallinity in the 30 nm Pt nanoparticles. Furthermore, the onset potential plots show narrower distributions than the $E_{1/2}$ plots. This is more apparent when the events are plotted in histograms, shown in Figure 5.6, where there is a higher probability of a particle displaying a given E_{onset} within the smaller range than for the $E_{1/2}$. This can be observed for all the nanoparticle batches but is most prominent for the 12 and 50 nm diameter gold nanoparticles. These histogram plots show the count and the probability that a nanoparticle from the given size will display the level of hydrazine oxidation at the given potential and further illustrate the differences between the different sized nanoparticles. The probability of the onset potential being located at a more negative potential is lower for the 5 nm Au NPs than for the 12 nm or 50 nm particles. This is because the smaller particles have more events that are kinetically limited, shifting the distribution to more positive potentials as compared to the larger particles. Alternatively, for the platinum nanoparticles, the 4 nm particles have the highest probability values observed between the three types of Pt NPs while the 30 nm particles have the lowest probability. This apparent reversal of the trends between Au and Pt is actually misleading because it is due to the fact the larger particles sometimes display more negative onset and $E_{1/2}$ potentials than the smaller particles, which spreads the probability distribution. Additionally, the distribution of the onset potentials and the $E_{1/2}$ potentials is overlapping much more for all sizes of the gold nanoparticles than compared to the platinum nanoparticles. This shows that the platinum nanoparticles are displaying sluggish reaction kinetics on the platinum surface where a much larger potential must be applied to increase the

current from the onset potential current to the $E_{1/2}$ current. The separation between the onset potential and $E_{1/2}$ distributions for the 30 nm platinum nanoparticles increases as compared to the 4 nm platinum nanoparticles, whereas the separation decreases for the 50 nm gold nanoparticles compared to the 5 nm Au nanoparticles. All of the distribution separations are larger for the platinum than for the gold nanoparticles meaning the Au NPs, despite needing higher potentials for the oxidation of hydrazine, display faster oxidation kinetics once the onset potential is reached and only a small increase in potential leads to a more substantial increase in current.

By averaging the responses from all of the events and plotting them versus the inverse of the radius (average radius from TEM measurements) a clearer trend emerges. The oxidation potentials for hydrazine on Au nanoparticles form a linear trend with the inverse of the radius of the particles, as seen in Figure 5.7A and Figure 5.7B. All of the tested gold and platinum nanoparticles have more positive $E_{1/2}$ and E_{onset} than their corresponding bulk metals. The E_{onset} and $E_{1/2}$ were measured at 107 and 204 mV vs Ag/AgCl for bulk gold, which are fairly close to the most active 50 nm gold nanoparticles. The bulk gold values were negatively shifted by approximately 21 mV (E_{onset}) and 28 mV ($E_{1/2}$) than the 50 nm Au nanoparticles. On the other hand, the E_{onset} and $E_{1/2}$ for bulk platinum were located at -244 and -349 mV vs Ag/AgCl, respectively, which are much further from the most active nanoparticles, in stark contrast to the gold nanoparticles. The bulk platinum was shifted by approximately 248 mV (E_{onset}) and 319 mV ($E_{1/2}$) more negative than the averaged 30 nm Pt NP potentials, also plotted versus the inverse of the nanoparticle radius in Figure 5.7C and Figure 5.7D. In these plots we again see that the smaller 4 nm Pt NPs are shifted to more positive potentials as compared to the larger 30 nm Pt NPs.

It is important to point out that the normal procedure of using onset or half-wave potential to compare catalytic activity of nanoparticles, as is traditionally done in ensemble measurements,^{50,51} should be carefully evaluated for single particle experiments. Despite well documented evidence from many studies that smaller nanoparticles should be more active catalysts,⁵² an opposite trend has been observed from our single-particle experiments. The observed increase in anodic overpotential at single nanoparticles, however, is in part due to an increased mass transport rate, a well-known effect due to size reduction at nanoscale electrodes.^{53,54} The mass transport coefficient at an ultramicroelectrode, defined as $m = D/r^{21,55}$, increases as the electrode radius r becomes smaller. Compared to previous ensemble experiments,

a key advantage of single-particle study is the elimination of overlapping diffusion layers of redox species in an ensemble.¹⁵ This results in the formation of an ultrafast radial type diffusion profile around each nanoparticle. Previous reports have indeed shown that the nanoparticle activities will increase with increasing nanoparticle loading (i.e. decreased nanoparticle distance)¹⁵ and single small nanoparticles will display higher overpotentials than single larger nanoparticles due to the increased mass transport.²¹

We first believed that there could have been a substrate effect where the carbon electrode was causing the positive shift in oxidation potential observed in single particle collision experiments. Such effect is especially strong in the case of platinum nanoparticles, where the substrate can either have a constructive or destructive effect on the activity.⁵⁶ Additionally, the capping ligands on the nanoparticle surface could have been interfering with the smaller nanoparticles activity. While these effects may have a subtle effect on the overall potential shift, we believe the increasing mass transport is the dominating influence. In order to further test our hypothesis, we have conducted cyclic voltammetry experiments using platinum nanoelectrodes that are free of interfering ligands and substrate effects. A clear positive shift similar to the nanoparticles has been observed on the platinum nanoelectrodes for the oxidation of hydrazine, seen in Figure 5.8. The plot shows how the $E_{1/2}$ shifts to more positive potentials as the radius decreases. These electrodes do not have the same substrate effects or ligand effects and we still observe the average $E_{1/2}$, which is located at similar potentials as the Pt NPs, shifting positively with decreasing radius.

The increased mass transport effects experienced by small nanoparticles have implications for single particle experiments where the activity is determined directly from the experimental CVs. When comparing electrocatalytic activity on single nanoparticles of different sizes, simply looking at the onset potential or $E_{1/2}$ from the experimental CVs will lead to a misinterpretation of the results. In order to obtain a more accurate picture of the nanoparticle activity, the experimental results must be combined with kinetics simulations in order to extract their electrocatalytic activity. For particles of same size where the mass transfer effect does not play a significant role, such comparison is still valid and relatively easy to compare particle activity.

A direct comparison of E_{onset} and $E_{1/2}$ between the 4 nm and 10 nm Pt particles has revealed a clear ligand effect in nanoparticle electrocatalysis. Despite a predicted positive potential shift on the 4 nm Pt particles from increasing mass transport, Figure 5.7C and Figure 5.7D, have shown a

clear positive shift on the 10 nm Pt particles compared to the 4 nm particles indicating lower overall catalytic activity. This is contradictory to our original hypothesis where we thought the 10 nm Pt particles would have been more active. These particles are mostly single crystalline cubic shaped particles, possessing {100} crystal faces which are known to have higher activities for hydrazine oxidation than the more abundant {111} crystal faces present on typical citrate capped platinum nanoparticles.^{57,58} The lower activity is most likely due to the nature of the larger polyacrylate capping molecules used in their synthesis. The use of polyacrylate results in an altered chemical environment compared to the citrate ligands used in the preparation of other nanoparticles, which may make it more difficult for the hydrazine to adsorb onto the Pt surface and will also change the electron density of the platinum particle surface in a different manner than the citrate ligands, which can also decrease the particle activity.⁵⁹ Thus, higher potentials may be needed to overcome this ligand effect. This effect is combined with the mass transport effects which decrease the activity even more than the 4 nm particles.

5.3.2 Electron Transfer Simulation Model

A major benefit of the FSCV technique is the ability to extract useful kinetic information from single catalytic nanoparticles. Here, hydrazine oxidation CVs collected on single nanoparticles are simulated with COMSOL®, a finite-element simulation program, by incorporating Butler-Volmer kinetics. We first considered a typical redox couple where an oxidized species O is reduced to R as following,



with k_c and k_a being the cathodic (reduction) and anodic (oxidation) rate constants respectively. These rates can be expressed according to Butler-Volmer kinetics as:

$$k_c = k_o * \exp\left[-\alpha\left(\frac{nF}{RT}\right)(E_{app} - E^o)\right] \quad (4)$$

$$k_a = k_o * \exp\left[(1-\alpha)\left(\frac{nF}{RT}\right)(E_{app} - E^o)\right] \quad (5)$$

Where k_o is the standard heterogeneous electron transfer rate constant, α is the charge transfer coefficient, n is the number of electrons involved in the reaction, F is the Faraday constant, R is the gas constant, T is the absolute temperature and E_{app} is the applied potential with E^o is the standard

potential for the reaction. The oxidation of adsorbed hydrazine is a totally irreversible reaction having a one-electron rate determining step as the initial oxidation step followed by the remaining three one-electron oxidation steps that are considered to be very fast.^{46,60,61}



For a totally irreversible reaction of this type where the initial step is rate determining, the overall result is given by the forward rate constant.⁶² In the case of hydrazine oxidation the forward rate constant is the anodic rate term k_a . The flux of the diffusing hydrazine molecules to the nanoparticle surface can then be expressed as,

$$j = -k_o * \exp\left[\beta\left(\frac{F}{RT}\right)(E_{app} - E^o)\right] * C_R \quad (8)$$

where C_R is the concentration of reactant (hydrazine) at the electrode surface. The values of both α and k_o were varied in the simulation until the simulated CV closely matched the experiment. A spherical geometry was assumed for the nanoparticles in the simulation and a discussion of the simulation environment can be seen in Figure 5.9A below along with a table of the physical constants used (Table 5.2). The geometry is color coded to the physical properties attributed to the simulated surface and is not drawn to scale for clarity. The simulation utilized a 2-Dimensional axial symmetry where surface 1 was set as the axis of symmetry. The entire geometry is rotated by 360° around the axis of symmetry effectively simulating a 3-Dimensional environment. The nanoparticle surface, surface 5, is the only surface that is active electrochemically and is resting on an inert surface which represents the surface of the catalytically inert carbon electrode. The remaining surfaces are simulating the bulk solution. Pictured next to the simulation environment in Figure 5.9B is a typical concentration profile color plot of a simulated 12 nm nanoparticle simulated with $\alpha = 0.5$ and $k_o = 0.0001$ m/s and 25 V/s scan rate taken at the time when the potential was at the maximum in the triangle sweep (36 ms out of 72 ms total). The diffusion profile at the nanoparticle is clearly visible where the concentration of reactant goes to zero near the nanoparticle surface and in the space between the nanoparticle and the insulating surface. The concentration profile is seen to increase up to nearly bulk concentrations at ~100 nm distance from the nanoparticle surface.

Figure 5.10 presents four example CVs with the simulated oxidation wave along with the parameters used in the simulation. Figure 5.10A and Figure 5.10B are from a 12 nm and a 50 nm Au nanoparticles and Figure 5.10C and Figure 5.10D are from a 4 nm and 30 nm Pt nanoparticles, respectively. The simulation overall matches quite well with the experiments but for the larger particles the simulation begins to deviate from the experimental curve. One possible reason is the mismatch in particle shapes. The simulation assumed perfectly spherical particles whereas the TEM images reveal that they can diverge from spherical geometry, especially for the larger particles. The 30 nm Pt nanoparticles appear rough and the 50 nm Au nanoparticles can be more oblong.

The simulation has revealed one remarkable difference between Au and Pt nanoparticles. The values for α used to simulate CVs for Pt nanoparticles were always greater than 0.5 but typically had to be smaller than 0.5 for gold nanoparticles. The necessarily high value of the transfer coefficient on Pt results in the simulated CVs having a smaller current response with a given potential change akin to the experimental curves. This was also observed for the hydrazine oxidation CVs collected on platinum nanoelectrodes, which when simulated had similar values for α and k_0 and can be seen in Figure SI7. This means that for the platinum nanoparticles there is a smaller current increase with increasing potential than for gold resulting in a somewhat elongated CV response, despite platinum's superior catalytic activity possibly indicating a competing surface reaction/species. The results shown in Figure 5.10 also show that the heterogeneous electron transfer rate constant for gold is several orders of magnitude smaller than platinum.

A summary of the average values of the α coefficient and k_0 can be seen in Table 5.3. It is clear that the electron-transfer rate constant increases as the particle size decreases, indicating an apparent increase in the activity at the nanoparticle surface as the radius decreases. This trend is observed for both platinum and gold nanoparticles and all have larger values for k_0 than the bulk values which were 6.5×10^{-7} cm/s and 4.25×10^{-4} cm/s for bulk gold and platinum respectively.

This trend was also observed for the platinum nanoelectrode hydrazine oxidation CVs, which when simulated, had similar values for the α coefficient and k_0 and can be seen for two nanoelectrodes in Figure 5.11. These example nanocatalysts are free of interfering ligands and were simulated to compare the values of the α coefficient and k_0 to the values obtained from the simulated single nanoparticles. The simulated CVs match very well to the experimental CVs although there is some deviation observed for the 47 nm radius electrode. The values of α were

0.725 and 0.8225 for the 305 nm radius and the 47 nm radius electrodes respectively. The values of k_o for the 305 nm radius electrode and the 47 nm radius electrode were 3.25×10^{-3} cm/s and 1.25×10^{-1} cm/s respectively. The disk shaped platinum nanoelectrodes exhibit similar trends in the value for α and the value of k_o as was observed for the simulated single platinum nanoparticles. The oxidation wave is again elongated giving a similar CV shape as with the single nanoparticles. This is important because the deviation of α from the usual 0.5 is also observed for the nanoelectrodes, supporting the single nanoparticle simulation data. Additionally, the value of k_o is larger for the smaller radius platinum nanoelectrode similar to the nanoparticle results.

The increased activity of the smallest nanoparticles, based in increasing values of k_o for smaller particles, is supported by Rotating Disk Electrode (RDE) experiments, where the smallest nanoparticles displayed the highest kinetic current densities. Figure 5.12A shows hydrazine oxidation CVs using a Rotating Disk Electrode (RDE) from 100 rpm to 500 rpm for 5 nm Au NPs and Figure 5.12B is the same but for 4 nm Pt NPs. By increasing the rotation rate of the electrode the mass transport of reactant will be increased and the kinetic current density of the nanoparticles can be determined. The active nanoparticle surface areas were determined using the underpotential deposition (UPD) of copper where a monolayer of copper adatoms forms on the nanoparticles surface. The charge associated with stripping the monolayer off can be used to calculate the catalyst surface area.⁶³⁻⁶⁵ To evaluate the activity of the nanoparticles, the kinetic current density was determined from the Koutecký-Levich equation seen below.^{62,66,67}

$$\frac{1}{j_T} = \frac{1}{j_K} + \frac{1}{j_D} = \frac{1}{j_K} + \frac{1}{BC_o\omega^{1/2}} \quad (9)$$

Where j_T is the total measured current density, j_K is the kinetic component of the current density and j_D is the diffusion component of the current density and $B = 0.62nFAD^{2/3}\nu^{-1/6}$ where ω is the rotation rate (in radians/s), n is the number of electrons, F is the Faraday constant, A is the geometrical area of the electrode, ν is the kinematic viscosity of water, D and C_o are the diffusion coefficient and concentration of the reactant, respectively. Levich plots were made by plotting the inverse of the measured current density (j_T^{-1}) vs. $\omega^{-1/2}$ for each of the nanoparticles, which can be seen in Figure 5.12C and Figure 5.12D. From these plots the respective kinetic current densities from the different nanoparticles were determined from the intercept of the line. The kinetic current densities for the gold nanoparticles were calculated to be 303 mA/cm² for the 5 nm particles, 278

mA/cm^2 for the 12 nm particles and $208 \text{ mA}/\text{cm}^2$ for the 50 nm particles at 0.8 V. The kinetic current densities for the platinum nanoparticles were calculated to be $435 \text{ mA}/\text{cm}^2$ for the 4 nm particles, $123 \text{ mA}/\text{cm}^2$ for the 10 nm particles and $400 \text{ mA}/\text{cm}^2$ for the 30 nm particles at 0.5 V. For each set of nanoparticles the smallest sized particle has the highest kinetic current density and supports the result in the main text where the smallest particles were found to have the largest heterogeneous electron transfer coefficient, indicating the highest activity. Additionally, the citrate capped platinum nanoparticles displayed the highest values for the kinetic current density compared to the gold nanoparticles. Whereas the 10nm PA capped Pt nanoparticles had the lowest kinetic current density of all the particles most likely due to the large capping agent hindering the reaction kinetics.

Also listed in Table 5.3 is the averaged α coefficient for each NP size determined from Tafel plots derived from the experimental CVs for the same set of events that were simulated. These Tafel plots, shown in Figure SI9, were plotted from the CVs in the region where the oxidation current began to increase until slightly before the $E_{1/2}$ potential. From the Tafel plots, values for α were calculated from the slope of the line and when compared to that obtained from the simulations there is a good match between the two. The x-intercept of the Tafel line was also used to calculate the exchange current density (j_o) for the set of sample events and it was found that on the gold nanoparticles there was very little exchange current and it seemed to decrease as the radius decreased. Conversely, on the platinum nanoparticles the exchange current density was several orders of magnitude larger and on average increased with decreasing radius. The large exchange current density is most likely due to the adsorption/desorption of protons from the solution.

Even though these experiments were performed in 50 mM phosphate buffer at pH 7.4, there is still a response from the adsorption/desorption of hydrogen on platinum which was unexpected as seen in Figure 5.13. The regions of hydrogen desorption on the positive scan of a platinum UME electrode overlaps with the region where hydrazine oxidation begins. The hydrogen ions will block catalytic surface sites on the platinum and compete with the hydrazine molecules. Similarly, proton adsorption has also been observed to interfere with the electrocatalytic reduction of oxygen on platinum, where the oxygen reduction current decreases as protons begin to adsorb on platinum.⁶⁸ The effect is much more pronounced for the nanoparticles and nanoelectrodes as compared to the platinum UME because of the low concentration of hydrogen ions in solution (pH

7.4). We think this competition effect, along with the increased mass transfer effects, may substantially shift the hydrazine oxidation to more positive potentials relative to the bulk, as discussed previously. This effect is significantly reduced on gold nanoparticles due to the weaker affinity for hydrogen leading to a smaller potential shift.

5.3.3 Thermodynamic Analysis

The ability to determine a single nanoparticle voltammetric response combined with simulation allows for detailed investigation into the thermodynamics of redox reactions at single particles. We have used this strategy to calculate the Gibbs free energy of activation for the hydrazine oxidation on both gold and platinum nanoparticles. Thermodynamically, the change in activity can be calculated from the standard heterogeneous electron transfer coefficient based on transition state theory developed by Marcus.^{69,70} The form of the expression for a heterogeneous electron transfer reaction at an electrode surface is,^{69,70}

$$k_o = k_{el} Z_{het} \exp\left(\frac{-\Delta G}{RT}\right) \quad (10)$$

where k_{el} is the electronic transmission coefficient (typically taken as unity for adiabatic processes)^{69,70} Z_{het} is the heterogeneous collision frequency factor, ΔG is the Gibbs free energy of activation and R and T are the universal gas constant and temperature respectively. The collision frequency factor is defined as;⁶⁹⁻⁷¹

$$Z_{het} = \left(\frac{k_b T}{2\pi\mu}\right)^{1/2} \quad (11)$$

where μ is the reduced mass of the molecule and the nanoparticle (assuming a very large mass for the nanoparticle μ reduces to the mass of the reactant molecule, hydrazine = 5.32×10^{-26} kg) and k_b is Boltzmann constant. The calculated ΔG is positive and decreases with the particle size, meaning the energy barrier decreases with decreasing nanoparticle size. The gold nanoparticles have larger magnitudes for ΔG than the platinum particles, which is consistent with the higher overpotentials for the oxidation of hydrazine on gold than platinum. For the gold nanoparticles there is a larger shift in ΔG for the 5 nm particles compared to the 12 nm and 50 nm particles. All of the nanoparticle batches had calculated values of ΔG that were below the values for the bulk metals (58.38 kJ/mol for bulk gold and 42.31 kJ/mol for bulk platinum). A comparison of ΔG between

platinum nanoparticles also showed a decreasing trend as the size decreased. However, the different Pt particles have very similar values for ΔG and did not show the same trend as the gold nanoparticles. This could be due to the fact that the particles used in the study had different capping agents, crystal faces and surface roughness.

To further explain the trend seen in the gold nanoparticles we calculated a predicted shift of the Gibbs free energy of activation based on a theoretical extrapolation where we assumed the particles were spherical and the change in energy is due to size of the particle alone. The shift of Gibbs free energy of the reaction on nanoparticles from bulk values has been predicted previously and takes the form of the Gibbs-Thompson relation,^{6,72-74}

$$\Delta G_{NP} = \Delta G_B \pm \Delta G_r = \Delta G_B \pm \frac{2v\sigma_r}{r} \quad (12)$$

where ΔG_B is the bulk free energy of activation, ΔG_r is the size dependent free energy of activation, v is the partial molar volume of the element ($1.021 \times 10^{-5} \text{ m}^3/\text{mol}$ for gold and 9.1×10^{-6} for platinum)⁷² and r is again the nanoparticle radius. The change in Gibbs free energy can have either a positive or a negative effect on the activation barrier depending on the nature of the reaction. In this case the effect decreases the Gibbs free energy for the nanoparticle relative to the bulk, indicating a lowering of the energy barrier. The variable σ_r is the size (radius) dependent surface energy of the particle which has the following form,⁷⁵

$$\sigma_r = \sigma_B \left(1 - \frac{1}{\left[\frac{2d}{h} - 1 \right]} \right) \exp \left(-\frac{2S_B}{3R} \frac{1}{\left[\frac{2d}{h} - 1 \right]} \right) \quad (13)$$

where σ_B is the surface tension of the bulk material (1880 erg/cm^2 (1.88 J/m^2) for Au and 3240 erg/cm^2 (3.24 J/m^2) for Pt)⁷², d is the diameter of the nanoparticle, h is the atomic diameter (0.289 nm for Au and 0.277 nm for Pt)⁷⁶, S_b is the cohesive entropy of the material which is equal to E_b/T_b . E_b is the bulk cohesive energy (3.81 eV (367.6 kJ/mol) for Au and 5.84 eV (563.46 kJ/mol) for Pt)⁷⁷ and T_b is the bulk solid vapor transition temperature (3129 K for Au and 4098 K for Pt)⁷⁸. The calculated curve for the value of ΔG_{NP} shows the largest deviation from bulk at approximately 1 nm radius and then is seen to increase very rapidly again. By plotting the theoretical size dependent free energy curve (calculated with equation 12 and 13) and plotting the experimentally determined Gibbs free energy of the different sized nanoparticles (calculated with equation 10 and 11) we see

that gold follows the theoretical curve but platinum does not, shown in Figure 5.14. The two largest diameter gold nanoparticles follow the calculated curve and show a small difference between the two but the smallest diameter nanoparticles have a large deviation, which is again consistent with the calculated curve. The platinum nanoparticles are seen to decrease in the value of ΔG_{NP} with decreasing size but do not fall in line with the calculated curve. The deviation of the platinum nanoparticles from the theoretical curve may be due to the structural and surface differences between the different sized particles in addition to the hydrogen adsorption competition. On average, the gold nanoparticles have very similar shapes, roughness and ligands whereas the platinum nanoparticles vary between particles.

5.4 Conclusions

In summary, the use of fast-scan cyclic voltammetry has enabled us to investigate and understand electrocatalytic activity of single platinum and gold nanoparticles of different sizes, shapes and capping ligands for the oxidation of hydrazine. The overpotential for hydrazine oxidation on single nanoparticles generally increases as the radius decreases. The increase in overpotential and the lower apparent activity on the nanoparticles can be largely due to an increase in the mass-transfer coefficient in addition to a size-dependent catalytic effect. We have also determined that the capping agent could play a more substantial role in the activity than the nature of the nanoparticle crystallinity and surface orientation. Numerical simulation of nanoparticle CVs from each batch of nanoparticles allows us to determine the electrocatalytic parameters, such as electron-transfer rate constant and the transfer coefficient, of single nanoparticles. The Gibbs free energy of activation was also calculated from the standard heterogeneous electron transfer rate constant and was found to be smaller for the nanoparticles than compared to bulk metals, indicating a lower energy barrier. The change in the Gibbs free energy with changing nanoparticle size also follows a theoretical thermodynamic model very well for gold but not for platinum. We believe the competition between hydrazine and adsorbed hydrogen ions for surface sites on the platinum surface, in part, explains the deviation of the platinum nanoparticles from the theoretical prediction. Single nanoparticle analysis using FSCV combined with simulations of the nanoparticles voltammetric response can be a powerful tool in many aspects of fundamental catalytic analysis.

5.5 Tables and Figures

Table 5.1 Nanoparticle Size TEM Analysis

The average diameters, standard deviation and number of particles measured for the various nanoparticle sizes used in the study as determined from TEM measurements. The nanoparticles were capped with citrate ligands unless otherwise noted.

Nanoparticle	Average Size (nm)	Number Measured
5 nm Au	5.02 ± 1.07	293
12 nm Au	12.29 ± 0.90	229
50 nm Au	49.73 ± 8.24	278
4 nm Pt	4.22 ± 1.14	271
10 nm PA capped Pt	9.54 ± 1.88	162
30 nm Commercial Pt	29.37 ± 3.95	332

Table 5.2 Physical Constant used in Nanoparticle Simulations

Table of the physical constants used in the simulation of the single nanoparticle hydrazine CVs using Butler-Volmer kinetics. Diffusion Coefficient of hydrazine and hydrazine formal potential taken from listed references.^{47,49}

Variable	Expression	Description
C_b	10 [mol/m ³]	Bulk Concentration
D_o	1.39E-9 [m ² /s]	Diffusion Coefficient of Hydrazine ⁴⁹
n	4	Number of Electrons
F	96485 [C/mol]	Faradays Constant
R	8.314 [J/(mol K)]	Gas Constant
T	298 [K]	Temperature (in Kelvin)
E_o	-0.56 [V]	Hydrazine Formal Potential (vs Ag/AgCl) ⁴⁷
α	Variable	Charge Transfer Coefficient
k_o	Variable	Heterogeneous ET Rate Constant
v	25 or 50 [V/s]	Voltage Scan Rate

Table 5.3 Single Nanoparticle Kinetics Summary

The different nanoparticle values for the charge transfer coefficient (α) determined from simulation and experimental Tafel plots, the heterogeneous electron transfer coefficient (k_o), the exchange current density (j_o) and the Gibbs free energy of activation (ΔG_{NP}). Ten different nanoparticles from each nanoparticle subset were investigated in detail for their kinetic parameters (60 in total).

	α (Simulation)	k_o (cm/s)	α (Tafel plot)	j_o (A/m ²)	ΔG_{NP} (kJ/mol)
5 nm Au	0.540 ± 0.062	$8.75 \pm 11.7 (10^{-5})$	0.545 ± 0.051	3.00 ± 2.66	48.04 ± 3.54
12 nm Au	0.477 ± 0.047	$9.64 \pm 17.3 (10^{-6})$	0.489 ± 0.047	11.49 ± 7.23	53.85 ± 3.16
50 nm Au	0.501 ± 0.052	$7.08 \pm 14.5 (10^{-6})$	0.509 ± 0.059	26.54 ± 29.60	54.91 ± 3.31
4 nm Pt	0.742 ± 0.021	$8.71 \pm 6.47 (10^{-2})$	0.777 ± 0.014	4750 ± 2125	29.49 ± 1.24
10 nm Pt ^(a)	0.775 ± 0.010	$7.66 \pm 2.78 (10^{-2})$	0.807 ± 0.012	4184 ± 1854	29.58 ± 0.88
30 nm Pt	0.758 ± 0.019	$4.23 \pm 1.76 (10^{-2})$	0.783 ± 0.021	1947 ± 748	31.14 ± 1.14

^(a) Cubic nanoparticles capped with polyacrylate.

Figure 5.1 Nanoparticle Collision Electrocatalytic Amplification

(A) Schematic illustration showing the generalized process of a catalytic metal nanoparticle colliding with an inert electrode where in situation (I) there is no hydrazine oxidation reaction and in situation (II) the nanoparticle diffuses through solution and collides with the inert electrode, sticking to it, and begins to oxidize the hydrazine in solution. (B) A graph of normalized current CVs of different material electrodes where the catalytic activity of the different materials determines the potential the hydrazine is oxidized at. All CVs were taken in 10mM hydrazine with 50 mM PB (pH 7.4) at 50mV/s scan rate.

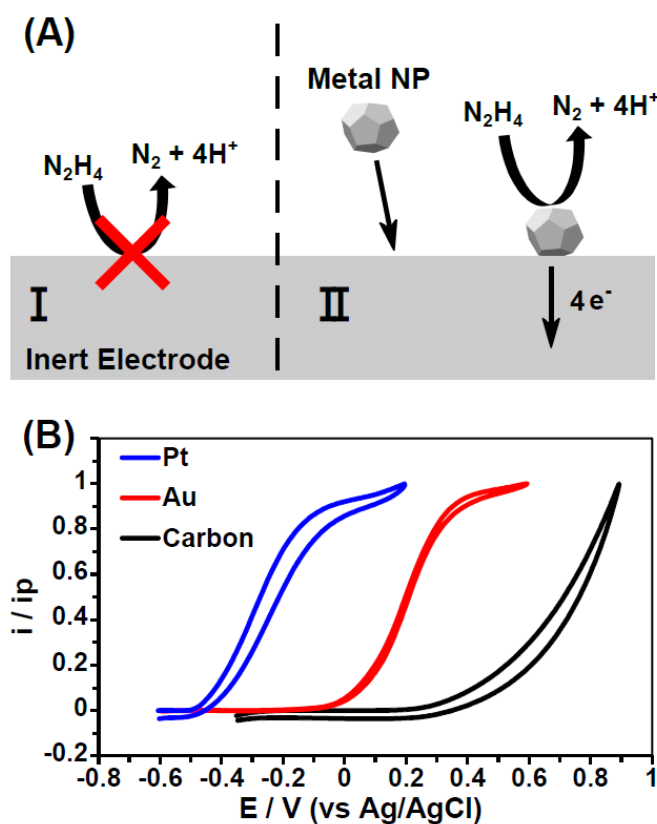


Figure 5.2 Gold Nanoparticle TEM Analysis

TEM images with corresponding size distribution histograms and Gaussian probabilities for the different gold nanoparticles. (A) and (B) correspond to the 5 nm gold nanoparticles, (C) and (D) correspond to the 12 nm gold nanoparticles and (E) and (F) correspond to the 50 nm gold nanoparticles.

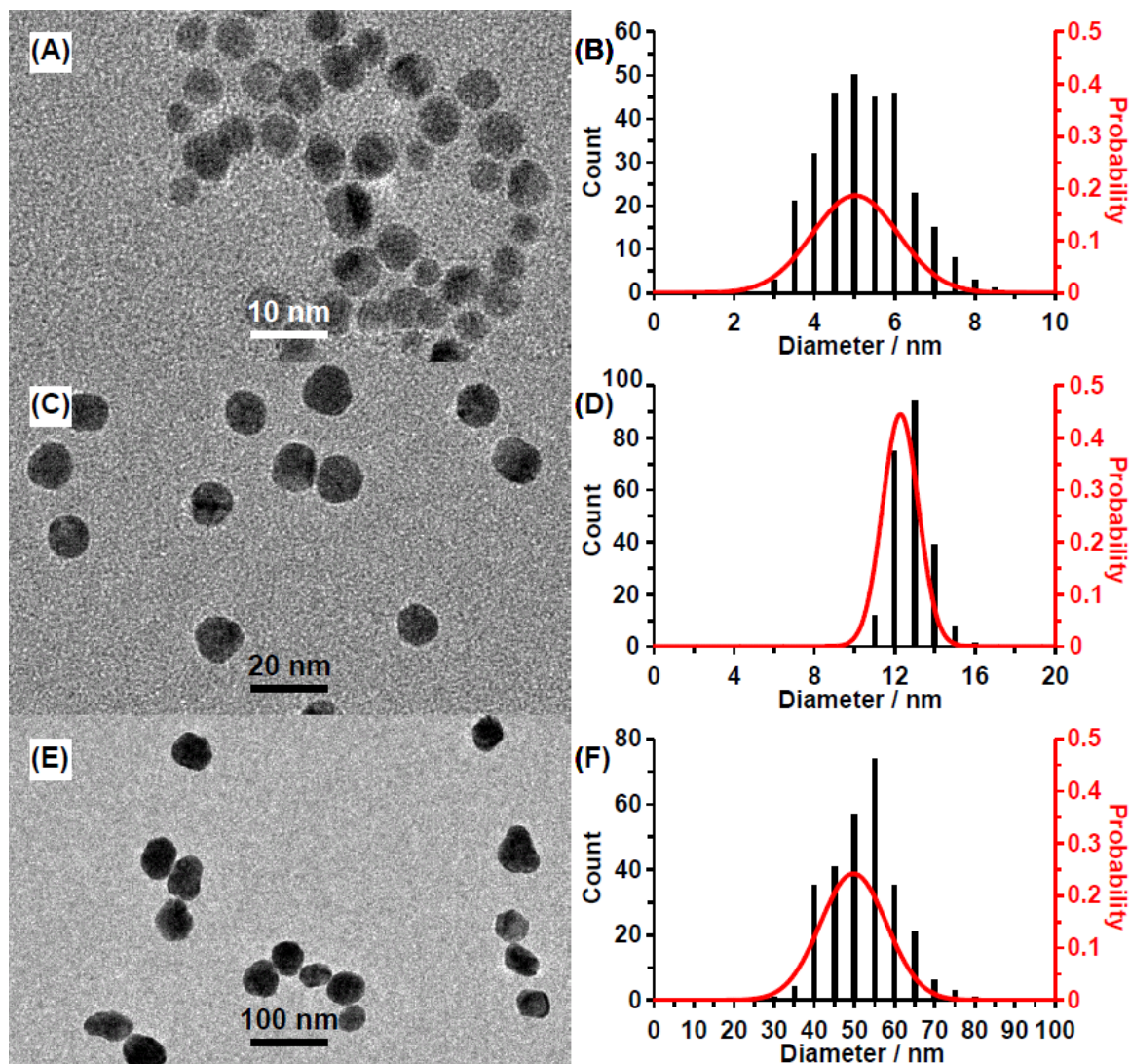


Figure 5.3 Platinum Nanoparticle TEM Analysis

TEM images with corresponding size distribution histograms and Gaussian probabilities for the different platinum nanoparticles. (A) and (B) correspond to the 4 nm platinum nanoparticles, (C) and (D) correspond to the 10 nm PA capped platinum nanoparticles and (E) and (F) correspond to the 30 nm platinum nanoparticles.

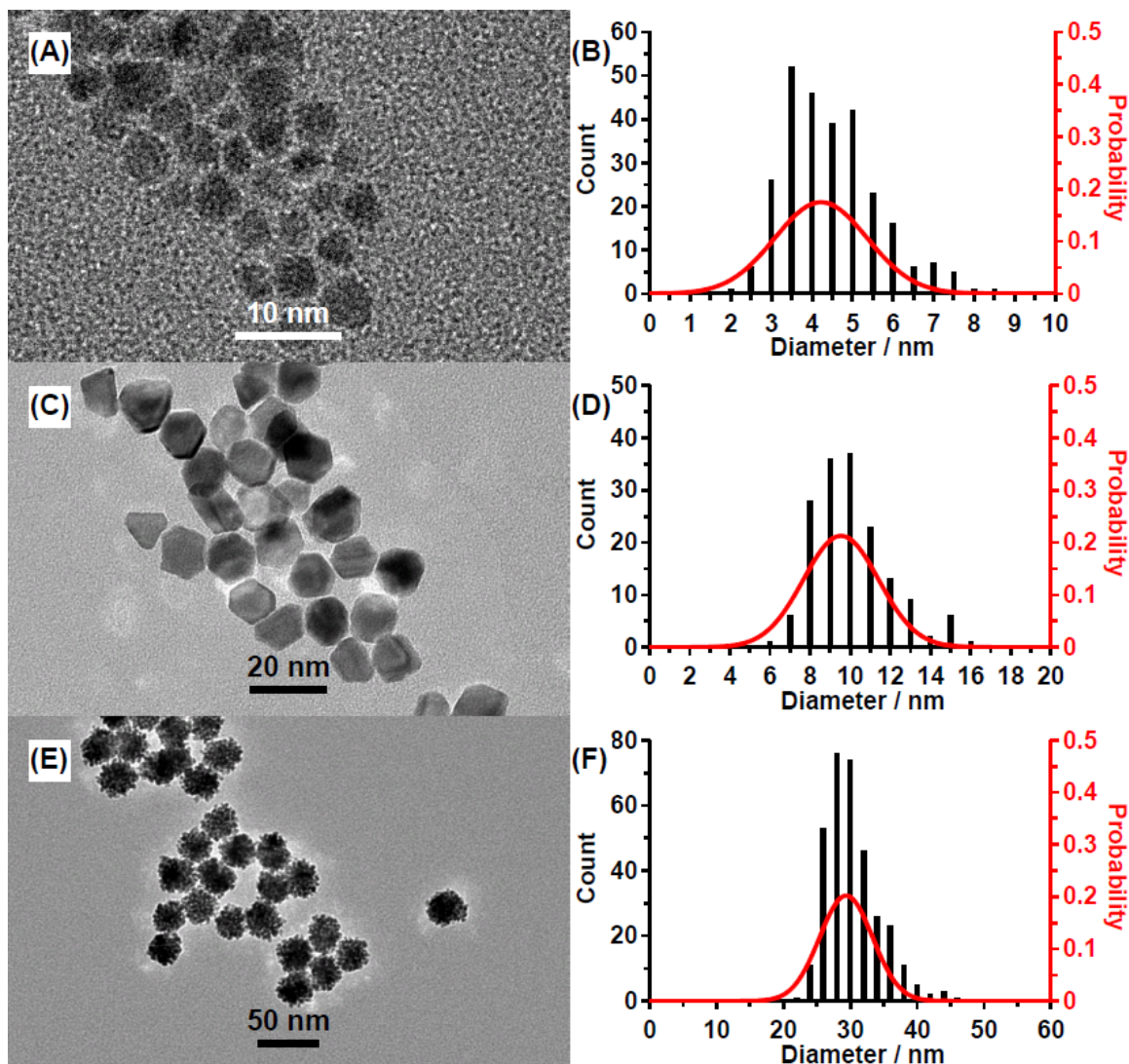


Figure 5.4 Nanoparticle Collision FSCV Analysis

(A) A typical FSCV color plot showing the current response from 12 nm Au NPs colliding with the carbon electrode. (B) Current vs time trace taken from the color plot in (A) where the potential was 0.465 V (black line) in the forward scan direction. (C) Single NP CVs from the events seen in (B), the events are numbered and color coded. The background was readjusted for each CV to subtract out the previous NP events. The solution was 10mM hydrazine in 50 mM PB (pH 7.4) with a scan rate of 25V/s the concentration of 12 nm Au NPs after addition to solution was ~ 12.5 pM.

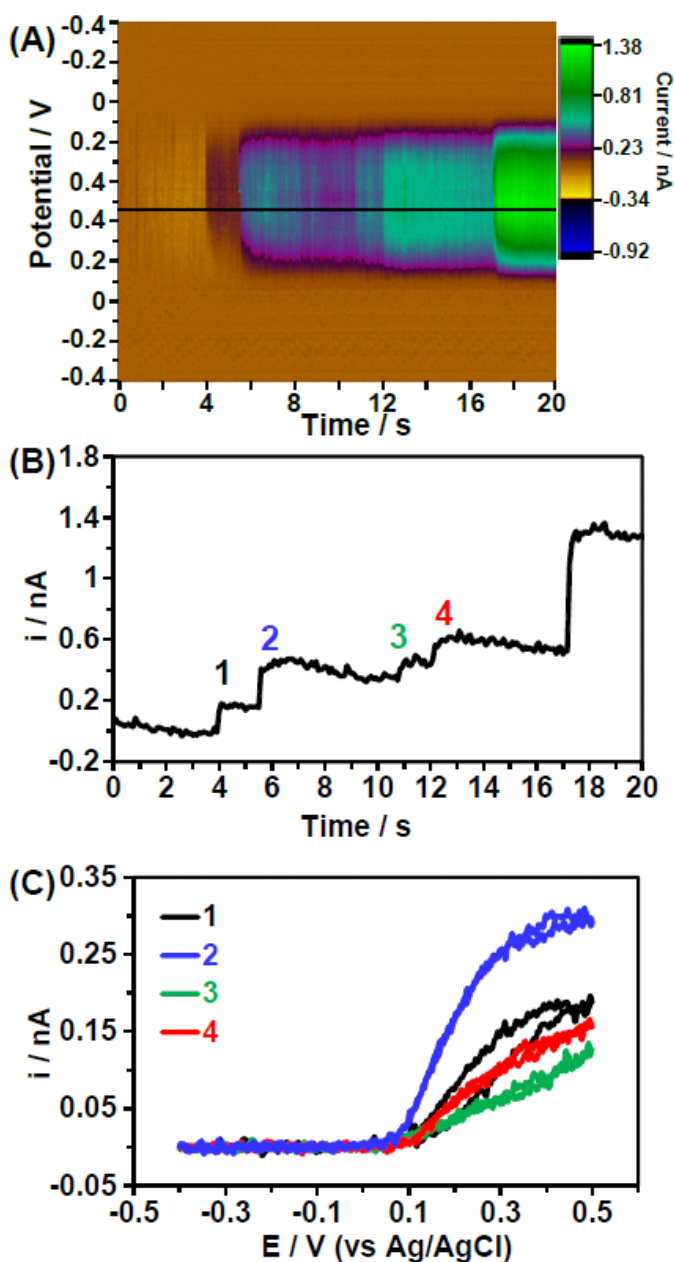


Figure 5.5 Single Nanoparticle Collision Events

Scatter plots showing the $E_{1/2}$ and onset potential (potential at 20% of peak current) versus the peak current for gold nanoparticles (A) and (B) and platinum nanoparticles (C) and (D). The points plotted for the onset potential are from the same events seen in the $E_{1/2}$ plots and all are plotted in reference to Ag/AgCl.

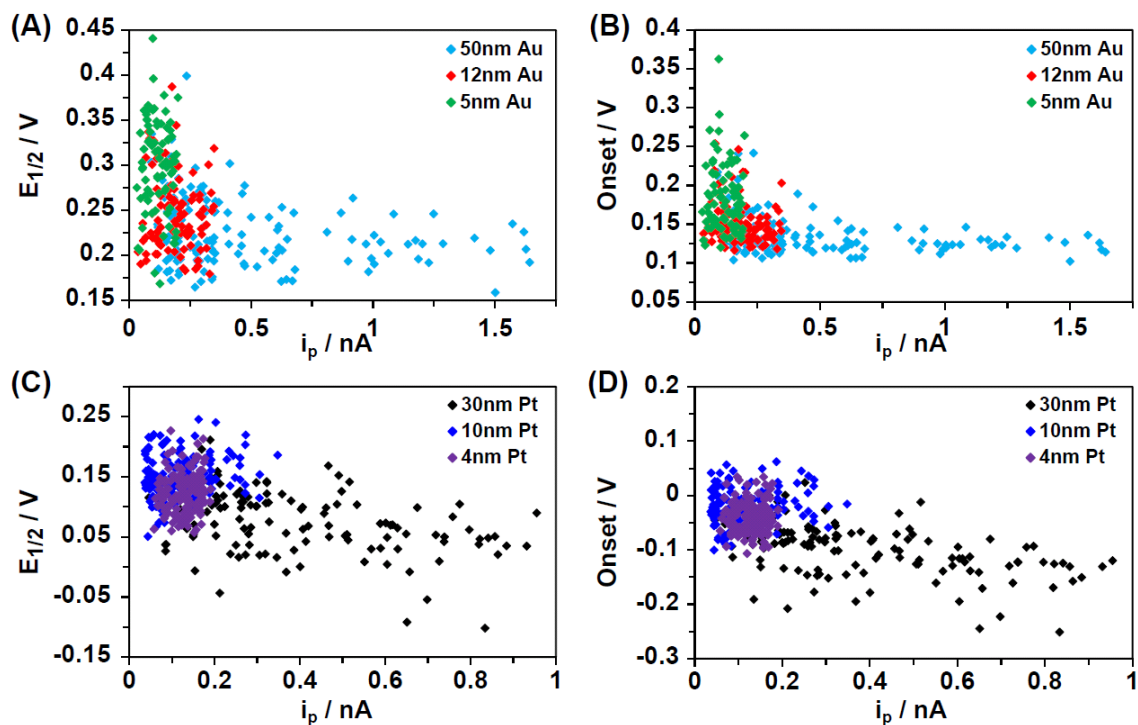


Figure 5.6 Nanoparticle Hydrazine Oxidation Activity Histograms

Histograms showing the count (left axis) and probability of the location of the $E_{1/2}$ and onset potential for the different nanoparticles. (A) 5 nm Au, (B) 12 nm Au, (C) 50 nm Au, (D) 4 nm Pt, (E) 10 nm Pt cubes and (F) 30 nm Pt nanoparticles.

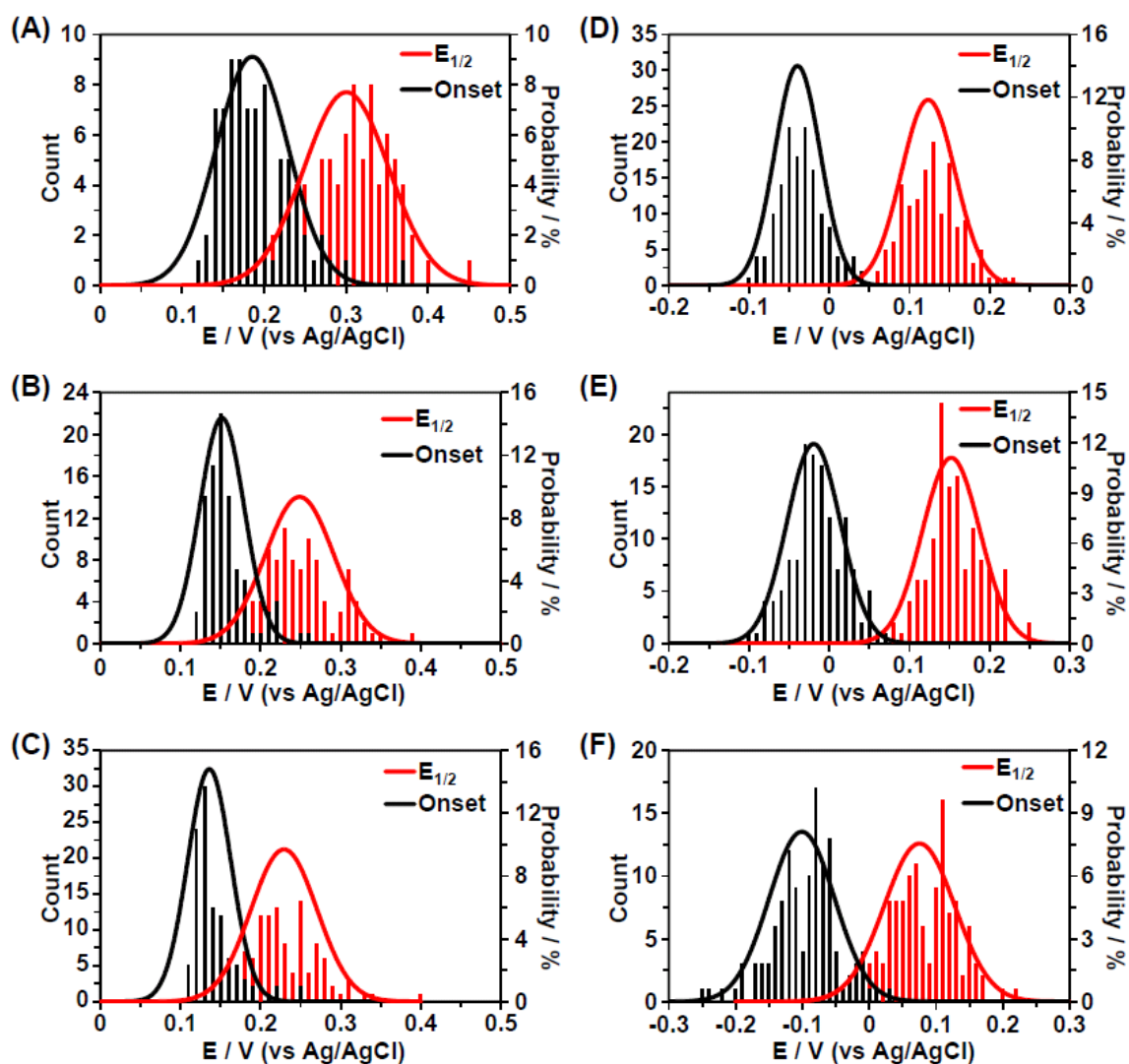


Figure 5.7 Averaged Nanoparticle Hydrazine Oxidation Activities

Plots of the averaged $E_{1/2}$ and averaged onset potentials from all the nanoparticle events seen in the scatter plot averaged for each specific nanoparticle size and plotted as the inverse of the radius. (A) and (B) are from the gold nanoparticles and (C) and (D) are from the platinum nanoparticles. The gold nanoparticle plots display a very linear relation when graphed versus the inverse radius but the platinum nanoparticles do not. Error bars represent one standard deviation of the mean.

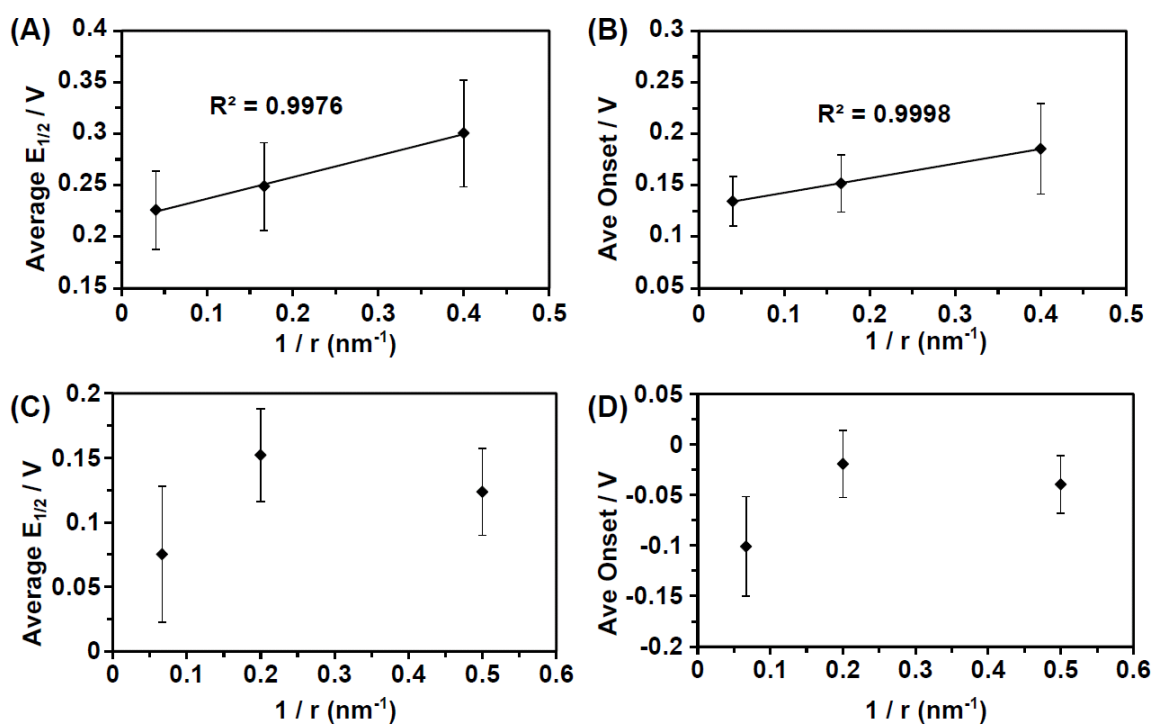


Figure 5.8 Platinum Nanoelectrode Hydrazine Oxidation Activity

Plots showing the shift of the $E_{1/2}$ as a function of the radius for glass sealed platinum nanoelectrodes. CVs taken in 10 mM hydrazine with 50 mM PB at 50 mV/s scan rate. Error bars represent one standard deviation of the mean.

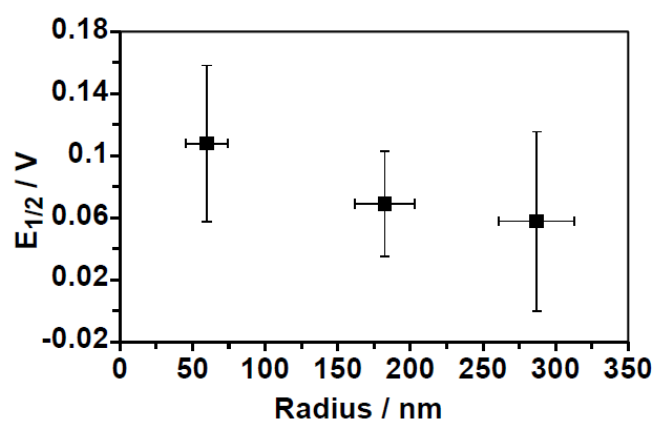


Figure 5.9 Single Nanoparticle Simulation Environment

(A) Simulation environment for the COMSOL single nanoparticle simulations showing the different surfaces where only the nanoparticle surface (surface 5) is electroactive in the simulation. Also seen in (B) is a screen grab (zoomed into the nanoparticle) of the concentration profile for a simulated 12 nm diameter nanoparticle simulated using a 25 V/s sweep rate, $\alpha = 0.5$ and $k_o = 0.0001$ m/s taken at a time in the simulated CV when the potential was at the maximum during the triangle sweep.

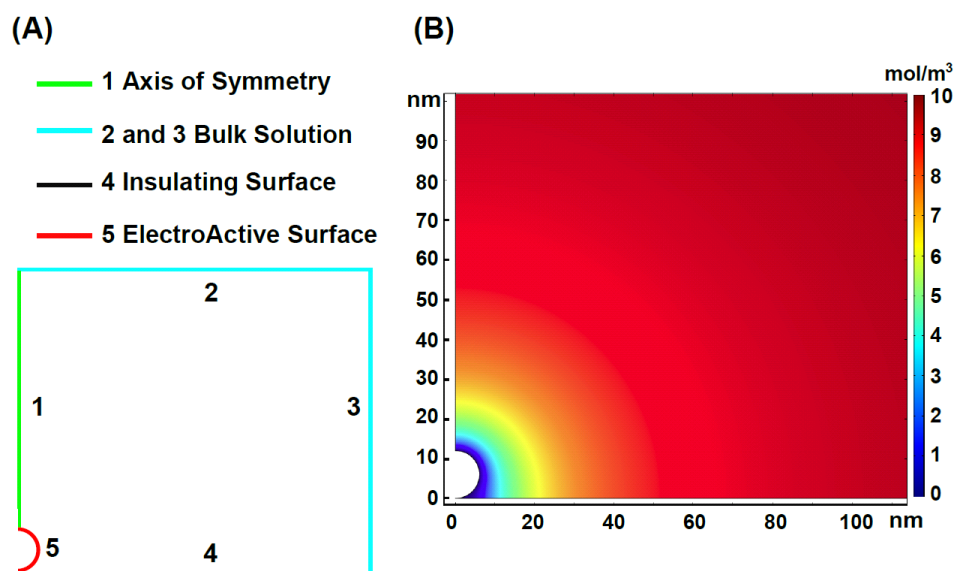


Figure 5.10 Single Nanoparticle Simulated CVs

Example simulation CV curves from (A) a 12 nm Au NP, (B) a 50nm Au NP, (C) a 4 nm Pt NP and (D) a 30 nm Pt NP. Also seen in each CV plot is the simulation CV obtained for each experimental CV using the listed values of the charge transfer coefficient (α) and the heterogeneous electron transfer coefficient (k_o). Only the forward scans are shown and each experimental CV was taken in 10 mM hydrazine with 50 mM PB (pH 7.4) at 25 V/s scan rate.

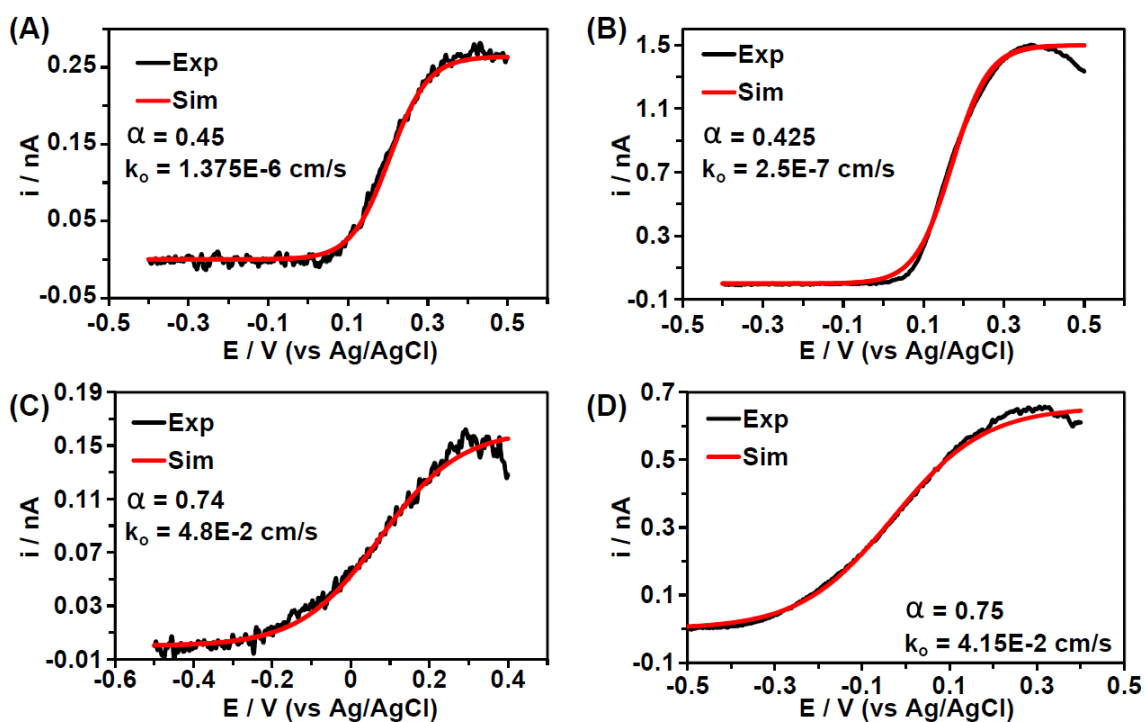


Figure 5.11 Platinum Nanoelectrode Simulated CVs

Representative hydrazine oxidation CVs from platinum disk nanoelectrodes along with the simulated CVs for (A) a 305 nm radius nanoelectrode and (B) a 47 nm radius nanoelectrode. Only the forward part of the CVs is shown for clarity. CVs were taken in 10 mM hydrazine with 50 mM PB at 50 mV/s scan rate.

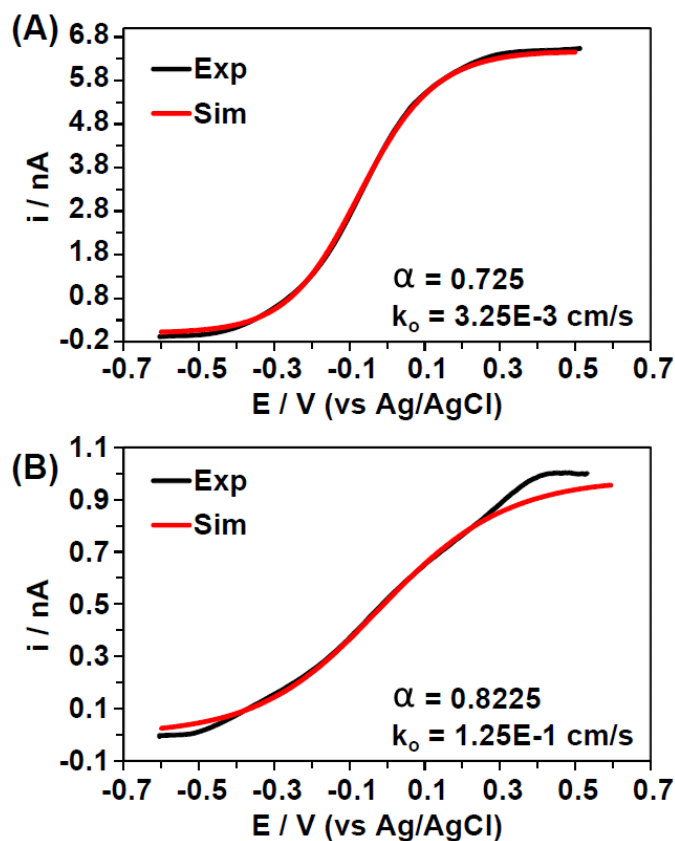


Figure 5.12 Rotating Disk Electrode Plots

(A) Plot showing CVs from 5 nm Au nanoparticles and (B) 4 nm Pt nanoparticles at several rotating rates. Levich plots of the RDE voltammogram data for (C) for the Au nanoparticles taken at 0.8 V and (D) for the Pt nanoparticles taken at 0.5 V. CVs were taken in 10 mM hydrazine 50 mM PB at 100 mV/s.

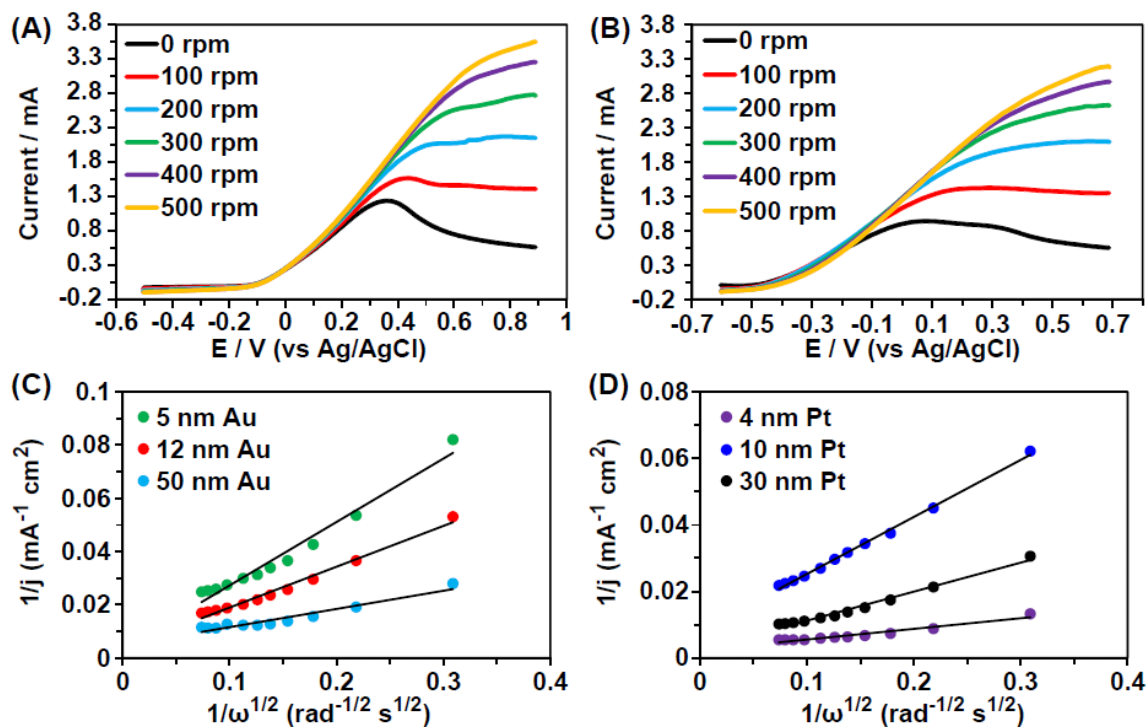


Figure 5.13 Platinum Surface Interaction with Hydrogen Ions

(A) Plot showing a 25 μm diameter platinum UME in argon bubbled 50 mM phosphate buffer and (B) a plot where the hydrogen ion desorption peaks from the microelectrode in (A) are normalized to a CV from a platinum nanoparticle in 10 mM hydrazine with 50 mM PB showing the overlapping regions of the hydrogen ion desorption and the hydrazine oxidation (from the Pt NP).

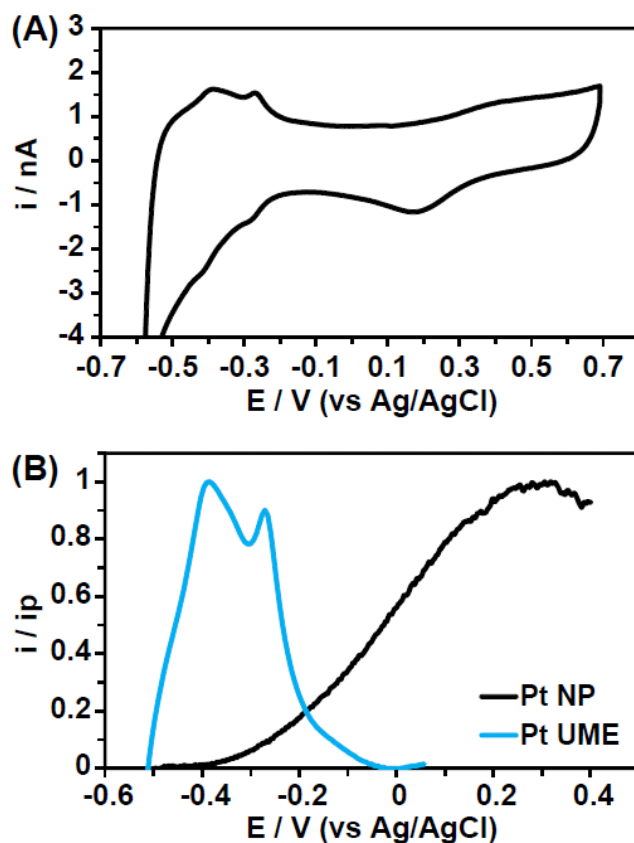
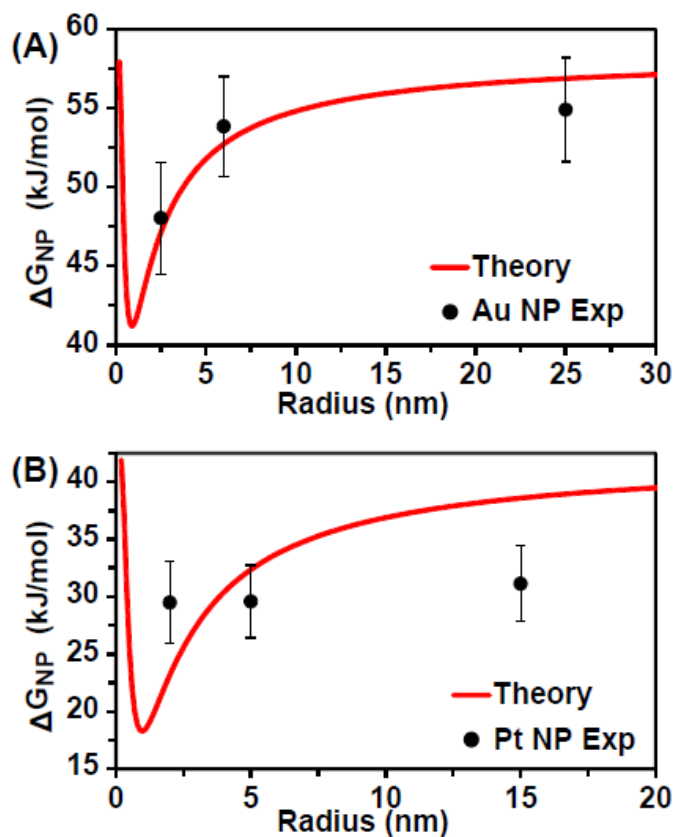


Figure 5.14 Gibbs-Free Energy Change

The average change in Gibbs-Free energy of activation of the different nanoparticle sizes calculated using the heterogeneous electron transfer coefficient obtained by simulating the CVs for a few nanoparticles. Also shown in each plot is the theoretical prediction of the change in ΔG_{NP} as predicted from equation 12. Error bars represent one standard deviation of the mean.



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Chapter 6 A Study of the Formation and Quick Growth of Thick Oxide Films Using Platinum Nanoelectrodes as a Model Electrocatalyst**

6.1 Introduction

Platinum is one of the most active electrocatalytic materials for numerous key reactions in energy conversion and storage.¹⁻⁵ Some reactions, including the Oxygen Evolution Reaction (OER)^{6,7} take place at high applied anodic potentials while others, such as oxidation of methanol,⁸ hydrazine^{9,10} and borohydride^{11,12} take place at more mild conditions and are all relevant to fuel cell operation. The kinetics of these oxidation reactions can be strongly affected by the presence of surface metal oxides.^{6,10} Understanding the oxidation behavior of such catalysts at oxidizing potentials is important for fully understanding the kinetics of the catalytic reactions.^{1,6,13}

Oxidation of bulk platinum metal has been extensively studied and has resulted in many great contributions although the process is still not fully understood.^{1,14} It has been demonstrated that thick platinum oxide can form under conditions of high galvanostatic current densities¹⁵ or high potentiostatic anodization.¹⁶ Other studies have also shown that the oxide layer thickness can be increasingly grown with a fast potential cycling^{17,18} or in very harsh conditions.^{15,19} Conway and coworkers have shown that the formation of different oxides can be independent of one another where the typically formed thin oxide (also known as α -oxide) could be selectively reduced and reformed without reducing the thick oxide layer (also known as β -oxide) implying that the thin oxide formed on the metal surface beneath the thick oxide layer.^{20,21} Biegler and Woods²² reached the conclusion that even at high anodic potentials (2.98 V vs NHE) a limit of 2.66 oxygen atoms/platinum atom is achieved with only monolayer coverage and was later supported using ellipsometry by Parsons and Visscher.²³ Later Conway and coworkers demonstrated that a thick platinum oxide layer can be grown without limits to the thickness of the film when the applied potential exceeds 1.9 V (vs NHE) for extended periods of time (>12 hours) and that oxide growth follows a direct

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logarithmic growth law with time at a constant potential.^{1,24,25} Recently it has been determined that the growth of oxide on platinum is limited to a few monolayers at anodic potentials up to 1.50 V.²⁶

Typically these studies do not observe or discuss growth of thick platinum oxide layers by holding the electrode potential at relatively low anodic potentials. However, many materials exhibit different properties when scaled down to nanometer dimensions.²⁷ One excellent example is the recent study reported by Mirkin and coworkers on the dissolution of platinum on nanoscale platinum electrodes at moderately negative cathodic potentials during the Oxygen Reduction Reaction (ORR).²⁸ The growth of platinum oxides resulting in the loss of electrochemically active surface area can impact fuel cell operation utilizing platinum nanoparticles by inhibiting the catalytic reaction on the oxide surface.²⁸⁻³⁰

Here, we report on the growth of thick platinum oxide films under relatively low anodic polarization potentials on platinum electrodes of nanoscale dimensions. This platform can be thought of as a model for platinum nanocatalysts with implications for fuel cell operation where even at lower operating potentials there may be unwanted formation of oxidized films on the platinum nanocatalyst, reducing its efficiency. The growth of these films on platinum nanoelectrodes appears to be much faster than previously reported and in fact can be observed directly through Electron Microscopy (EM). The use of EM and electrochemistry has enabled us to obtain an apparent growth rate of the platinum oxide, which exceeds any growth rate documented to date that we are aware of. In addition, the oxide film exhibits signs that it may be soft/malleable with a high degree of structural irreversibility.

6.2 Experimental

6.2.1 Chemicals and Materials

All aqueous solutions were prepared using deionized water (>18 MΩ cm) produced in a Barnstead Nanopure water purification system. Ferrocene methanol (FcMeOH, Aldrich 97%), anhydrous sodium sulfate (Na₂SO₄, J. T. Baker), Sulfuric Acid (H₂SO₄, Fisher), Argon (Ar, Praxair, >99%) Pt microwire (25 μm diameter, Alfa Aesar, 99.99%) were all used as received from the manufacturers.

6.2.2 Electrochemical Measurements

Electrochemical data was recorded using a computer-controlled Dagan Chem-Clamp voltammeter/amperometer and data was recorded using an in-house virtual instrumentation program written in LabVIEW (National instruments) on a desktop PC equipped with a PCI-6251 (National Instruments) data acquisition card. A Hg/Hg₂SO₄ reference electrode (CH Instruments, Inc.) was used for all CVs and experimental CV data was manually baseline corrected. The Hg/Hg₂SO₄ reference electrode was used to prevent chloride contamination which is known to block platinum oxidation at lower potentials.³¹ All potentials presented are referenced to a Ag/AgCl reference electrode unless otherwise noted. Sulfuric acid solutions were bubbled with argon for >30 minutes prior to use to ensure the solution was free of dissolved oxygen before anodic polarization. All experiments were done at ambient room temperature.

6.2.3 Scanning Electron Microscopy and Energy Dispersive X-ray Spectroscopy

Scanning Electron Microscope (SEM) images were obtained using a field-emission microscope (FEI Sirion) equipped with a through the lens secondary electron detector with a resolution of 1 to 3 nm at the Nanotech User Facility located at the University of Washington. All samples were sputter coated with a 2-3 nm thin conducting layer of gold/palladium or carbon prior to SEM imaging. Energy Dispersive X-ray Spectroscopy (EDS) data was obtained using an Oxford X-max 80 mm² Silicon Drift Detector.

6.3 Results and Discussion

6.3.1 Fabrication and Characterization of Pt Nanoelectrodes

The procedure to prepare the platinum disk nanoelectrodes is described in detail elsewhere.³²⁻³⁴ However to briefly summarize, a 25 μ m diameter platinum wire was placed in a fused silica capillary tube (O. D.: 1 mm, I. D.: 0.3 mm, Sutter Instrument Co.) and one end sealed closed using an oxygen/hydrogen flame. The fused silica capillary was then placed in a P-2000 laser pipette puller (Sutter Instrument Co.) and vacuum applied to the unsealed end of the capillary. The laser was used to heat and seal the fused silica around the platinum without pulling the capillary. Then the platinum/fused silica assembly was pulled (Pull parameters: Heat = 750 Filament = 2, Velocity = 60, Delay = 140, Pull = 250) resulting in two ultrasharp tips with the platinum nanowires

sealed inside. The tips were then electrically contacted using tungsten wires and conductive silver paste (DuPont). To expose the electrodes a high speed beveling process was employed utilizing a diamond lapping film (3M, 0.5 μm diamonds Ted Pella Inc.) attached to a rapidly rotating wheel (7500 rpm). The electrode was polished by slowly approaching the wheel while visually monitoring using an inverted optical microscope.

The platinum nanoelectrodes were characterized by SEM and steady-state Cyclic Voltammetry (CV). The polished platinum nanoelectrodes are flush with the glass insulating layer, as shown in Figure 6.1. The platinum nanoelectrode shown in Figure 6.1A located at roughly the center of the glass tip is not perfectly round but more oval shaped. Figure 6.1B shows a more uniformly shaped platinum electrode with a diameter less than 500 nm.

Figure 6.2A shows the voltammetric response of two platinum nanoelectrodes in 2 mM ferrocene methanol (FcMeOH), one having a radius of 219 nm and the other 122 nm (calculated from equation 1). Both electrodes show sigmoidal shape CV response typical for a conventional UME of this size.³⁵ The diffusion limited steady-state currents of the electrodes were then used to calculate the radii of the electrodes using the steady-state current equation for a planar disk electrode,³³⁻³⁵

$$i_{ss} = 4nFDC_b r \quad (1)$$

where n is the number of electrons transferred per redox molecule, F is Faraday constant, D is the diffusion coefficient of the redox molecule (for FcMeOH $D = 6.7 \times 10^{-6} \text{ cm}^2/\text{s}$),³⁶ C_b is the bulk concentration of the redox molecule and r is the radius of the electrode. The steady-state CVs were not only used to determine the sizes of the electrodes but are also used to determine any general changes to the area of the electrodes because an increase in the diffusion-limited current indicates an increase in the radius and geometric area of the electrode.

Sulfuric acid scans of the platinum electrode were used to determine the regions of platinum oxidation/reduction as well as the relative cleanliness of the platinum surface after exposure. A representative scan from a 124 nm radius nanoelectrode is shown in Figure 6.2B and a 25 μm diameter Pt UME in Figure 6.2C. The hydrogen adsorption/desorption peaks are observed at potentials below 100 mV (vs Ag/AgCl) on the forward and backward scans respectively.^{35,37} These peaks are from the adsorption/desorption of hydrogen ions in solution onto the platinum surface

and closely match the representative sulfuric acid scan of the 25 μm Pt UME. Also seen in the sulfuric acid scan for the nanoelectrode is an increase in current during the anodic sweep starting at approximately 500 mV and continuing to increase until the sweep reverses. This is slightly different from the 25 μm Pt UME electrode where two distinct current increases are observed, one starting at ~ 570 mV which increases and plateaus to a steady current and another current increase located at approximately 940 mV. These current increases are due to the oxidation of the platinum surface forming platinum oxides initially in the form of an adsorbed layer of oxygen followed by the formation of sub-monolayer coverage of PtO .¹⁴ In the case of the 25 μm Pt UME the second increase, starting at 940 mV, may possibly be attributed to the onset of an interfacial place exchange whereby the oxygen ions in the PtO , initially formed at lower potentials, exchange positions with platinum atoms in the metal surface forming a bilayer PtO structure.¹⁴ During the cathodic sweep a single large peak is observed (in addition to the hydrogen peaks at lower potentials) centered at ~ 500 mV which is due to the reduction of the compact α -oxide layer, formed during the anodic sweep.^{1,21} Interestingly the reduction peak for the nanoelectrode in 2B is centered at ~ 450 mV, indicating that the oxide film formed on the nanoelectrode is more electrochemically irreversible and requires a lower potential for reduction during the cathodic sweep. Additionally, the nanoelectrode surface may also undergo oxidation with an increased rate of initial oxide formation and place exchange at a given potential and the different oxidation mechanisms may proceed at lowered potentials compared to bulk platinum. This can be seen in sulfuric acid scans where the initial oxidation current for the nanoelectrode begins at a lower potential than the 25 μm Pt UME and also does not level off but continues to increase with increasing potential. The ~ 47 mV lower potential needed to reduce the oxide and the increasing oxidation with the anodic potential sweep on the nanoelectrode may be due to the increased adsorption energy of oxygen to the platinum surface of the nanoelectrode as compared to a bulk platinum surface and has been previously observed with other platinum nanostructures.^{27,38-40} The magnitude of the potential shift for the oxide reduction peak for a nanoelectrode of that diameter was unexpected but smaller than some reported shifts for small diameter Pt nanoparticles.^{27,38} This effect might be enhanced by the specific crystal faces present at the electrode surface where for a given specific crystal orientation the oxide reduction peak will shift to more negative potentials, but will also shift the onset of oxide formation in the positive direction.⁴¹

6.3.2 Potential Step Experiments

Oxidation of the platinum by anodic polarization was accomplished by first holding the electrode at 0 mV vs. Ag/AgCl in argon bubbled 0.5 M H₂SO₄ and then quickly stepping it up to a 1200 mV potential where the electrode was held for the duration of the oxidation experiment. If the electrode was reduced after the oxidation, then the potential was stepped back to 0 mV. The most prominent feature from the potential step current-time trace is the large current spike, called the peak current, and can be seen in Figure 6.3A. This current-time trace is obtained from a 100 nm radius electrode stepped to 1200 mV and shows a peak current spike of ~2.8 nA that quickly decays to a steady residual current of ~38 pA larger than the original baseline current. The residual current from the current-time trace is taken as the average current 5 minutes after the potential step and has contributions from both the OER as well as the oxidation of platinum. The residual current measurement was taken after 5 minutes in order to give a fairly accurate result of the differences between the potential steps while not allowing sufficient time to drastically change the electrode surface. Figure 6.3B shows how the peak current changes with potential when the nanoelectrode is stepped from 0 mV to a given positive potential. It is expected that the peak current increases as the potential steps are increased due to the double layer capacitance charging at the surface of the electrode.³⁵

There is a small increase in the peak current as the stepping potential is increased to ~500-600 mV but essentially there is very little change until the stepping potential reaches 1100 mV where a larger increase is observed. The small increase observed at 500-600 mV may be due to the onset of platinum oxidation which is assumed to be limited to sub- or mono- layer thicknesses but has a slow growth rate at low potentials.^{1,25} This is also observed with the residual currents, shown in Figure 6.3C, where again the current essentially does not increase until the stepping potential is 1100 mV or above. At that potential it is apparent that there is an increase in the rate of the platinum oxidation reaction or possibly a new reaction has started. At 1200 mV there is again a large increase in residual current compared to the previous step but as the potential is stepped higher the currents increase less dramatically. The OER is expected to contribute to the current at these increased potentials but its rate is dependent on the pH of the solution.⁴² In a sufficiently acidic solution the OER would not proceed at a significant rate until a high potential was reached.⁴³ Nonetheless, it would still be present when platinum oxidation is occurring making it difficult to determine the specific current that can be attributed to the platinum oxidation. The residual

current increase observed at 1100 mV may be due to the onset of multilayer platinum oxidation at a potential much lower than previously described.¹

The Pt nanoelectrode used in the increasing potential step experiments was visually inspected by SEM imaging, shown in Figure 6.4A and 6.4B. The SEM images show that the platinum surface appears to have grown out from the initial location, seen in the central circular region, and reveals an increased surface area. Figure 6.4C shows the CVs of the same electrode in 2 mM FcMeOH before and after the increasing potential step experiment. The initial current of the nanoelectrode is ~47 pA at 0.1 V which gives a calculated electrode radius of ~91 nm which very closely matches the measured radius of 94 nm from the central circular region in the SEM image. After the experiment the steady-state current has increased to ~114 pA at 0.1 V which is a 243% increase.

6.3.3 Prolonged Anodic Polarization

We then decided to test what would happen if the high applied potential was held for a prolonged amount of time. Figure 6.5A and Figure 6.5B shows the results of the oxidation of a platinum nanoelectrode held at 1200 mV for 90 minutes and removed from the 0.5 M H₂SO₄ while still under anodic polarization in order to prevent the reduction of the oxidized platinum. The SEM images clearly show growth of the electrode and protrusion out of the surrounding glass insulation. Energy Dispersive X-ray Spectroscopy (EDS) measurements of this electrode are shown in Figure 6.6 and verify that the protrusion is indeed the platinum nanoelectrode. A representation of what we believe is physically occurring as the platinum oxide is growing and expanding can be seen in the Schematic in Figure 6.5C. The Schematic illustrates that the platinum electrode is encased in a rigid insulator and that the increasing volume resulting from the platinum oxide formation causes the soft film to protrude out of the insulator forming a rounded hemispherical structure. Previous studies have found that there is a possibility of surface reactions occurring at the sidewall of a glass sealed Pt nanowire.^{44,45} Platinum oxidation and film growth would certainly occur at the Pt/glass interface but would expand and constrict the opening, limiting the growth rate. If there was a substantial contribution from PtOx growth at the sides of the nanowire where the Pt/glass interface is located, then we would expect to see a more ring-like structure protruding from the glass instead of the rounded, centrally located structure observed in the SEM images. However, the schematic

illustrates the additional effect of oxide growth into the nanowire from the sides or increased growth rate from the edges of the electrode causing the oxide to grow radially into the Pt nanowire, but the fact remains we don't know what exactly is occurring within the nanowire. The bulk growth and resulting protrusion of the oxidized platinum is due to the increasing volume of the platinum oxide as oxygen atoms are incorporated into the crystal lattice of the platinum through the previously discussed interfacial place exchange mechanism.¹⁴ Additionally as the oxide layer thickens and the oxygen is incorporated into the lattice structure there may be a formation of voids from the buckling of the platinum atoms, further expanding the oxide layer and possibly causing some instability of the oxide film.⁴⁶

6.3.4 Protruding Oxide Reduction

If this platinum oxide film is reduced after it has grown out of the glass insulation the surface area is found to increase due to the highly irreversible processes that take place as the oxide film is growing. Figure 6.7A and Figure 6.7B show SEM images of a Pt nanoelectrode that had been oxidized for 60 minutes at 1200 mV and then reduced by switching the potential back to 0 mV. The images show that the electrode is protruding out of the glass insulating layer and its surface appears rougher, or faceted, compared to the electrode shown in Figure 6.5. The increase in geometric surface area exposed to the redox solution would increase the resulting steady-state current after the oxidation and reduction of the platinum surface. This can be seen in Figure 6.7C. The limiting current for the electrode before the oxidation/reduction step is ~ 125 pA yielding a calculated radius of 241.8 nm when equation 1 is used and closely matches the SEM measured radius of ~ 227 nm. After the oxidation/reduction step the current increases to ~ 187 pA and the CV exhibits sudden current fluctuations (increasing and decreasing) that may be due to a somewhat porous and unstable nature of the reduced platinum, where perhaps small particles become dislodged and/or new areas become available for the redox reaction. This can be seen in the SEM images where small particulates are littering the area around the protruding nanoelectrode. The incorporation of oxygen into the growing oxide film and possible void formation, discussed earlier, results in the highly structurally irreversible oxide growth. Upon reduction the platinum is unable to reform a compact and uniform crystal structure resulting in the rough and unstable surface observed in the SEM image.

The method of steady-state cyclic voltammetry also allows for the determination of an approximate growth rate for the platinum oxide film. By using a platinum electrode where the disk surface is initially recessed into the quartz insulator and measuring the increase in the diffusion-limited steady-state current, a change in the recessed depth can be calculated using equation 2,⁴⁷⁻⁴⁹

$$i_{ss} = \frac{4\pi n F D C_b r^2}{4L + \pi r} \quad (2)$$

where the constants are the same as previously defined for equation 1 and L representing the depth of the electrode recess. Figure 6.8A again shows an SEM image of a 142 nm radius platinum nanoelectrode that has been oxidized at 1200 mV for 90 minutes and then reduced at 0 mV. Figure 6.8B shows the same electrode but is tilted to show the recessed depth of the electrode that is clearly recessed into the quartz. The radius of the electrode was measured from the SEM images and used with the steady-state current of ~18.8 pA in the 2 mM FcMeOH solution to calculate an initial depth of ~324 nm before the oxidation procedure.

After the oxidation and reduction, an increased steady-state current of ~25.0 pA was used to obtain a final recessed depth of ~217 nm. The calculated depth closely matches the SEM measured value of ~204 nm, which was measured at an angled view. This means that the electrode increased in volume to fill-in 107 nm (~33% of the recessed depth) and gives a lower limit of the oxide film growth to be ~1.2 nm/minute, for this particular electrode. We call this a lower limit because we assume that some volume may have been lost due to the reduction step whereby some oxygen would be driven out of the crystal lattice thus decreasing the total volume. This electrochemically calculated value is comparable to an average growth rate of 1.58 ± 0.99 nm/min which was obtained from visually measuring the PtOx protruding from the glass insulators. The electrochemically calculated rate is lower than the visually measured rate possibly because of the recessed nature of the nanoelectrode which can hinder the mass transport. The increased mass transfer resistance means the acidic protons generated from the OER would have more difficulty diffusing away from the electrode and could lower the local pH making the Pt oxidation less favorable at the electrode surface, slowing the oxide growth. Interestingly, after reduction of this oxide, the steady state redox CV did not exhibit much variation in current, and may be due to oxide layer growth confined by the quartz insulator limiting its growth to just one direction. When reduced, the oxide layer was able to form a more compact structure as compared to that in Figure

6.7 where the protrusion allowed it to grow radially outward, thus increasing the disorder and making it more difficult to re-align its crystal structure upon reduction.

It is apparent that the platinum oxidation on nanoscale electrodes is not limited to a few monolayers and questions still remain regarding why the oxide growth differs from that of bulk platinum, and we will continue to investigate this interesting result. The growth of thick oxide films on platinum nanoelectrodes at relatively low anodic potentials may be indicative of intrinsic stress in the platinum crystal structure where growth of the oxide layer is facilitated by the higher strain energy. The growth rate of the thick platinum oxide may also be largely dependent on the crystal face present at the surface of the electrode and a few studies have stated that crystal faces will influence oxide growth rate.²⁴ We feel it important to note that growth of thick oxide films is not always observed and that surface contaminants, likely from the polishing step, may hinder the growth process.

6.4 Conclusions

We have investigated the growth of thick platinum oxide films on platinum nanoelectrodes at low anodic holding potentials. The potential step experiments reveal a critical potential where the residual current at the nanoelectrode increases due to both onset of platinum oxidation and the OER. The growth of the oxide causes the growing film to protrude out of the glass insulator, indicating the soft nature of the film. The diffusion-limited steady-state current measurements of a simple redox molecule was used to evaluate the minimal growth rate of the oxide film in a recessed platinum nanoelectrode. It appears that the growth rate can be as high as 1.2 nm/min at 1200 mV (vs Ag/AgCl) hold potential. This may be a consequence of the nanoscale dimensions of these platinum electrodes where oxygen adsorption energy is increased compared to bulk platinum and may explain why the oxidation behavior and the subsequent growth of the oxide film is different from that of bulk platinum electrodes. Further investigation is needed to more accurately evaluate the growth rate and also to determine the nature of the oxide film that is grown in this method.

6.5 Figures

Figure 6.1 Platinum Nanoelectrode SEM Images

SEM images of freshly polished platinum nanoelectrodes showing the electrode surfaces flush with the glass insulator.

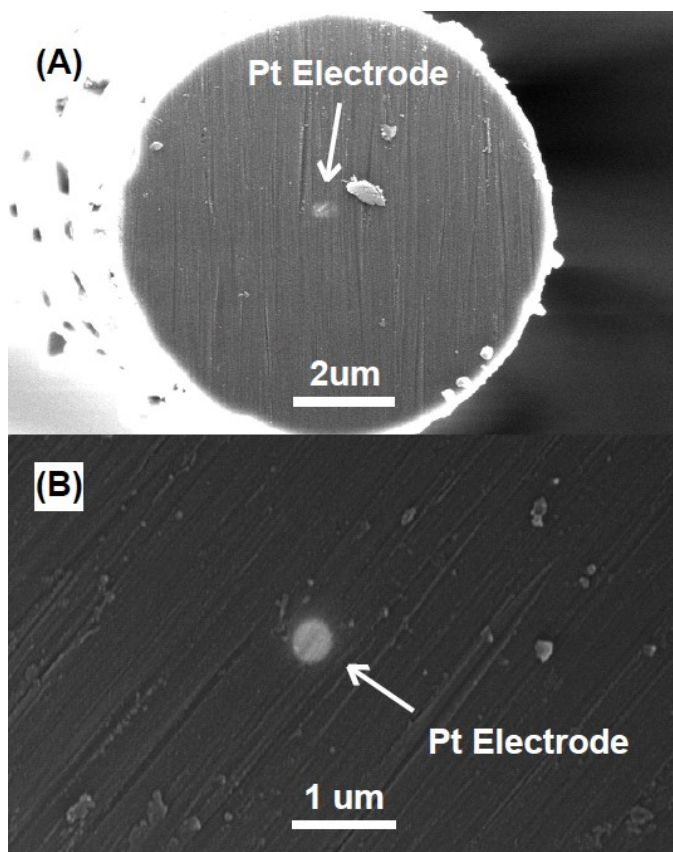


Figure 6.2 Electrochemical Characterization

A) CVs of two platinum nanoelectrodes with different radii in 2 mM FcMeOH with 100 mM Na_2SO_4 at 50 mV/s scan rate and B) a 124 nm radius Pt nanoelectrode in 0.5 M H_2SO_4 at 100 mV/s scan rate and C) a 25 μm diameter Pt electrode in 0.5 M H_2SO_4 at 100 mV/s scan rate.

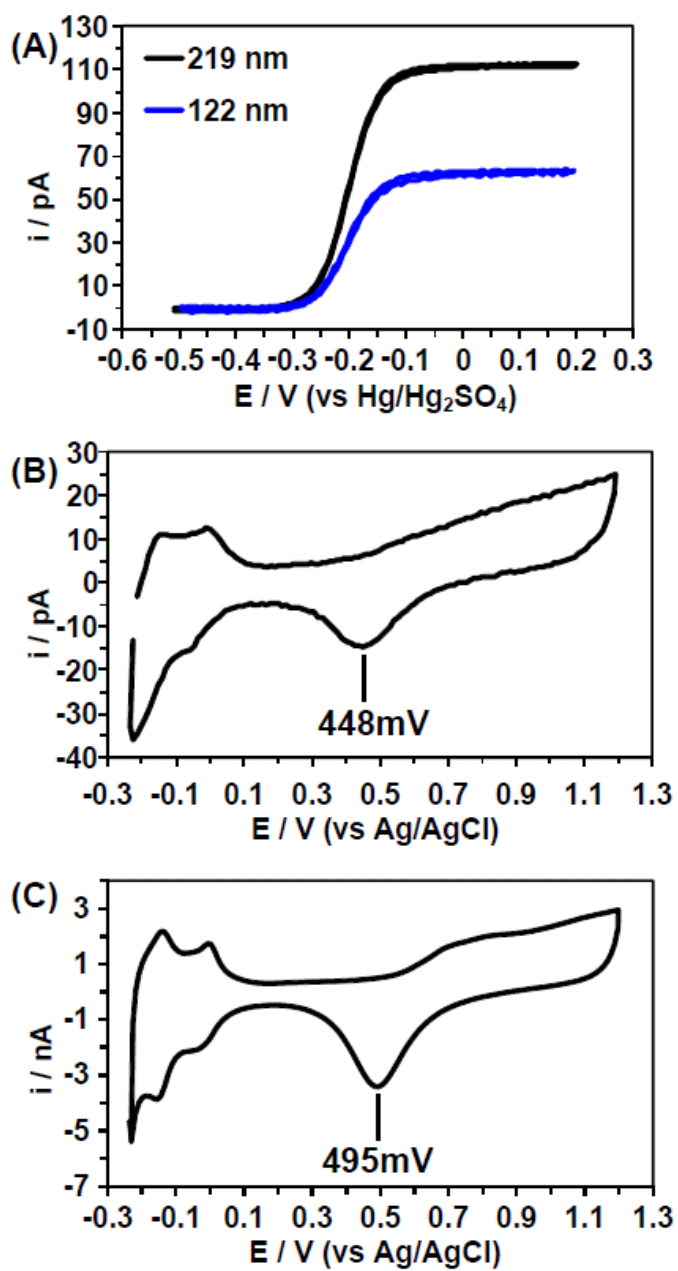


Figure 6.3 Potential Step Current Response

A) Potential step chronoamperometric trace at 1200 mV from a 100 nm radius Pt nanoelectrode in 0.5 M H_2SO_4 where the initial peak current (red dot in (B)) is observed to decay to a non-zero residual current (red dot in (C)). B) Peak current observed at each potential step and C) residual current observed for each potential step measured as the average current 5 minutes after the potential step. All potential steps were recorded using the same electrode.

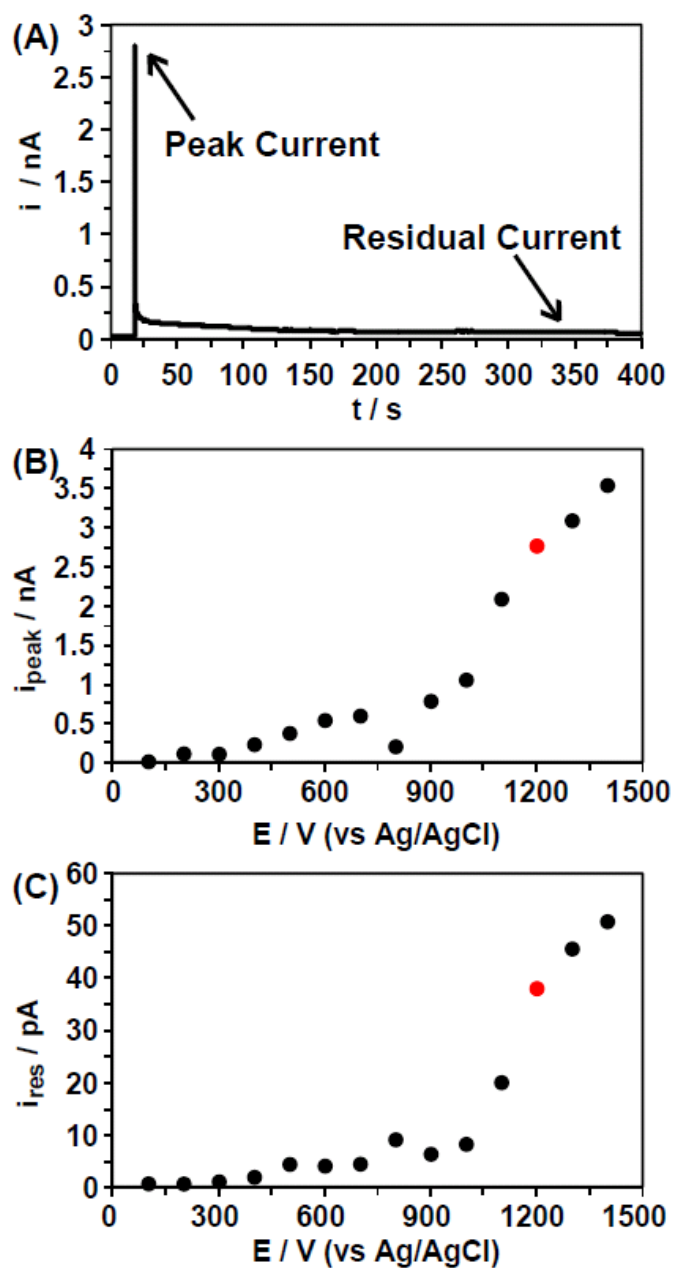


Figure 6.4 Surface Growth After Potential Step Experiments

A) and B) are SEM images showing the electrode used in the increasing potential step experiment where it appears the platinum surface area has significantly increased compared to the initial circular region at the center. C) Diffusion-limited steady-state CVs in 2 mM FcMeOH with 100 mM Na_2SO_4 supporting electrolyte before and after the increasing potential step experiment showing a substantial increase in the current. Scan rates were 50 mV/s for both CVs.

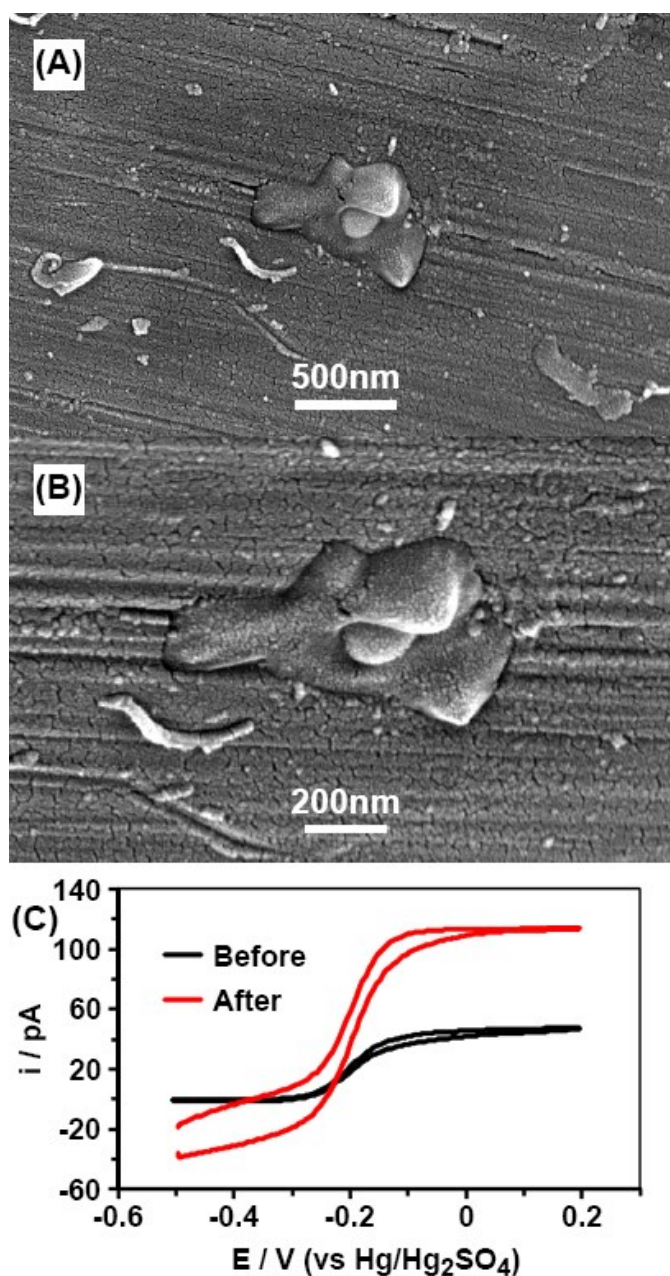


Figure 6.5 Protruding Oxide Growth with Schematic

A) SEM image of an electrode after Anodic oxidation at 1200 mV for 90 minutes. B) The side view of the same electrode as in (A) showing the protruding nature of the Pt oxide growth. C) Schematic showing the hypothesized growth of the Pt oxide where the surrounding glass insulation forces the increasing volume of Pt oxide to grow out of the glass pore in a radial direction.

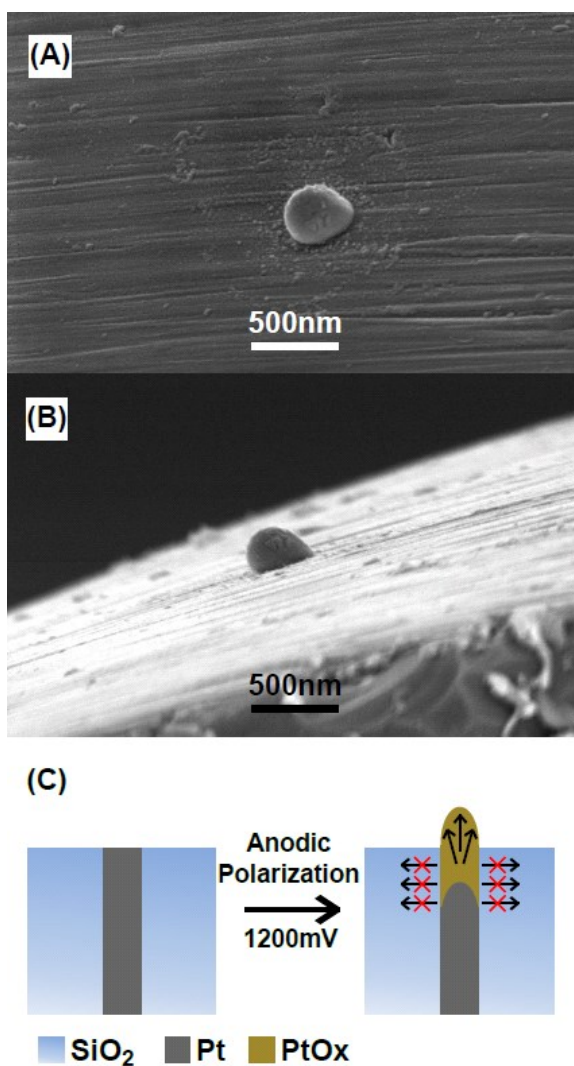


Figure 6.6 Oxide Growth EDS Analysis

EDS image of the anodically oxidized platinum nanoelectrode shown in Figure 6.5A and 6.5B. A) All color plots overlaid on the EM image showing the location of the platinum coincides with the bulge. B) Only the platinum EDS color plot, C) the silicon color plot and D) the oxygen color plot.

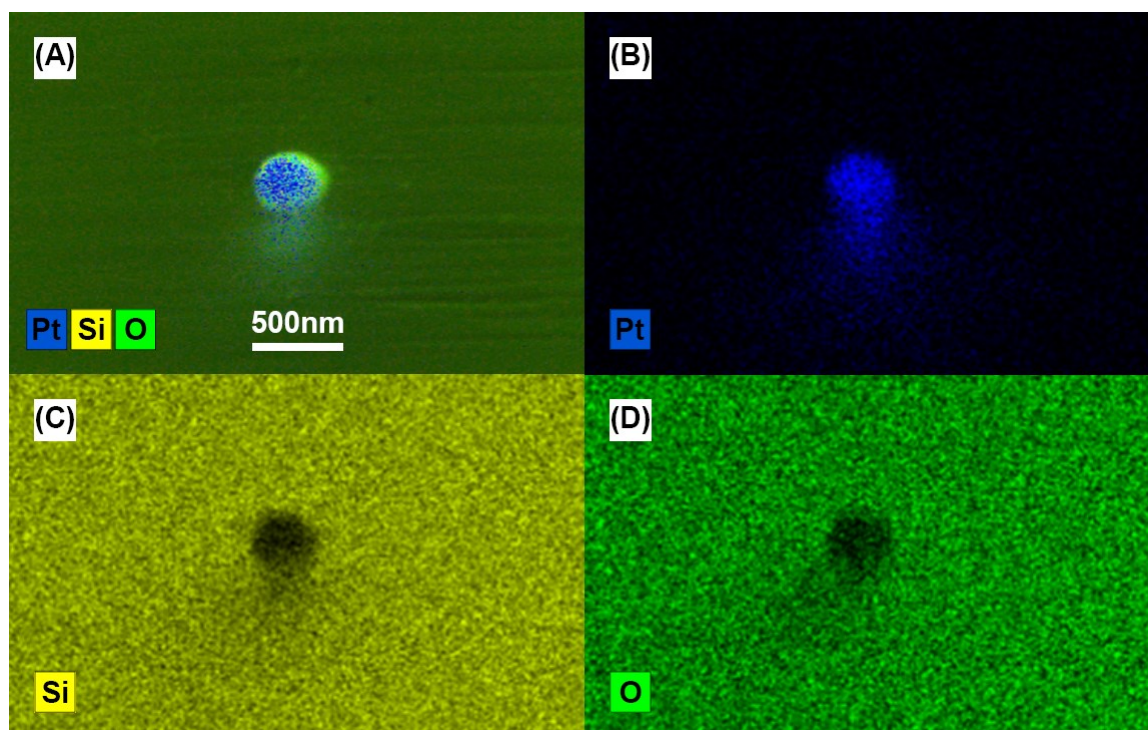


Figure 6.7 Protruding Oxide Electro-Reduction

A) and B) SEM images of an electrode oxidized for 60 minutes at 1200 mV and then reduced at 0 mV showing the more crystalline (faceted) nature of the Pt surface. C) CVs in 2 mM FcMeOH before and after the oxidation/reduction step showing an increase in the limiting current (100 mM Na₂SO₄ supporting electrolyte 50 mV/s scan rate).

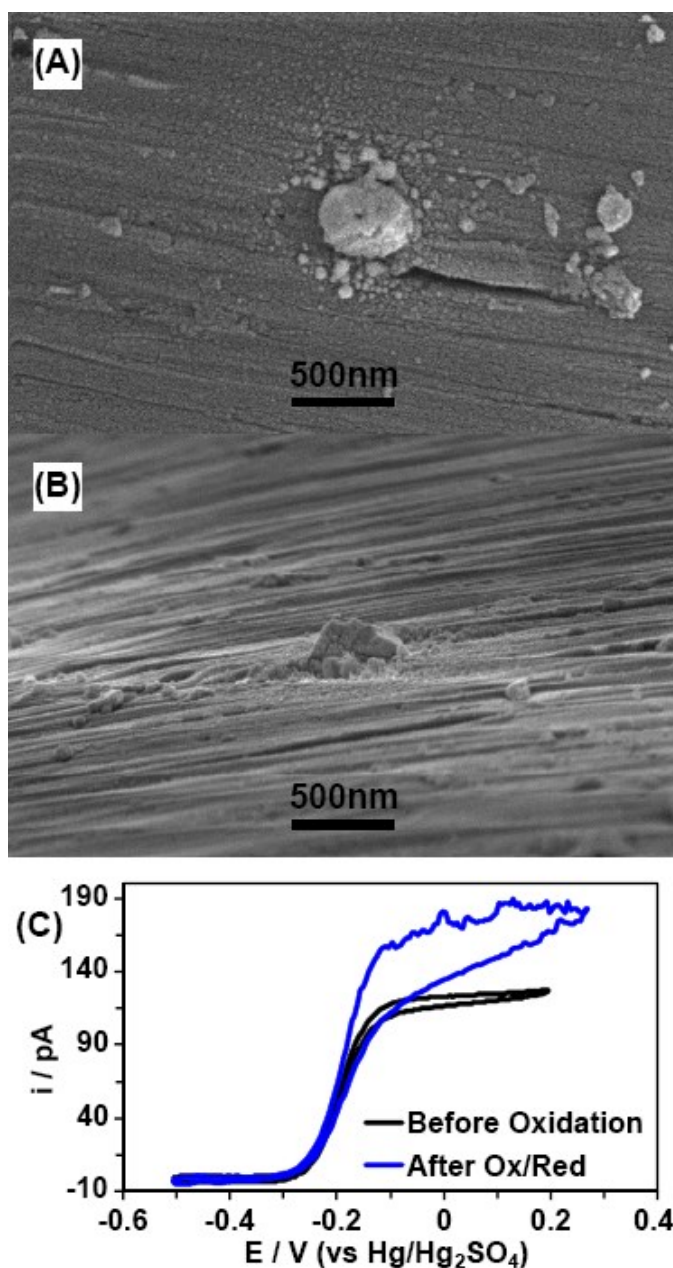
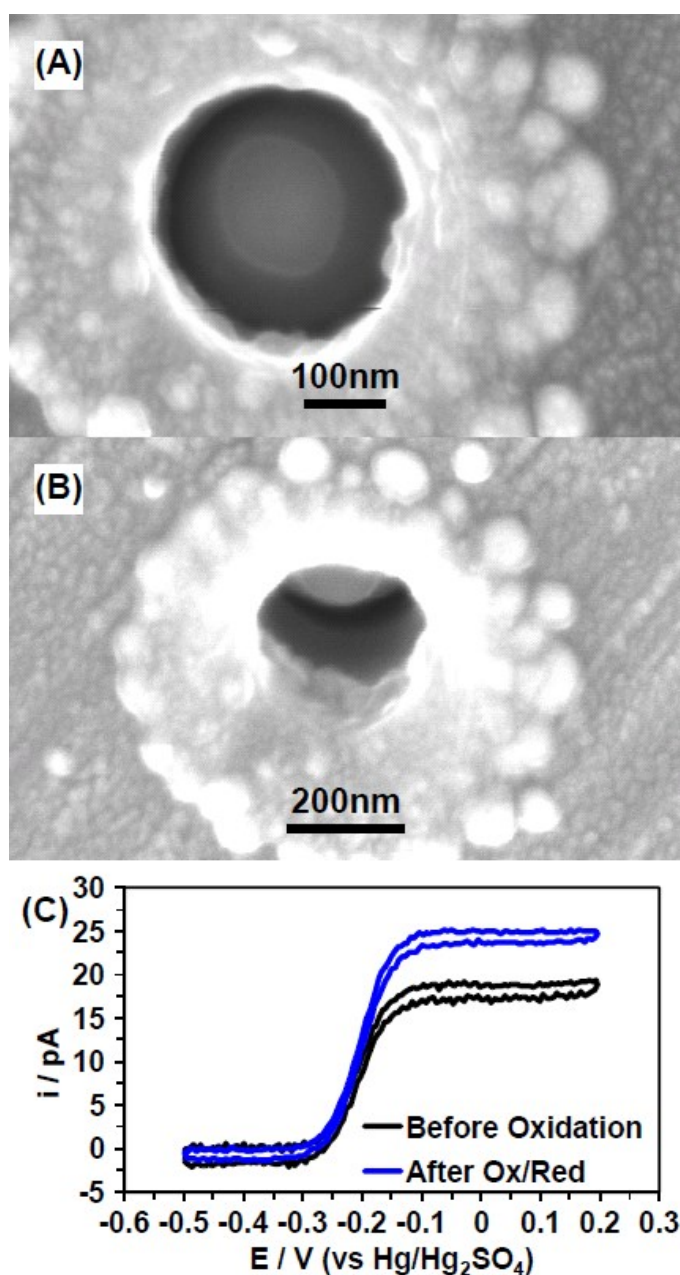


Figure 6.8 Recessed Nanoelectrode Oxide Growth

A) and B) are SEM images of a recessed platinum nanoelectrode that was oxidized for 90 minutes at 1200 mV and then reduced at 0 mV. The SEM image in (B) is at a tilted angle to show the electrode surface and the sidewall of the recess. C) CVs from the electrode shown in (A) and (B) showing the steady state currents before oxidation and after oxidation where the increased current indicates a less recessed electrode surface.



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Chapter 7 Fluorescence Coupling for Direct Imaging of Electrocatalytic Heterogeneity^{††}

7.1 Introduction

The ability to spatially and temporally resolve electrochemical processes has become increasingly important for many investigations in the past several decades, particularly for electrocatalysis studies¹ and studies involving heterogeneous electrode surfaces² and biological redox processes.³ Among the most widely applied electrochemical imaging methods is scanning electrochemical microscopy (SECM), which relies on the rastering of an ultramicroelectrode over a substrate of interest to obtain topographical or electrochemical information.^{4,5} SECM has proven to be extremely valuable for applications, such as mapping a catalytic surface,^{6,7} studying molecular transport at localized domains,⁸⁻¹¹ and imaging single biological cells.^{12,13} In addition to the stand alone technique, SECM has been combined with other imaging techniques, such as atomic force microscopy (AFM)¹⁴ and scanning ion-conductance microscopy (SICM).¹⁵⁻¹⁷ Despite these outstanding properties, it is necessary, however, with SECM to make a compromise between image spatial resolution, scan time, and size of working area. Several attempts have been reported to overcome this limitation, most notably by Girault and co-workers who have used flexible linear microelectrode arrays to minimize the total scan duration.^{18,19} However, if faster temporal information is desired for transient or short-lived processes, a scanning technique will not suffice.

Tao and co-workers have recently introduced an elegant electrochemical imaging method, which utilizes surface plasmon resonance (SPR) to detect local changes in current density^{20,21} or electrochemical impedance^{22,23} and to perform square wave voltammetry²⁴ at thin film gold electrodes. Their method can obtain data comparable to a conventional voltammetric response over various regions of an electrode with excellent sensitivity for small redox species, such as $\text{Ru}(\text{NH}_3)_6^{3+}$ or TNT. However, this method requires the use of a thin-film gold electrode, which may limit its application in certain processes. Additionally, certain redox processes involving larger electroactive molecules may likely involve relatively little change in the index of refraction and thus

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a weak signal. Another challenge with this technique may be the deconvolution of local SPR changes due to heterogeneity of the electrochemical current from irregularities due to electrode surface functionalization's themselves. To address the aforementioned challenges it would be desirable to use an array of thousands or more individually and simultaneously addressable microelectrodes. This, however, presents several major challenges, both in the array fabrication and the complex and costly electronics/data acquisition requirements for monitoring such an extreme number of channels. The Ewing group has extended the traditional limit to the numbers and size of microelectrode arrays for electrochemical analysis^{25,26} including a recent report using an array containing 15 ultramicroelectrodes.²⁷ This has allowed for the direct imaging of transient exocytosis events from single cells. In order to significantly increase the number of simultaneously addressable electrodes and to spatially resolve smaller features, an alternative method for addressing individual microelectrodes and monitoring their current is necessary.

Here we report a new electrochemical approach, called fluorescence-enabled electrochemical microscopy (FEEM), to locally monitor electrochemical current on large electrochemical arrays. This method couples a fluorogenic redox reaction to the redox reaction of interest so that one can use fluorescence microscopy to examine a conventional faradaic reaction on individual microelectrodes. Extending this strategy on a closed bipolar electrochemical array allows one to simultaneously monitor thousands of electrodes. Figure 7.1a illustrates the basic principles of FEEM. At the core of the setup is a closed bipolar electrode,^{28,29} which along with its surrounding insulative substrate completely separates the two solution compartments. One solution compartment contains an oxidizable redox analyte (R), while the other contains a buffered solution of resazurin (S). No direct electrical contact is made to the bipolar electrode from the external circuit thus simplifying the electrical setup. Instead, a small bias voltage is applied to two electrodes to couple the redox reactions on the bipolar electrode. The oxidation of R to O at the anodic pole is coupled to the two-electron, two-proton fluorogenic reduction of resazurin (Figure 7.1b). Optical monitoring of the fluorescent product of this reaction, resorufin (P), provides a convenient and sensitive way to measure the electrochemical signal of the analyte.

The use of fluorescence microscopy to study electrochemical processes is itself not a new concept. Fluorescence-voltage single molecule spectroscopy (F-V/SMS)³⁰ and single-molecule spectroelectrochemistry (SMS-EC), developed by Barbara and Bard and their co-workers^{31,32} has led

to much related work for the study of electron transfer kinetics³³ and electrocatalytic reduction^{34,35} of single organic dyes. While all of these studies demonstrate applications of fluorescence-based electrochemical detection, their usefulness is strictly limited to investigations into the properties of a limited number of redox active fluorophores or special fluorogenic redox reactions. FEEM instead relies on the fluorogenic reaction only to report the rate of electrochemical processes involving redox species with no inherent fluorescence of their own. This makes possible the broad application of FEEM to study nearly any redox active species.

A unique advantage of this method is the ability to individually and simultaneously address a large number of parallel microelectrodes (e.g., >104) and optically monitor their faradaic response. The absence of a direct connection and the conversion of an electrochemical current signal to a fluorescence signal allow for the use of a large array of parallel bipolar electrodes. This provides a new means to spatially and temporally resolve electrochemical processes. In this report we first provide the initial demonstration of FEEM using two series-coupled microelectrodes. Next, electrochemical arrays containing thousands of ultramicroelectrodes are used to image redox species discharged from a glass micropipet. Finally, due to the growing interest in electrocatalyst screening,^{36,37} we demonstrate the use of FEEM to map catalytically active hot spots on a carbon fiber electrode array, which was selectively patterned and modified with Pt. Although this simple demonstration here uses only two materials, it can be easily scaled up for high-throughput, parallel, multicomponent screening of electrocatalysts.

7.2 Experimental

7.2.1 Chemicals and Materials

Ferrocene (Fc, Fluka Analytical), ferrocenemethanol (FcMeOH, Aldrich), hydrogen peroxide (30%, J.T. Baker), tetra-n-butylammonium hexafluorophosphate (TBAPF₆, Aldrich), potassium chloride (J.T. Baker), sodium sulfate (Fisher Chemicals), sodium hydroxide (J.T. Baker), monosodium phosphate (Fisher), disodium phosphate (J.T. Baker), platinum(IV) chloride (Aldrich), sulfuric acid (EMD Chemicals), and reagent grade acetonitrile (MeCN, Aldrich) were all used without further purification. Resazurin sodium salt (Aldrich) containing resorufin in small quantities was purified using previously established procedures.³⁸ A Barnstead Nanopure water purification system was used to provide >18 MΩ·cm deionized water for all aqueous solutions.

7.2.2 Fabrication of Bipolar CF Electrode Arrays and Pt Deposition

Carbon pultrusion rods (OD 0.280–4 mm) consisting of hundreds or thousands of individual 6 μm -diameter carbon fibers within an insulative epoxy binder were obtained from DPP Pultrusion through the distributor A2Z Corp. Sections of the rods were further sealed in Epo-Tek 301epoxy (Epoxy Technologies, Inc.) to further increase rigidity and provide additional isolation between both ends of the rods. Thin cross sections of the resulting carbon fiber/epoxy rods were cut and then polished to the desired final thickness from ~ 0.1 to 4 mm. CF arrays to be selectively patterned with Pt were first patterned with photoresist. Samples were spin coated with adhesion promoter (Micro Prime MP-P20 (20% hexamethyldisilazane (HMDS), 80% propylene glycol monomethyl-ether acetate (PGMEA)), then with AZ1512 photoresist (AZ Corporation). Patterning was accomplished using a chromium-on-glass UV mask and a Newport UV Flood Exposure System with a 500 W Hg lamp followed by developing to expose the selected carbon fibers (AZ351 developer AZ Corporation, diluted 1:5 developer:DI H₂O). Pt was deposited on exposed carbon fibers using a solution of 1 mM PtCl₄ and 0.5 M H₂SO₄ in a bipolar deposition configuration. To provide electron transfer at the anodic poles of the CF array a solution of 2 mM FcMeOH in 0.1 M KCl was used and a potential pulse of -1.6 V for 200 ms followed by a resting potential of 0 V for 800 ms. The voltage was applied to two Ag/AgCl QREs for a total of 5 min.

7.2.3 FEEM Apparatus Setup

An Olympus IX70 inverted microscope equipped with an IX-FLA inverted reflected light fluorescence observation attachment was used for all fluorescence experiments. Illumination was provided using an Olympus U-ULS100HG 100 W mercury burner. A filter set consisting of a HQ535/50 excitation filter, a Q565lp dichroic mirror, and a HQ610/75 emission filter was used. Video/images were recorded using an Andor iXon+EMCCD camera cooled to -80 °C and a Dell PC equipped with Andor SOLIS software. Electric potential was applied to two AgCl-coated Ag wire quasi-reference electrodes through a Chem-Clamp potentiostat (Dagan) connected to an EG&G 175 programmer. Voltammetric response was recorded using a PCI-6251 (National Instruments) card on a Dell PC using in-house LabVIEW 8.5 software (National Instruments). A scan rate of 200 mV/s was used for all potential sweep experiments unless noted otherwise.

7.2.4 Video Acquisition and Processing

Andor SOLIS software was used for all video/image recording and post processing. Video was recorded at a frame rate of 19.81 Hz for the experiments shown in Figure 5 and 33.887 Hz for all other experiments. A preamplifier gain setting of 5.1 was used. Time derivative of fluorescent intensity is presented as a moving average for Figure 3b ($n = 30$) and Figure 6 ($n = 10$) to smooth short-term fluctuations in fluorescent signal.

7.2.5 Scanning Electron Microscopy

Scanning Electron Microscopy (SEM) images were obtained using a field-emission electron microscope (FEI Sirion). Samples were sputter coated with a thin layer (2–3 nm) of Au/Pd prior to imaging.

7.3 Results and Discussion

7.3.1 Fluorescence Coupling on a Closed Bipolar Electrode

Here, we first use a simple closed bipolar electrode to demonstrate electrochemical coupling between the oxidation of ferrocene and the reduction of resazurin. Two 25 μm diameter Au disk electrodes were connected in series to create a closed bipolar electrode, as shown in the schematic in Figure 7.2. The anodic pole was placed in an acetonitrile solution containing 2.5 μM ferrocene and 0.1 M TBAPF₆, while the cathodic pole was placed in an aqueous solution containing 50 μM resazurin and 50 mM phosphate buffer (pH = 7.4). The solution surrounding the cathodic pole was illuminated (with a Hg lamp and a HQ535/50 excitation filter) to excite resorufin fluorescence. A triangular potential waveform 0–1.4 V was applied on the bipolar cell at a scan rate of 200 mV/s to oxidize ferrocene. This process was coupled to the reduction of resazurin to generate resorufin as a fluorescent product on the cathodic pole. Figure 7.3a shows five background corrected snapshots at selected voltages taken from a video recording a burst of fluorescence throughout the course of the potential sweep experiment. The sixth panel in Figure 7.3a is a plot of the fluorescence intensity versus time for the region over the electrode surface. The fluorescence signal seen here is the product of coupling the two electrochemical reactions, the oxidation of ferrocene and the fluorogenic reduction of resazurin, through the closed bipolar electrode.

For comparison Figure 7.3b shows the voltammetric responses of a 25 μm diameter Au disk electrode in 2.5 μM Fc in a conventional two-electrode cell (blue) and the corresponding closed bipolar configuration as used in the above fluorescent experiment (red). It can be seen here that the current–voltage response of the bipolar configuration is somewhat broader than the response from the conventional cell, and the curve is shifted to higher potentials. This change in wave slope is the result of coupling these two electrochemical processes and is not itself an indication of kinetic limitations.³⁹ Additionally, the position of the curve (i.e., the half-wave potential) can be approximated by taking the difference between formal potentials for the reactions at each of the two poles of the bipolar electrode. A more detailed discussion of the voltammetric response of closed bipolar electrodes can be found in our recent work.^{28,39} The black curve shown in Figure 7.3b is the time derivative of the fluorescent intensity, dI/dt , at different applied potentials during the forward scan from 0 to 1.2 V. A nice correlation can be seen between the “fluorescence current” (black curve) and the corresponding electrochemical current (red curve). The total fluorescent count should be proportional to the total number of fluorescent resorufin molecules, which, by Faraday’s law ($Q = nFN$), is proportional to the total charge passed through the bipolar electrode. As such, the time derivative of the fluorescence count, dI/dt , could generate a response linearly correlated to the faradaic current response. A more detailed explanation and derivation of the relationship between the Faradaic current and the time derivative of the fluorescence intensity are given in the supplemental section at the end of this chapter. Lei et al. have also recently shown the correlation between the derivative of fluorescence intensity and measured electrochemical current for the quasi-reversible oxidation of cresyl violet.³³ Here, due to the relatively low concentration of ferrocene, the oxidation reaction on the anodic pole limits the overall faradaic response of bipolar electrode, and the resulting “fluorescent voltammetric response” in Figure 7.3b is representative primarily of the oxidation of ferrocene. At short time intervals this relationship holds true, however, other factors, such as photobleaching, diffusion of fluorescent product resorufin and, at elevated potentials, further reduction of resorufin to the nonfluorescent dihydroresorufin,³⁴ may lead to a more convoluted signal at extended times. Quantification of the fluorescent response and its exact relationship to electrochemical current are an inherently difficult task. This would require consideration of the extinction coefficients and quantum efficiencies of both the fluorescent product and the redox active precursor, the detector efficiency as well as other less easily quantifiable factors, such as those discussed above. For this reason we believe that FEEM, in its

present configuration, is more useful for measurements of relative electrochemical response. Additional controls and standards could be introduced into an experimental configuration to yield a more quantifiable result.

Figure 7.4 shows the results of several additional FEEM experiments for the oxidation of dopamine over the course of a potential sweep. The oxidation of dopamine and the reduction of resazurin are both two-electron electrochemical processes. Thus, we anticipate that there is a 1:1 ratio between the total oxidized dopamine on the anodic pole and the generated resorufin on the cathodic pole. Indeed, here we see a linear correlation between peak fluorescence intensity and dopamine concentration. In this present experimental configuration, the limit of detection was ~ 1 μM , which corresponds to an oxidation limiting current of ~ 10 pA on the 25 μm diameter gold ultramicroelectrode.⁴⁰ However, other parameters including volume and concentration of the resazurin solution and method of fluorescence monitoring may be adjusted in order to increase sensitivity. A more systematic study is needed to better understand the relationship between fluorescence generation and electrochemical current including the possible use of other fluorogenic reporter reactions to improve sensitivity as well as to detect reducible analytes.

7.3.2 Fluorescence-Enable Electrochemical Imaging

A unique advantage of this method is that it can be used on an array of ultramicroelectrodes to image dynamic and heterogeneous redox processes. We demonstrate this concept using a carbon-fiber ultramicroelectrode array. Figure 7.5a illustrates a scheme of an experiment designed to electrochemically image redox species. Here we use this array to detect and image FcMeOH molecules as they are released from a glass micropipet. An SEM image of the microelectrode array is shown in Figure 7.6. This array consisted of nearly 1000 parallel carbon fibers, each with a diameter of ~ 6 μm and a length of ~ 200 μm , insulated from each other by epoxy. A constant voltage of 800 mV was applied between the two Ag/AgCl driving electrodes in the anodic (top) and cathodic (bottom) solution compartments. The 3 μm inner diameter tip micropipet containing an aqueous solution of 2 mM FcMeOH with 0.1 M Na_2SO_4 was placed at the left most edge of the array adjacent to the anodic poles (top) and discharged for 5 s at 1 PSI. A burst of fluorescence was immediately observed at the corresponding location on the cathodic poles of the bipolar array. An image showing the initial burst of fluorescence is presented in the top left panel of Figure 7.5b and demonstrates the ability to spatially resolve transient presence of FcMeOH near the surface of the

carbon electrodes. A series of six snapshots is presented in Figure 7.5b showing the growing fluorescent signal with time as more FcMeOH molecules are released from the pipet. The mass transport of FcMeOH at the anodic side of the array is visualized in this process. One drawback of this method, however, is the loss of spatial resolution due to diffusion of the fluorescent product along the surface of the microelectrode array. Figure 7.7 shows the fluorescence intensities for select regions both to the right of the pipet tip location over the array and to the left of the tip over the insulating substrate. It can be seen that the intensity decays more rapidly with distance to the left than with an equal distance to the right, indicating that transport of the analyte on the dark side of the array can be discerned from the diffusion of the fluorescent product alone. Diffusion of resorufin will of course lead to a decrease in spatial resolution at extended experiment times. This can possibly be hindered or even completely prevented by immobilizing these fluorescent molecules on the surface of the bipolar electrodes. However this may significantly decrease our upper limit of detection by lowering the concentration of fluorogenic reaction precursor available at or near the electrode surface. We are currently investigating methods to immobilize resazurin onto the electrodes without adversely affecting our detection limit.

To further explore the spatial resolution provided by FEEM in its present setting, a carbon-fiber array was patterned with photoresist on the anodic side (top) to physically block the oxidation of FcMeOH on selected regions of the bipolar electrode array. Only the carbon fiber surfaces inside the Husky pattern, shown in Figure 7.8a, are exposed to FcMeOH solution, while the rest of the areas are covered with photoresist. No photoresist was placed on the cathodic side of the array where the fluorescence was observed. The FEEM image shown in Figure 7.8b provides a clear representation of the oxidation of 2 mM FcMeOH at the anodic poles of the array, and the pattern is well resolved. There are however noticeable distortions to the image seen in Figure 7.8b as compared to the pattern in Figure 7.8a. For example, in the fluorescent signal we see a brighter section at the jaw line of the Husky, flanked by two less intense regions. This distortion is likely due to irregularities in the original carbon fiber array, such as lateral crosstalk or convergence/divergence of adjacent wires. We have found that very thin cross sections of the array, as thin as 100 μm , greatly reduce image distortions. We are working to incorporate highly ordered nanowire arrays into our setup to virtually eliminate this issue. The resolution of FEEM is currently limited by the size of each of the individual carbon fibers of the array, $\sim 6\ \mu\text{m}$ for the arrays

used here. However, we anticipate greatly increasing the spatial resolution through the use of metallic nanowire arrays.

7.3.3 Electrochemical Imaging of Electrocatalytic Heterogeneity

Development of new electrocatalysts requires quick and rigorous screening to determine their activity. As a result, there has been an increasing demand for improved high throughput screening methods. FEEM provides an excellent platform for quick, parallel screening of electrocatalytic materials. To demonstrate the use of FEEM for electrocatalyst screening, a simple experiment was carried out where a carbon fiber bipolar electrode array was selectively patterned with platinum on one side and used to study the electrocatalytic oxidation of hydrogen peroxide (Figure 7.9a). SEM images of the array (Figure 7.9b) show the five regions where Pt $\sim$ 200 nm thick was electrochemically deposited on individual carbon fibers within the array. The remaining bare carbon fibers were unmodified. A solution of 10 mM H_2O_2 in 0.1 M NaOH was placed on the dark side of the array with the Pt-coated carbon fibers (Pt-CF). A voltage ramp from -400 to 700 mV was applied on the bipolar array to allow for the oxidation of H_2O_2 . A large contrast in the oxidation signal can be clearly seen between the Pt-covered region and the remaining bare fibers. Figure 7.9c shows an FEEM image (top) and corresponding line scan (bottom) taken at the peak fluorescence intensity from a video recorded during the potential sweep. The five regions corresponding to the Pt-CFs are well resolved in the fluorescence image showing the much higher electrocatalytic activity of Pt to H_2O_2 oxidation versus bare carbon fiber.

In a subsequent experiment the hydrogen peroxide solution was replaced with 2 mM FcMeOH in 0.1 M KCl, and the potential was swept from 0 to 1 V. Unlike H_2O_2 , FcMeOH is oxidized by an outer-sphere mechanism, and therefore the electron transfer kinetics is relatively independent of the electrode material. This can be visualized using FEEM as shown in Figure 7.9d, where the entire array fluoresces almost uniformly. The voltammetric response of a single bare carbon fiber and resulting Pt-CF after deposition in the same solutions of H_2O_2 and FcMeOH are shown in Figure 7.9e,f, respectively. As expected the oxidation of hydrogen peroxide is strongly dependent upon the electrode material, showing a much greater current response after Pt deposition. The response of the bare CF and Pt-CF in FcMeOH, on the other hand, is very similar in magnitude. Slight differences in charging current and a more peak shaped response with the Pt-CF are likely due to increased surface roughness and an increased contribution due to linear diffusion.

The time derivative of the fluorescent signal intensity, like in the FEEM experiment using single electrodes shown in Figure 7.3, can be used to obtain information comparable to traditional electrochemical current signal. The fluorescent voltammetric response from the FEEM videos for the oxidation of H_2O_2 and FcMeOH is shown in Figure 7.10a and 7.10b, respectively. Like the conventional voltammetric response, the fluorescent voltammetric response shows a clear difference in the catalytic activity for a region of bare carbon fibers versus a region of Pt-CF with hydrogen peroxide oxidation but little difference in the response for FcMeOH oxidation. This simple demonstration of the possible application of FEEM to electrocatalyst screening uses only two materials, platinum and carbon fiber. However, large scale use of this method to interrogate an array containing hundreds of parallel, multicomponent materials could be realized with little additional cost or technical requirements. Furthermore, significant improvements to the resolution of FEEM can be expected through the use of highly uniform, dense electrochemical arrays.

7.4 Conclusions

In summary, we have studied the electrochemical coupling of a fluorogenic reduction reaction and conventional oxidation reactions (e.g., oxidation of Fc, dopamine, and H_2O_2) on closed bipolar microelectrodes and their array. The generation of a fluorescent product allows one to use highly sensitive fluorescence microscopy to observe electrochemical kinetics and monitor electrocatalytic heterogeneity over large electrochemical arrays. This is a unique electrochemical imaging approach to study many conventional electrochemical oxidation reactions with excellent spatial and temporal resolutions. We have shown the correlation between the derivative of fluorescence intensity and the electrochemical current and are currently carrying out additional studies in order to quantify this relationship. The use of fluorogenic oxidation reactions, such as the oxidation of cresyl violet or amplex red, may be used in future experiments to allow for the extension of this method to the detection of reducible analytes. We have briefly shown the applicability of FEEM to electrocatalyst screening and believe that it could serve as a useful platform for high throughput, multicomponent, and parallel testing. The future incorporation of arrays of bipolar nanoelectrode into the FEEM configuration holds the possibility for reaching submicrometer or even diffraction-limited resolution.

7.5 Figures

Figure 7.1 Fluorescence Enabled Electrochemical Microscopy

(a) A schematic illustrating the basic principle of FEEM and (b) the fluorogenic reduction of resazurin.

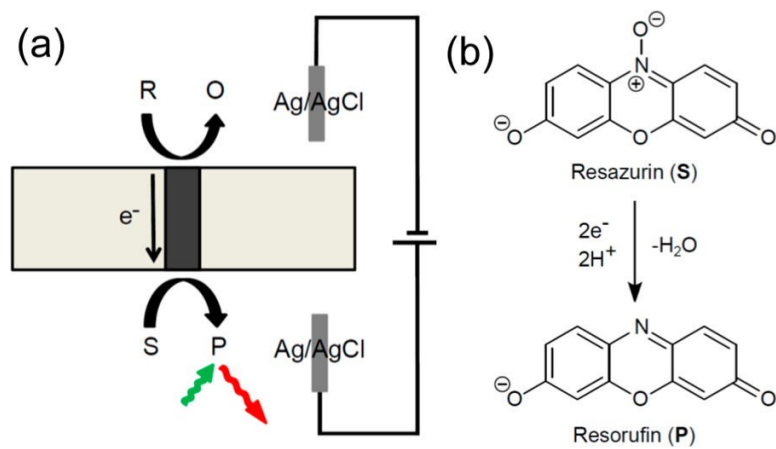


Figure 7.2 Bipolar UME Setup

Schematic for experimental FEEM setup in which two microelectrodes are connected in series to create the bipolar electrode.

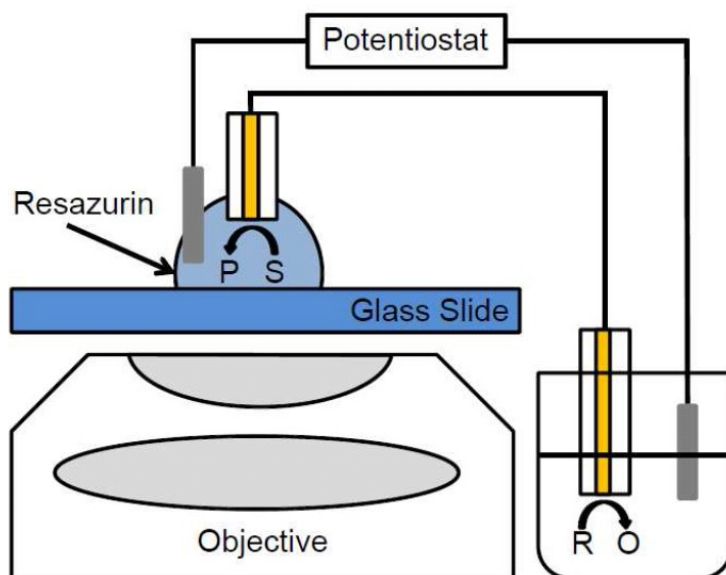


Figure 7.3 FEEM UME Voltammetric Response

(a) A series of fluorescence images over the course of a potential sweep experiment (0–1.4 V, 200 mV/s) for the detection of 2.5 μM Fc using 50 μM resazurin in a 50 mM phosphate buffer pH = 7.4. The last panel shows the total fluorescence counts plotted as a function of time during the voltage sweep. (b) Voltammetric response of a 25 μm Au disk electrode in 2.5 μM Fc (blue curve), the response when the same electrode is connected in series to another 25 μm Au disk electrode in 50 μM resazurin (red curve) and the time derivative of the fluorescence intensity (black trace) for the experiment shown in (a) as a function of potential from 0 to 1.2 V.

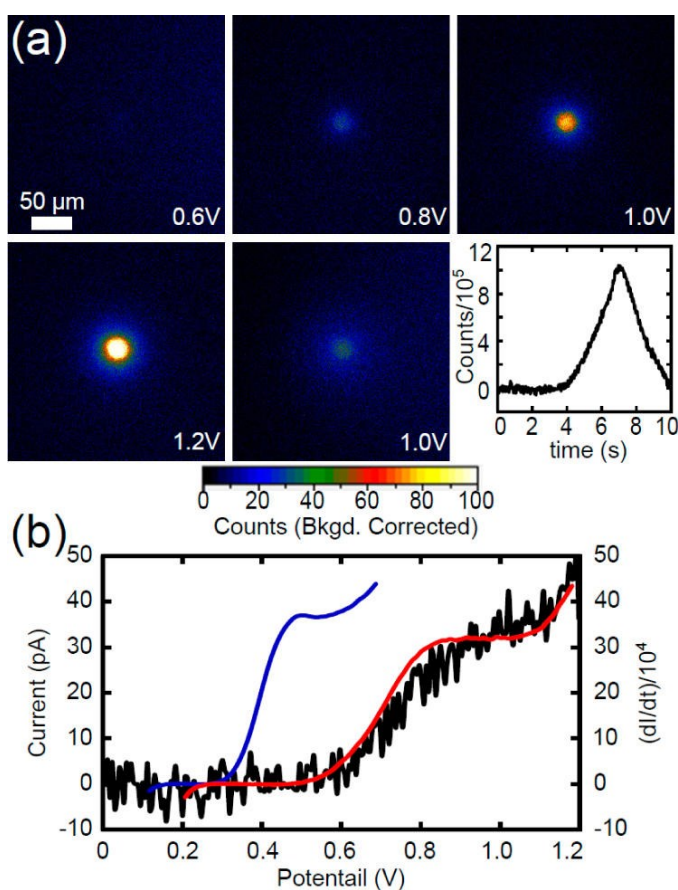


Figure 7.4 FEEM Fluorescence Concentration Response

Fluorescence intensity for several FEEM experiments during a potential sweep (0.4 –1.6 V, 200 mV/s) for the oxidation of dopamine (DA) using two series coupled, 25 μm diameter Au disk electrodes and the concentration dependence of the peak fluorescence intensity (inset).

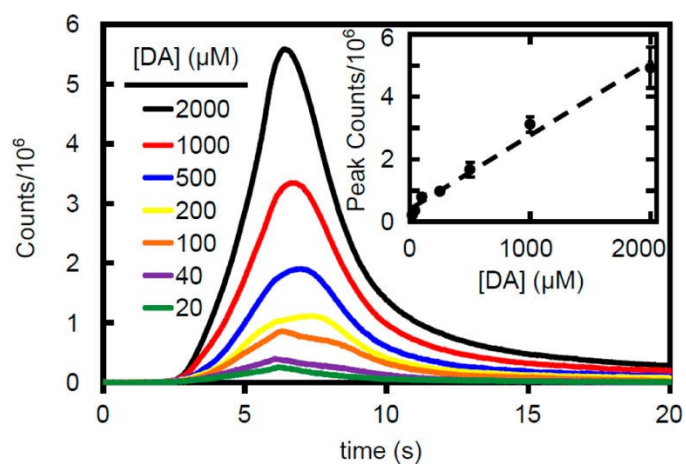


Figure 7.5 Analyte Mass Transport FEEM Imaging

(a) Schematic diagram showing the setup to image release of FcMeOH from a glass micropipet with an array of carbon-fiber ultramicroelectrodes. The FcMeOH molecules are oxidized on the top surface of the carbon electrodes generating resorufin on the bottom surface of the carbon rods. (b) Fluorescence snapshots recorded from an experiment in which a solution of 2 mM FcMeOH with 0.1 M Na_2SO_4 was discharged from a 3 μm micropipet for 5 s at 1 PSI onto the left most side of a CF array with a total diameter of 300 μm . Potential was held at 800mV.

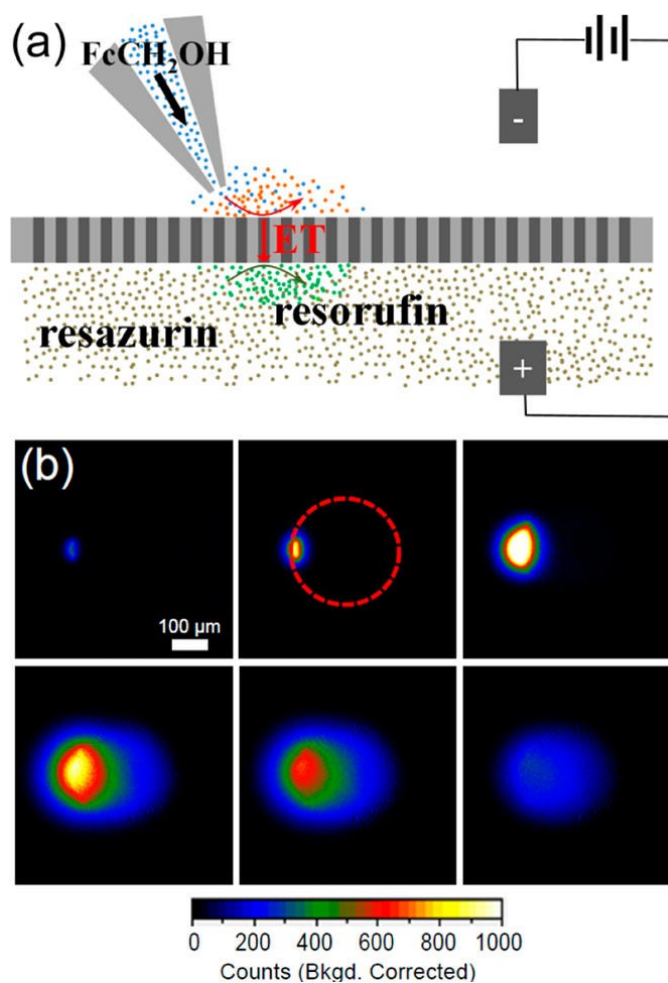


Figure 7.6 Carbon Fiber Bipolar Array SEM Image

SEM image of a CF array with a total diameter of 300 μm . Each fiber is about 6 μm in diameter. The thickness of the array is around 200 μm . The inset shows a magnified portion of the array where the individual carbon fibers are more clearly seen.

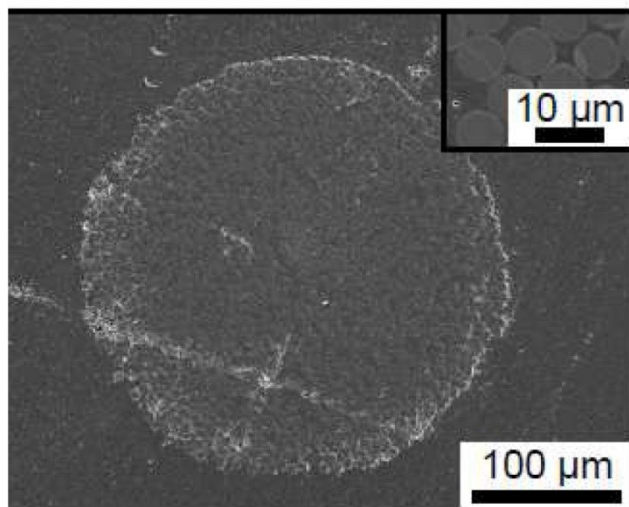


Figure 7.7 Fluorescence Intensity at Different Positions on The Array

Fluorescence intensity for the FEEM experiment in Fig 7.5 at various positions (a) to the right over the CF array showing mass transport of analyte and diffusion of resorufin and (b) to the left showing only diffusion of resorufin for 10x10 pixel regions shown as red squares in (c). It can be seen that the signal decays much more rapidly to the left with time and distance indicating that signal over array is indicative of FcMeOH mass transport and can be distinguished from diffusion of resorufin alone.

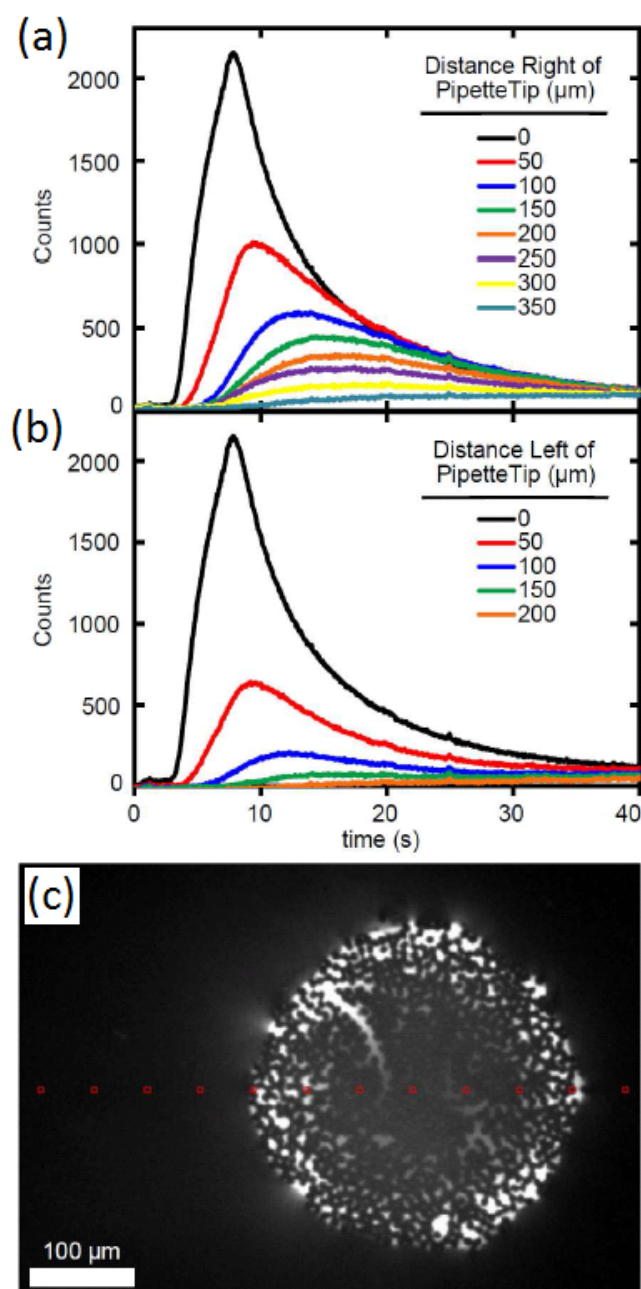


Figure 7.8 FEEM Imaging of Patterned Array

(a) Optical micrograph of a CF array patterned with photoresist and (b) a FEEM image of the oxidation of 2 mM FcMeOH at the patterned anodic side of the array.

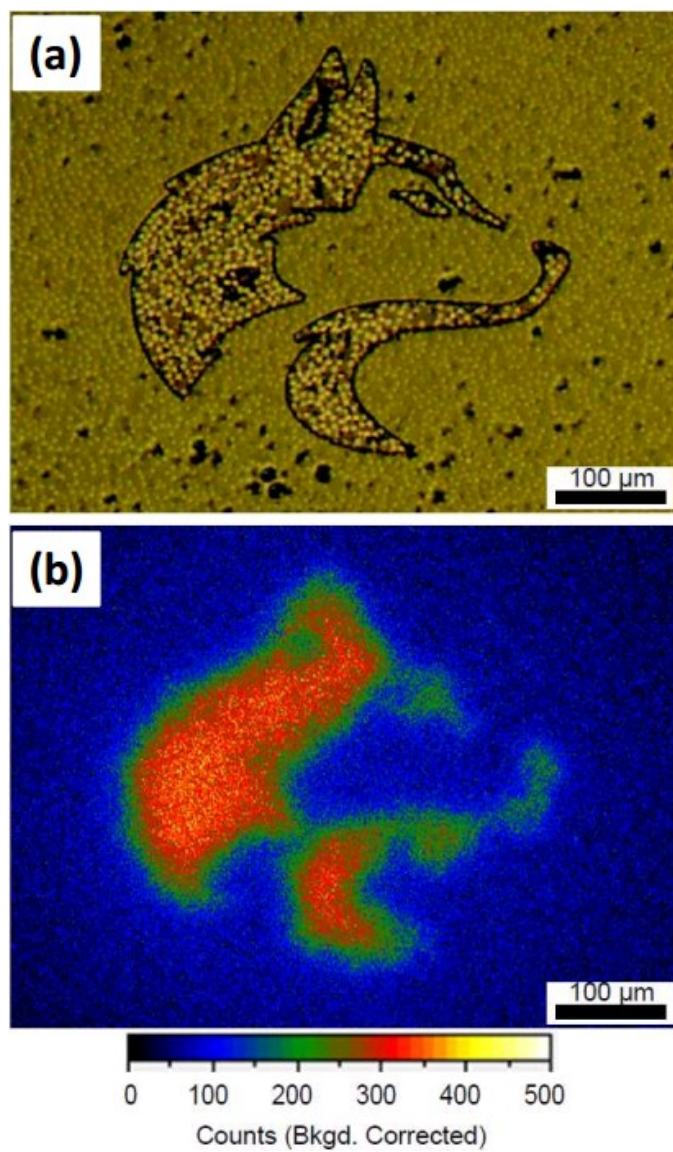


Figure 7.9 Imaging of Electrocatalytic Heterogeneity

(a) Schematic showing the experimental design. (b) SEM image showing the pattern of Pt deposition on the CF array surface with an inset showing a region of Pt deposition. (c) FEEM image (top) and line scan (bottom) showing the oxidation of 10 mM H_2O_2 in 0.1 M NaOH at catalytically active “hot-spots” where Pt was deposited on a CF array. (d) FEEM image for the same Pt patterned CF array showing the nonselective oxidation of 2 mM FcMeOH in 0.1 M KCl. (e,f) Cyclic voltammetric response of a single 5 μm diameter CF electrode in 10 mM H_2O_2 and 2 mM FcMeOH, respectively, before and after Pt deposition on the electrode surface.

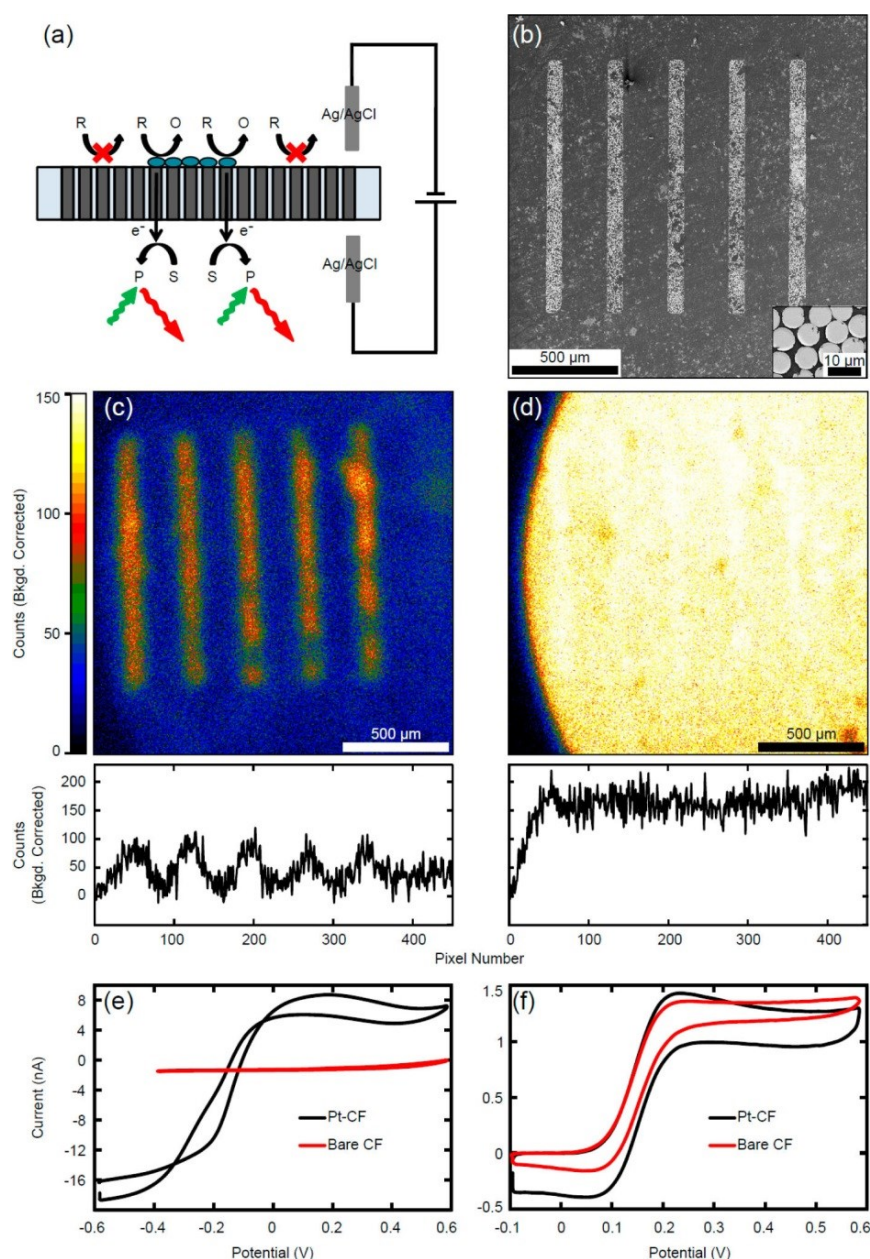
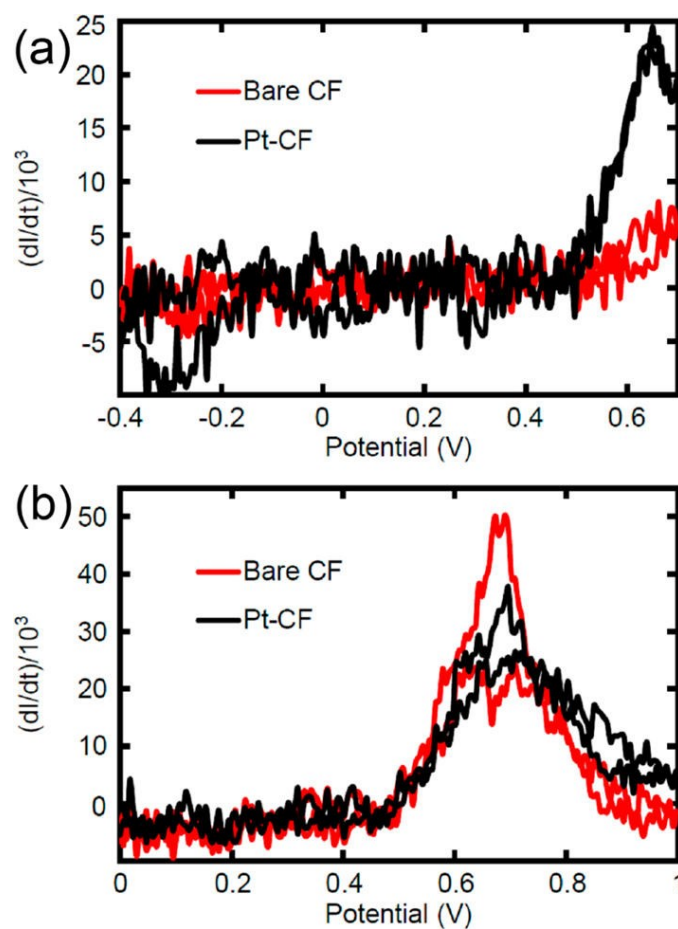


Figure 7.10 Fluorescence Derivative Plots

Time derivative of the fluorescence intensities for the experiment shown in Figure 7.9 as a function of potential for (a) the catalytic oxidation of 10 mM H_2O_2 at a Pt patterned CF array and (b) the oxidation of 2 mM FcMeOH in 0.1 M KCl at the same Pt patterned CF array.



7.6 Supplemental Information: Derivation of the relationship between the Faradaic current on a closed bipolar electrode and the time derivative of the fluorescence intensity

Assuming that all fluorophores can be treated identical, the overall fluorescence intensity from fluorophores in detection volume can be described as follows:

$$I(t) = N(t) \cdot \kappa \cdot I_{ex}(r) \cdot S(r) \cdot \sigma(\lambda) \cdot \phi(\lambda) \quad (1)$$

where, $I(t)$ is the time-related fluorescence intensity collected on the CCD detector, $N(t)$ is the number of fluorophores in the detection volume, κ is the overall detection efficiency, $I_{ex}(r)$ is spatial distribution of the excitation energy with the maximum amplitude I_o , $S(r)$ is the optical transfer function of the objective pinhole combination which determines the spatial collection efficiency of the setup, $\sigma(\lambda)$ and $\phi(\lambda)$ are the absorption cross-section (absorption extinction coefficient) of the fluorophore and the quantum yield, respectively.

Given Faraday's law, $Q = nFN$, where n is the number of electrons transferred in the process and F is Faraday's constant, the Faradaic current on the bipolar electrode can be expressed as,

$$i = \frac{dQ}{dt} = nF \frac{dN}{dt} \quad (2)$$

Combing equations (1) and (2), we can obtain an expression relating the electrochemical current of a fluorogenic redox reaction, i , to the change in fluorescence intensity.

$$i = \frac{nF}{\kappa \cdot I_{ex}(r) \cdot S(r) \cdot \sigma(\lambda) \cdot \phi(\lambda)} \frac{dI}{dt} \quad (3)$$

Alternatively, we can derive a similar liner relationship between the electrochemical current and the fluorescence intensity from a "bulk" perspective. Fluorescence intensity can be quantified using the Beer-Lambert law where at low fluorophore concentrations simplifies to the following expression,

$$I = I_o k \phi \ln(10) \epsilon b C \quad (4)$$

where I is the fluorescence intensity, I_0 is the excitation light intensity, k is a constant for the system that includes the detection efficiency and other geometric instrumentation parameters, b is the path length of illuminated sample and ϕ is the quantum yield, ε is the extinction coefficient and C is the concentration of the given fluorophore. Converting concentration into number of fluorophores, N , in the volume given by bA_I , where A_I is the area illuminated gives:

$$I = I_0 k \phi \ln(10) \frac{\varepsilon N}{A_I} \quad (5)$$

$$\frac{dI}{dt} = \frac{I_0 k \phi \ln(10) \varepsilon}{A_I} \frac{dN}{dt} \quad (6)$$

Given Faraday's law, $Q = nFN$, where n is the number of electrons transferred in the process and F is Faraday's constant, the Faradaic current on the bipolar electrode is

$$i = \frac{dQ}{dt} = nF \frac{dN}{dt} \quad (7)$$

We can then obtain an expression relating the electrochemical current of a fluorogenic redox reaction to the change in fluorescence intensity.

$$i = \frac{nFA_I}{I_0 k \phi \ln(10) \varepsilon} \frac{dI}{dt} \quad (8)$$

For resorufin, the quantum efficiency ϕ is ~ 0.97 (in neutral to basic solutions) and the extinction coefficient ε (570nm) is $57000 \text{ M}^{-1} \text{ cm}^{-1}$.³⁴

7.6 References

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Chapter 8 The Oxygen Reduction Reaction at Graphene Edges with Various Layer Numbers

8.1 Introduction

Graphene (or graphite for multi-layered crystals) possesses a highly stable six membered ring structure composed of sp^2 hybridized carbon atoms, where the conduction band and the valence band of a single sheet of graphene meet at the Fermi energy level.¹ Graphene has become a widely studied material since its initial isolation and its complex electrical properties first elucidated.^{2,3} Many electrochemical applications have been proposed for this new material including chemical sensors,⁴⁻⁶ energy storage^{4,7,8} and energy production.^{9,10} A substantial amount of effort has been focused on the use of graphene in heterogeneous catalyst materials, which are typically been made from reduced graphene oxide and used mainly as a catalyst support for metal nanoparticles.¹¹⁻¹⁵ Additionally, metal free electrocatalysts are being vigorously investigated to replace expensive noble metal catalysts, which makes graphene^{16,17} and Carbon Nanotubes (CNTs)^{18,19} very attractive materials.

Investigation of graphene properties has led to some contradictory conclusions, including how the number of layers present in a graphene sheet affects its electrochemical performance.^{20,21} These studies typically involve large amounts of the material deposited onto macroscopic electrodes, and thus, the results are an average of the ensemble and not from individual nanostructures. Especially in the case of graphene, bulk catalytic investigations are severely hindered by the large presence of exposed basal plane surfaces. It has been shown that the graphite basal plane is not as catalytically active as the edge plane.²² The resulting measurements are therefore skewed by the large surface area of the exposed basal plane preventing truly accurate measurement of the edge plane activity.

The role of the individual graphene sheets have not been extensively investigated and furthermore the nature of the catalytic activity as a function of layers present for a given graphene sheet is unknown. It is important to study the contribution of individual graphene layers to a specific catalytic reaction in order to more precisely determine how they will contribute to the activity of a composite electrocatalyst material. Recently, individual graphene sheets have been electrically contacted and used to investigate their electrochemical voltammetric responses.^{23,24}

However, these studies focused on electron transfer rate constants for simple redox molecules and not catalytic reactions.

Here we present an initial insight into the catalytic activity of individual graphene sheets and the effect the number of layers has on the catalytic activity for the Oxygen Reduction Reaction (ORR). Additionally, the unique method employed to construct these graphene electrodes eliminates exposed basal plane, leaving the electrochemical response solely due to the edge plane. To our knowledge, this is the first report about the layer dependence of graphene sheets for their activity towards the ORR, as measured from graphene edges. We found that there may be an increase in the catalytic activity for the ORR from the edge plane of few layer graphene sheets as compared to single and bi-layer graphene sheets, but the opposite observation is seen for the kinetic activity where the lower numbered layer sheets display better kinetics.

8.2 Experimental

8.2.1 Chemicals and Materials

All aqueous solutions were prepared using deionized water ($>18\text{ M}\Omega\text{ cm}$, Barnstead Nanopure Systems) and all chemicals and materials were used as received from the manufacturers. Quartz and silicon substrates were thoroughly cleaned and sonicated with DI water, Acetone and IPA and allowed to dry in an oven. Flake Graphite (Asbury Carbons), Single crystal $\langle 100 \rangle$ Silicon wafers double side polished (Silicon Quest International Inc.), Polished quartz wafers (UniversityWafer.com), grade V-5 muscovite mica (Structure Probe Inc.), Acetone (Mallinckrodt Baker), Isopropyl alcohol (Mallinckrodt Baker), Ethyl Acetate (EMD), Cellulose Acetate Butyrate (average $M_n = 30,000$, Sigma Aldrich), Epo-tek 2-part epoxy resin (Epoxy Technology 301 epoxy), Ferrocene methanol (FcMeOH, Aldrich 97%), Sodium Acetate tri-hydrate (J. T. Baker), Ferricyanide ($\text{K}_3\text{Fe}(\text{CN})_6$, Sigma-Aldrich 99%), Ferrocyanide tri-hydrate ($\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$, Fluka), Potassium Hexachloroiridate (III) (K_3IrCl_6 , Sigma Aldrich), Sodium Hydroxide (J. T. Baker), Sulfuric acid (H_2SO_4 , Fisher), Nitrogen (N_2 , $>99.99\%$ Praxair) and Oxygen (O_2 , $>99.99\%$ Praxair).

8.2.2 Physical Vapor Deposition

Physical Vapor Deposition (PVD) was used to make electrical contact to the graphene where gold pellets (99.999% High Purity, Kurt J. Lesker) were placed in Tungsten metal evaporation boats

next to Chromium coated Tungsten rods (99.999% High Purity, Kurt J. Lesker) for deposition of Au/Cr electrodes using an in-house, two source, PVD system.

8.2.3 Cyclic Voltammetry

Diffusion limited steady-state cyclic voltammograms were recorded using a computer-controlled Dagan Chem-Clamp voltammeter and data was recorded using an in-house virtual instrumentation program written in LabVIEW (National Instruments) on a desk top PC equipped with a PCI-6251 (National Instruments) data acquisition card. A commercially available Ag/AgCl reference electrode (Bioanalytical Sciences, Inc.) was used as reference electrodes for all CVs and data was manually baseline corrected and slope corrected. Solutions used for ORR were bubbled with Oxygen or Nitrogen for greater than 20 minutes prior to use to ensure the solution was saturated with the desired gas.

8.2.4 Atomic Force Microscopy

Atomic Force Microscopy (AFM) was performed using a Veeco Dimension 3100 Scanning Probe Microscope operating in tapping mode using OTESPA cantilever tips. The microscope was placed within a noise and vibration isolation table and images presented in this paper have been flattened to remove the background curvature of the substrate surface, but are otherwise free of modification.

8.2.5 Raman Spectroscopy

Raman spectroscopy was performed using a Horiba Jobin Yvon T64000 Raman spectrometer equipped with a Spectrum One liquid nitrogen cooled CCD detector. An Argon ion laser (488 nm wavelength) was used for excitation with a power density of approximately 12 mW at the sample location. Additionally, a band pass filter was used (Thorlabs) to filter out unwanted laser wavelengths and a holographic notch filter (Kaiser Optical systems, Inc.) was used to eliminate the 488 nm laser line before reaching the diffraction grating (1200 grooves/mm).

8.2.6 Scanning Electron Microscopy

Scanning Electron Microscope (SEM) images obtained using a field-emission microscope (FEI Sirion) equipped with a through lens secondary electrode detector with a resolution of 1-3 nm at the

Nanotech User Facility located at the University of Washington. Graphene samples were not sputter coated with a thin conducting layer (2-3 nm) of Au/Pd for SEM imaging unless otherwise noted.

8.3 Results and Discussion

8.3.1 Fabrication of Single Sheet Graphene Electrodes

The generalized fabrication of the single sheet graphene electrodes can be seen in Figure 8.1 and involved making contact to the edge of the graphene sheet with a gold electrical contact then sealing the entire device in epoxy resin to fully insulate it. After the graphene was insulated it was very carefully polished to expose just the end of the sheet where the ORR was then tested. A finished graphene electrode can be seen in Figure 8.2A where the gold is contacting the graphene sheet on a quartz substrate, the image was captured prior to insulating in epoxy resin. To make the graphene electrodes, the graphene sheets were first isolated from larger graphite flakes using scotch tape and deposited onto a clean silicon chip with a 300 nm coating of thermally grown SiO₂. Once the graphene samples were located using an optical reflectance microscope, their respective layer numbers were determined using Atomic Force Microscopy (AFM) and Raman spectroscopy. A characteristic AFM topographic image of a single sheet of graphene is shown in Figure 8.2B where the inset shows the line scan with the step height measured from two marked points.

The AFM scans were used to ensure the Raman signal was accurate in determination of the number of layers for most of the graphene samples. The Raman spectrum of graphene consists of a few main peaks^{25,26} including the D peak, G peak and 2D peak. These peaks can be seen in a typical Raman spectrum of a few layer graphene in Figure 8.2C. The D peak, termed the disorder peak, is located at $\sim 1350\text{ cm}^{-1}$, the G peak, located at $\sim 1600\text{ cm}^{-1}$, and the 2D peak, located at $\sim 2700\text{ cm}^{-1}$, is the 2nd order of the D peak and will change shape as the number of layers change.²⁵ Figure 8.3A shows how the 2D will change shape based on graphene layer number from 1 layer up to 5 layers and the bulk graphite spectra also shown for comparison. With just a single layer of graphene present the 2D peak shows a single Gaussian shaped peak, however, as soon as there is more than one layer the peak shows multiple energy transitions which change further upon addition of more layers. The graphene sheets of different layer numbers will give unique Raman spectra up to a maximum of approximately 5 or 6 layers, after which the Raman spectra is too similar to that of bulk graphite. The 2D peak shape can be used to qualitatively determine the number of layers in a given

graphene sheet, however using the ratio of the areas of the G and 2D peaks gives a quantitative way to determine layer number. This is because as the number of layers increase, the G peak intensity will increase and by integrating both peaks at the FWHM you obtain a G/2D ratio that is linear with the number of layers, up to a maximum of 5 and maybe 6 layers (7 layers and more have very similar ratios and cannot be easily identified). A plot of this ratio as a function of the number of layers is presented in Figure 8.3B. This ratio plot shows a region represented by blue dots where the ratio increases very linearly with layer number, followed by red dots that show similar ratios for the G/2D peaks.

After the graphene sample thicknesses were determined, the graphene sheets were transferred from the silicon chip to a quartz substrate using a method termed “wedging” described by Schneider et al.²⁷ Gold contacts were then patterned onto the graphene sheets, as described previously, using a thermal evaporator and a physical “shadow” mask that prevented the gold from depositing underneath it. Using this non-lithographic technique, the bulk of the graphene sheets were not damaged, as can happen during other lithographic techniques such as Electron Beam Lithography. Once the graphene was contacted a degassed epoxy resin (epotek) was coated onto the graphene electrode and gold contact to completely seal them into an insulating medium.

8.3.2 Electrochemical Characterization

The electrochemical voltammetric response of the graphene electrodes, once exposed, was characterized by Cyclic Voltammetry (CV) with various simple redox molecules, such as Ferrocene methanol (FcMeOH). Figure 8.4 shows two characteristic CVs in FcMeOH from two different electrodes, 8.4A is from a 1 layer graphene electrode and 8.4B is from a 4 layer graphene electrode. The steady state diffusion limited current observed is proportional to the area of the electrodes and knowing the number of layers present, taken to be the width of the electrode (0.5 nm per layer²⁸), the exposed length can be determined using the diffusion limited steady state current equation for a band electrode,²⁹

$$i_{ss} = \frac{2\pi nFAD C_b}{w \ln\left(\frac{64Dt}{w^2}\right)} \quad (1)$$

where F is Faradays constant, n is the number of electrons A and w are the area and width of the band electrode, D and C_b are the diffusion coefficient and bulk concentration of the redox molecule

respectively. A good approximation can be made for the time component, t , can be approximated as $t = (RT/Fv)^{30}$ where R is the universal gas constant, T is the temperature in kelvin and v is the potential scan rate. Using the diffusion coefficient of FcMeOH ($6.7 \times 10^{-6} \text{ cm}^2/\text{s}$)³¹ the area of the electrode can be calculated from the diffusion limited steady state current. The current density for both the simple redox reaction and the catalytic ORR were determined from the calculated area of the graphene electrodes.

8.3.3 The Oxygen Reduction Reaction

The main goal of this work was to conduct cathodic ORR studies at the edges of individual graphene sheets with various layers. Figure 8.5A shows a single layer graphene electrode response for the ORR in alkaline media. When the solution is saturated with oxygen, a large reduction current is observed after the potential is swept past -100 mV. This reduction current is directly attributable to the ORR as it is absent in the nitrogen saturated solution. Characteristic ORR CV curves for all the tested electrodes were normalized using their respective current at -0.4 V and graphed on the same plot, shown in Figure 8.5B, and shows the respective activities for the ORR for the different graphene electrodes used in this study. Also shown in Figure 8.5B are both polycrystalline gold and edge plane Highly Oriented Pyrolytic Graphite (HOPG) for reference.

It does appear that there is a layer number dependency in the alkaline ORR activity, in terms of the $E_{1/2}$. It is clear from this plot that all the graphene electrodes, from 1-4 layers, are much more active for the ORR than the HOPG, where the edge plane HOPG shows an average $E_{1/2}$ for the ORR of $\sim -340 \text{ mV}$ (vs. Ag/AgCl) which is around 180 mV more negative in potential for the ORR than the $E_{1/2}$ of even the least active graphene electrode, which turns out to be the single layer graphene electrode, showing an $E_{1/2}$ average of $\sim -163 \text{ mV}$ for the ORR. It is very interesting that the single layer, is in fact, the least active graphene electrode for the ORR with bi-layer graphene being very similar to it with an average $E_{1/2}$ of $\sim -159 \text{ mV}$. From this data it seems that there is something unique about the few layer graphene samples, in that they display an $E_{1/2}$ that is shifted to the right of the single and bi-layer graphene samples. The best graphene electrode used in this study turns out to be the three layer graphene with an $E_{1/2}$ of $\sim -106 \text{ mV}$ for the ORR with the four layer graphene activity half way between that of the three layer graphene and the bi-layer graphene, having an average $E_{1/2}$ of around -134 mV. The differences in the activity for the ORR in terms of the $E_{1/2}$ for the different layered graphene can be seen in Figure 8.6A. The apparent number of

electrons involved in the ORR was estimated using the band electrode equation, the ORR current and concentration of dissolved oxygen in 1M NaOH with its respective diffusion coefficient ($C_{O_2} = 8.4 \times 10^{-7} \text{ cm}^3/\text{s}$, $D_{O_2} = 1.65 \times 10^{-5} \text{ cm}^2/\text{s}$)³². This is called the apparent electron number because there are also other kinetic parameters that are lumped into the estimate including the adsorption of oxygen and desorption of the catalyzed species (whether it is H_2O or H_2O_2). According to this estimate of the apparent electron number, there seems to be a decrease in reaction kinetics as the number of layers increases where for the 4 layer graphene the apparent electron number involved is approximately 1, which is equivalent to the bulk HOPG. Whereas the electron number is increased in three layer to 1.74 and further increases to 2.384 in single layer graphene.

The graphene current density for both the catalytic ORR and the simple redox molecule oxidation FcMeOH were calculated using the maximum experimentally observed currents and the calculated exposed graphene electrode area and can be seen in Figure 8.6B. The current density increases as the number of layers decreases as expected due to the increased mass transport coefficient, which is proportional to the critical dimension of the electrode.³³ The current density for the ORR at the graphene electrodes is far in excess compared to the current density from the HOPG electrode which is approximately 0.0007 A/cm^2 compared to 2.27 A/cm^2 for the 4 layer graphene electrode. For the single and bi-layer graphene electrodes, the current density for the ORR is an order of magnitude greater than the 4 layer graphene with the density being in excess of 20 A/cm^2 .

Electronic band doping may account for the increased thermodynamic activity of the few layered graphene for the ORR. It has been previously shown that different chemical environments, from adsorbed chemical species such as NO_2 ³⁴ or I_2 ³⁵ will reduce the population of electrons in the graphene electronic bands, which results in a p-doped state. They found that these adsorbed species will p-dope the electronic band structure of the graphene, but inner layers of the graphene sheet will be partially shielded from these doping effects.^{34,35} This means that the inner layers of the few layer graphene sheets will be less p-doped than the outer layers. Additionally, the single and bi-layer graphene are more susceptible to the doping and may require scanning the potential to more negative values in order to reach the reduction potential for the ORR. It has also been shown that gold will p-dope the electronic bands of graphene sheets.³⁶ The unintentional doping of the graphene by gold may be a result of the fabrication procedure employed in this study. It is very likely that some unwanted gold atoms are deposited underneath the “shadow” mask onto the

graphene sheets during the deposition step. During the thermal evaporation step the gold ad-atoms would have increased mobility and could have traveled along the surface and depositing on the graphene surface. Additionally, the deposited gold metal ad-atoms may have helped to stabilize the adsorbed oxygen reduction intermediates during the ORR at the single sheet graphene electrodes.

8.4 Conclusions

Our initial results indicate that graphene is a much more active ORR electrocatalyst than bulk graphite and that there is a layer dependence on the specific activity of the graphene for the ORR. More interestingly, it appears that the few layer graphene samples are better ORR electrocatalysts than the single and bi-layer graphene. The possibility of the graphene electronic band p-doping may explain the increased ORR activity, as measured by the $E_{1/2}$, of the few layer graphene compared to the single and bi-layer graphene. The ORR kinetics appears to be slowed as the number of layer increases and is similar to the bulk HOPG at 4 layers. More investigation of single graphene sheets are necessary to determine the nature of this increased activity and whether it is truly a layer dependence or a consequence of the fabrication, resulting in a higher level of p-doping in the single and bi-layer graphene compared to the few layered graphene.

8.5 Figures

Figure 8.1 Graphene Electrode Fabrication Schematic

Schematic of the generalized fabrication steps used to make the single graphene sheet nanoelectrodes. The graphene would be transferred to a quartz substrate where a gold contact would be patterned onto the sample and the whole substrate sealed in epoxy resin and carefully polished to expose the edge of the graphene.

1. Graphene transferred to Quartz

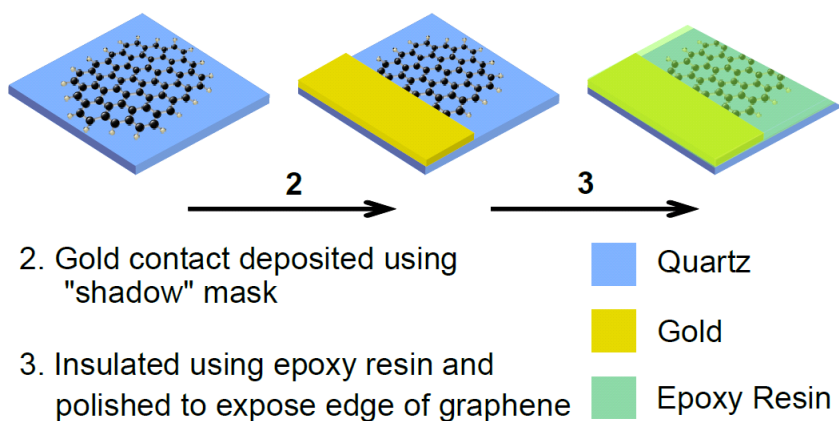


Figure 8.2 Single Graphene Sheet Characterization

A) Optical image of a finished graphene electrode before application of the epoxy resin showing the graphene on the quartz substrate and the gold contact. B) AFM topographic images of a single layer graphene sheet. The inset shows the height profile for the line in the image with the step height measured between the two markers. C) Characteristic full Raman spectrum of a few layer graphene sheets.

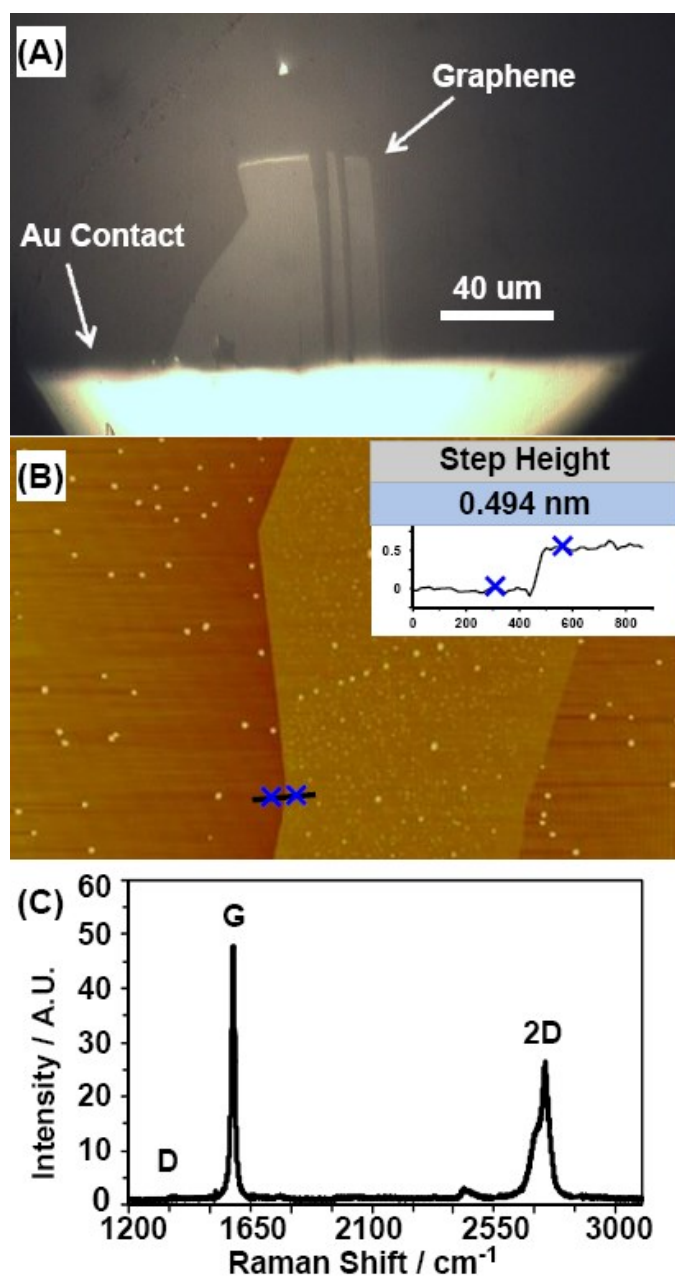


Figure 8.3 Raman Spectroscopy Graphene Peak G/2D Ratio Change

(A) Raman spectra from various layer graphene sheets showing how the 2D peak shape changes as the number of layers increases. B) Relationship between the G and the 2D peak area intensities showing a linear increase in the G/2D peak area ratio as the number of layers increases with the HOPG peak ratio also shown.

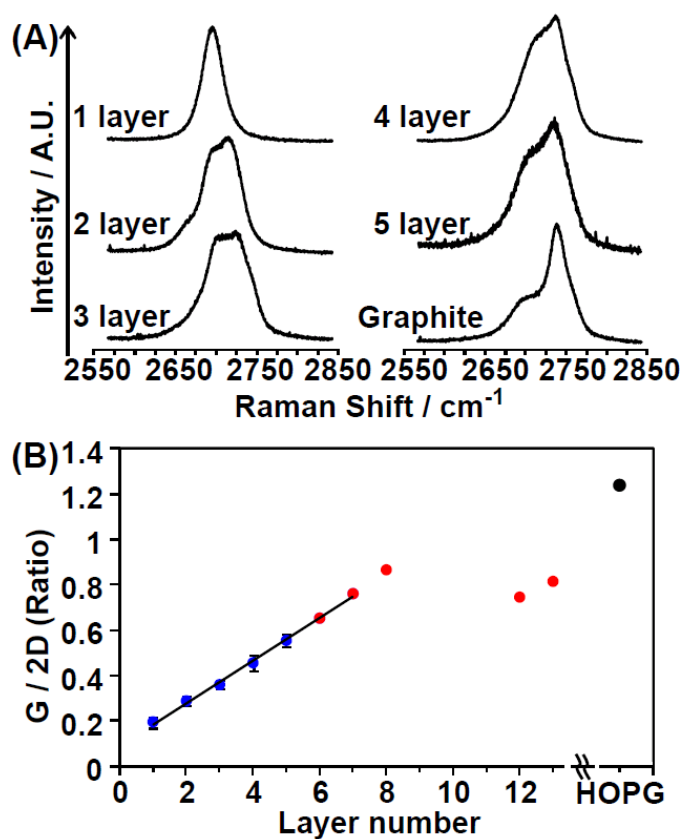


Figure 8.4 Electrochemical Response of Graphene Electrodes

CVs of redox molecules FcMeOH for A) 1 layer and B) 4 layer graphene electrodes both in 2 mM FcMeOH with 100 mM sodium acetate supporting electrolyte, 50 mV/s scan rate. The limiting current was used to calculate the lengths of the exposed graphene sheets.

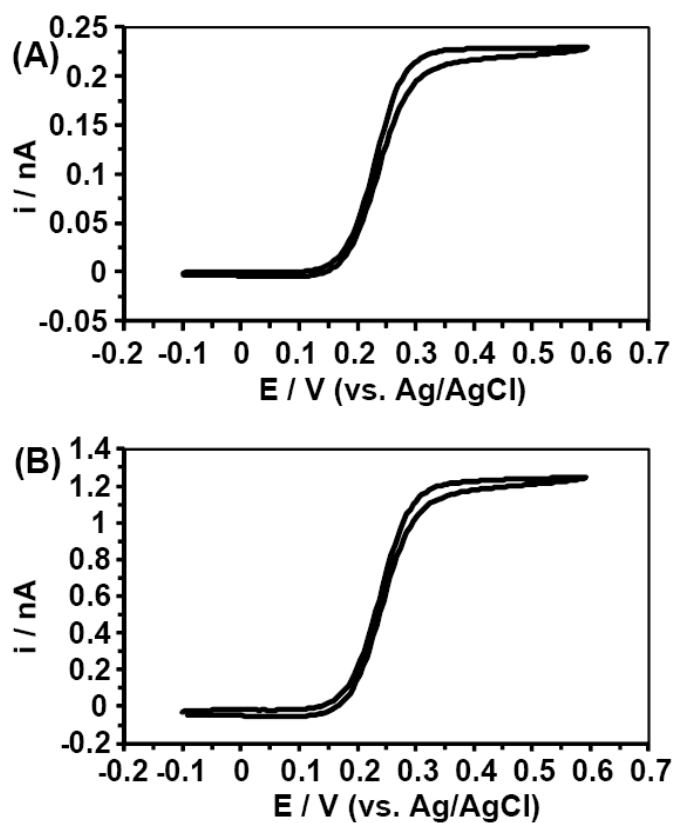


Figure 8.5 Graphene Oxygen Reduction Reaction

A) CVs of a 1 layer graphene electrode in either N₂ or O₂ saturated 0.5 M H₂SO₄. B) ORR CVs normalized to the current at -0.4 V, showing just the forward scan direction for clarity.

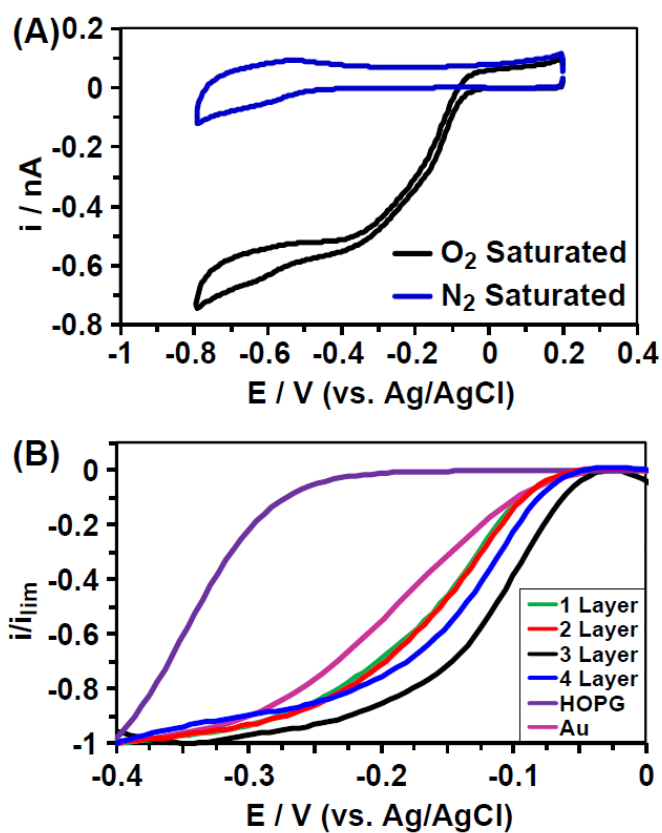
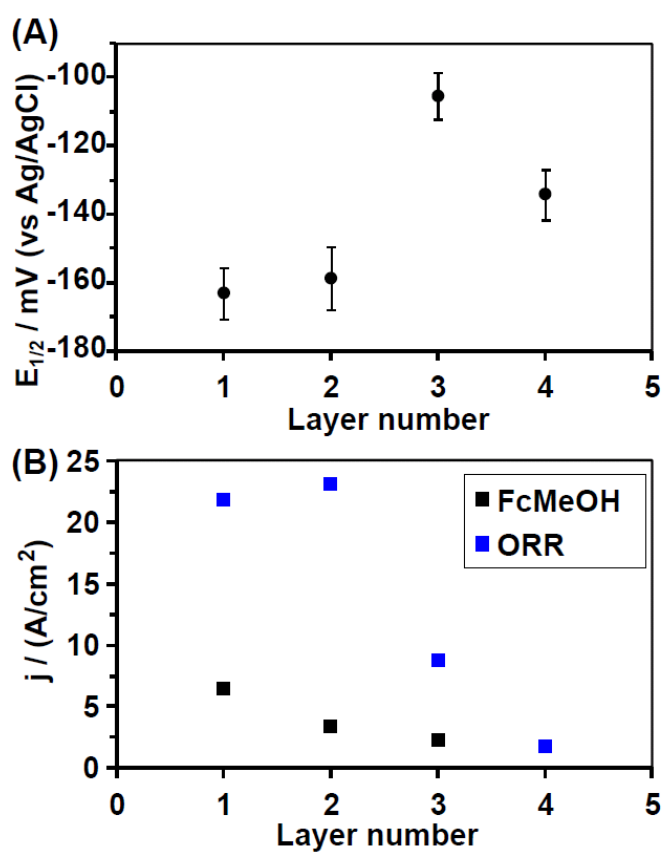


Figure 8.6 Sheet Layer ORR Activity Dependence

A) Relationship between the ORR $E_{1/2}$ and the sheet layer number, scale bars represent on standard deviation from the average. B) Current density for the ORR and FcMeOH oxidation as a function of layer number.



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Chapter 9 An On-Chip Recessed Ring-Disk Ultramicroelectrode with a 200 nm Ring-Disk Gap Used for Scavenging of Redox Molecules^{††}

9.1 Introduction

Electrochemical detection of dopamine and other catecholamines from single cells using microelectrodes has been an invaluable analytical technique for the determination of cellular signaling processes.¹⁻⁶ Carbon fiber electrodes (CFEs) are most commonly used for exocytosis, even at a single vesicle level.^{1,2,5} Many avenues have been pursued to investigate exocytosis by constructing new types of microelectrodes. Some recent examples include; microchip-based electrodes allowing for the study of exocytosis from the bottom of the cell,⁷⁻⁹ electrochemical arrays that give spatial resolution,¹⁰ and highly sensitive electrodes modified with gold nanoparticle networks¹¹.

Despite decades of research to determine the nature of exocytotic release processes, many questions still remain.^{1,6,12} Exocytotic events are documented to be variable in both the current magnitude and the event kinetics.^{1,6,12} Some of the smaller events are suspected to be partial release events, termed “kiss and run”,^{2,13,14} and the long duration of others may be due to diffusion of molecules to the electrode from release sites further away from the electrode.^{2,12,15} Some of the larger events are theorized to be nearly simultaneous, multiple release events¹² or larger vesicles that fully release their contents in a short period of time.^{16,17}

Here we report a new on-chip microelectrode that has been fabricated and electrochemically tested, which can be useful to investigate single-cell exocytosis. As shown in Figure 9.1, the electrode consists of a disk microelectrode a few microns in size that is slightly recessed by a few hundred nanometers into the insulating substrate below a second ring electrode located within the insulating material. In this work, we focus on the fabrication of such chip-based electrodes and detailed discussion and comparison of their electrochemical responses under steady-state conditions to the modeled responses using finite-element simulations and, finally, we demonstrate the electrodes use for single cell experiments. The cells under investigation rest on top

^{††} This chapter is adapted with permission from Percival, S. J.; Gunderson C. G.; Zhang, B. “An On-Chip Recessed Ring-Disk Ultramicroelectrode with a 200-nm Ring-Disk Gap Used for Scavenging of Redox Molecules” *In Preparation to be Submitted*

of the disk electrode in the indentation where they can be stimulated to release neurotransmitters. The transmitter molecules released from the side of the cell which is in close proximity to the disk are quantified using amperometric methods. The purpose of the second ring electrode is to “scavenge” any neurotransmitter molecules that may be released from vesicles further away from the disk electrode by oxidizing it before it can diffuse to the disk. We found that the presence of the nanoring electrode can effectively reduce diffusive flux of redox species to the bottom disk electrode. The nanoscale separation of the two electrodes is ideal for these types of investigations because freely diffusing dopamine from vesicles released above the ring would be eliminated. Therefore, a more detailed assessment of the cellular signaling process is possible in terms of proportion between full release events and “kiss and run” events. To the best of our knowledge this is the first chip-based microelectrode system for redox molecule scavenging designed towards single-cell exocytosis applications. Similar electrode systems have been reported before but had much larger ring disk separations and were used for generator collector studies.¹⁸ Additionally, because the electrodes can be made on a flat, transparent substrate, this device setup could be modified by using a transparent conductive coating electrode to allow simultaneous monitoring of the cells by conventional fluorescence microscopy or Total Internally Reflected Fluorescence (TIRF) microscopy.¹⁹⁻²²

9.2 Experimental

9.2.1 Chemicals and Materials

All aqueous solutions were prepared using deionized water (>18 MΩ cm, Barnstead Nanopure Systems). All chemicals and materials were used as received from the manufacturers: acetone (Mallinckrodt Baker), isopropyl alcohol (IPA, Mallinckrodt Baker), ferrocene methanol (FcMeOH, Aldrich 97%), sodium sulfate anhydrous (J. T. Baker), potassium hexachloroiridate (K_3IrCl_6 , Aldrich), Ferricyanide ($\text{K}_3\text{Fe}(\text{CN})_6$, Sigma-Aldrich 99%), Ferrocyanide ($\text{K}_4\text{Fe}(\text{CN})_6$, Fluka 99.5%), dopamine hydrochloride (Sigma), photoresist AZ1512 with AZ351 developer (AZ Corporation, developer diluted 1:5 developer:DI H_2O), gold etch (Transene - TFA (KI/I_2)), chrome etch (Transene - $((\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ with HClO_4). Single cell experiments were performed in an isotonic saline solution prepared with 150 mM NaCl (J. T. Baker), 5 mM KCl (Mallinckrodt Baker), 1.2 mM MgCl_2 (J. T. Baker),

5mM glucose (Sigma), 10 mM HEPES (Fisher), and 2 mM CaCl_2 (J. T. Baker) and the pH was adjusted to 7.4 with concentrated NaOH (J. T. Baker).

9.2.2 Physical Vapor Deposition

Thin films of gold were deposited by Physical Vapor Deposition (PVD) where high purity Au pellets (99.999% High Purity, Kurt J. Lesker) were placed in Tungsten metal evaporation boats and along with Chromium coated Tungsten rods (99.999% High Purity, Kurt J. Lesker) for deposition of Au/Cr electrodes using an in-house resistive heating two source PVD system.

9.2.3 Plasma Enhanced Chemical Vapor Deposition

Thin films of low stress silicon oxide (SiO_2) or silicon nitride (Si_3N_4) were deposited using Plasma Enhanced Chemical Vapor Deposition (PECVD) in an Oxford Instruments Plasma Lab 100 equipped with a heated sample chuck heated to 350 °C operating in a 650 mtorr environment. The feed gases used include SiH_4 , NH_3 and NO_2 with flow rates of 8.5 sccm SiH_4 , and 710 sccm NO_2 with 162 sccm N_2 for SiO_2 deposition or 18 sccm SiH_4 and 24 sccm NH_3 with 980 sccm N_2 for Si_3N_4 deposition.

9.2.4 Reactive Ion Etching

Plasma Reactive Ion Etching (RIE) of thin films was performed using a TRION Phantom Reactive Ion Etcher operating with RF power of 300 W with 75 sccm of SF_6 and 15 sccm O_2 at 50 mtorr operating pressure.

9.2.5 Electrochemical Data and Finite Element Numerical Simulations

A volume of redox solution was dropped onto the top of the electrode chips to perform cyclic voltammetry (CV) experiments. An Ag/AgCl quasi-reference electrode was used as reference electrode for all CV experiments without the need for a counter electrode and the data was manually baseline corrected. Steady-state voltammograms were recorded using a PC-controlled Dagan Chem-Clamp (Dagan Corporation, Minneapolis, MN) voltammeter and data was recorded using an in-house virtual instrumentation program written in LabVIEW (National instruments) on a Dell PC equipped with a PCI-6251 (National Instruments) data acquisition card. Single cell amperometric data was recorded with an Axopatch 200B amplifier (Molecular Devices; Sunnyvale, CA) and monitored in real time via the AxoScope software package (version 10.2, Molecular

Devices). The output was digitized at 20 kHz and filtered at 2 kHz with an internal four pole Bessel filter and analyzed without subsequent filtering. Amperometric peaks were identified and characterized with the MiniAnalysis software detection algorithm (Synptosoft, Decatur, GA). Peaks were detected if the local maxima and the area under the curve exceeded a threshold of five times the root mean squared noise for a flat 2 s time period when no cell was located on the electrode. All simulations done were performed using COMSOL Multiphysics version 3.4 software installed on a Dell Precision T7400 (Intel Xeon E5430 dual die quad core, 1333 MHz FSB, 2.66 GHz, 8 GB DDR2 SDRAM).

9.2.6 Scanning Electron Microscopy and Atomic Force Microscopy

Scanning Electron Microscope (SEM) images were obtained using a field-emission microscope (FEI Sirion) equipped with a through lens secondary electrode detector with a resolution of 1-3 nm at the Nanotech User Facility located at the University of Washington. All samples were sputter coated with a thin conducting layer (~3 nm) of Au/Pd for SEM imaging. Atomic Force Microscopy (AFM) was performed using a Veeco Dimension 3100 Scanning Probe Microscope operating in tapping mode using OTESPA cantilever tips. The microscope was placed within a noise and vibration isolation table and images presented in this paper have been flattened to remove the background curvature of the substrate surface (a typical procedure due to normal AFM operation), but are otherwise free of modification.

9.2.7 Cell Culturing

PC12 cells were purchased from the American Type Culture Collection (Manassas, VA) and maintained as previously described.^{11,23} Briefly, PC12 cells were grown on mouse collagen IV-coated culture dishes (BD Biosciences; Bedford, MA) in phenol red free RPMI 1640 (Mediatech; Manassas, VA) supplemented with 10% equine serum (HyClone; Logan, UT), 5% fetal bovine serum (HyClone; Logan, UT), and 100 units/ml penicillin/streptomycin (HyClone; Logan, UT). Cells were kept in a 7% CO₂ atmosphere at 37 °C and subcultured every 7 to 9 days or when cell confluency was reached. Cells were used for all experiments between 4 and 7 days after subculturing.

9.2.8 Single Cell Experimental Setup

Electrochemical recordings of single cells were made on an reflective microscope (Olympus BX51) positioned on a vibration isolation table (Model 63-563, Technical Manufacturing Corporation, Peabody, MA) inside a home built faraday cage. The working electrode was epoxied into a petri dish and with the electrical contacts sticking up the sides of the dish and insulated from the cell bathing solution. Exocytosis was stimulated at approximately 55 s intervals with a 5 s, 25 psi pulse (Eppendorf/Brinkman Instruments; Hauppauge, NY) from a glass micropipette containing isotonic saline with elevated K^+ (100 mM). The dish where the electrode was held was warmed to 37 ± 1 °C using an automatic temperature controller (Model TC-344B, Warner Instrument Corp., Hamden CT) fitted to the microscope stage. Constant potentials were applied to the electrodes with respect to a single Ag/AgCl quasi-reference electrode placed in the cell bathing solution. The constant potential was applied to the ring electrode using a DC power supply (BK Precision 1610; Yorba Linda, CA).

9.3 Results and Discussion

9.3.1 Electrode Fabrication and Characterization

Polished quartz substrates (University Wafer) were cut and cleaned by sonication in DI H_2O , acetone then IPA and dried for 10 minutes at 60 °C. The cleaned substrates were patterned with cut glass cover slips used as shadow masks for physical vapor deposition (PVD) of the metal electrodes. Figure 9.2 shows the fabrication procedure of these electrodes. First, a 5 nm Cr adhesion layer and a 50 nm gold layer were deposited on a quartz substrate. A thin layer (~200 nm) of insulator (SiO_2 or Si_3N_4) was then deposited using an Oxford Instruments Plasma Lab 100 system and the substrate was patterned with shadow masks to deposit the second layer of 50 nm Au with a 5 nm Cr that would later become the ring electrode, with a total thickness of 55 nm. This was insulated with another insulating layer (~300 nm layer) and then patterned with a few micron sized circle using a Heidelberg-MicroPG-101 laser direct write tool. The substrates were spin coated with a 1-2 μm AZ1512 and patterned using 6-8 μm diameter circular patterns. The photoresist was hardened at 90 °C for 10 minutes to increase the plasma etch resistance. Reactive Ion Etching (RIE) was then used to etch away the insulating layer down to the top metal layer (later to become the ring electrode layer). Then the gold, followed by the chrome adhesion layer, were etched away using Transene-

TFA gold etch and Transene Chrome etch forming the ring electrode and exposing the insulator underneath. The final RIE step was performed to etch away the now exposed insulating layer to uncover the bottom disk electrode followed by a piranha etch (Careful: Piranha solution is extremely reactive and corrosive) to completely remove the photoresist. Contact was made to the electrode leads using tungsten wires and conductive silver paste (DuPont). With the fabrication method presented here various types of electrodes can be made with different geometries or materials tailored to suit the needs of the application.

SEM and AFM were employed to characterize the ring-disk UMEs to ensure they were properly made. Figure 9.3A and Figure 9.3B show SEM images of a typical 3.25 μm -radius electrode. The gold disk is recessed below the silica film and the 55 nm thick Au/Cr ring electrode is embedded into the insulator slightly above the disk. The magnified SEM image in Figure 9.3B shows some slight non-uniformity of the silica edge likely due to over etching of the top layer of silica. Figure 9.3C and Figure 9.3D are AFM images of another electrode 3.75 μm in radius with a recession of approximately 550 nm into the surface. This measured depth is consistent with the predicted depth based on the thickness of each film. The SEM and AFM images also indicate that the insulating surface is etched more than desired, resulting in a slight over exposure of the gold nanoring electrode. Additionally, the AFM image shows that some residual photoresist is sometimes present after the acetone wash which was what warranted an extra cleaning step with piranha solution to fully remove it.

These on-chip recessed ring-disk UMEs were further characterized using cyclic voltammetry. Figure 9.4A shows the voltammetric response of both the disk and ring from a 4 μm radius electrode in a solution containing 2 mM Ferrocene Methanol (FcMeOH). Both electrodes show sigmoidal shape CV response typical for a conventional UME of this size.²⁴ The steady-state limiting current, i_{ss} , for a recessed disk electrode can be predicted from the electrode radius, r , and the depth, L , from equation 1,^{18,25,26}

$$i_{ss} = \frac{4\pi n F D C_b r^2}{4L + \pi r} \quad (1)$$

where n is the number of electrons transferred per redox molecule, F is Faraday constant, D is the diffusion coefficient of the redox molecule and C_b is the bulk concentration of the redox molecule.

The limiting currents for a 4 μm radius electrode are measured to be 1.75 nA for the disk electrode and 1.02 nA for the ring (both values taken from the forward CV scan at 450 mV). The limiting current for the recessed disk of this radius and a 550 nm depth in 2 mM FcMeOH ($D = 6.7 \times 10^{-6} \text{ cm}^2/\text{s}$)²⁷ is calculated to be 1.760 nA from equation 1, which is approximately a 0.6% difference from the measured value. Additionally, the sigmoidal shapes of the CVs for both the disk and ring indicate that there is minimal, if any, solution leakage or gaps in-between the metal and the insulator. Figure 9.4B shows the voltammetric response of the same 4- μm -radius electrode used for the CVs in 2A but this time in 5 mM K_3IrCl_6 with limiting currents of 3.37 nA and 1.69 nA for the disk and ring respectively (both values taken from the CVs at 1 V in the forward scan).

The responses from the disk and ring from a 3.75 μm radius electrode in 5 mM $\text{K}_3\text{Fe}(\text{CN})_6$ (Ferricyanide) with 1.5 M KCl and 5 mM $\text{K}_4\text{Fe}(\text{CN})_6$ (Ferrocyanide) with 1.5 M KCl are shown in Figure 9.4C and Figure 9.4D. The supporting electrolyte for the both Ferricyanide and Ferrocyanide was increased to 1.5 M in an attempt to get relatively good diffusion limited steady-state CVs for these redox molecules because they are known to be a surface sensitive redox molecule.²⁸ The increased supporting electrolyte will decrease the electrical double layer thickness²⁴ allowing the molecule to interact with the electrode surface more easily. The current from the 3.75 μm radius disk and ring in Ferricyanide (taken from -0.1 V in Figure 9.4C) was -4.66 nA and -2.73 nA respectively. The current from the 3.75 μm disk and ring in Ferrocyanide (taken from 0.5 V in Figure 9.4D) was 4.00 nA and 2.41 nA respectively. The predicted disk current from equation 1 for Ferricyanide (using $D = 7.6 \times 10^{-6} \text{ cm}^2/\text{s}$)²⁴ was -4.634 nA giving a percent difference of $\sim 0.6\%$. However, in Ferrocyanide, the predicted current from equation 1 (using $D = 6.3 \times 10^{-6} \text{ cm}^2/\text{s}$)²⁴ is 3.842 nA giving a percent difference of 4.05% which is rather large when compared to the Ferricyanide current deviation. The small deviance of the experimental current from predicted current indicates that the electrodes do not have gaps between the metal layers and the insulating layer. It is interesting to note that the CV responses for K_3IrCl_6 are less well defined than the other redox species, which is curious because the similarly charged Ferricyanide does not show the same hysteresis behavior. Perhaps this effect would be reduced if the supporting electrolyte was increase to the same concentration as the Ferricyanide.

In each case the ring current is lower than the disk current, as expected for electrodes of this size, and shows the area of the exposed gold for the disk is larger and indicates the insulator has

been etched away completely in the RIE step. For each set of CVs the ring limiting current is approximately $\sim 50 - 60$ % of what the disk current is, the ratio ($i_{\text{ring}} / i_{\text{disk}}$) is 58.3 %, 50.2 %, 58.6 % and 60.3 % of the disk current for FcMeOH, K_3IrCl_6 , Ferricyanide and Ferrocyanide respectively. These differences are within a few percentage points of each other even though a different diameter electrode was used for ferricyanide and Ferrocyanide than for the first two redox molecules. Besides the ratio for K_3IrCl_6 , all the ratios very closely match the predicted values for the $i_{\text{ring}} / i_{\text{disk}}$ ratio from the simulations which is further discussed below. The values obtained from the simulation show the $i_{\text{ring}} / i_{\text{disk}}$ current ratio is 58.4 % for a 4 μm radius electrode, and 58.6 % for a 3.75 μm radius electrode.

9.3.2 Numerical Simulation

The electrochemical responses of these electrodes were further studied and verified by simulating both their steady-state limiting current and the entire CV responses using a method, discussed further in the supporting information, previously described by White and coworkers.²⁹ The simulation was performed using finite-element method with COMSOL® Multiphysics. The simulated results were compared to the experimental CVs of the electrodes. To simulate the CVs, the electrode surface concentrations are set with a simulated potential dependent concentration equation and the flux of the molecules to the surface from the bulk solution is measured.

The faradaic current is assumed to be completely originated from the diffusive transport of the molecules from the bulk solution to the electrode surface where the flux is measured. The redox molecules are assumed to be 1-electron reversible oxidations, $\text{R} \rightarrow \text{O} + \text{e}^-$ for FcMeOH or reductions, $\text{O} + \text{e}^- \rightarrow \text{R}$, for $\text{K}_3\text{Fe}(\text{CN})_6$ where O and R are assumed to have the same diffusivities. The concentration of the reactant (R) and product (O) at the electrode surface are denoted as $C_{\text{R},\text{s}}$ and $C_{\text{O},\text{s}}$. The mass balance equation for an electrochemical reactions such as these is expressed as $C_{\text{b}} = C_{\text{R},\text{s}} + C_{\text{O},\text{s}}$ where C_{b} is the bulk concentration of the redox molecules.

The transient simulations employed the use of a triangle wave equation to simulate the applied potential to the electrode surfaces.

$$E(x) = \left(\frac{2}{\pi}\right) \sin^{-1}[\sin(\pi x)] \quad (2)$$

Using this simple function and the Nernst equation $E = E^\circ + (RT/nF)\ln(C_{O,s}/C_{R,s})$; where E° is the formal potential of the redox molecule, R is the universal gas constant, T is the absolute temperature in kelvin, a new triangle potential waveform equation can be made by replacing x with $(t * (1/2)v/E_{range})$, where t is the time step and v is the scan rate, and multiplying it by the E_{range} , where E_{range} is the range of the potential wave. This gives the following equation for the triangle waveform.

$$E(t) = \left(\frac{2}{\pi}\right) E_{range} \sin^{-1} \left[\sin \left(\frac{\pi t v}{2 E_{range}} \right) \right] \quad (3)$$

A simulated triangular potential waveform can be seen in Figure 9.5A which is simulated with E_{range} equal to 0.4 V and using a scan rate of 0.05 V/s. Using the mass balance equation, Nernst equation and the triangular waveform equation, the concentration of R (or O) at the electrode surface can be determined at time t by rearranging the equations into;

$$C_{R,S}(t) = \frac{C_b}{\left[1 + \exp \left(\frac{nF}{RT} \right) (E(t) - E^\circ) \right]} \quad (4)$$

where $E(t)$ is the triangular potential waveform equation 3. An example plot of the concentration at the electrode over time can be seen in Figure 9.5B. This equation is set as the concentration boundary conditions for the electro-active surface in the simulation. The current is then taken as the simulated flux of molecules (in units of mol/s) to the electrode multiplied by nF to convert the number of moles into current. For the transient simulations that involve the flux at the disk while the ring is turned on to scavenge diffusing redox molecules, equation 4 is put into the boundary condition for both electrode surfaces.

The geometry used to model the electrodes is assumed to be a perfect circle with completely flush sidewalls and is shown in Figure 9.6A. Here, numerical simulation was carried out using axis symmetry with surface 1 as the axis of symmetry where the simulation environment is rotated 360° around the axis of symmetry. Surfaces 3 and 8 are set with concentrations equal to the bulk solution concentration, C_b . The surfaces 4, 6 and 7 are set as insulating surfaces (i.e. no flux) leaving surfaces 2 and 5 as the electroactive surfaces of the disk and the ring electrodes respectively. The electrode side wall was modeled as a 550 nm recession with a 200 nm insulating layer above the disk electrode followed by a 55 nm wide section in the surface of the side wall, due

to the 5 nm chrome layer and 50 nm of gold, and a final 295 nm insulating layer above the ring electrode.

The electrodes modeled in the simulations have disk currents with < 0.5% difference as compared to equation 1 for any given electrode radius. Due to this small variability in the simulated disk current from the calculated current the subsequent simulations of the ring current and the scavenging mode current at the disk were then modeled with confidence in the results. Figure 9.6B shows a comparison of the simulated CVs of a 4 μm radius ring-disk UME in a simulated environment of 2 mM FcMeOH and the experimental CVs of a 4 μm radius electrode in 2 mM FcMeOH both at a scan rate of 50 mV/s. The simulation CVs are in close agreement with the experimental CVs although the latter show some minor slope to the steady-state current curve. This result shows the model matches the real electrode geometry well enough and is suitable for simulating the scavenging CVs.

The simulated ring current was 57.12% of the disk current and as is previously discussed, the experimental limiting currents on the ring electrode is around 50-60% of that on the disk electrode for the ring-disk UMEs with radii between 3-4 μm . The limiting current on the recessed disk should be approximately proportional to its radius when $r \gg L$ where the diffusive flux to the ring can be a small fraction of that on the disk. Here L is $\sim 0.55 \mu\text{m}$ for all electrodes in this work. On the other hand, the ring electrode can be viewed as a nanoband electrode with a band width of 55 nm and band length of $2\pi r$. Because the limiting current on a nanoband electrode is proportional to its length, the limiting current on the ring electrode should also be proportional to the radius of the ring when the radius is comparable or greater than the diffusion layer. For a nanoelectrode, the diffusion layer thickness can be approximated by 10 times its critical dimension at short time scales, or in this case, $\sim 550 \text{ nm}$. Therefore, the ratio of the two limiting currents should approach a constant as r increases. Conversely, when r is comparable to or even smaller than the depth L , the mass transfer resistance of the redox molecules to the recessed disk electrode could be sufficiently large so that the limiting current on the ring electrode is greater than that on the disk.

In order to more quantitatively understand the above prediction, we went on to simulate the limiting current on both the ring and the disk for electrodes with radii between 0.25 to 4.25 μm . Figure 9.7A shows the simulated steady-state limiting current on the disk electrode (○) in the when

the ring is left at open circuit, the ring electrode (Δ) when the disk is left at open circuit, and their ratio ($\bullet$) plotted as a function of the radius of the disk. As shown in Figure 9.7A, the limiting current on the UME disk is nearly linearly related to the radius of the electrode so as is the limiting current on the ring electrode. The current on the disk is almost always greater than that on the ring except when the radius of the electrode is smaller than ~ 550 nm or roughly the depth of the recess. The ratio of the limiting current ($i_{\text{ring}} / i_{\text{disk}}$) decreases as the radius increases and flattens when the radius is much greater than the depth and reaches a constant at or near 0.5, which is in agreement with our prediction of approaching constant value at large values of r . This indicates that the current ratio becomes independent of the radius of the electrode when the size of the electrode is much greater than its depth.

Figure 9.7B displays the simulated results when both the ring and the disk are simultaneously biased with a large over potential so that the effective surface concentration of redox species is zero. The limiting current collected on both electrodes dropped due to strong competition of the electrodes for the redox species or overlap in their diffusive fluxes. It can be qualitatively seen that the limiting current drops much more quickly on the ring electrode than on the disk electrode as the radius of the electrode increases. The limiting current on the disk electrode overall shows a nearly linear relationship with its radius which is similar to the results in Figure 9.7A. However, the relationship is more complicated on the ring electrode and the current increases slower with radius. The current ratio between the ring and the disk now quickly decreases with increasing radius to nearly zero when radius is greater than $4 \mu\text{m}$. This result shows that when the electrode is sufficiently large, the electrochemical current on the disk is nearly unaffected by the presence of the nanometer-sized ring electrode in an open electrochemical cell.

9.3.3 Redox Scavenging

The redox molecule scavenging experiments were conducted by applying a DC voltage to the ring electrode and a cyclic potential sweep to the disk electrode with one common reference electrode in solution and the current was recorded for the disk electrode only. The potential applied to the ring electrode was large enough to oxidize (or reduce) the redox species in the solutions. The voltage chosen for each redox molecule tested was picked to be at least 200 mV more positive (or negative for reduction) than the $E_{1/2}$ for the molecule being studied. Figure 9.8A shows the results of a typical scavenging experiment of a $3.75 \mu\text{m}$ radius electrode in 2 mM FcMeOH

where the limiting current of the disk is reduced when the ring electrode is turned “ON” compared to that when the ring is turned “OFF”. Simulations of the redox scavenging show similar results compared to the experimental data (Figure 9.8B) however, the reduction in current is seen to be more in the simulation than is observed experimentally. The reduction in current for the disk when the ring is “ON” compared to “OFF” is 11.6% for the experimental results and 14.12% reduction for the simulated results. The current difference of the disk when the ring is “ON” did not match the simulated results and was in fact below the predicted decrease in current by 17.8%. This may be due to the fact the simulation assumed the electrode geometry was perfectly circular and the side walls of the recession were straight and without irregularities. However, the AFM and SEM images clearly show that the real electrodes are imperfect and some variations to the simulation can be expected. Another possible reason is that the gold ring electrode could be slightly over etched during the electrode preparation process. As such, the redox flux to the ring electrode could actually be below what it should be due to additional mass transfer resistance. Perhaps these small variations are not as noticeable when taking normal CVs but are magnified when performing the scavenging experiments and the deviations become more significant.

A summary of the decrease in disk current operating in scavenging mode for some different electrodes and redox molecules is presented in Table 9.1 along with the simulated data corresponding to each electrode-redox combination. The diffusion coefficient used for dopamine is $5.9 \times 10^{-6} \text{ cm}^2/\text{s}$.³⁰ For all the redox molecules tested (with the given electrode sizes) the difference in current was below what the calculated predicted difference was from the simulations. Interestingly, the percent decrease seen in the simulated disk current was most dependent on the radius of the electrodes and not on the redox molecule diffusion coefficient or concentration. In the simulation, as the electrode radius becomes smaller, the change of the disk current will increase when the ring is turned “ON” compared to the ring “OFF” disk current, as was discussed previously. For a 3.75 μm radius electrode, both the 2 mM Ferrocene Methanol and 2.5 mM Ferricyanide simulated current decrease was 14.12% where the experimental decrease was seen to be 11.6% and 11.2% for FcMeOH and Ferricyanide respectively. The decrease in current for each redox molecule is approximately the same and this shows that the electrode size is more important to the decrease in current than the different redox molecules. However, when a cell is placed in the cavity of the electrode a much larger percentage of the redox molecules (dopamine) will be scavenged by the

ring electrode, hopefully eliminating them.

9.3.4 Single Cell Exocytosis

To perform the single cell exocytotic experiments PC12 cells were transferred from the growth media into isotonic saline solution where the ring disk electrode was located. The cells were then very carefully placed on the electrode surface using a manipulation pipette to move them into position. Figure 9.9A shows an amperometric trace recorded from the disk electrode of a ring disk electrode with a single PC12 cell placed directly on top of it. The trace shows a current spike as the ring is biased to +700 mV and another when the disk is biased to +700 mV. After the disk is turned on, the current sharply increases and then exponentially decays down to a steady current. After the cell is stimulated it begins to exocytose which is then detected at the disk electrode as current spikes. We believe the scavenging ring electrode is reducing or eliminating the freely diffusing dopamine that may be released farther away from the disk because, as can be seen in Figure 9.9B, there is a larger population of short lived events when the ring is "ON" compared to when it is "OFF". We believe this indicates that the ring reduces the number of long duration events that the disk detects which could be events that occur above where the ring is located. The event duration can be elongated due to the diffusion of the dopamine molecules long distances to the electrode surface.³¹ The disk is detecting only events that are located in very close proximity to the disk electrode preventing the molecular diffusion profile of the event from spreading out and we observe more short lived events.

Figure 9.10 shows a histogram of the calculated dopamine contents detected from the individual vesicles. The dopamine was calculated from the amperometry current traces by integrating the current over time. This integrated current corresponds to the number of dopamine molecules oxidized in each current spike. The histogram shows that the average dopamine content is roughly equal for the ring disk electrode when the ring is turned "ON" and scavenging the redox molecules and when it is "OFF". Additionally, the dopamine content for the events detected with the ring disk electrodes is very similar to the content detected with the carbon fiber microelectrodes that are typically used for single cell exocytotic studies. This method may allow for more accurate analysis of cellular vesicle exocytotic release durations. However many more single cell experiments need to be done in order to obtain statistically significant results and verify this conclusion.

9.4 Conclusion

On-chip recessed ring-disk UMEs, ranging in radii from 3 to 4 μm , have been fabricated by laying down successive layers of metal and insulator then etching through the layers to expose the patterned electrodes. This method allows for easy control over the size of the UME and the ring-disk distance with nanometer precision. These electrodes have been characterized using electron microscopy and AFM as well as steady-state cyclic voltammetry. The electrochemical response has been modeled in a computer simulation and compared to the experimental data. The simulated CV responses closely match the experimental CVs but are not as exact in modeling the scavenging behavior of the different redox molecules. The scavenging ring eliminates a percentage of the freely diffusing electroactive molecules before they reach the disk electrode and the scavenged percentage is proportional to the electrode radius. We have demonstrated that the electrodes can be used for single cell exocytotic experiments and have observed that when the ring is turned “ON” and is scavenging redox molecules the population of events detected at the disk electrode with low half width times increases relative to when the ring is “OFF”. Many more experiments need to be performed to determine if there is any real statistical difference between typical single cell exocytotic events and those when a scavenging electrode is present to eliminate the dopamine released above the ring before it can be detected by the disk. A more detailed analysis of PC12 cells with electrodes utilizing this specific geometry will be conducted in future studies.

9.5 Tables and Figures

Table 9.1 Redox Molecule Scavenging Summary

A comparison of the current on the disk electrode when the ring is either in the “ON” state and the ring is acting as a molecular scavenger or when it is “OFF”. Both the simulated and experimentally observed results are shown.

Electrode radii & redox conc.	Measured Disk current			Simulated Disk current		
	Ring “OFF” (nA)	Ring “ON” (nA)	Difference %	Ring “OFF” (nA)	Ring “ON” (nA)	Difference %
3.75 μm 2 mM FcMeOH	1.64 (at 0.45 V)	1.45 (at 0.45 V)	11.6	1.629	1.399	14.12
3.75 μm 2.5 mM $\text{K}_3\text{Fe}(\text{CN})_6$	-2.14 (at -0.2 V)	-1.90 (at -0.2 V)	11.2	-2.310	-1.984	14.12
3.25 μm 2 mM dopamine	2.33 (at 0.7 V)	2.01 (at 0.7 V)	13.7	2.426	2.053	15.37

Figure 9.1 Recessed Ring-Disk Redox Scavenger Schematic

A schematic showing the cross-section of a recessed ring-disk UME and the proposed mode of operation for the electrode as a redox scavenger with the diffusive flux to the electrodes shown.

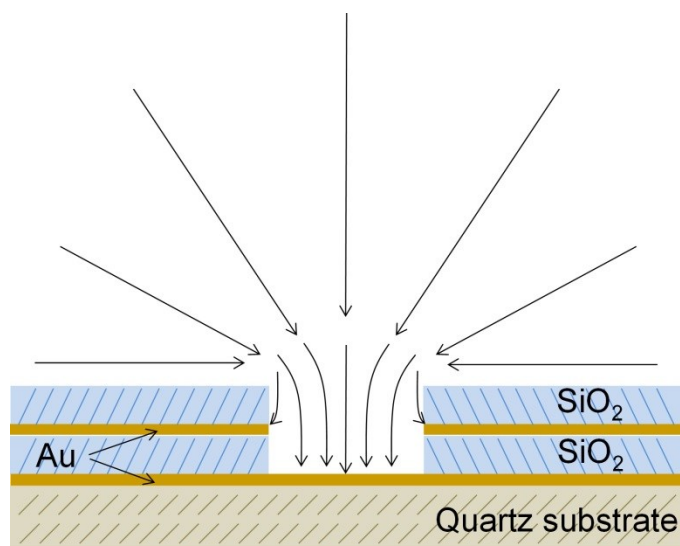


Figure 9.2 Schematic of Fabrication Steps

Fabrication of a recessed ring-disk UME depicting the various steps to make an electrode including the deposition of the gold layers that will become the electrodes and the insulating layers followed by UV photolithographic patterning and etching of the various layers.

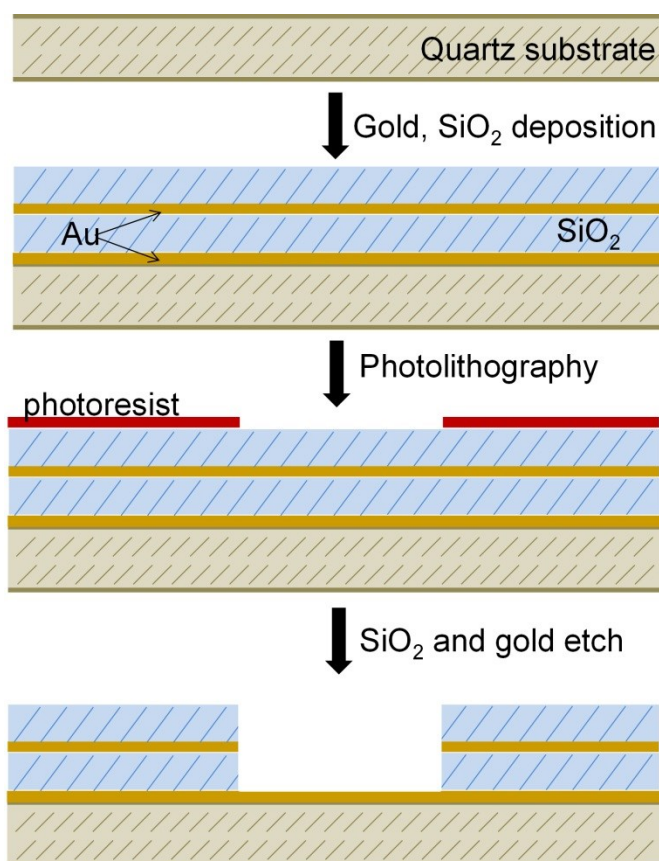
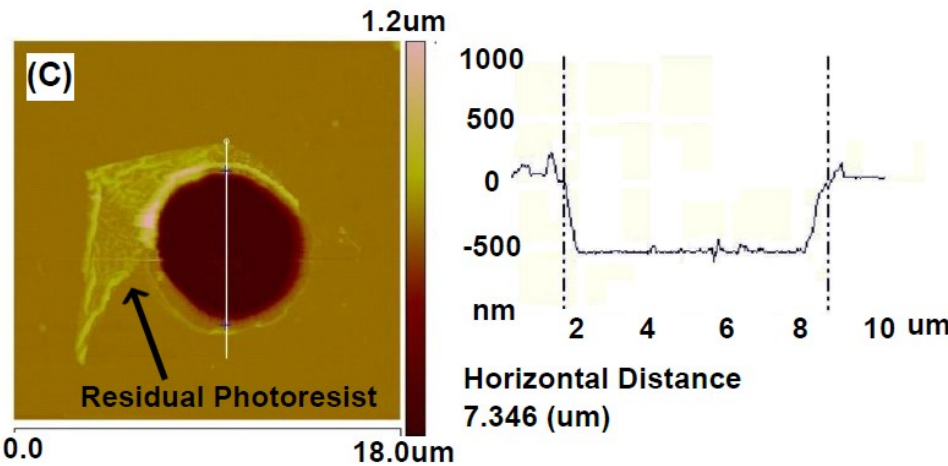


Figure 9.3 Electrode SEM and AFM Characterization

(A) An SEM image of a 3.75 μm radius ring-disk UME. (B) Increased magnification SEM image of the gold ring electrode located within the SiO_2 sidewall. (C) AFM image of another 3.75 μm radius electrode showing the depth and diameter of the recess. The AFM image (C) shows a circular electrode with a dark center and a lighter ring. A vertical line is drawn across the center, and a cross-section profile is plotted to the right. The profile shows a deep recess in the center, with the depth reaching approximately -500 nm. The horizontal distance of the recess is 7.346 μm . The label 'Residual Photoresist' points to the material surrounding the electrode. The color scale on the left ranges from 0.0 to 18.0 μm .

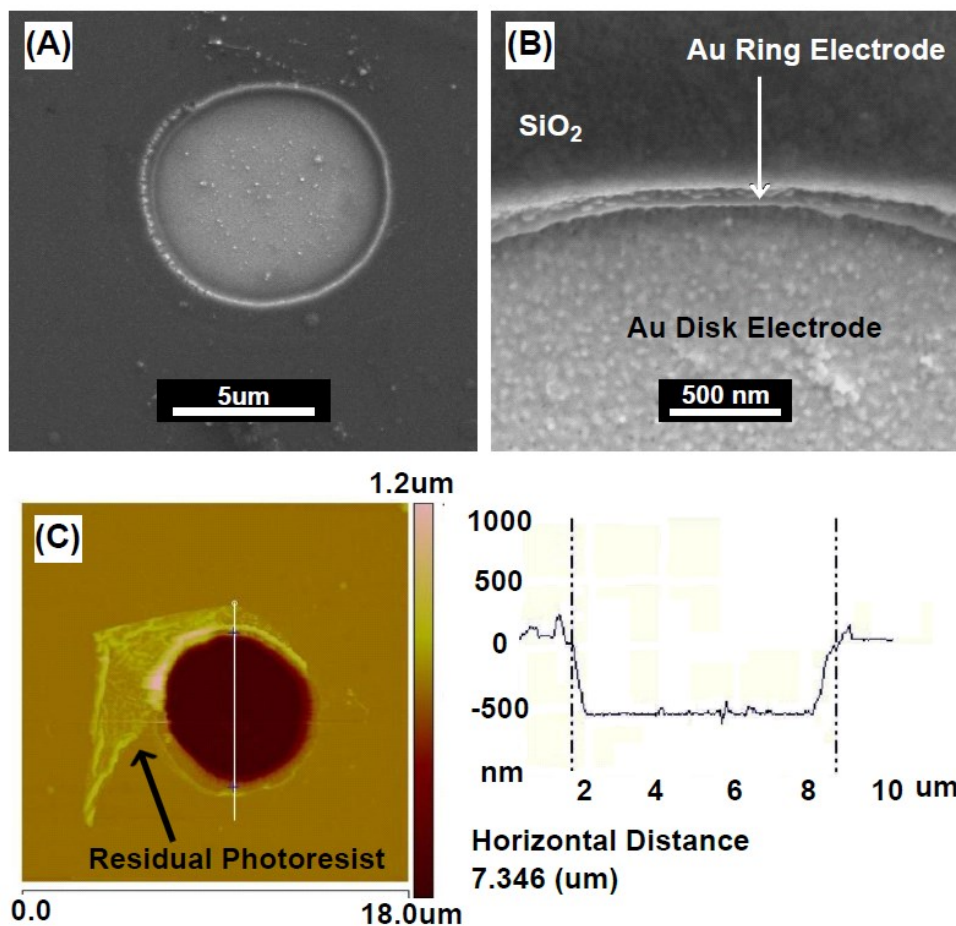


Figure 9.4 Recessed Ring Disc Electrochemical Response

CVs of ring and disk electrodes for 2 different 4 μm radius electrodes with different redox molecules. (A) A 4 μm radius ring-disk UME in 2 mM FcMeOH with 0.1 M Na_2SO_4 and (B) 5 mM K_3IrCl_6 with 0.2 M Na_2SO_4 . (C) A different 4 μm radius ring-disk UME in 5 mM $\text{K}_3\text{Fe}(\text{CN})_6$ with 1.5 M KCl and (D) in 5 mM $\text{K}_4\text{Fe}(\text{CN})_6$ with 1.5 M KCl. Scan rates were 50mV/s for all CVs.

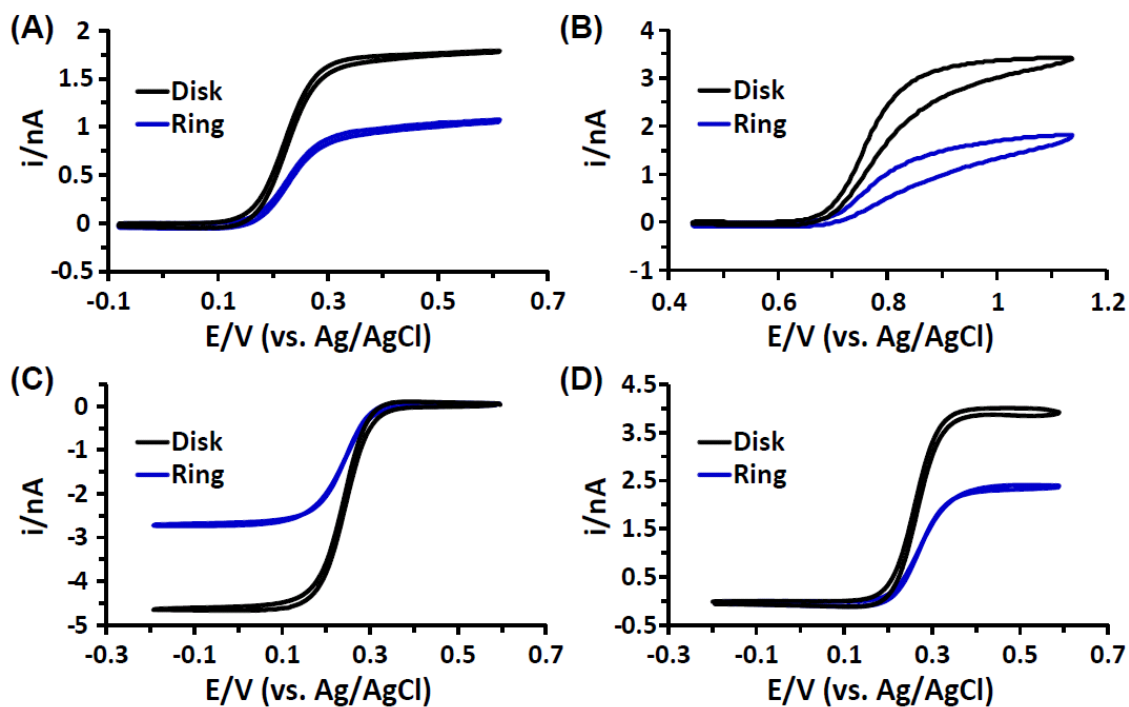


Figure 9.5 Simulated Potential Wave and Concentration Curve

(A) Simulated voltage-time plot prepared using equation 3 from the supporting text. E_{range} was set equal to 0.4 V and a scan-rate of 0.05 V/s was used. (B) A graph of concentration (normalized to the bulk concentration) over time calculated using equation 4 where the concentration is seen to go from the bulk concentration to 0 and back to bulk concentration. The concentration was calculated using the same parameters as the voltage time plot seen in (A) with an E° of 0.2 V.

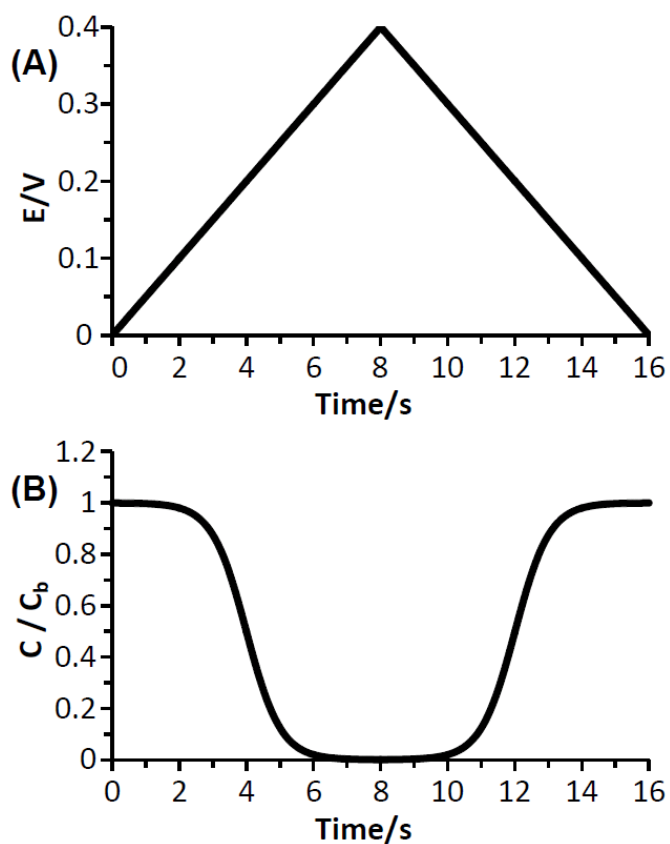


Figure 9.6 Simulation Geometry and Simulated CVs

(A) Electrode geometry used to model the ring-disk UME. Electroactive surfaces are colored red and the section containing the ring electrode (surface 5) is expanded for clarity (i.e. not drawn to scale).

(B) A comparison of the simulated CVs vs. the experimental CVs for an 4 μm radius electrode in 2 mM FcMeOH and 0.1 M Na_2SO_4 at 50 mV/s.

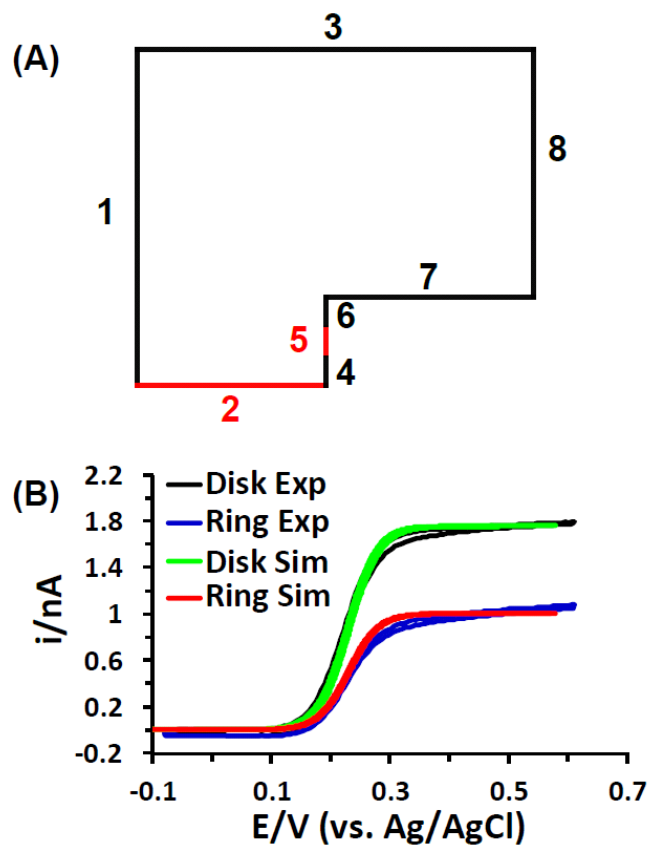


Figure 9.7 Ring Disk Simulated Current Comparison

(A) Simulated steady-state limiting current on the disk electrode (○) in the when the ring was left at open circuit, the ring current (Δ) when the disk is left at open circuit, and their ratio (●) plotted as a function of the radius. (B) Simulated steady-state limiting current on the disk electrode (○) in the presence of an applied ring voltage, the ring current (Δ) in the presence of an applied disk voltage, and their ratio (●) plotted as a function of the radius of the disk.

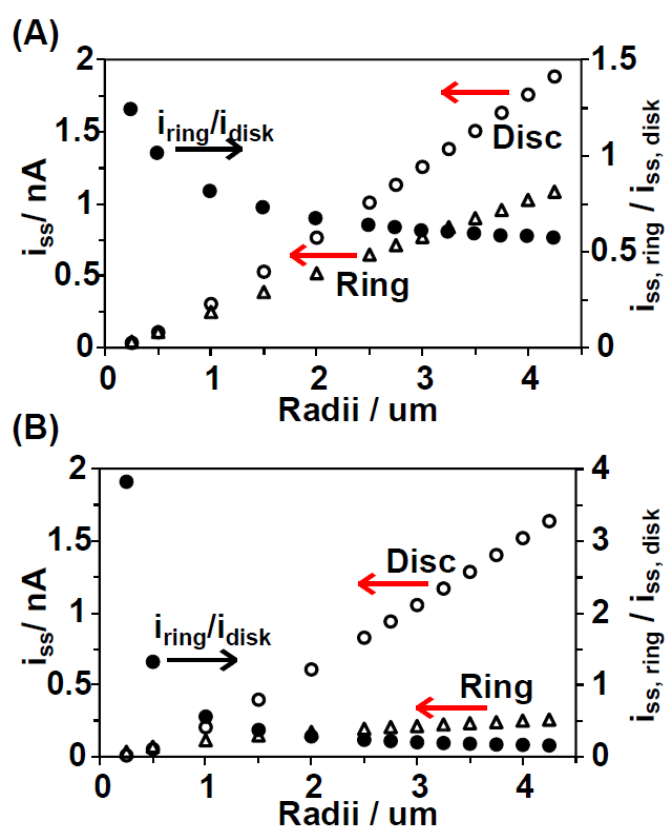


Figure 9.8 Redox Scavenging Simulated and Experimental CVs

(A) Experimental CVs at 50 mV/s of the disk of a 3.75 μm radius disk electrode without voltage applied to the ring electrode and with 400 mV (vs. Ag/AgCl) applied to the ring electrode in 2 mM FcMeOH and 0.1 M Na_2SO_4 . (B) Simulated CVs at 50 mV/s of a 3.75 μm radius disk electrode in 2 mM FcMeOH with and without the ring voltage turned on.

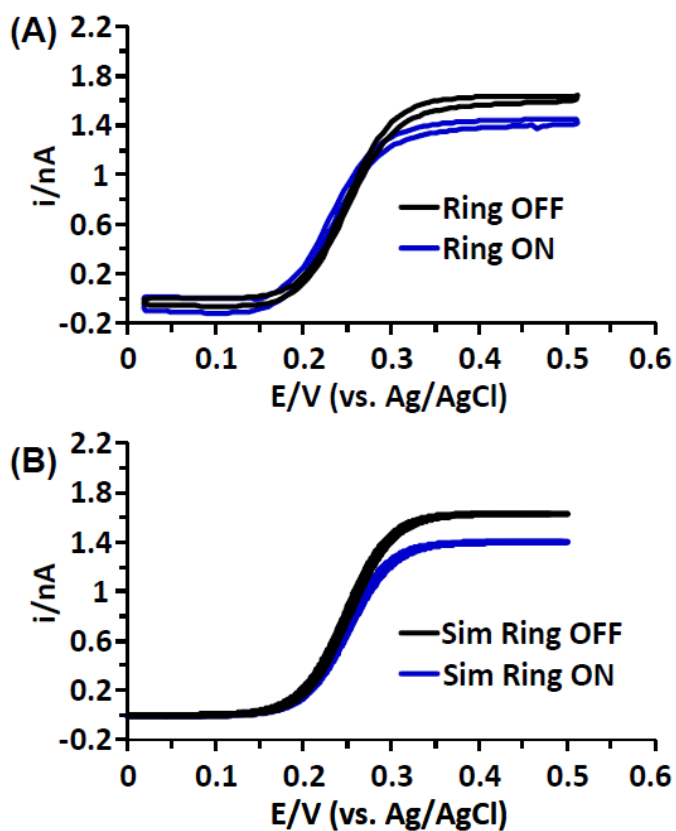


Figure 9.9 Single Cell Exocytotic Event Detection

(A) Experimental Amperometric trace of a single PC-12 cell on a ring disk electrode showing many exocytotic events after the ring and disk have both been turned on to +700 mV applied potential and the stimulation solution injected. (B) Histogram plots showing the average half widths of the events when the ring is turned “OFF” and when it is turned “ON” (number of events: $N_{\text{ON}} = 28$ and $N_{\text{OFF}} = 50$).

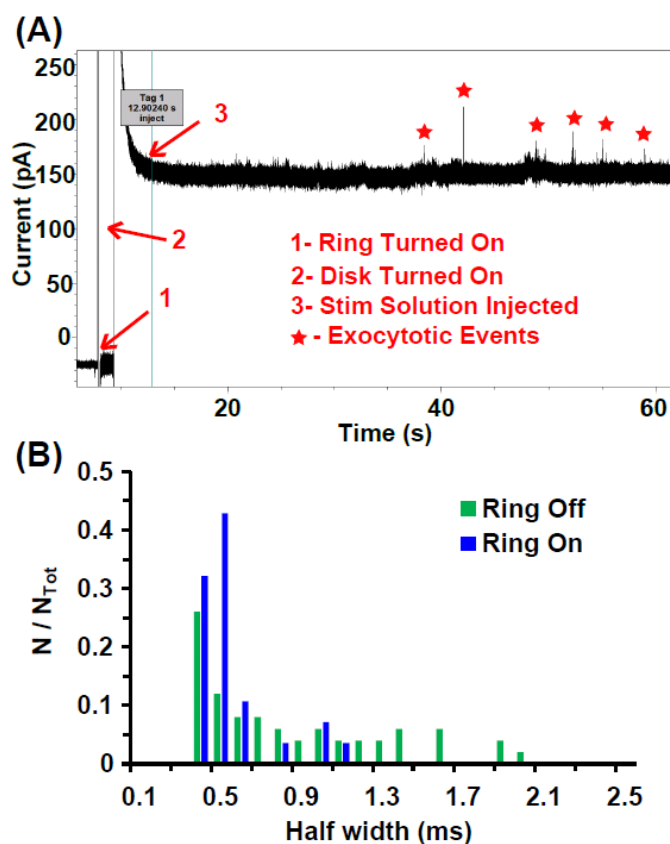
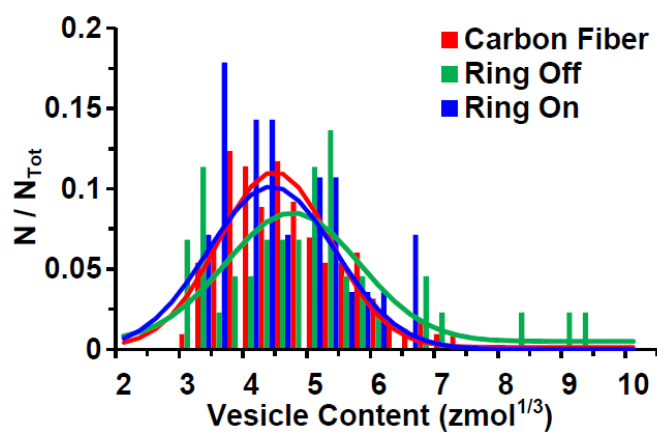


Figure 9.10 Vesicle Dopamine Content

Histogram showing the distribution of dopamine content in the vesicles that is amperometrically detected from single PC12 cells using the ring disk electrodes operating with the ring in both the “ON” and “OFF” states and with a typical carbon fiber electrode for comparison.



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Chapter 10 Gold Nanowire and Carbon Film TEM Chip Electrodes

10.1 Introduction

Metal nanoparticles are a very common catalyst for many different reactions, both electrochemical¹ and gas phase heterogeneous catalysis². The catalytic behavior of the nanoparticles can change depending on shape³ or substrate interface.⁴⁻⁶ By changing the shape of the nanoparticle, different crystal faces are exposed and the catalytic activity can be strongly affected by the crystal face.^{7,8} Determining the nature that a nanoparticles shape has on the catalytic activity is an important aspect of heterogeneous catalysis experiments but can be very hard to accurately determine. There have been many methods developed to help determine the catalytic activity of single nanoparticles.⁹⁻¹² One such method involves immobilizing a single nanoparticle at the end of a nanoelectrode and, after performing the desired electrochemical testing, imaging the nanoparticle using a Transmission Electron Microscope (TEM).^{13,14} However, performing the experiments may alter the nanoparticle by atomic migrations that can alter the surface¹⁵, dissolve¹⁶, or de-alloy¹⁷ the nanoparticle.

The technique of *in-situ* Environmental-TEM (E-TEM), involves imaging a sample in an environment that would typically not be possible under normal TEM operation.^{18,19} This technique has allowed some very detailed studies to be done on nanoparticle growth,²⁰ nanoparticle restructuring²¹ and nanoparticle catalysis.²² Any sample that is to be put into the TEM must in be small enough to fit into the sample holder and able to withstand the high energy electron beam, while being thin enough to be transparent to the electron beam. Construction of nanoelectrodes for the purpose of investigating the catalytic activity and resulting nanoparticle behavior during *in-situ* E-TEM imaging, to the best of our knowledge, has not been done.

We have constructed new types of electrodes on silicon TEM chips where either a gold nanowire is placed over a thin support membrane and cut forming a nanoscale electrode or an electroactive carbon film is deposited on the membrane and selectively patterned to expose only a small portion of it. These new chip electrodes will allow investigations on single nanoparticle electrocatalysis during E-TEM imaging experiments where real time imaging of nanostructures under changing environmental conditions will provides unprecedented details about the changes the nanostructure will incur. In the case of the gold nanowire TEM electrodes, a single, specifically

shaped, nanoparticle will be immobilized onto the gold nanoelectrode where it will be tested and imaged using the TEM with the added advantage of a side on viewing angle. Alternatively, a nanoparticle can be selectively grown on the end of the gold nanowire providing insight into the nucleation and growth of the nanoparticle under an applied potential. In the case of the carbon film electrodes, they will have a larger area to do ensemble studies of nanoparticle growth or catalysis where the change or nucleation will be viewed from an axis perpendicular to the electrode surface. Additionally, carbon is a very catalytically inert material to make the electrode surface from (as opposed to gold) and thus will not interfere with the electrochemical data recorded from the nanoparticle catalysts experiments.

10.2 Experimental

10.2.1 Chemicals and Materials

All aqueous solutions were prepared using deionized water (>18 M Ω cm, Barnstead Nanopure Systems) and all chemicals and materials were used as received from the manufacturers. Silicon substrates were thoroughly cleaned and sonicated with DI water, Acetone and IPA and allowed to dry in an oven. Single crystal <100> Silicon wafers double side polished (Silicon Quest International Inc.), hydrofluoric acid (HF, 48 wt% conc. Sigma Aldrich), Acetone (Mallinckrodt Baker), Isopropyl alcohol (Mallinckrodt Baker), Ethanol (200 proof, Decon Labs), Ferrocene methanol (FcMeOH, Aldrich 97%), Ferrocyanide tri-hydrate ($K_4Fe(CN)_6 \cdot 3H_2O$, Fluka), KCl (Mallinckrodt Baker), KOH (Fisher Scientific) 1,6-Hexanedithiol (96%, Sigma Aldrich), photoresist AZ1512 with AZ351 developer (AZ Corporation, developer diluted 1:5 developer:DI H₂O), Graphite (99.999%, Ted Pella), Ethyl Acetate (EMD), Cellulose Acetate Butyrate (average M_n = 30,000, Sigma Aldrich), gold wire (99.99%, Kurt J. Lesker), Poly Vinyl Pyrrolidone (PVP, average M_w ~55,000, Sigma Aldrich), hydrazine (anhydrous 98%, Sigma Aldrich), monobasic potassium phosphate (KH_2PO_4 , J. T. Baker), dibasic potassium phosphate (K_2HPO_4 , J. T. Baker), 30 nm diameter platinum nanoparticles (sodium citrate capped, dispersed in 2 mM citrate, NanoComposix, Inc. San Diego, CA).

10.2.2 Low Pressure Chemical Vapor Deposition and Carbon Thin Film Deposition

An approximately 50 nm layer of silicon nitride was deposited on the bare silicon wafers using a Low Pressure Chemical Vapor Deposition (LPCVD) ThermcoNitride system operating at ~800 °C at an operational pressure of 250 mtorr with dichlorosilane ($SiCl_2H_2$) and ammonia (NH_3) as the

gaseous precursors. Carbon was deposited using NRC 3117 electron beam evaporator with a 10 kV, 1 amp Temescal CV-10 power supply with automatic beam sweep and a Inficon XMS-3 deposition monitor where a graphite crucible filled with graphite was used as the material source.

10.2.3 UV Photolithography and Reactive Ion Etching

A Newport Flood exposure source with a UV light power was 8.94 mW at 360 nm exposure wavelength and exposures were typically 8-9 seconds in duration. Substrates were spin coated with an approximately 1-2 μm thick layer of AZ1512 before UV light exposure. AZ315 used to develop the exposed photoresist. The Reactive Ion Etching of the thin nitride films was performed using a TRION Phantom Reactive Ion Etcher operating with RF power of 300 W with 75 sccm of SF_6 and 15 sccm O_2 at 50 mtorr operating pressure.

10.2.4 Electron Microscopy and Focused Ion Beam Milling

Scanning Electron Microscope (SEM) images were obtained using a field-emission microscope (FEI Sirion) equipped with a through lens secondary electrode detector with a resolution of 1-3 nm at the Nanotech User Facility located at the University of Washington. All samples were sputter coated with a thin conducting layer (~ 3 nm) of Au/Pd for SEM imaging. Focused Ion Beam Milling (FIB) was done using a FEI XL830 Dual Beam FIB/SEM system with a liquid gallium source equipped with a through the lens detector and a continuous dynode electron multiplier for secondary electron, backscattered electron and secondary ion imaging. Transmission Electron Microscopy (TEM) imaging was performed on a FEI Tecnai G2 F20 S-Twin operating at 200kV using a single tilt sample holder and carbon coated Formvar copper TEM grids (Ted Pella).

10.2.5 Synthesis of Decahedra Gold Nanoparticles

Gold nanoparticle with decahedra shapes were synthesized according to a polyol reduction process²³ where poly(vinyl pyrrolidone) (PVP) was used to stabilize the gold nanoparticles. In this reaction 2.0 g of PVP was dissolved into 25 ml of Di-ethylene glycol (DEG) and refluxed for 5 minutes in a mineral bath. A solution of 2.0 ml of DEG containing 20 mg of HAuCl_4 was added to the boiling solution and allowed to reflux for 10 minutes. At the end of the reaction the solution was a deep purple color and was allowed to cool to room temperature while stirring. The mixture centrifuged at 6,000 rpm for 30 minutes and the precipitate collected and washed with ethanol to remove residual polymer and re-suspended in ethanol.

10.2.6 Electrochemical Measurements

Steady-state cyclic voltammograms (CVs) were recorded using a computer-controlled Dagan Chem-Clamp voltammeter/ampereometer and data was recorded using an in-house virtual instrumentation program written in LabVIEW (National instruments) on a desktop PC equipped with a PCI-6251 (National Instruments) data acquisition card. A commercially available Ag/AgCl reference electrode (Bioanalytical Sciences, Inc.) was used as reference electrode for all CVs. Amperometric detection of nanoparticles was done using a MiniDigi 1A (Molecular Devices, Sunnyvale, CA) operating at 1kHz frequency collection rate.

10.3 Results and Discussion

10.3.1 Silicon Wafer Anisotropic Wet Etching

The individual silicon TEM chips that would become the device substrates for both types of TEM chip electrodes were made in house from single crystal silicon wafers possessing a {100} crystal face. These chips were etched out of the wafers using well established standard micro fabrication methods commonly employed to make integrated circuits and micro electromechanical devices.²⁴⁻²⁶ The wafers were patterned and anisotropically etched to produce small chips using a 50 nm thick layer of Si_3N_4 that will act as the KOH wet etch mask and later form the window located in the center. The chips final diameter was designed to be ~ 3 mm with a 5 μm or 50 μm window in the center where the 50 nm silicon nitride membrane is covering it. A schematic showing the generalized fabrication steps to produce the TEM chips is shown in Figure 10.1A.

The {100} oriented silicon wafers were first coated with the 50 nm layer of silicon nitride using Low Pressure Chemical Vapor Deposition (LPCVD). The wafers were then patterned using UV photolithography and a UV contact mask. The mask was made with a 21x21 array of the chip patterns in the approximately 4x4 inch area, which means that for every 4-in wafer processed an estimated 250 individual chips are produced (after correcting for the shape of the wafer and possible damaged/un-usable chips). After patterning the thin layer of silicon nitride with the UV photolithography the exposed layer will be etched away using Reactive Ion Etching (RIE) exposing the silicon metal underneath. The remaining nitride layer will act as the KOH wet etch mask during the anisotropic silicon etching process where the KOH will etch silicon but does not appreciably etch silicon nitride. The KOH wet etch is an anisotropic etch where the crystal faces of the silicon wafer

etch at vastly different rates as the {100} crystal faces etch much faster than the {111} crystal faces, with a 400:1 etch rate ratio of {100}:{111}.²⁴ The patterned wafers were etched in a solution of 30 wt% KOH heated to 80 °C under constant stirring. After the silicon was etched through the thickness of the wafer the individual chips would begin to release from the remaining silicon frame. An optical image of half of a 4 inch wafer that has been patterned and etched can be seen in Figure 10.1B. A few individual TEM chips can be seen still attached to the silicon frame that remains. To verify that the dimensions of the TEM chips were correct, SEM images were taken to measure the dimensions of a sample of chips. A typical finished chip can be seen in the SEM image Figure 10.1C where the nanometer thick silicon nitride window can be seen in the center of the chip and the diameter of the almost circular chip is ~2.7 mm indicating successful design and patterning of the silicon wafer. These chips can also be used for some types of TEM analysis in addition to substrates that the gold nanowire electrodes and carbon film electrodes are made on top of.

10.3.2 Fabrication of Gold Nanowire TEM Chip Electrodes

Using the silicon TEM chips, a gold nanowire is placed on top of the silicon nitride window then insulated and a portion exposed to form a gold nanodisk electrode at the center of the chip. A schematic of the gold nanowire TEM chip electrode can be seen in Figure 10.2A where the nanowire directly above the silicon nitride window has been cut open and it is picture with a single gold nanoparticle attached to the exposed end of the electrode (as one proposed use for these electrodes).

The gold nanowires to be placed on top of the window were made by a laser assisted mechanical pulling process described in detail elsewhere²⁷ but quickly; a small amount of gold is first sealed into a large quartz tube under vacuum and then quickly hand pulling²⁸ it into a micron sized diameter wire that is still encased in the quartz. This wire pre-form is then cut into 1-cm sections and inserted into a quartz capillary (Outer Diameter: 1 mm, Inner Diameter: 0.3 mm). The Au/quartz ensemble was then pulled in the laser puller (P-2000, Sutter Instruments) using the pulling parameters (Heat = 725, Filament = 3, Velocity = 100, Delay = 110, Pull = 225) resulting in two sharp quartz tips with the gold nanowires sealed inside. These nanowires were then etched out of the quartz encasement onto bare silicon using concentrated hydrofluoric acid. Once washed the gold nanowires could be transferred onto the silicon nitride TEM chip window. This was accomplished using a process termed “wedging”, described by Schneider et al.²⁹, where a

nanostructure is encased in a polymer (such as cellulose acetate butyrate) and then moved to the desired location/substrate. The polymer was then removed using oxygen plasma and the back end of the gold nanowire contacted with a thermally evaporated gold contact pad and the whole surface encased in another layer of PECVD silicon nitride to insulate it. The wire and insulating silicon nitride were then cut open over the window using Focused Ion Beam (FIB) milling exposing the electrode and creating an inlaid disk nanoelectrode where the surface is normal to the silicon TEM chip substrate. This means that if viewed through a TEM the side of the gold nanoelectrode would be visible. A typical gold nanowire TEM chip electrode can be seen in Figure 10.2B where the gold nanowire can be distinguished from the surrounding insulator due to the charging effects of the electron beam and can be seen running up to the silicon nitride window (the large brighter rectangular section) where it is cut open with the FIB. The size of the disk electrode can be determined by visually measuring it using the FIB immediately after cutting it open (as is shown in Figure 10.2C). The size can also be determined from the diffusion limited steady state current of simple redox molecule. The equation that will relate the radius of the electrode, r , to the faradaic current is seen in equation (1) below;³⁰

$$i_{ss} = 4nFDC_b r \quad (1)$$

where n is the number of electrons transferred in the redox reaction, F is Faradays constant, D is the diffusion coefficient of the redox molecule and C_b is the concentration of the redox molecule in bulk solution. The magnitude of the current will also indicate whether a nanoparticle has successfully attached to the surface of the electrode due to the increase surface area of the spherical nanoparticle. The gold nanoparticles are attached to the nanoelectrode through chemical linkage molecules of 1,6-hexanedithiol that will first be used to modify the surface of the nanoelectrode forming a Self-Assembled Monolayer³¹ (SAM) onto which a gold nanoparticle can also attach. In Figure 10.3A are some typical CVs from a SNPE before modification where the redox current is due solely to the bare gold nanoelectrode and after the dithiol SAM and nanoparticle attachment. After attachment, an increase in current is observed and corresponds to the increased surface area of a nanoparticle on the nanoelectrode that indicates the modification was successful. Upon testing for the Oxygen Reduction Reaction (ORR) in alkaline media we discovered that the ORR does not show increased ORR activity as compared to a gold microelectrode (not shown) and may be due to the

PVP capping agent that was employed to synthesize the nanoparticles hindering the reaction or blocking the catalytic sites.

The gold nanoelectrode seen in the TEM image shown in Figure 10.3B has a single nanoparticle attached to the electrode and corresponds to the same SNPE electrode from the Ferrocyanide CVs in Figure 10.3A showing the increase in current from the nanoparticle attachment. Unfortunately, the electrode was situated a short distance from the edge of the silicon nitride film and as such had to be imaged through the film. However, from the image we can determine the approximate size of the nanoparticle and compare it to the calculated size of the nanoparticle based on equation (2) below, which is the steady state current at a sphere.³⁰

$$i_{ss} = 4\pi nFD C_b r \quad (2)$$

Where all the constants are the same as for equation (1) but r is now the radius of the sphere. Using the steady state current from the nanoparticle CV in Figure 10.3A the radius of the particle was calculated as 102.6 nm radius which is in close agreement to the visually measured value of 109.7 nm radius from the TEM image in Figure 10.3B. The agreement between the measurements shows that nanoparticles can be attached to the TEM chip gold nanoelectrodes and evaluated electrochemically. A larger diameter gold electrode with multiple particles attached can be seen in Figure 10.3C where there is a clear image of the particles. This would be an ideal imaging situation of the attached nanoparticles where the nanoparticles size and shape can be clearly observed and even the region between nanoparticle and the electrode can be seen, as in Figure 10.3D. This region between the electrode and the particle is where the SAM is attached to the electrode at one end and the nanoparticle at the other. The fact that the nanoparticle is not directly touching the electrode surface means that the electrons involved in any electrochemical reaction must tunnel through the interface from the electrode to the nanoparticle (or vice versa).³² It may be possible to determine the effect of the electron tunneling based on the size of the gap between them, which can be increased by increasing the linker molecules length, and how that distance affects the nanoparticles electrochemical response. In future experiments it will be necessary to have the end of the electrode extend to the edge of the Nitride film in order to clearly image the attached nanoparticle.

10.3.3 Selective Patterning of Carbon TEM Chip Electrodes

Using the same silicon TEM chip substrates as in the previous section, carbon electrodes can be made by depositing a layer of ultra-thin carbon onto the top of the TEM chip. This thin layer of carbon will later serve as the electrode surface onto which many experiments can be performed.³³ These electrodes will have the benefit of a large area electrode that can be imaged either after the experiment or, in the case of the In-situ E-TEM imaging experiments, during the procedure. Because the end goal is to perform High Resolution TEM (HRTEM) imaging on the carbon electrodes, we deposit the carbon thick enough to be conductive but as thin as possible. The onset of the conductivity of this type of carbon has been found previously to be at $\sim 5.6 \pm 0.5$ nm thickness, after which the conductivity will increase linearly with thickness.³⁴ With this in mind, we deposited a carbon layer 7 nm thick on the top side of the TEM chips in order to be sure the films were conductive.

After the carbon deposition, the majority of the carbon surface had to be insulated leaving only a small section exposed directly above the transparent silicon nitride window. To accomplish this goal the chips were selectively patterned using a modified UV photolithographic procedure, as seen in Figure 10.4A, where the top of the chip was coated in a layer of UV photoresist. Then, only the backside of the chip was exposed to the UV light which will be transmitted through the silicon nitride window, thus exposing the photoresist directly above the window, but nowhere else. Once developed only the carbon on top of the silicon nitride window will be exposed from the photoresist. An SEM image of a representative carbon electrode chip can be seen in Figure 10.4B where the square shaped silicon nitride support window can be seen in the center of the image with a layer of developed photoresist bordering the window. A magnified image of the photoresist layer at the edge of the window can be seen in Figure 10.4C where there is clearly a thickness to the photoresist layer.

The chips were then characterized electrochemically after developing the photoresist layer and making contact to the carbon layer. Some diffusion limited steady state CVs can be seen in Figure 10.5A taken in 2 mM FcMeOH from different chips that had different sized support windows (resulting in different sized carbon electrodes). Based on the limiting current from the CVs and approximating the electrode as a pseudo disk electrode, the electrochemical response can be compared to the SEM measured sizes using equation (1) for a disk geometry electrode. The SEM

measured size of the electrode is the averaged radius measured from the diagonal and the edges of the square. The calculated radius for the electrode labeled 1 was $29.2\text{ }\mu\text{m}$, from the limiting current of 15.19 nA , which is very similar to the measured radius of $28.1\text{ }\mu\text{m}$ (a 3.76% difference in size), but as the electrode size decreases the electrochemically measured size deviates from the visually measured value. For electrode 2 the electrochemically calculated radius was $4.93\text{ }\mu\text{m}$ (from a 2.55 nA limiting current) while the SEM image measured radius was $6.2\text{ }\mu\text{m}$ with a percent difference of 20.43%. For electrode 3 the percent difference continues to increase where a $0.89\text{ }\mu\text{m}$ radius (electrochemically calculated from 0.46 nA) gives a 41.78% difference compared to the visually measured $1.53\text{ }\mu\text{m}$ radius. This increasing deviation is likely due to the fact that it is recessed into a layer of photoresist where, as the size of the electrode decreases, the aspect ratio between the electrode size and the photoresist thickness will increase leading to an increased mass transfer resistance.³⁵ This means that as the size of the recessed electrode decreases, the mass transfer resistance will increase, decreasing the overall flux of the reactive species to the electrode more than expected for an electrode level with the insulating surface, leading to a larger decrease in the limiting current. This will not affect the proposed use of these electrodes where they will be utilized as a platform to perform nanoparticle characterization experiments.

Figure 10.5B shows an amperometric trace of a carbon TEM chip electrode in 10 mM hydrazine where a constant potential is applied to the electrode and the successive nanoparticle collision events can be observed from the increase in current. The increase in current is due to the fact that the platinum nanoparticles oxidize the hydrazine at a potential where the electrode will not (carbon is an inert material for hydrazine oxidation at this potential). When a nanoparticle collides with the inert electrode the nanoparticle will begin to oxidize the reactant and there will be a current change.⁹ The chips offer the unique advantage that the nanoparticles can be observed, using dark field microscopy³⁶, as they collide with the electrode while their electrochemical response recorded where then the specific nanoparticles can be correlated to their catalytic activity. Additionally, if these chips were to be used in E-TEM experiments, observing the electrochemical nucleation and growth of nanoparticles or the structural changes of nanoparticles when a potential is applied, then the electrodes must allow for High Resolution TEM (HRTEM) imaging. Figure 10.5C shows a HRTEM image of a single gold nanoparticle that was detected amperometrically colliding with a carbon TEM electrode in hydrazine solution. This image shows the atomic lattice of the gold nanoparticle where the atomic spacing of the $\{100\}$ and $\{111\}$ crystal planes is measured to be $2.04\text{ \AA}$

and 2.35Å respectively.^{37,38} This example image demonstrates that the atomic lattice of the gold nanoparticle can be imaged with detailed clarity even through the layer of carbon and silicon nitride support membrane.

10.4 Conclusion

In conclusion, new TEM chip based electrodes have been designed and fabricated using silicon nitride coated silicon TEM chips as the substrate support. These chips were patterned and etched out of single crystal silicon wafers using well established UV photolithography and anisotropic wet etching techniques. Gold nanowires were then placed on top of the silicon nitride membranes, further insulated and cut open using a FIB to expose a cross section of the nanowire. The gold nanowire electrode TEM chips have been demonstrated as viable platforms for single nanoparticle and SAM investigations. Alternatively, carbon was deposited onto the TEM chips forming an electroactive surface that was selectively patterned by a modified UV photolithography method. These carbon TEM chip electrodes have been demonstrated as viable platforms to perform single nanoparticle electrochemical detection and are also suitable to do HRTEM imaging of the nanoparticles on the carbon surface. Future work will include using the different TEM chip electrodes to perform environmental TEM studies where different phenomena can be studied in great detail. These studies can include electrochemical nucleation and nanoparticle growth or atomic rearrangement of nanoparticles when under an applied potential.

10.5 Figures

Figure 10.1 Silicon Wafer Patterning and Anisotropic Wet Etching

(A) Generalized schematic depicting the fabrication steps used to make the TEM chips from a single crystal silicon wafer where the wafer is patterned and anisotropically wet etched to release the chips. (B) is an optical image showing half of a single crystal wafer that has been patterned and etched where a few of the TEM chips remain loosely attached to the silicon wafer frame. (C) An SEM image of a single TEM chip showing the silicon nitride support window and that the size is approximately 3 mm in diameter.

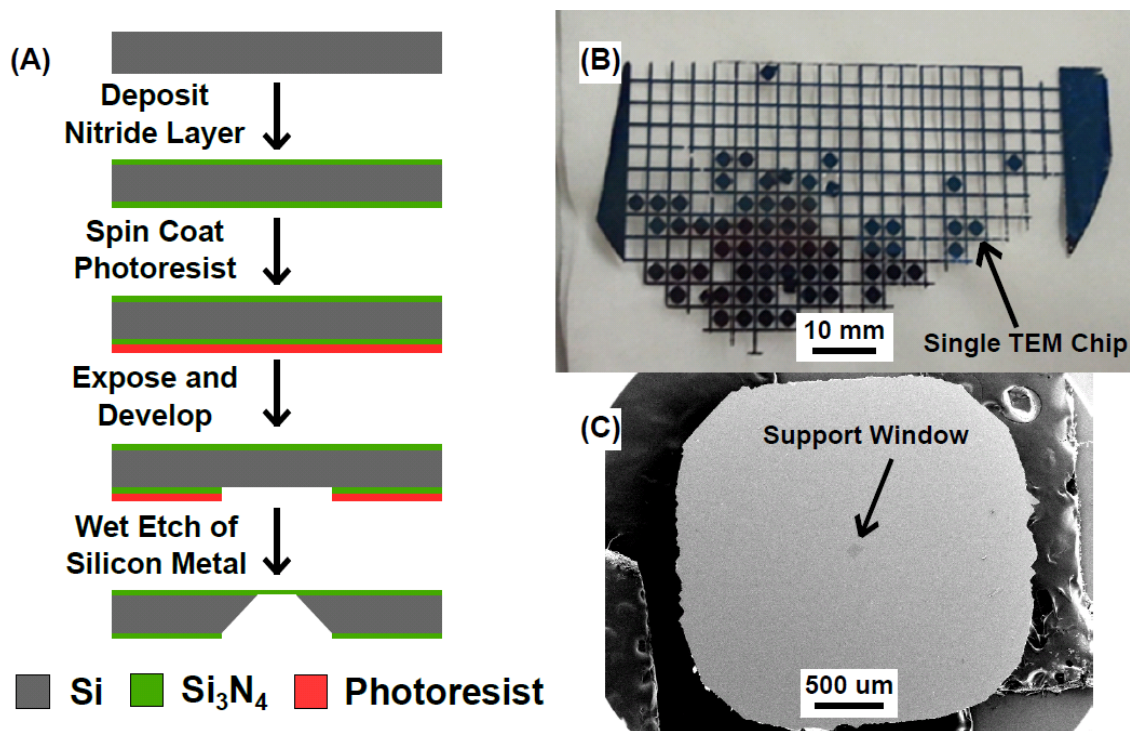


Figure 10.2 Gold Nanowire TEM Chip Electrode

(A) Schematic of the proposed Au nanoelectrode on a 3 mm TEM chip with a gold nanoparticle attached to the nanoelectrode at the center of the chip where an opening is cut into the Si_3N_4 window. (B) An SEM image of a Au nanoelectrode TEM chip that has been cut open using an FIB where the nanowire can be seen extending onto the silicon nitride window and C) SEM image of an exposed gold disk nanoelectrode viewed straight on.

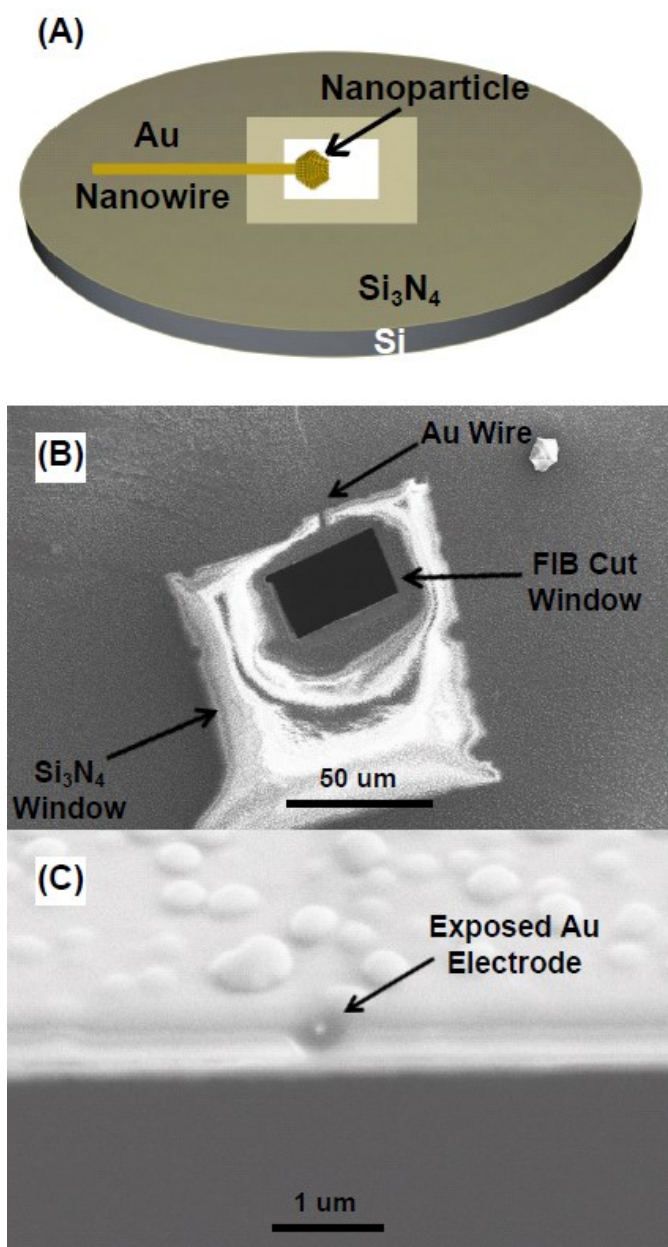


Figure 10.3 Gold Nanowire Nanoparticle Attachment and TEM Imaging

(A) CVs from a gold nanoelectrode TEM chip recorded before and after dithiol SAM and nanoparticle modification in $K_4Fe(II)(CN)_6$ with 1.5 M KCl supporting electrolyte at a 50 mV/s scan rate. (B) TEM image of the gold nanoparticle attached to the electrode that was tested in (A) and appears to have a single nanoparticle attached. (C) A TEM image of a larger nanoelectrode with multiple particles attached showing the ability to image the nanoparticles with very high resolution. (D) A highly magnified image of a single gold nanoparticle attached to a gold nanoelectrode where the interface between the electrode and nanoparticle is visible and is seen to be less than 1 nm.

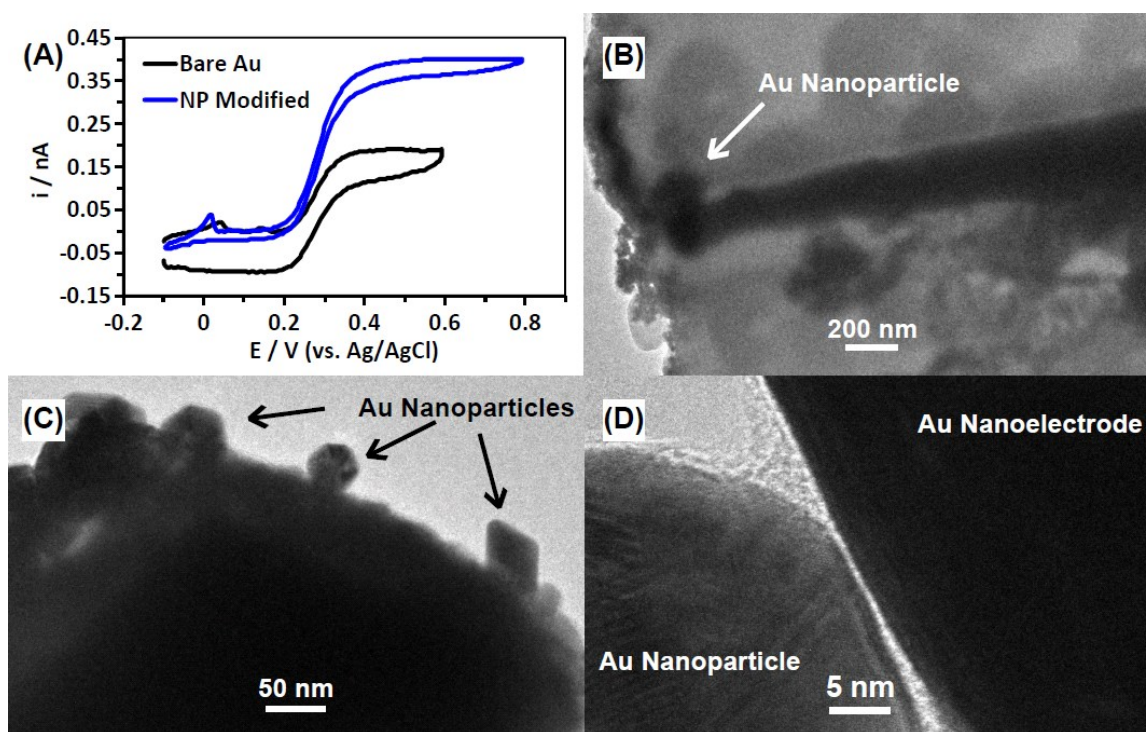


Figure 10.4 Carbon TEM Chip Electrode Selective Patterning and Characterization

(A) Generalized schematic showing the modified UV photolithographic procedure to selectively pattern the carbon electrode where the chip is exposed to the UV light from the backside allowing the light to transmit through the transparent silicon nitride window and exposing only the photoresist on top of the window. After development the carbon directly above the window will be uncovered leaving the rest insulated under the remaining photoresist. (B) SEM image of a typical carbon electrode TEM chip that has been selectively patterned where the thick photoresist layer can be seen and the exposed carbon is outlined by the red dashed square. (C) A magnified SEM image of the corner of the carbon electrode further showing the thick photoresist layer and the well-defined features from the patterning process.

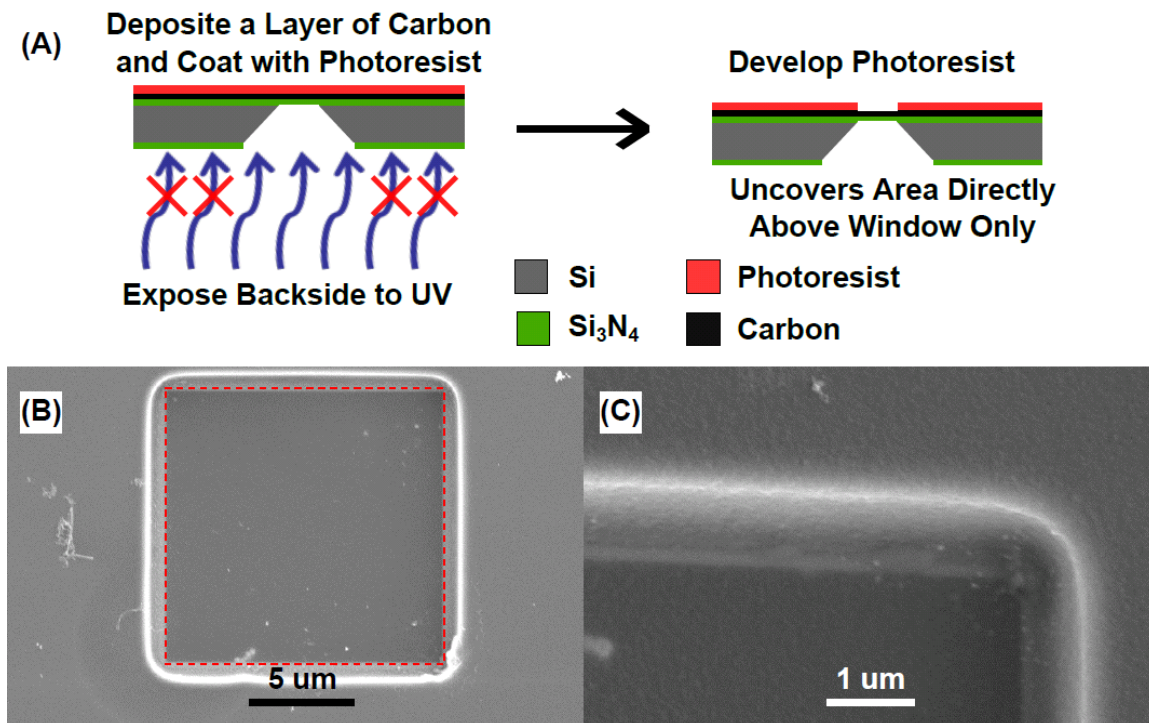
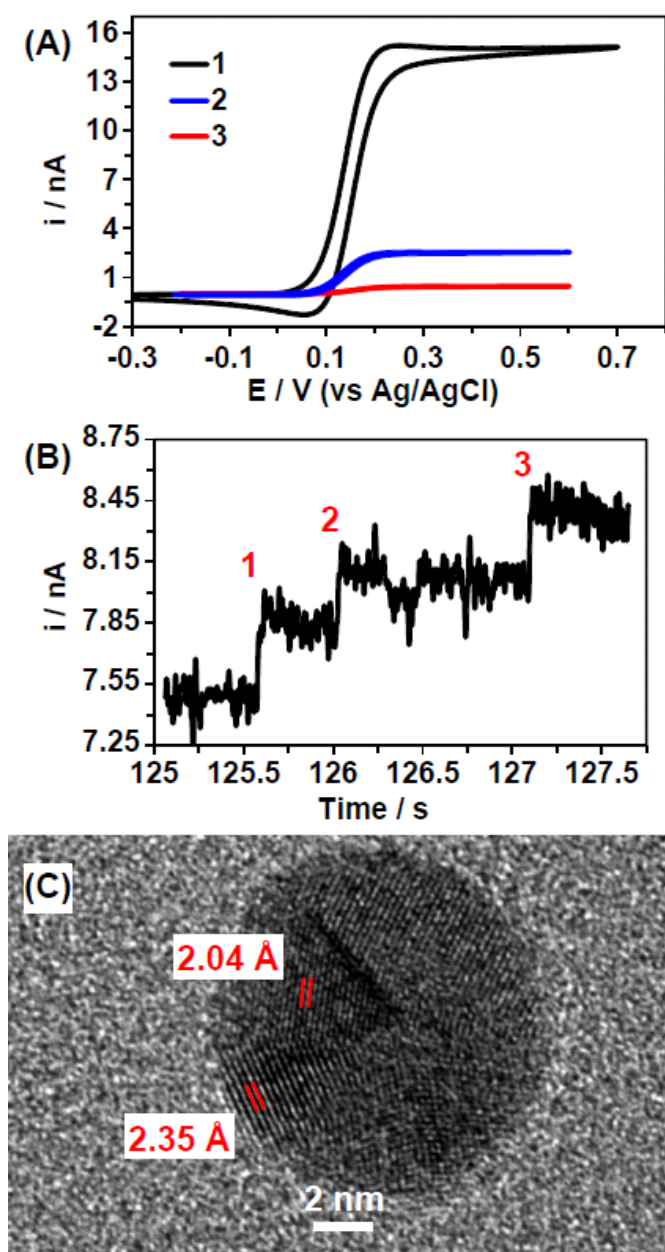


Figure 10.5 Carbon TEM Chip Voltammetric Response and Nanoparticle Detection

(A) CVs from three different sized carbon electrode TEM chips in 2 mM FcMeOH with 100 mM KCl supporting electrolyte at 50 mV/s scan rate. (B) Amperometric trace of a typical carbon TEM chip electrode in 10 mM N_2H_4 with 50 mM PB where three 30 nm platinum nanoparticle collision events are observed and labeled, marked by the sudden increase in current. (C) HRTEM image of a single gold nanoparticle on a carbon electrode where the nanocrystals atomic lattice is clearly visible, with the {100} and {111} crystal planes measured.



10.6 References

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Vitae

Stephen J. Percival was born and raised in Reno, Nevada. Throughout his life he had been interested in all aspects of science but finally, in his senior year of high school, decided to study chemistry where he found he was able to help other students who did not understand the material. Stephen received the Governor Guinn Millennium Scholarship from the State of Nevada which allowed him to attend Truckee Meadows Community College (TMCC) where he graduated with his Associates of Science. At TMCC he fortuitously took a math class and was placed into a group for a class project where he met and fell in love with his future wife, Tara. After attaining his Associates of Science, he then transferred to the University of Nevada, Reno (UNR) where he earned his Bachelor's degree in Professional Chemistry with a minor in Mathematics. Attending UNR opened his eyes to the world of chemistry research under his advisor Dr. Sean Casey and allowed him to experience first-hand the process of research. Stephen received an NSF EPSCoR undergraduate research fellowship which helped support him and allowed him to conduct research on "The Self Assembly Properties of Perylene Diimides". This presented further opportunity where he was asked to hold multiple positions as an undergraduate student Teaching Assistant at both TMCC and UNR where he again enjoyed helping students understand the intricacies of the chemical sciences. After experience in scientific research he knew he would not be satisfied ending his education with a bachelor's degree and decided to attend graduate school at the University of Washington, Seattle. Stephen and Tara moved to Seattle where he joined Bo Zhang's lab and has since been working on nanomaterial electrocatalysis and has mentored many undergraduate and graduate students, helping them learn the ins-and-outs of performing scientific research. After graduation, Stephen plans on continuing his work in the fields of electrochemistry, heterogeneous catalysis and nanotechnology.