CHARACTERIZATION OF WATER OXIDATION CATALYSTS FOR IMPLEMENTATION IN A DYE-SENSITIZED PHOTOELECTROSYNTHESIS CELL (DSPEC)

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ABSTRACT
Katherine E. Michaux: CHARACTERIZATION OF WATER OXIDATION CATALYSTS FOR IMPLEMENTATION IN A DYE-SENSITIZED PHOTOELECTROSYNTHESIS CELL (DSPEC)
(Under the direction of Royce W. Murray)

Chapter One is an introduction to solar energy conversion and the Dye-Sensitized Photoelectrosynthesis Cell (DSPEC). It goes into detail about the development of the individual parts of the DSPEC, including the semiconductor electrodes, photosensitizers and catalysts that have been implemented in similar devices. It then gives a brief history of the use of iridium oxide nanoparticles as water oxidation catalysts.

Chapter Two describes the film formation process for iridium oxide nanoparticles, focusing particularly on the electroflocculation technique. Studies were performed which determined the mechanism of electroflocculation, focusing on the short electroflocculation time periods. Three different electroflocculation methods – constant potential, potential pulsing and potential cycling – were implemented and the resulting iridium oxide nanoparticle films were compared electrochemically and microscopically. Electroflocculation was also compared to chemical flocculation and a direct pH change method of film formation.

Chapter Three is a general characterization chapter on iridium oxide nanoparticles, using a variety of analytical techniques to probe the structure, surface chemistry and reactivity of these nanoparticles. It probes the pH effect on electroflocculated NPs electrochemically and relates it to its reactivity as a water oxidation catalyst. UV-Vis spectroelectrochemistry of the iridium oxide nanoparticles is discussed and the individual spectra of each Ir oxidation state is presented. Raman spectroscopy of the freely diffusing iridium oxide nanoparticles and
electroflocculated nanoparticles demonstrates the increase in crystallinity via electroflocculation. SEM demonstrates the morphology of the electroflocculated films. Change in surface charge of the iridium oxide nanoparticles with respect to pH is depicted with zeta potential measurements. Finally, XPS of various forms of the iridium oxide nanoparticles shows the different forms of iridium within the nanoparticles, likely distinguished by surface and core iridium sites.

**Chapter Four** details the behavior of iridium oxide nanoparticles in organic media through a few different methods. First, the behavior of an electroflocculated iridium oxide nanoparticle film is examined in an aprotic solvent, as well as the changes in the electrochemical behavior when a proton source is added. A hot injection thermal degradation synthesis of iridium oxide nanoparticles is also explored. Exchange into organic media via valeric acid capping ligands is discussed. This leads to the ferrocenation of the iridium oxide nanoparticles using a Click reaction with a phosphate terminated ligand. Electrochemical tagging of the iridium oxide nanoparticles elaborates on the surface chemistry and diffusion coefficient in aprotic media.

**Chapter Five** explores a dip-coated layer-by-layer synthesis of a chromophore-catalyst photoanode assembly consisting of a Ru(II) polypyridal dye and iridium oxide nanoparticle catalyst. Preparation of Ru(II) polypyridyl-iridium oxide nanoparticle (IrO$_x$ NP) chromophore-catalyst assemblies on a FTO|nanoITO|TiO$_2$ core/shell by a layer-by-layer procedure is described for application in Dye Sensitized Photocathodes Cells (DSPEC). Significantly enhanced, bias-dependent photocurrents with Lumencor 455 nm 14.5 mW/cm$^2$ irradiation are observed for core/shell structures compared to TiO$_2$ after derivatization with [Ru(4,4’-PO$_3$H$_2$bpy)$_2$(bpy)]$^{2+}$ (RuP$_2$) and uncapped IrO$_x$ NPs at pH 1 and pH 5.8 in HClO$_4$ and NaSiF$_6$ buffers, respectively, with a Pt cathode. Photocurrents arising from photolysis of the resulting photoanodes,
FTO|nano|ITO|TiO$_2$|-RuP$_2$,IrO$_2$, are dependent on TiO$_2$ shell thickness and applied bias, reaching 0.2 mA/cm$^2$ at 0.5 V vs AgCl/Ag with a shell thickness of 6.6 nm. Long term photolysis in the NaSiF$_6$ buffer results in a marked decrease in photocurrent over time due to surface hydrolysis and loss of the chromophore from the surface. Long term stability, with sustained photocurrents, has been obtained by Atomic Layer Deposition (ALD) of overlayers of TiO$_2$ to stabilize surface binding of -RuP$_2$ prior to the addition of the IrO$_X$ NPs.

**Chapter Six** focuses on the electrochemical characterization of three novel Ru(II) quaterpyridine complexes and the assessment of their potential for benzyl alcohol oxidation catalysis. The terminal ligands for these complexes are varied between CH$_3$CN, Cl and vinyl pyridine. Their electrochemical behavior in acetonitrile and aqueous media are reported. When dissolved in aqueous media, an exchange of the CH$_3$CN ligands with H$_2$O allows the complexes to reach higher oxidation states, suggesting potential for water oxidation catalysis. Benzyl oxidation catalysis is also explored; two of the three complexes are catalysts for this reaction.
To my brother, Woody. Thanks for growing up with me and tolerating my older sibling abuse. This dissertation is for you and I can’t wait to read yours.
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<tr>
<td>A</td>
<td>Area of the Electrode</td>
</tr>
<tr>
<td>A (unit)</td>
<td>Ampere</td>
</tr>
<tr>
<td>Å</td>
<td>Angstrom</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
</tr>
<tr>
<td>AgBF₄</td>
<td>Silver Tetrafluoroborate</td>
</tr>
<tr>
<td>Ag/AgCl</td>
<td>Silver/Silver Chloride Reference Electrode</td>
</tr>
<tr>
<td>ALD</td>
<td>Atomic Layer Deposition</td>
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<tr>
<td>Al₂O₃</td>
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<td>Gold</td>
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<tr>
<td>BDD</td>
<td>Boron Doped Diamond Electrode</td>
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<td>BF₄⁻</td>
<td>Tetrafluoroborate Anion</td>
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<td>bpy</td>
<td>2,2’-bipyridine</td>
</tr>
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<td>BTU</td>
<td>British Thermal Unit</td>
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<tr>
<td>C</td>
<td>Carbon, Elemental</td>
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<td>DPV</td>
<td>Differential Pulse Voltammetry</td>
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<tr>
<td>DSA</td>
<td>Dimensionally Stable Anode</td>
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<td>Fe_2O_3</td>
<td>Iron Oxide</td>
</tr>
<tr>
<td>Fe_3O_4</td>
<td>Iron Oxide</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>-------------</td>
</tr>
<tr>
<td>FTO</td>
<td>Fluorine-Doped Tin Oxide</td>
</tr>
<tr>
<td>FTO</td>
<td>nanoITO</td>
</tr>
<tr>
<td>Ga</td>
<td>Gallium</td>
</tr>
<tr>
<td>GaP</td>
<td>Gallium Phosphide</td>
</tr>
<tr>
<td>GC</td>
<td>Glassy Carbon Electrode</td>
</tr>
<tr>
<td>H⁺</td>
<td>Proton</td>
</tr>
<tr>
<td>H₂</td>
<td>Hydrogen, Molecular</td>
</tr>
<tr>
<td>HClO₄</td>
<td>Perchloric Acid</td>
</tr>
<tr>
<td>HER</td>
<td>Hydrogen Evolution Reactoin</td>
</tr>
<tr>
<td>HNO₃</td>
<td>Nitric Acid</td>
</tr>
<tr>
<td>HPT</td>
<td>Hydride Proton Transfer</td>
</tr>
<tr>
<td>hr</td>
<td>Hour</td>
</tr>
<tr>
<td>hr⁻¹</td>
<td>Inverse Hour</td>
</tr>
<tr>
<td>H₂O</td>
<td>Water</td>
</tr>
<tr>
<td>H₂O₂</td>
<td>Hydrogen Peroxide</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest Occupied Molecular Orbital</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>Sulfuric Acid</td>
</tr>
<tr>
<td>H₂PO₃</td>
<td>Phosphonic Acid</td>
</tr>
<tr>
<td>H₃PO₄</td>
<td>Phosphoric Acid</td>
</tr>
<tr>
<td>H₂PO₄⁻</td>
<td>Monobasic Phosphate Anion</td>
</tr>
<tr>
<td>HPO₄⁻²</td>
<td>Dibasic Phosphate Anion</td>
</tr>
<tr>
<td>PO₄³⁻</td>
<td>Tribasic Phosphate Anion</td>
</tr>
<tr>
<td>i_c</td>
<td>Catalytic Current</td>
</tr>
</tbody>
</table>
$i_L$  Limiting Current for a Catalytic Reaction

$i_{\text{lim}}$  Limiting Current for a Microelectrode CV Experiment

$i_p$  Peak Current

$I_{\text{SS}}$  Steady-State Current

$\text{In}$  Indium

$iR$  Current Times Resistance

$\text{Ir}$  Iridium, Elemental

$\text{Ir}^{\text{III}}$  Iridium (III) Oxidation State

$\text{Ir}^{\text{IV}}$  Iridium (IV) Oxidation State

$\text{Ir}^{\text{V}}$  Iridium (V) Oxidation State

$\text{Ir}^{\text{VI}}$  Iridium (VI) Oxidation State

$\text{Ir}^{\text{IV/III}}$  Iridium 3+, 4+ redox couple

$\text{Ir}^{\text{V/IV}}$  Iridium 4+, 5+ redox couple

$\text{Ir} \, 4f_{5/2}$  Iridium 4f\textsubscript{5/2} Electron Orbital

$\text{Ir} \, 4f_{7/2}$  Iridium 4f\textsubscript{7/2} Electron Orbital

$\text{Ir(acac)}_3$  Iridium Acetylacetonate

$[\text{IrCl}_6]^{-2}$  Iridium(IV) Chloride Anion

$\text{IrO}_x$  Iridium Oxide Nanoparticles

$\text{IrO}_x \cdot n\text{H}_2\text{O}$  Hydrated Iridium Oxide Nanoparticles

$\text{IrO}_2$  Iridium Oxide, Bulk Material

$[\text{Ir(OH)}_6]^{-2}$  Iridium(IV) Hydroxide Anion

$\text{ITO}$  Tin-doped Indium Oxide

$j$  Current Density

xxxiv
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>( j_0 )</td>
<td>Exchange Current Density</td>
</tr>
<tr>
<td>( k )</td>
<td>Boltzmann Constant in J/K</td>
</tr>
<tr>
<td>( k_{\text{cat}} )</td>
<td>Catalytic Rate Constant</td>
</tr>
<tr>
<td>( k_{\text{obs}} )</td>
<td>Observed Rate Constant</td>
</tr>
<tr>
<td>( \text{K}_2\text{IrCl}_6 )</td>
<td>Potassium hexachloroiridate</td>
</tr>
<tr>
<td>( \text{L} )</td>
<td>Liter</td>
</tr>
<tr>
<td>( \text{LED} )</td>
<td>Light Emitting Diode</td>
</tr>
<tr>
<td>( \text{LUMO} )</td>
<td>Lowest Unoccupied Molecular Orbital</td>
</tr>
<tr>
<td>( \text{M} )</td>
<td>Molar (mol/L)</td>
</tr>
<tr>
<td>( \text{mA} )</td>
<td>Milliamp</td>
</tr>
<tr>
<td>( \text{mC} )</td>
<td>Millicoulomb</td>
</tr>
<tr>
<td>Mebimpy</td>
<td>2,6-bis(1-methylbenziidazol-2-yl)pyridine</td>
</tr>
<tr>
<td>( \text{MeCN} )</td>
<td>Acetonitrile</td>
</tr>
<tr>
<td>( \text{mg} )</td>
<td>Milligram</td>
</tr>
<tr>
<td>( \text{MgSO}_4 )</td>
<td>Magnesium Sulfate</td>
</tr>
<tr>
<td>( \text{MHz} )</td>
<td>Megahertz</td>
</tr>
<tr>
<td>( \text{min} )</td>
<td>Minute</td>
</tr>
<tr>
<td>( \text{mL} )</td>
<td>Milliliter</td>
</tr>
<tr>
<td>( \text{mM} )</td>
<td>Millimolar (mmol/L)</td>
</tr>
<tr>
<td>( \text{mmol} )</td>
<td>Millimole</td>
</tr>
<tr>
<td>( \text{mol} )</td>
<td>Moles</td>
</tr>
<tr>
<td>( \text{mV} )</td>
<td>Millivolt</td>
</tr>
<tr>
<td>( \text{mW} )</td>
<td>Milliwatt</td>
</tr>
</tbody>
</table>
n  Number of Electrons

\( n_c \)  Number of Electrons Involved in the Catalytic Reaction

\( n_p \)  Number of Electrons Involved in the Peak Reaction

N  Number of Moles

\( N_2 \)  Nitrogen, Molecular

Na  Sodium

NaHCO₃  Sodium Bicarbonate

NaN₃  Sodium Azide

nanoITO  Nanoscopic Tin-Doped Indium Oxide Films

NaOH  Sodium Hydroxide

Na₂SiF₆  Sodium Hexafluorosilicate

\((\text{NH}_4)_2\text{Ce(NO}_3)_6\)  Cerium Ammonium Nitrate

NHE  Normal Hydrogen Electrode

Ni  Nickel

NiO  Nickel Oxide

\( N_3\text{IrO}_x \)  Iridium Oxide Nanoparticles with Azide Terminated Capping Ligand

nm  Nanometer

NP  Nanoparticles

O  Oxygen, Elemental

O₂  Oxygen, Molecular

OER  Oxygen Evolution Reaction

Os  Osmium

PCET  Proton Coupled Electron Transfer
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEC</td>
<td>Photoelectrolysis Cell</td>
</tr>
<tr>
<td>PhCHO</td>
<td>Benzaldehyde</td>
</tr>
<tr>
<td>PhCHOH</td>
<td>Benzyl Alcohol</td>
</tr>
<tr>
<td>pic</td>
<td>Picoline</td>
</tr>
<tr>
<td>PMAA</td>
<td>Poly(methacrylic acid)</td>
</tr>
<tr>
<td>PO₄⁻³</td>
<td>Phosphate Anion</td>
</tr>
<tr>
<td>POCl₃</td>
<td>Phosphoryl Chloride</td>
</tr>
<tr>
<td>PSII</td>
<td>Photosystem II</td>
</tr>
<tr>
<td>Pt</td>
<td>Platinum</td>
</tr>
<tr>
<td>Q</td>
<td>Charge in coulombs</td>
</tr>
<tr>
<td>QCM</td>
<td>Quartz Crystal Microbalance</td>
</tr>
<tr>
<td>qpy</td>
<td>Quaterpyridine</td>
</tr>
<tr>
<td>r</td>
<td>Hydrodynamic Radius of a Nanoparticle</td>
</tr>
<tr>
<td>r₀</td>
<td>Radius of a Microdisk Electrode</td>
</tr>
<tr>
<td>R</td>
<td>Gas Constant in J/mol K</td>
</tr>
<tr>
<td>Rh</td>
<td>Rhodium</td>
</tr>
<tr>
<td>RHE</td>
<td>Reversible Hydrogen Electrode</td>
</tr>
<tr>
<td>RMS</td>
<td>Root Mean Square</td>
</tr>
<tr>
<td>rpm</td>
<td>Rotations Per Minute</td>
</tr>
<tr>
<td>RRDE</td>
<td>Rotating Ring Disk Electrode</td>
</tr>
<tr>
<td>RT</td>
<td>Room Temperature (ca. 25 °C)</td>
</tr>
<tr>
<td>Ru</td>
<td>Ruthenium</td>
</tr>
<tr>
<td>RuO₂</td>
<td>Ruthenium Oxide</td>
</tr>
</tbody>
</table>
RuP₂

[\text{Ru}(4,4'\text{-PO}_3\text{H}_2\text{bpy})_2(bpy)]^{2+}

s

Second

[S]_{\text{bulk}}

Concentration of Substrate in Bulk Solution

SAM

Self-Assembled Monolayer

SEM

Scanning Electron Microscopy

Si

Silicon

SIROF

Sputtered Iridium Oxide Films

SnO₂

Tin Oxide

Sn:In₂O₃

Tin-Doped Indium Oxide (ITO)

T

Temperature

TBAOH

Tetrabutylammonium Hydroxide

TBAP

Tetrabutylammonium Perchlorate

TBAPF₆

Tetrabutylammonium Hexafluorophosphate

TDMAT

Tetrakis(dimethylamido)titanium

TEM

Transmission Electron Microscopy

TFA

Trifluoroacetic Acid

THF

Tetrahydrofuran

Ti

Titanium

TiO₂

Titanium Dioxide

TO

Turnover

trpy

2,2'6',2''-terpyridine

UV-Vis

Ultraviolet-Visible Spectroscopy

V

Volts
VP  Vinyl Pyridine
WE  Working Electrode
WO₃  Tungsten Oxide
WOC  Water Oxidation Catalyst
XANES  X-Ray Absorption Near Edge
XAS  X-Ray Absorption Spectroscopy
XPS  X-Ray Photoelectron Spectroscopy
vs.  Versus
ZnO  Zinc Oxide
α  Transfer Coefficient
Γ_{cat}  Coverage of Catalyst
Γ_{Ir}  Coverage of Iridium in mol/cm²
ΔE_p  Difference in Potential of the Oxidative and Reductive Peak for a Redox Couple
ΔG  Gibbs Free Energy
η  Viscosity in cP
µA  Microamp
µg  Microgram
µL  Microliter
µm  Micrometer
µM  Micromolar
ν  Scan Rate
ω  Rotation Rate
% w/w  Percent weight by weight
°C Degrees Celsius
CHAPTER 1: Introduction to the Dye-Sensitized Photoelectrolysis Cell (DSPEC)

1.1 SOLAR ENERGY AS A RENEWABLE SOURCE

Over the past few decades, the global energy demand has significantly increased due to growing economies, advances in technology and increased access to that technology. Figure 1.1, from the International Energy Outlook of 2013 published by U.S. Energy Information Administration, depicts this trend and further predicts how this demand will increase through 2040.\(^1\) There is need for a renewable efficient energy source to meet this perpetually increasing demand.

Research has focused on developing and improving renewable energy sources, such as wind, hydroelectric and solar energy sources. As almost 600 quadrillion BTU hits the earth’s surface every hour directly from the sun, improving solar energy conversion techniques to harvest this energy has been a major focus of current research. Photovoltaic devices are the current technology that has reached commercial use. However, their use of semiconductor material limits the maximum efficiency at which these devices can function. This limit is based on the Shockley-Quiesser limit, and the maximum efficiency of a silicon photovoltaic device is ca. 29%.\(^2\) Most modern photovoltaic cells are close to achieving this value. On top of this, they also present the dilemma of their electrical output being directly proportional to the influx of sunlight. As the majority of energy consumption occurs at times after the sun has set, a method of storing this energy must also be obtained.
Battery materials have been proposed as a storage method for solar energy. Most recently, Tesla Motors announced the production of at-home versions of their car batteries, Powerwall©, that can pair with photovoltaic materials for solar energy storage. However, the materials for such high power density batteries can become quite expensive. Batteries are also prone to losing their charging and discharging ability over time, largely due to loss of structural integrity of the cathodes and anodes. An alternative to this is to use a different method of storing solar energy, by mimicking plants and storing this energy in chemical bonds, as is done in photosynthesis.

One of the most sought after reactions for storing energy in chemical bonds is the splitting of water into molecular oxygen and hydrogen. Per its mass, hydrogen has one of the highest energy densities of any molecule. As a fuel, it has the added benefit of producing water as its only side product, eliminating the production of greenhouse gases. Generating hydrogen from the splitting of water involves two half reactions: the oxidation of water to oxygen gas and protons and the reduction of those protons to hydrogen gas. The major obstacle in this reaction is the large activation energy of water oxidation required in the thermodynamically uphill

![Figure 1.1: Annual global energy demand by decade since 1990, as well as the predicted increase over the next 35 years.](image)
reaction. While the free energy change ($\Delta G$) of this reaction corresponds to 1.23 eV, an energy within the solar spectrum, it often requires more energy (i.e. overpotential, $\eta$) due to a large kinetic obstacle from the multielectron process. This large overpotential results in a need for either a semiconductor with a large enough band gap energy to compensate for this increase in energy requirement or a catalyst to lower the overpotential of the water oxidation reaction.

The semiconductor requirements for water splitting involve a large band gap energy, a conduction band energy with a potential more negative than the formal potential ($E^0$) of the $H^+/H_2$ reaction and a valence band energy with a potential more positive than the formal potential of the $O_2/H_2O$ reaction. One such material that fits these requirements is TiO$_2$, which has a band gap of ca. 3 eV. In 1972, Honda and Fujishima first demonstrated solar water splitting via illumination of a TiO$_2$ semiconductor photoanode coupled with a Pt cathode.$^4$ However, the conduction band of TiO$_2$ is just barely more negative than that of the proton reduction reaction, which leads to slow overall water splitting. Finding a semiconductor material that is efficient and stable in the conditions for both the oxygen evolution reaction (OER) and the hydrogen evolution reaction (HER) has been a challenge. Because of this, dual band gap cells have been explored, where a p-type semiconductor material is combined with an n-type semiconductor material to more efficiently split water.$^2$ The use of two different semiconductor materials in one cell with complementary band gaps to absorb different regions of the solar spectrum results in an increase of overall efficiency of these devices.
The development of photocathode semiconductor materials has largely focused on phosphide, sulfide, telluride and selenide materials, consisting of various ratios of Ga, Cd and In. This focus is due to their conduction band being sufficiently negative, as shown in Figure 1.2. Due to the large overpotential, the addition of a Pt catalyst to the semiconductor/liquid interface has been implemented. It was found that using catalytic metal particles, instead of a metal film, improved efficiency for H₂ production, likely because a continuous metal film blocks light absorption by the semiconductor. By limiting the coverage of the catalyst to island-like structures, the electrode material is essentially transparent.

Conversely, photoanode semiconductor materials for water oxidation have been largely oxide based. The valence band on these materials consist of O 2p orbitals, with the valence orbitals of the metals serving as the conduction band. Because of this, the valence band of these materials are all very similar, while the conduction band is varied based on which metal ions are present; examples include TiO₂, Fe₂O₃, WO₃ and ZnO (Figure 1.2).
band energies tend to be significantly higher than the OER potential, the excess energy that is absorbed escapes via thermal relaxation, resulting in poor efficiency.

Unassisted solar water splitting has been widely reported using a combination of the n-type TiO$_2$ semiconductor electrode combined with the p-type GaP.$^{16,17,18,19,20}$ Efficiencies up to 1% were reported, largely due to the instability of the p-GaP photocathode. These were all examples of some of the first photoelectolysis cells (PEC). Combination of a PEC device with a photovoltaic (PV) device has also been explored, where the light that isn’t absorbed by the PEC semiconductor is instead absorbed by the PV. This provides a bias that is required to split water.$^{21}$

In a similar manner, Grätzel combined a dye-sensitized solar cell (DSSC) with a WO$_3$ photoanode to increase efficiency.$^{22,23,24}$ DSSC devices generally contain a high surface area semiconductor, such as TiO$_2$, with dyes bound to the surface to absorb light and inject the resulting excited electron into the semiconductor material. This, in turn, can create a bias which is sufficient to split water. By implementing a molecular dye, DSSC devices incorporate a material with a tunable absorption.$^{25}$ It is difficult to control the band gap energies of metal oxide semiconductor materials. Organometallic complexes, however, have much greater tunability, as changing the metal center and surrounding ligands can adjust the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO). Manipulating the structure of these complexes or organic dyes can be seen as the equivalent of changing the band gap of the semiconductor material. With the addition of a dye, the absorption characteristic of the device can be shifted towards the visible region of the solar spectrum and the need for an external bias can be decreased or eliminated.$^{26}$
DSSC devices have other advantages as well. The implementation of the dye splits the duties of the semiconductor material. The dye serves the purpose of absorption, while the semiconductor electrode’s sole responsibility is charge separation of the injected electron and the resulting holes. Most DSSC devices implement a high surface area, mesoporous semiconductor structure, which results in high loading of the dye, and use TiO$_2$ as their base, which is a relatively cheap material, reducing cost of the overall device. Because of this, they also are simple to fabricate, lightweight and are flexible in design. The use of a dye attached to mesoporous semiconductor base has also been applied to the photocathode as well, with NiO serving as the base. The combination of both an n-type DSSC with a p-type DSSC has also been explored for its advantages. By manipulating the absorption of each dye molecule so that they’re complementary to each other, the theoretical maximum efficiency is greater than 40%, significantly higher than a single device. Currently, the efficiency is much less ideal, but strides have been made to further improve the function of these devices.

While strides have been made to improve the stability and efficiency of photoanode and cathode materials for water splitting, the large overpotentials required, especially for water oxidation, result in higher energy requirements needed for water splitting. To reduce these high overpotentials, electrocatalysts have been added on the surfaces of both semiconductor electrodes. Pt has proven to be the ideal electrocatalyst for the HER, with a low overpotential of 50 mV at 10 mA/cm$^2$. Electrocatalysts for the OER have proven to be more elusive; some examples of these are discussed in Section 1.4. The DSSC, when combined with electrocatalysts for water oxidation and reduction, leads to the development of the Dye-Sensitized Photoelectrosynthesis Cell (DSPEC), discussed below.
1.2 **The Dye-Sensitized Photoelectrosynthesis Cell (DSPEC)**

The Dye-Sensitized Photoelectrosynthesis Cell (DSPEC) was originally proposed by Thomas J. Meyer in 2005. The goal of these devices is to take common resources, such as \( \text{H}_2\text{O} \) and \( \text{CO}_2 \) and yield a fuel entirely from sunlight to store solar energy for later use. This device consists of two semiconductor electrodes with chromophore catalyst assemblies, as pictured in Figure 1.3. At the photoanode, a chromophore is excited via sunlight and injects an excited electron into the semiconductor material. The chromophore then oxidizes the catalyst, attached by a bridging ligand, which in turn oxidizes water to \( \text{O}_2 \) and \( \text{H}^+ \). The protons then travel across a membrane to the photocathode, where they are reduced to some type of fuel by another chromophore-catalyst assembly. The fuel that is produced can be manipulated based on what catalyst is present at the cathode. Examples include \( \text{H}_2 \), \( \text{CH}_4 \), \( \text{CH}_3\text{OH} \) and \( \text{CH}_3\text{CH}_2\text{OH} \). The example shown in Figure 1.3 illustrates the flow of electrons throughout the device, from the

![Diagram of DSPEC](image)

**Figure 1.3:** Schematic of the Dye-Sensitized Photoelectrosynthesis Cell, where sunlight is used to oxidize water and use the resulting protons to reduce \( \text{CO}_2 \) to \( \text{CH}_4 \).
excitation of the photoanode chromophore over to the photocathode, where the catalyst specifically reduces CO$_2$ and H$^+$ to form CH$_4$.

DSPEC devices are very similar in structure to the DSSC devices discussed above. They both consists of the mesoporous semiconductor material for high surface area electrodes, as well as high loading concentrations of each dye. The major difference between the two is the addition of electrocatalysts at both the photoanode and photocathode in the DSPEC. DSSC devices use an electron mediator in order to regenerate the ground state of each dye. In a DSPEC, the catalyst is responsible for regenerating the ground state of the dye. On the photoanode side of the device, the catalyst reduces the chromophore back to its ground state by donating an electron. After successive electron donations, the catalyst then oxidizes the desired reagent, in this case water, to form molecular O$_2$ and H$^+$. This dependence on the catalyzed reaction to regenerate the chromophore is what distinguishes the DSPEC from the DSSC.

There are major challenges to be overcome on both sides of the DSPEC device, including efficient absorption by the chromophore, limiting back electron transfer within the system, photoanode and photocathode stability and lowering the overpotential required for both the cathodic and anodic reactions. As the topic of this dissertation focuses on the photoanode half of this device, this introduction will focus on the development of that half of the device.

1.3 THE PHOTOANODE

There are many requirements for the photoanode and its individual parts that must be met, in order for the DSPEC device to function and split water. The first condition is relatively obvious: the semiconductor electrode, photosensitizer dye and water oxidation catalyst must all be photo- and electrochemically stable under the conditions of the
device. This is easier said than done, as the stability conditions for the dye can be very different than those for the catalyst and the semiconductor material. The second requirement is that the sensitizer must absorb in the visible part of the solar spectrum, in order to maximize how much of the light is going to towards water splitting and not waste. Ideally, the dyes would be fixed to the semiconductor surface by a linker that is stable under aqueous conditions. Finally, the HOMO and LUMO of the dye must be at sufficient energies for the flow of electrons that is required for water oxidation in this setup. The HOMO must be at a potential more positive than of the onset of water oxidation for the particular catalyst it is paired with. Conversely, the LUMO energy level must be more negative than the conduction band of the semiconductor in order to be able to inject excited electrons.

Examples of some popular chromophores in the literature that have been utilized in DSSC and DSPEC devices are featured in Figure 1.4.26 All of these dyes incorporate highly conjugated pi systems for efficient molecular absorption in the UV-Visible region of the solar spectrum and then electron transfer into the desired semiconductor surface. Most of the dyes consist of polypyridal ligands paired with Ru centers and are derivatized from [Ru(bpy)₃]²⁺, a gold standard for a chromophore in these types of devices. Most importantly, all of these photosensitizers have a linker which can anchor them to the metal oxide semiconductor surface. The linkers are generally either carboxylic acid or phosphonic acid groups, which are known to interact with metal oxide surfaces. Carboxylic acids are generally considered a weaker interaction than the phosphonic acid groups, which form covalent bonds with metal oxide surfaces. Phosphonic acid groups, however, are prone to hydrolysis attack as pH increases.51 Because of this, significant research has been focused on ways to further stabilize the chromophore linkage to the semiconductor surface, especially in higher pH media, where the
thermodynamic potential of water oxidation is shifted to more negative potentials and should require less potential bias to proceed.

Figure 1.4: Examples of the structures of commonly used chromophores for DSSC and DSPEC devices.

Stabilization of these linkers has been thoroughly explored. One proposed method is to cover the chromophore with an electronically and ionically conductive material, such as Nafion or other electropolymerized films. Modifying the ligands of the chromophores to include vinyl groups is another method. When the potential of an electrode is cycled with these chromophores
freely diffusing in solution, the vinyl groups will polymerize and form a film on the electrode surface, stabilizing the chromophore in the process.\textsuperscript{53,54,55,56,57} More recently, physically blocking the anchoring group with a metal oxide material, such as Al\textsubscript{2}O\textsubscript{3} or TiO\textsubscript{2}, has been explored.\textsuperscript{58,59,60,61,62,63,64,65,66,67} Atomic layer deposition was implemented in order limit the metal oxide film growth to less than 1 nm in thickness. By limiting film growth to this thickness, the linker is covered, but not the entire chromophore, in order to maintain both the maximum absorption and ET to the catalyst. These thin films have shown promise is stabilizing phosphonic acid groups at pH values up to 13.\textsuperscript{68}

Improvements in the semiconductor electrode have also been made by altering the structure. Nanostructured semiconductors, such as rods, have shown enhancement in photocurrent.\textsuperscript{69,70} This is due to the decreased path length for the excited electron to travel from injection to the conductive circuit. Because this is shorter, there is less chance of recombination.\textsuperscript{3} Core/shell electrodes have also been developed, which involve a thin semiconductor shell surrounding a conductive core.\textsuperscript{71,72} This maintains the high surface area of the mesoporous titania with nanostructured optically transparent conductive materials such as tin-doped indium oxide.\textsuperscript{74} The thin semiconductor layer limits back electron transfer to the dye and improves electron injection into the circuit.

\textbf{1.4 Catalysts for Water Oxidation}

Choosing the right catalyst for water oxidation is imperative for improving the overall efficiency for a DSPEC device. One of the major hurdles in developing an effective device is the overpotential required for water oxidation. A higher overpotential results in an increase in the energy required for reaction to proceed, meaning less of the solar spectrum can be employed. By implementing a water oxidation catalyst with a lower overpotential, light with longer
wavelengths, i.e. in the visible region and near IR region, have the potential to be used to split water. This improves the solar energy conversion efficiency, as more of the solar spectrum can be applied towards water splitting.

There are two major requirements for an efficient water oxidation catalyst. The first is that it must be able to create a sufficient amount of O$_2$, at a low overpotential, i.e. this reaction should occur at the rate at which the chromophore is injecting electrons into the semiconductor electrode. This means electron transfer must be fast between the chromophore and catalyst and within the catalyst to oxidize water. The other condition is that the catalyst must be photo- and electrochemically robust under the conditions of water oxidation for extended periods of time. Both molecular, homogeneous catalysts and heterogeneous catalysts have been explored. This dissertation delves into the characterization of IrO$_X$ NPs, a heterogeneous water oxidation catalyst, and three new Ru polypyridal complexes, which have shown potential as water oxidation catalysts.

1.4.1 Homogeneous Catalysts

Originally, catalysts for water oxidation were synthesized to structurally mimic Photosystem II (PSII), the main player in natural photosynthesis that produces oxygen gas (O$_2$). In this system, O$_2$ is generated from splitting water molecules. H$_2$O is oxidized by manganese sites within the complex that are bonded together by μ-oxo bridges. Using this as an inspiration, various mono-, di-, tri- and tetrametallic complexes have been suggested as catalysts using ruthenium, manganese, rhodium, osmium and iridium metal centers. They have polypyridal ligands, such as bipyridine, tripyridine, and phenanthroline which are good oxidizers due to their ability to accept electrons in the conjugated pi system and transfer them to the metal centers. Some of the more prominent molecular catalysts are featured in Figure 1.5.
All of these molecular catalysts consist of a metal center that can access high oxidation states, such as 4+, 5+ or higher. These high oxidation states are required for water oxidation catalysis. Organometallic complexes which cannot access these states have repeatedly shown lack of catalytic activity. A relatively new trend in research has been to synthesize seven coordinate Ru complexes, where there is an open site on the metal center that can react with H₂O. Licheng Sun et al. has observed fast water oxidation rates with Ce(IV) as a chemical oxidant with complexes with this structure, seen in the top two complexes in Figure 1.5, although
their stability as a monomer has been questioned. Ir complexes, such as the one in the middle of Figure 1.5, have also shown promise as water oxidation catalysts. However, their stability is limited and they have shown to decompose into the heterogeneous water oxidation catalyst, iridium oxide nanoparticles (IrO\(_x\) NPs).\(^{75,76,88}\)

The most successful molecular water oxidation catalysts developed have largely consisted of precious metal centers, such as Ru, Rh, Ir and Os. However, there has been a push recently to explore complexes derived of first row transition metals, such as Co, Cu, Ni and Fe, in order to reduce the cost of the DSPEC devices.\(^{94,95,96,97,98,99,100}\) The Meyer laboratory, in particular, has had luck with Co, Cu and Fe complexes showing water oxidation electrocatalytic properties. The overpotentials for these complexes, however, need to be much higher than their Ru complex equivalent in order to observe the same rate of activity.

**1.4.2 Metal Oxide Heterogeneous Catalysts**

While these systems are able to catalyze the water oxidation reaction, they are complex to synthesize, requiring multiple step syntheses, especially in the case of the tri- and tetrametallic complexes. An alternative and still effective catalyst choice is a metal oxide heterogeneous catalyst. Due to the high density of oxygen sites on the surface of these materials, they have a propensity towards water oxidation catalysis. However, it has been found that not all metal oxides catalyze water oxidation to the same extent. Rasiyah and Tseung proposed in 1984 that redox potentials for the metal oxidation states in the materials affect their ability to effectively oxidize water.\(^{101}\) Those whose redox potentials closely aligned with the formal potential of the water oxidation reaction would have the highest activity. They were able to establish a linear relationship between the redox couple potentials of the metal oxide catalysts and the overpotential required for water oxidation catalysis. A volcano plot, depicted in Figure 1.6, demonstrates the relationship between the overpotential required for water oxidation catalysis
and the metal-oxygen bond strength at the surface of these materials. Essentially, there is a minimum overpotential reached with the materials whose metal-oxygen bond strength is ca. -100 kJ/mol, with the ideal materials being RuO$_2$ and IrO$_2$. For those materials whose bond strength is more positive than the maximum, the materials are less readily oxidized, thereby increasing the overpotential required for water oxidation. Those with more negative bond strengths are very easily oxidized, which results in an abundance of the absorbed intermediate and thus an increased overpotential.

While less expensive materials, such as Co$_3$O$_4$, NiO$_2$ and Fe$_2$O$_3$ have been explored as water oxidation catalysts, they have yet to achieve comparable activity to their more expensive counterparts. Both IrO$_2$ and RuO$_2$ are currently used as commercially available dimensionally stable anodes (DSAs), where they are thermally deposited onto a metal.

Figure 1.6: “Volcano plot”, developed by S. Trasatti, relating the metal-oxygen bond strength of each material to the overpotential required for water oxidation catalysis.
oxide semiconductor, such as TiO$_2$ or SnO$_2$. Both IrO$_2$ and RuO$_2$ bulk materials have the advantage of being highly reactive, especially in acidic media, but RuO$_2$ in particular can have stability issues at high overpotentials and in more alkaline solutions. To make the film more stable, RuO$_2$ can be mixed with IrO$_2$ or deposited at higher temperatures to form a more crystalline structure. As a film becomes more crystalline, however, the number of exposed active catalytic sites decreases due to decreased surface area, resulting in a decrease in catalytic activity. In this respect, increasing the active surface area of the film should increase the catalytic activity, thus giving rise to the contribution of nanoscience – most specifically iridium oxide nanoparticles – in the area of water oxidation research.

1.5 Iridium Oxide Nanoparticles

Iridium oxide nanoparticles (IrO$_x$ NPs), both freely diffusing and deposited as films, have been explored as electrocatalysts for water oxidation and have proven to be very efficient. In a study performed by Yagi et al., the electrocatalytic effects on water oxidation of colloidal IrO$_x$ nanoparticles (50 – 100 nm diameter) as an amorphous monolayer on an tin-doped indium oxide (ITO) electrode were studied and the turnover frequency for this system was determined to be between 2.3 x 10$^4$ and 3.5 x 10$^4$ h$^{-1}$. In comparison, electrodes modified with ruthenium complexes, which are the homogeneous catalysts with the next most efficient turnover frequency, have reported turnover rates that are smaller by an order of magnitude or more than that of this system. The Ru-red/Pt-black system, for example, demonstrated a turnover frequency of 1500 h$^{-1}$ and the complex $[(\text{NH}_3)_3\text{Ru}^{II}\langle\mu-\text{Cl}\rangle_3\text{Ru}^{III}(\text{NH}_3)_3]^2^+$ was only shown to have a turnover rate of around 200 h$^{-1}$ in conjunction with a Ce$^{IV}$ oxidant. Furthermore, the overpotential needed for the oxidation of
water using the colloidal IrO$_x$ nanoparticles was about 0.4 V, which was much lower than others previously reported.$^{115}$

More recently, IrO$_x$ nanoparticles of a smaller size have been explored as electrocatalysts by numerous groups, in particular those of Murray and Mallouk.$^{110-113,116}$ Because of the nanoparticle’s small size, generally in the 1 – 2 nm range, their reactivity differs from that of the larger colloidal IrO$_2$ nanoparticles, due to the increase in surface area. Murray and coworkers demonstrated that the nanoparticles can be deposited onto the electrode by electrofloculation; the nanoparticles retain their individual shape and size, as determined by TEM of the dislodged film. Electrofloculation is a film formation technique, where the nanoparticles flocculate, not aggregate, together when a potential bias is applied. Studies of the pH dependence of the redox couples from the film, Ir$^V$/Ir$^{IV}$ and Ir$^{IV}$/Ir$^{III}$ revealed that as the pH of the solution increased, the formal potentials of the couples shift proportionally according to the Nernst equation, and are thus Nernstian behaved. As the thermodynamic potential of water oxidation is also Nernstian behaved, the overpotential for water oxidation was nearly independent of pH, revealing that the nanoparticles retain their catalytic activity across a wide range of pH.$^{110-111}$

A relationship between the production of O$_2$ and the thickness of the film was also demonstrated by Murray et al.$^{111}$ As the coverage, $\Gamma$, of IrO$_x$ nanoparticles increased, the production of O$_2$ increased proportionally, indicating that the kinetics are not adversely affected by the increasing thickness of the film. At a $\Gamma_{Ir}$ of 7 x 10$^{-8}$ mol/cm$^2$ and applied potential of 1.3 V vs. Ag/AgCl, a steady state current of 91 mA/cm$^2$ was achieved, which is about 40 times higher than that reported previously. In addition, the turnover frequency achieved by the films was similar to those earlier reported, between 1.6 x 10$^4$ and 2.2 x 10$^4$ hr$^{-1}$. These films are quite thick, comparatively, and are charged to the Ir$^{VI}$ state throughout very quickly, indicating that the
electron transfer through the film is fast. This is due to a mesoporous structure of the film, which allows transport of water and ions to flow easily through the film, and the increased surface area, which results in an increase of accessible reactive sites. Furthermore, this film had an overpotential of 0.25 V vs. Ag/AgCl at a current density of 0.5 mA/cm² for the OER, which was significantly lower than the 0.4 V reported by Yagi et al.\textsuperscript{111}

While the nanoparticles of Murray and coworkers were prepared in a basic solution at pH 13, the nanoparticles synthesized by Mallouk and coworkers were synthesized using the same method and then were adjusted to a pH of 1 by the addition of HNO\textsubscript{3}.\textsuperscript{27, 38, 71, 114, 116} The proposed mechanism involves the formation of [Ir(OH)\textsubscript{6}]\textsuperscript{2-} and IrO\textsubscript{X}·nH\textsubscript{2}O from [IrCl\textsubscript{6}]\textsuperscript{2-} in a basic solution. As the pH of the solution is lowered, the [Ir(OH)\textsubscript{6}]\textsuperscript{2-} condenses to form IrO\textsubscript{X}·nH\textsubscript{2}O. The partial condensation of the iridium centers of the nanoparticles led to slightly increased electrocatalytic activity for the nanoparticle electroflocculated films, which decreased the overpotential for the oxidation of water to 0.22 V vs. Ag/AgCl independent of pH, roughly 30 mV less than that of Murray et al. Mallouk et al. suggested this was due to consumption of the Ir\textsuperscript{IV} in the acidic condensation method, although the difference in overpotential could be considered negligible in comparison.\textsuperscript{27, 116}

IrO\textsubscript{X} NPs freely diffusing in solution have also proven to be efficient heterogeneous electrocatalysts.\textsuperscript{110, 112} It was found that the current produced from water oxidation catalysis when rotating the electrode was almost independent of the rotation rate, \(\omega\). This suggests the rate determining step in the process is the electron transfer between the Ir\textsuperscript{VI} and the H\textsubscript{2}O. The current efficiency was found to be nearly 100% at a current density of 0.5 mA/cm\textsuperscript{2}. The overpotential needed for the 100% current efficiency was determined to be 0.29 V vs. Ag/AgCl, which is comparable to that of the IrO\textsubscript{X} film made of the same nanoparticles. The turnover frequency of
O₂ was also similar to that of the nanoparticle films and independent of the concentration of IrOₓ. Consequently, it was concluded that the kinetics are very similar in both the film and freely diffusing NPs, indicating that the reaction is limited by its kinetics, not by mass transport.¹¹⁰,¹¹¹

While it has been established that these 2 nm IrOₓ NPs are excellent catalysts for water oxidation based on their low overpotential and high turnover rate, little is known about the NPs themselves or how they behave. The Murray lab has investigated this, including the research in this dissertation. In the same study mentioned above, 96% of the known concentration of Ir sites present in solution were able to undergo reduction from Ir⁶⁺ to Ir³⁺. This suggests that the entire nanoparticle is electrochemically reactive, where each Ir site is able to undergo redox chemistry. This may be due to the small size of the nanoparticle, which facilitates electron transfer between iridium sites. Because the electron transfer is fast, each one of the Ir sites is able to be reduced and oxidized.¹¹¹

The Murray lab also studied the same IrOₓ NPs in solution, when stabilized by phosphate ligands.¹¹² In a Pourbaix diagram of formal potential, E°', vs. pH, the Ir⁶⁺/⁵⁺ E° and Ir⁴⁺/³⁺ E°' at low pH of the NPs in solution followed a similar pattern as that of the electroflocculated NPs. They each had a slope of around 70 mV/pH, suggesting a one e⁻, one H⁺ transfer. The Ir⁴⁺/³⁺ E°' in solutions above pH 6, however, differed by having a slope of 116 mV/pH, which implies a one e⁻, two H⁺ transfer in basic media. It is thought that this change from the film is due to the surface oxide acid-base sites of the NPs; when the NPs are electroflocculated, these sites become inactive, resulting in a one e⁻, one H⁺ process at the pH values above 6.

Another important observation from this study is that both phosphates and carboxylates ligate and stabilize the IrOₓ NPs.¹ This led to a study by the Murray lab as well where the NPs
were attached to a Au slide via a self-assembled monolayer (SAM) of carboxylated alkanethiolates.\textsuperscript{113} The longer carbon chains lead to decreased electron transfer (ET) for the monolayers, as measured by a change in $\Delta E_{\text{peak}}$, which increased with increasing chain length. The overpotential for water oxidation also shifts with increasing chain length. A higher overpotential was required to reach the same current level for longer alkane chains. This change in overpotential demonstrates that the kinetics of water oxidation can be controlled by varying the chain length of the SAMs, opening up a new way to study the kinetics of water oxidation.

The research presented in this dissertation largely focuses on these small iridium oxide nanoparticles. Film formation and characterization of IrO$_x$ NPs will be discussed, as well as their behavior in non-aqueous media. By fully understanding the behavior, structure and surface chemistry of IrO$_x$ NPs, we can learn more about what makes them such efficient catalysts for the OER and apply that knowledge towards the development of less expensive materials. The implementation of these catalysts into a DSPEC device will also be discussed, including a novel assembly method with a Ru(II) polypyridal based chromophore on core/shell electrodes. Finally, the last chapter will take a left turn and discuss the electrochemical characterization of three novel Ru(II) quaterpyridine complexes, as well as their potential to serve as benzyl alcohol oxidation and water oxidation catalysts.
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CHAPTER 2: Film formation of Iridium Oxide Nanoparticles

2.1 INTRODUCTION

Iridium oxide nanoparticles (Ir$^{IV}$O$_X$ NPs) deposited as films are highly efficient electrocatalysts for the oxidation of water.$^{1-10}$ Yagi et al.$^{127g}$ showed that colloidal IrO$_X$ nanoparticles (50 – 100 nm diameter) spontaneously adsorb as an amorphous monolayer on an indium tin oxide (ITO) electrode surface. These coated surfaces electrocatalyzed water oxidation at 1.3V vs Ag/AgCl at a turnover frequency (mol O$_2$/mol Ir) of ca. 6.6 s$^{-1}$ (23,000 hr$^{-1}$) and at pH 5.3, with an overpotential of water oxidation reaction of ca. 0.4 V. While the turnover rate and over-potential were attractive, only a small percentage of the Ir sites in the film were electrochemically activate.

Thermal hydrolysis of K$_2$IrCl$_6$ solutions produces much smaller (ca. 2 nm dia.) Ir$^{IV}$O$_X$ nanoparticles which in films on electrodes are also very active water oxidation catalysts, as our laboratory$^{1,2,5,6}$ and that of Mallouk$^{4,9,10}$ have shown. The TO frequencies of Ir sites for water oxidation by these nanoparticles are similar to those observed by Yagi$^{127g}$ but the electrochemical over-potentials are significantly smaller. Additionally, nearly 100% of the Ir centers undergo electrochemical transformations, reflecting$^{5,6}$ facile transport of electronic and ionic charge throughout the nanoparticle films.

The formation of IrO$_X$ nanoparticle films on electrodes occurs by their electrofloculation,$^5$ in which the nanoparticles retain their individual shape and size (as opposed to aggregation to form larger nanoparticles by the cementing together of smaller ones.) IrO$_X$ nanoparticle films can also be formed by anodic electrolysis of [Ir(OH)$_6$]$^2$ solutions.$^{10}$ The
quantities of nanoparticles deposited in their electroflocculated films—expressed as $\Gamma_{\text{IrO}_2}$, mol Ir/cm$^2$—can be adjusted by the duration of the electrofloculation process.$^5$ The rate of production of O$_2$ by water oxidation is proportional to nanoparticle coverage over a ca. 300-fold range, indicating that charge and ion transport kinetics are somewhat tolerant to increasing film thickness. Deposition of an Ir oxide like material has also been reported from the decomposition of a soluble Ir complex upon oxidation.$^{11}$

While the previous research shows that films of IrO$_X$ NPs are efficient catalysts for water oxidation, little is known about how electrofloculation of the NPs occurs. The electrofloculation process may influence structure and catalytic activity. Because of the key connection of water oxidation rate to nanoparticle coverage, a fuller understanding of the electrofloculation process than now available is desirable. The research presented seeks further insights based on voltammetry and microscopy techniques, notably scanning electron microscopy (SEM), atomic force microscopy (AFM), and an electrochemical quartz crystal microbalance (eQCM). We will show the topography of these films and propose a mechanism of flocculation based on these techniques.

Three different electrofloculation methods were also explored, including constant potential, potential pulsing and potential cycling. The electrochemistry and microscopy of these films are presented below as a comparison of the different electrofloculation techniques. Finally, two alternative flocculation methods not involving any applied potential will be discussed; they provide further insight to the film formation process of IrO$_X$ NPs. Understanding the film formation process is key in developing efficient heterogenous water oxidation catalyst films and the research presented delves into how different methods affect this film formation process as well as the film itself.
2.2 **EXPERIMENTAL**

2.2.1 **Electrochemical Experimental Setup**

Electrochemical experiments were performed in a conventional three electrode cell with Au-coated slide working, Pt wire auxiliary, and 3 M Ag/AgCl reference (BASi) electrodes, using a CH Instruments 760c potentiostat. This reference electrode, relative to RHE, is 0.2881 V. The Au-coated glass slides (Evaporated Metal Films, 239 Cherry St, Ithaca, NY 14850) had a 5 nm Ti layer on the glass over-coated by a 100 nm Au layer. Electroflocculating while rotating the electrode at 500 rpm was performed using a Pt ring, GC disk rotating ring disk electrode (RRDE). Changes in mass of IrO$_x$ films upon electroflocculation were monitored with a Gamry eQCM 10M™ Quartz Crystal Microbalance.

2.2.2 **Iridium Oxide Nanoparticle Synthesis**

The Ir$^{IV}$O$_x$ nanoparticles were synthesized using a Wohler method,$^{12}$ in which a 2.5 mM solution of K$_2$IrCl$_6$ (99%, Strem Chemicals) in nanopure H$_2$O was adjusted to pH 13 with 25% w/w NaOH (50% w/w, Fisher Scientific). The solution was heated at 90 °C for 20 minutes and then allowed to cool to RT and to rest for at least 24 hours after the synthesis.

For studies at lowered pH, the above nanoparticle solutions were adjusted to lower pH with either concentrated HClO$_4$ (GSF Chemicals), to a final pH of 2.5, or H$_3$PO$_4$ (Fisher Scientific), to a final pH of 1.5. For pH 7 and 10 NP solutions, concentrated H$_3$PO$_4$ was added to create 1.0 M PO$_4$$^{3-}$ solutions and then adjusted to their respective pH with 50% w/w NaOH.

2.2.3 **Electroflocculation of Iridium Oxide Nanoparticles**

For electroflocculations not monitored by QCM, Au slides were first cleaned by exposure to piranha solution (3:1 concentrated H$_2$SO$_4$ (Fisher Scientific) to H$_2$O$_2$ (30% w/w, Fisher Scientific)), and then rinsed with nanopure H$_2$O and dried under a stream of Ar gas. Piranha solution is highly oxidizing and should therefore be handled with care. For electroflocculation of
films monitored by QCM, Gamry Au coated and C coated 10 MHz crystals were used as delivered, without prior cleaning in order to reduce exposure of the crystal to harsh environments.

The films were formed from unstirred pH 13 IrO\textsubscript{x} nanoparticle solutions by applying a potential of 0.9 V \textit{vs.} Ag/AgCl. The duration of the applied potential was varied to generate different nanoparticle coverages. The films were rinsed with nanopure H\textsubscript{2}O and then CV was performed in 0.1 M NaOH to verify the presence of a film.

Three different electroflocculation techniques were further explored: constant potential, potential pulsing and potential cycling. The methods to determine the most efficient film formation process are discussed below. In order to accurately compare each technique, the total time spent at potentials more positive than the onset of water oxidation (0.6 V \textit{vs.} Ag/AgCl at pH 13) was kept constant at 10 minutes. After electroflocculation, all films were analyzed using cyclic voltammetry in a clean pH 13 buffer. The charge (Q) under the Ir\textsuperscript{IV/III} and Ir\textsuperscript{V/IV} waves were calculated. Using Faraday’s Law (Equation 2-1), where \(n\), \(F\) and \(N\) are the number of electrons, Faraday’s constant and the number of moles of analyte respectively, the coverage of Ir (\(\Gamma_{\text{Ir}}\)) was found.

\textbf{Equation 2-1}

\[
Q = nFN
\]

2.2.3.1 Electroflocculation via Constant Potential

In the constant potential experiments, a potential more positive than the onset of water oxidation was held for ten minutes. This potential varied from 0.6 to 1.9 V \textit{vs.} Ag/AgCl. The time was also varied, while keeping the potential applied constant at 1.2 V \textit{vs.} Ag/AgCl.
2.2.3.2 Electroflocculation via Potential Pulsing

Electroflocculation via potential pulsing involved pulsing between two potentials, one more positive than the onset of water oxidation and one more negative than the onset of water oxidation. For the remainder of this chapter, these will be referred to as the upper and lower potential limits, respectively. The upper potential limits explored were 0.6, 0.9 and 1.2 V vs. Ag/AgCl and the lower potential limits were 0, 0.2 and 0.6 V vs. Ag/AgCl. The pulse length of the upper potential limit was varied between 0.1, 0.2 and 0.5 s; the total time spent at the upper potential limit, however, remained constant at 10 minutes.

2.2.3.3 Electroflocculation via Potential Cycling

Electroflocculation via potential cycling consisted of cycling the potential between the upper and lower potential limits listed in the above section. The scan rates were varied between 0.01, 0.1 and 1 V/s. The number of sweep segments was adjusted so that the total time spent more positive than the onset of water oxidation was kept at 10 minutes.

2.2.4 Microscopy of the IrOx NP Films

Images of films were obtained from a Hitachi S-4700 Cold Cathode Field Emission Scanning Electron Microscope (SEM) and an Asylum Research MFP3D Atomic Force Microscope (AFM).

2.2.5 Chemical Flocculation of Iridium Oxide Nanoparticles

The nanoparticles were chemically flocculated from homogeneous solutions by either adding a solid oxidant NH₄Ce(NO₃)₆ (Aldrich) salt to an as synthesized pH 13 nanoparticle solution, or by adding a 1 mM solution of NH₄Ce(NO₃)₆ to the nanoparticle solution in 50 µL increments.
2.2.6 **Direct pH Change for Iridium Oxide Nanoparticle Precipitation**

A solution of as-synthesized IrO\textsubscript{X} NPs was adjusted to \(~\text{pH}~1\) with the addition of concentrated HClO\textsubscript{4} so that the final solution was 0.1 M HClO\textsubscript{4}. After sitting at room temperature for 24 hours, electroactive slides were dipped vertically in the solution for 1.5 hours in order to form a film on the surface.

2.3 **RESULTS AND DISCUSSION**

2.3.1 **Electroflocculation of Iridium Oxide Nanoparticles via Constant Potential**

As noted earlier, electroflocculation of IrO\textsubscript{X} nanoparticles onto an electrode is accomplished by applying a potential sufficiently positive to induce water oxidation catalysis. An example is shown in Figure 2.1 and Figure 2.2 where the film-forming applied potential was 0.9 V, for 10 minutes, in an as-synthesized pH 13 solution of nanoparticles. Voltammetry of a film of Ir\textsuperscript{IV}O\textsubscript{X} nanoparticles in 0.1M NaOH solution (pH 13) is illustrated in Figure 1. The nanoparticles undergo two Ir-centered redox reactions, Ir\textsuperscript{IV/III} and Ir\textsuperscript{V/IV}. At potentials more

![Figure 2.1](image_url)

**Figure 2.1:** Cyclic voltammetry of an electroflocculated IrO\textsubscript{X} NP film, depicting the Ir\textsuperscript{IV/IV} and Ir\textsuperscript{V/IV} redox waves and the onset of water oxidation in 0.1 M NaOH solution (pH = 13). Electrode area 0.071 cm\textsuperscript{2}.  

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positive than the latter reaction, large currents for water oxidation immediately appear. (These electrochemical processes are also seen when the nanoparticles are solutes in the electrolyte solution, and oxygen is evolved at a similar rate and over-potential.) The solution pH dependences of the formal potentials of the IrV/IV and IrIV/III couples of the nanoparticles, and of the onset of water oxidation (associated with the IrVI/V reaction), are all ca. 60 mV/pH unit. The overpotential for water oxidation, ca. 250 mV at 0.5 mA/cm², is independent of pH from 1.5 to 13, revealing a constant level of catalytic reactivity across pH.² Coulometry of nanoparticle solutions shows that ca. 100% of the Ir nanoparticle sites undergo the IrV/IV and IrIV/III reactions.²

The IrOx film formation process is general with respect to electrode material, including gold, glassy carbon (GC), platinum, tin-doped indium oxide (ITO) and titanium dioxide (TiO₂) surfaces. The formation of a film is readily confirmed by cyclic voltammetry in 0.1 M NaOH solution, in which two film redox couples are observed (Figure 2.1). The two waves are attributed to IrIV/III and IrVI/IV oxidation state changes, and can also be seen in solutions of IrOx nanoparticles. The IrIV/III peak in a nanoparticle film occurs at a somewhat more positive
potential for the IrOx films, as described previously.\textsuperscript{2,5} Once formed, the films are stable to exposure to various buffers and organic solvents within the limits described.

2.3.1.1 Electroflocculation with Rotation of Electrode

The film-forming process diminished by convection. Rotating the disk electrode during film-forming results in appearance of Ir\textsuperscript{IV/III} and Ir\textsuperscript{V/IV} waves in subsequent voltammetry, but the charge (Q) under the waves (which are proportional to the number of Ir sites present on the electrode) is significantly reduced (Figure 2.3). When using a rotating ring-disk electrode (500 rpm RRDE, Pt disk and GC ring), holding the disk potential in a pH 13 nanoparticle solution at 0.9 V for 10 minutes, film formation occurred on both disk and ring electrodes as evidenced by subsequently observed water oxidation catalysis. (Applying potential only to the Pt ring of the RRDE deposited IrOx film only on the ring.) This phenomenon is due to the convection created by rotating the electrode. The NPs flocculate at whichever electrode is polarized. When it is generated at the disk, some of the flocculated NPs are swept past the ring and therefore IrOx film formation is observed at both the disk and the ring. When the ring is polarized, the convection due to rotating doesn’t cause the flocculated NPs generated at the ring to pass the disk, so there is no precipitation observed at the disk. There is still NP precipitation at the ring because the flocculated NPs are created there.

\textbf{Figure 2.3}: Cyclic voltammetry in 0.1 M NaOH of the GC disk (a) and Pt ring (b) after electroflocculation of pH 13 IrOx NPs while rotating at 500 rpm.
From these observations, it can be concluded that while applied potential is essential for nanoparticle flocculation into a film, the flocculation process is moderately slow, allowing film formation on an electrode (the ring) to which potential is not applied but which is exposed to a bath of (disk-charged) nanoparticles.

2.3.1.2 Electroflocculation at Varying pH

Electroflocculation onto Au film electrodes was attempted from nanoparticle solutions at lowered pH (pH 1, 7 and 10), with varying degrees of success, as seen in Figure 2.4. The NPs in pH 10 solution appeared to flocculate just as readily as the as-synthesized pH 13 NPs, with comparable coverages seen in the CVs from charge (Q). The NPs in pH 1 and pH 7 solutions, however, did not electrofloccluate as readily, as their CVs showed a significant decrease in Q, presumably corresponding to a decrease in coverage. This suggests that the H\(^+\) formation at high pH is essential for flocculation. Also of note, the surface of the NPs at different pH values changes significantly, which greatly impacts the electrofloccluation.

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**Figure 2.4:** Cyclic voltammetry after the electroflocculation onto Au coated slides of different pH IrO\(_X\) NPs. CVs were performed in pH 1 phosphate buffer (pH 1 NPs), pH 10 phosphate buffer (pH 7 and 10 NPs) and 0.1 M NaOH (pH 13 NPs).
2.3.1.3 eQCM Monitoring of Electroflocculation

Observations during electroflocculation using an electrochemical quartz crystal microbalance (eQCM) were very informative. Figure 2.5 shows an example of electroflocculation onto a Au coated quartz crystal at an applied 0.9 V potential. While current flow commences immediately upon the potential application, the quartz crystal frequency, whose decrease reflects growth of nanoparticle mass rigidly bound to the Au surface, interestingly exhibits a delayed response, for a relatively prolonged period (indicated by the black arrow in Figure 2.5). This delay, or induction period, occurred only for the initial stage of film formation; if the applied potential was removed and then re-applied, mass changes were observed immediately. The lack of delay in mass accumulation occurred whether the same nanoparticle solution was used or was replaced by a fresh one. It appears that once formed, a nanoparticle film builds upon itself with relative ease. The induction period of the electrofloculation process was seen at different IrOx nanoparticle concentrations and electrodes.

Figure 2.5: Electrofloculation of IrOx NPs ([Ir] = 2.5 mM, pH 13) at 0.9 V vs. Ag/AgCl onto a Au coated quartz crystal, as monitored by eQCM. The measured current is the blue line; green corresponds to the change in mass obtained from the change in frequency of the quartz crystal. The black arrow indicates the end of the observed induction period. 1 μg increase in mass corresponds to roughly $1.67 \times 10^{-10}$ mol IrOx NPs/cm².
The length of time for the induction phase could vary with conditions, but the total charge passed during it was crudely similar between films, averaging \( \text{ca.} \ 85 \pm 8 \ \text{mC} \), regardless of nanoparticle concentration. This suggests a common scenario of the trigger for film deposition, such as a buildup of a local pH gradient at the electrode due to prolonged water oxidation. The currents are rather substantial. The above water oxidation charge corresponds to an average of \( 2 \times 10^{-7} \) moles of generated protons, which would neutralize an equivalent amount of base in the electrode interphase. The ca. 200 seconds of proton generation would create, roughly, a 0.01 cm thick diffusion layer at the electrode surface and a proton concentration of 0.1 M at the surface, i.e. sufficient to neutralize the 0.1 M NaOH near the electrode surface and create a pH gradient. This change in pH at the interface may trigger the initial flocculation of NPs and precipitation onto the electrode surface.

2.3.1.4 Microscopy of IrO\(_x\) NP Films at Early Electroflocculation Times

Atomic force microscopy (AFM) and scanning electron microscopy (SEM) were performed on various electroflocculated films of IrO\(_x\) NP films. For longer electroflocculation
40 times, 5 minutes or longer, both SEM and AFM showed porous, non-uniform islands of NPs, as seen in Figure 2.6.

Atomic Force Microscopy (AFM) was implemented to study the topography of the films, specifically as a function of electroflocculation time; AFM was chosen as an alternative to SEM for these experiments due to its higher spatial resolution. AFM agrees with the eQCM data reported above. AFM images of films after 0, 90 and 120 s of electroflocculation are in the Figure 2.7. Films electroflocculated for 120 seconds and shorter times all very closely resemble a blank gold slide, in terms of topography and roughness factor (RMS), with the 120 second film appearing slightly rougher than the rest. These results support the eQCM data where there was no net increase in mass for films electroflocculated for 120 seconds or less, again suggesting an induction phase. Figure 2.8 depicts a film electroflocculated for 180 seconds at 0.9 V in pH 13 IrO$_x$ NP solution. Small islands of what is presumed to be IrO$_x$ NPs are visible at this point, as
indicated by the blue boxes. This corresponds with the induction period seen in the QCM data, as for the first two minutes or so, there is very little change in topography.

![AFM images of Au coated glass slides subjected to 0 s (left) and 180 s (right) of electroflocculation. After 180 s, patches of IrOx NPs are visible, as indicated by the blue squares.](image)

**Figure 2.8:** AFM images of Au coated glass slides subjected to 0 s (left) and 180 s (right) of electroflocculation. After 180 s, patches of IrOx NPs are visible, as indicated by the blue squares.

### 2.3.2 Different Methods of Electroflocculation

#### 2.3.2.1 Constant Potential

Figure 2.9 depicts the coverages of Ir in mol/cm² obtained after electroflocculation at different potentials via constant potential by integrating both the IrIV/III and IrV/IV redox waves obtained by cyclic voltammetry in a pH 13 NaOH solution. Various scan rates were used and integrated and the standard deviation is representative of the variance of the Q over the difference scan rates. Ideally, there would be no variance and the coverage of iridium would be the same for both the IrIV/III and IrV/IV couples.

The overall trend for coverage of iridium with respect to electroflocculation potential is an increase of coverage with increase in potential. This is evident in the coverages calculated from the waves of both redox couples. This agrees with the proposed method of flocculation mentioned above, where the precipitation is induced via a local change in pH caused by water oxidation catalysis. As the applied potential increases, the rate of catalysis also increases and
protons are generated more quickly. This would lead to a larger localized pH change and theoretically, a greater number of precipitated nanoparticles.

At potentials above 1.2 V vs. Ag/AgCl, however, the trend breaks and we see a decrease in coverage. This is can also be explained through water oxidation catalysis. Another product of water oxidation is \( \text{O}_2 \) and if it is produced at a faster rate than which it can diffuse away, it will start to accumulate at the electrode surface. If the solution then becomes saturated past the solubility of \( \text{O}_2 \) in water, then the remaining \( \text{O}_2 \) will form bubbles at the electrode surface. These bubbles, which are visible during electroflocculation, will inhibit precipitation onto the electrode surface. At the higher applied potentials, enough bubbles are likely formed that it inhibits film formation, so we see a decrease in coverage.

The high applied potentials also resulted in a larger discrepancy between the coverages calculated from the \( \text{Ir}^{\text{V/IV}} \) and those from the \( \text{Ir}^{\text{IV/III}} \) waves. The average coverages for the \( \text{Ir}^{\text{V/IV}} \) wave of films formed at applied potentials greater than 1 V were an order of magnitude larger than those for the \( \text{Ir}^{\text{IV/III}} \) wave of the same films. These films agree with other findings from the

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**Figure 2.9**: Coverage of Ir (\( \Gamma_{\text{Ir}} \)) after electroflocculation at different potentials, using the chronoamperometry method. The coverages calculated from the \( \text{Ir}^{\text{IV/III}} \) couple is represented in blue and the coverages calculated from the \( \text{Ir}^{\text{V/IV}} \) couple are in red.
Murray lab\textsuperscript{129}, where there is an increase in conductivity between the two couples, resulting in a larger current and charge for the Ir\textsuperscript{V/IV} wave. What is unique about this finding, however, is that there is a correlation between whether this effect is observed and the applied potential during electrofloculation. This can also be due to bubble formation during the water oxidation catalysis. As mentioned above, at higher applied potentials, bubbles result from a build-up of O\textsubscript{2} at the electrode surface. As the IrO\textsubscript{X} NP films are mesoporous, these bubbles can also form within the film itself. This would cause breaks within the film and the decrease in connectivity between the different areas of IrO\textsubscript{X} NPs would lead to a decrease in conductivity. This would result in a discrepancy between the Q passed by the Ir\textsuperscript{IV/III} and Ir\textsuperscript{V/IV} waves.

Figure 2.10 depicts how coverage changes of the IrO\textsubscript{X} NP films with respect to how long the applied potential is held at 1.2 V vs. Ag/AgCl in as-synthesized pH 13 IrO\textsubscript{X} NP solution. At electrofloculation times shorter than 10 minutes, there is a trend of increasing film coverage with increasing electrofloculation time. Starting at 10 minutes, however, there is no trend with

\textbf{Figure 2.10:} Coverage of iridium ($\Gamma_{Ir}$) for the Ir\textsuperscript{V/IV} (red) and Ir\textsuperscript{IV/III} (blue) waves with respect to length of electrofloculation in min at 1.2 V vs. Ag/AgCl.
length of electroflocculation time. This is likely due to the high applied potential creating bubbles at the electrode surface and inhibiting film formation.

From these studies, it was concluded that the best conditions for electroflocculating IrOx NP films via the constant potential method were potentials below 1.0 V vs. Ag/AgCl in pH 13 IrOx NP solution. The reduced applied potential decreases the rate of water oxidation which creates bubbles that inhibit film formation at the electrode surface. The bubbles can also affect the conductivity throughout the film; when these films are used in potential devices, higher conductivity is preferable.

2.3.2.2 Pulsing the Potential

Compared to a typical cyclic voltammogram of IrOx NP films featured in Figure 2.1, pulsing the potential to induce electroflocculation yielded oddly shaped cyclic voltammetry (CV) of the films depending on the pulse length. These CVs are shown in Figure 2.11. The longest pulse length (0.5 s at the upper potential limit) yielded CVs most closely resembling that of those formed using the constant potential method. Two redox waves are observed, likely the same Ir^{IV/III} and Ir^{V/IV} waves identified previously. The shorter pulse lengths, however, formed films with slightly different electrochemistry. The two main redox waves at -0.3 and 0.1 V vs. Ag/AgCl are still both present, corresponding to the Ir^{IV/III} and Ir^{V/IV} redox couples. However, there also appears to be a third couple at 0.3 V vs. Ag/AgCl that previously wasn’t present in these films. This couple appears to be more diffusional in character, compared to the other two redox couples. The $\Delta E_p$ is much closer to the standard 60 mV separation expected for a diffusing species as opposed to the near 0 mV separation for species on the electrode surface. As the nanoparticle films are mesoporous, one explanation for these species could be unbound IrOx NPs diffusing through the film. In larger films, such as those formed via the constant potential
method and at longer pulse lengths, these could blend into the Ir$^{V/IV}$ wave for the film, thus

Figure 2.11: Cyclic voltammetry of the IrO$_x$ NP films formed via potential pulsing. The lower potential limit was 0 V vs. Ag/AgCl and the upper potential limit was varied between 1.2 V (green), 0.9 V (red) and 0.6 V (blue). The different pulse lengths were 0.1, 0.2 and 0.5 s at the upper potential limit. CVs were performed in fresh 0.1 M NaOH solution and the CVs shown above are at $\nu = 50$ mV/s.
accounting for the appearance of a much larger $\text{Ir}^{\text{IV/III}}$ wave compared to the $\text{Ir}^{\text{IV/IV}}$ wave. The $\text{Ir}^{\text{IV/III}}$ wave for the diffusional species is much more negative than that of the film and therefore wouldn’t be seen in the potential window above.

The other thing to notice is the significantly higher coverages associated with the longest pulse length (0.5 s). If an induction phase is still present for this method of electroflocculation, the longer pulse lengths would create a larger pH gradient at the electrode surface, which would lead to more flocculation and an increase in coverage of Ir. The coverage of each film with respect to the upper potential limit is shown in Figure 2.12. Also of interest, is the ratio of the coverage of $\text{Ir}^{\text{IV/III}}$ compared to that of $\text{Ir}^{\text{IV/IV}}$. Previously, that ratio for most films was less than one, as the $\text{Ir}^{\text{IV/IV}}$ wave was much larger than the $\text{Ir}^{\text{IV/III}}$ wave. With the pulsing, however, it is the $\text{Ir}^{\text{IV/III}}$ wave that is larger, and therefore has a higher coverage. The ratio of $\text{Ir}^{\text{IV/III}}$ to $\text{Ir}^{\text{IV/IV}}$ for nearly all of the films formed by pulsing the potential is greater than one. The difference in ratio could be due to the ability to distinguish the waves at 0.1 V and 0.3 V vs Ag/AgCl. If both of these waves are present in the thicker films and are indistinguishable from the each other, than integrating the two together would lead to the appearance of a higher coverage of Ir from the $\text{Ir}^{\text{IV/IV}}$ wave. The combined film and diffusional wave effect appears largely in films

![Figure 2.12: Coverage of iridium ($\Gamma_{\text{Ir}}$) with respect to the upper potential limit. Coverage for the $\text{Ir}^{\text{IV/III}}$ couple is on the left and that for the $\text{Ir}^{\text{IV/IV}}$ couple is on the right. The lower potential limit was 0 V vs. Ag/AgCl, while the upper potential limit is featured along the x-axis. Each pulse length is represented by a different symbol, 0.5 s as red squares, 0.2 s as green triangles and 0.1 s as purple circles.](image)
electroflocculated with high upper potential limits or applied potentials. These diffusional peaks may be caused by bubble formation within the film, which break off part of the IrOₓ NP flocculate, resulting in diffusional species within the film.

The lower potential limit was also varied for the same upper potential limits and pulse lengths discussed above. The CVs of the varied potentials are similar to those featured in Figure 2.11. The coverages from these films formed with a lower potential limit of 0.2 V vs. Ag/AgCl are shown in Figure 2.13. Those of the films flocculated with a lower potential limit of 0.6 V vs. Ag/AgCl are in Figure 2.14.

**Figure 2.13:** Coverages of iridium (Γₘ) for the Ir⁴⁺/³⁺ (left) and Ir⁵⁺/⁴⁺ (right) couples with a lower potential limit of 0.2 V vs. Ag/AgCl. The upper potential limit is shown on the x-axis and the different pulse lengths are in different colors, 0.5 s in red, 0.2 s in green and 0.1 s in purple.

By increasing the lower potential limit to 0.2 V from 0 V vs. Ag/AgCl, the ratio of Ir⁴⁺/³⁺ to Ir⁵⁺/⁴⁺ is much closer to one. The coverages calculated for each species are not statistically different from one another. The same trend is observed for the pulse length, where an increase in pulse length leads to higher coverage of Ir in both species. The upper potential limit, itself, however, doesn’t appear to have a significant effect on Ir coverage past 0.9 V vs. Ag/AgCl. Comparing the lower potential limit of 0.2 V to 0 V vs. Ag/AgCl, there is a slight decrease in iridium coverage by increasing the lower potential limit by 200 mV.

Only two upper potential limits were explored for the lower potential limit of 0.6 V vs. Ag/AgCl, as keeping the upper potential limit at 0.6 V vs. Ag/AgCl would be the same
experiment as the constant potential experiment at 0.6 V Ag/AgCl. The CVs of these films appear to have gone back to the usual trend seen in the constant potential flocculations, where the ratio of Ir$^{IV/III}$ to Ir$^{V/IV}$ is less than one. This makes sense, as the potential never dips below the onset of water oxidation catalysis. While there may be a decrease in the rate of catalysis at the lower potential limit, water oxidation is still occurring throughout the electroflocculation process and the films formed would be expected to behave similarly to those formed via the constant potential method. The increase in upper potential limit for these films still yields a higher coverage (although only two potentials were explored) and the longer pulse lengths yield higher Ir coverages as well.

2.3.2.3 Cycling the Potential

The films formed via cycling the potential in an as-synthesized IrO$_x$ NP solution all yielded similar cyclic voltammetry when put into a new 0.1 M NaOH solution. An example of these CVs are in Figure 2.15, where each CV is from a different film formed by cycling the potential at different scan rates. The examples shown have a lower potential limit of 0 V vs. Ag/AgCl and an upper potential limit of 0.9 V vs. Ag/AgCl during electroflocculation. The
waves for the Ir$^{IV/III}$ and Ir$^{V/IV}$ couples are relatively equal for this method, with the ratio of the two being slightly larger than one. The wave at 0.3 V vs. Ag/AgCl that is present in the pulsing method is not present in these cyclic voltammograms. This suggests that the freely diffusing IrO$_x$ NPs, if those are responsible for the couple at 0.3 V, are not trapped within the mesoporous film.

The coverages obtained for the Ir$^{IV/III}$ and Ir$^{V/IV}$ waves via potential cycling with a lower potential limit of 0 V vs. Ag/AgCl are shown in Figure 2.16. As hinted at in the previous paragraph, the coverage for the Ir$^{IV/III}$ couple is slightly higher than that of the Ir$^{V/IV}$. For the fastest scan rate (1 V/s), Ir coverage increases with increasing upper potential limit, as expected. With the slower scan rates (10 and 100 mV/s), there is no apparent trend with upper potential limit, with the exception of the Ir$^{IV/III}$ coverage for the 10 mV/s cycling which decreases with increasing upper potential limit. This could be the equivalent to the high applied potentials in the constant potential method, as the slower scan rate results in longer continuous time at potentials.
above the onset of water oxidation catalysis. This could lead to accumulation of O$_2$ at the electrode surface and therefore, film formation inhibition due to bubble formation.

Another important feature to note is the relatively small scatter in coverage with respect to scan rate, represented by the standard deviation on the graphs. These films are behaving more ideally, where the same charge is passed regardless of scan rate.

The lower potential limit was also varied for the potential cycling electrofloculation processes and the coverages obtained from the 0.4 V vs. Ag/AgCl lower potential limit are featured in Figure 2.18.

For the fastest scan rate (1 V/s), there is a slight increase in Ir coverage with increasing upper potential limit, although the difference in the Ir$^{IV/III}$ wave is statistically insignificant. There is no apparent trend for the film formed at 100 mV/s and the coverages for the slowest scan rate (10 mV/s) decrease with increasing upper potential limit. These are likely due to the same effect mentioned about the 0 V lower potential limit, where a slower scan rate can lead to the formation of bubbles at the electrode surface that inhibit electrofloculation. However, there are only two data points, so this should all be taken with a large grain of salt.

![Figure 2.16](image)

**Figure 2.16:** Coverages of iridium ($\Gamma_{Ir}$) from film formed via potential cycling with a lower potential limit of 0 V vs. Ag/AgCl for the Ir$^{IV/III}$ (left) and Ir$^{V/IV}$ (right) couples. The upper potential limit is represented along the x-axis and the scan rates are represented by different colors, 10 mV/s in blue, 100 mV/s in red and 1 V/s in green.
The coverages of Ir for the lower potential limit of 0.6 V vs. Ag/AgCl is exhibited in Figure 2.17. There is no apparent trend for upper potential limit or variance in scan rate. Again, there are only two data points so these “trends” are only so accurate. However, there does appear to be a trend for the lower potential limit and ratio of coverage of the Ir$^{IV/III}$ to Ir$^{V/IV}$ couples. The ratio of the Ir$^{IV/III}$ to Ir$^{V/IV}$ coverages for the films formed with a lower potential limit of 0 V vs. Ag/AgCl most closely resembled those of the potential pulsing, where the ratio is greater than one. The Ir coverages of the films electroflocculated with a lower potential limit of 0.6 V, however, more

**Figure 2.17:** Coverages of iridium ($\Gamma_{Ir}$) from film formed via potential cycling with a lower potential limit of 0.6 V vs. Ag/AgCl for the Ir$^{IV/III}$ (left) and Ir$^{V/IV}$ (right) couples. The upper potential limit is represented along the x-axis and the scan rates are represented by different colors, 10 mV/s in blue, 100 mV/s in red and 1 V/s in green.

**Figure 2.18:** Coverages of iridium ($\Gamma_{Ir}$) from film formed via potential cycling with a lower potential limit of 0.4 V vs. Ag/AgCl for the Ir$^{IV/III}$ (left) and Ir$^{V/IV}$ (right) couples. The upper potential limit is represented along the x-axis and the scan rates are represented by different colors, 10 mV/s in blue, 100 mV/s in red and 1 V/s in green.
closely resemble the films formed via the constant potential method, where the ratio of Ir\textsuperscript{IV/III} to Ir\textsuperscript{V/IV} is less than one. The films deposited with the lower potential limit of 0.4 V are right in the middle of these two extremes, where the ratio of Ir\textsuperscript{IV/III} to Ir\textsuperscript{V/IV} is very close to one. This trend is likely due to the time spent not above the onset of water oxidation. For the most negative lower potential limit (0 V vs. Ag/AgCl), there is more continuous time spent not at potentials above the onset of water oxidation. This time is equivalent to the lower potential limit pulse in the pulsing technique, so the electroflocculation methods create similar films. In these cases, there is more time for O\textsubscript{2} to diffuse away from the electrode surface, resulting in a decrease in bubble formation.

On the opposite side of the spectrum, the films formed via cycling with a lower potential limit of 0.6 V vs. Ag/AgCl never spend any time below the onset of water oxidation catalysis. There is a slight change in rate of catalysis, but this method is essentially identical to the constant potential method and they therefore deposit similar IrO\textsubscript{x} NP films. Bubble formation in the more positive lower potential limit case results in film breakage which contributes to the high Ir\textsuperscript{V/IV} charge and coverage, as seen in the constant potential films.

2.3.2.4 Comparison of Various Electroflocculation Methods

Figure 2.19: Cyclic voltammetry of films formed via different methods of electroflocculation. Constant potential and potential pulsing is represented on the left and potential cycling on the right. The different pulse lengths and scan rates for the potential pulsing and potential cycling respectively are noted in the legend. Each film was electroflocculated with the same amount of time spent above the onset of water oxidation catalysis. Each of these CVs is taken in 0.1 M NaOH at 50 mV/s.
2.3.2.4.1 Cyclic Voltammetry and Coverages of Ir of Different Electroflocculation Methods

Cyclic voltammetry of a representative film from each electroflocculation method is depicted Figure 2.19. Each of these films has an upper potential limit of 0.9 V vs. Ag/AgCl and a lower potential limit of 0 V vs. Ag/AgCl and they each spent an equivalent amount of time above the onset of water oxidation (10 minutes), although not continuously for the potential cycling and pulsing techniques. At first glance, the current passed for the film formed via the constant potential method is the lowest out of all of the films, followed by the shortest pulse length of potential cycling through the longest pulse length. The potential cycling appears to yield the thickest film (based off of current), although there is no trend within the potential cycling films with regard to scan rate. The overall shape is important to note as well. The film formed with the constant potential method exhibits a larger Ir\textsuperscript{V/IV} wave than Ir\textsuperscript{IV/III}. The films formed via potential pulsing have relatively equivalent Ir\textsuperscript{V/IV} and Ir\textsuperscript{IV/III} waves. The potential cycling films, however, have larger Ir\textsuperscript{IV/III} waves compared to the Ir\textsuperscript{V/IV} waves.

![Figure 2.20: Coverages of iridium (Γ\textsubscript{Ir}) for films formed via different electroflocculation methods, depicted in the legend on the right. The Ir\textsuperscript{IV/III} values are represented by circles, while the Ir\textsuperscript{V/IV} values are squares. The blue data points denote values obtained from a film formed via constant potential, while the green data points are from films flocculated by potential pulsing and the red from potential cycling. The lower potential limit is 0 V vs. Ag/AgCl for all films.](image-url)
The Ir coverages for the films created via the constant potential method, 0.1 s potential pulses and 1 V/s scan rates are displayed in Figure 2.20, as well as those from the upper potential limits of 0.6-0.65 V and 1.2 V vs. Ag/AgCl. Potential pulsing and cycling methods had a lower potential limit of 0 V vs. Ag/AgCl. Looking at the difference in coverage between the $\text{Ir}^{\text{V/IV}}$ and $\text{Ir}^{\text{IV/III}}$ waves, the potential pulsing remained the most consistent for each applied potential, where there was a slight discrepancy between coverage, but the overall ratio of the $\text{Ir}^{\text{IV/III}}$ and $\text{Ir}^{\text{V/IV}}$ waves was very close to one. The difference between the $\text{Ir}^{\text{IV/III}}$ and $\text{Ir}^{\text{V/IV}}$ waves increases with increasing upper potential limit for the potential cycling and constant potential methods; however, the ratio of $\text{Ir}^{\text{IV/III}}$ and $\text{Ir}^{\text{V/IV}}$ changes in opposite directions. For the potential cycling methods, the ratio increases, as the $\text{Ir}^{\text{IV/III}}$ couple becomes significantly larger than the $\text{Ir}^{\text{V/IV}}$ couple. For the constant potential methods, the ratio of $\text{Ir}^{\text{IV/III}}$ and $\text{Ir}^{\text{V/IV}}$ decreases with increasing applied potential as the $\text{Ir}^{\text{V/IV}}$ wave becomes much larger than the $\text{Ir}^{\text{IV/III}}$ wave.

Also of importance is the variance of calculated coverage with respect to scan rate, denoted by the standard deviations in Figure 2.20. As the upper potential limit and/or applied potential increases, the standard deviation also increases. If these were ideally behaved films, there would be no change in the charge passed, and therefore coverage of Ir, with respect to scan rate. Therefore, the most ideal films are formed at the lower applied potentials and/or upper potential limits.

There are significant changes to the IrO$_x$ NP films that are formed via different methods of electroflocculation, based on the shape of the cyclic voltammetry and the charge passed for each Ir redox couple. Ideally, the ratio of the two Ir redox couples would be equal and the charge underneath each of this couples would not vary with respect to scan rate. Based on these two criteria, the preferred method of electroflocculation would involve a low applied potential or
upper potential limit. However, this must be balanced with thickness of film, as a higher coverage of catalyst would result in higher rates of catalysis. Taking this into consideration, an upper potential limit of 0.9 V for either the potential cycling or potential pulsing method meets both the ideal electrochemical film behavior and film thickness requirements.

2.3.2.4.2 SEM of Film Formed via Different Electroflocculation Methods

Examples of images obtained by scanning electron microscopy (SEM) of the IrOₓ NP films are seen in Figure 2.21. The top row of images (a, b and c) are all films made using the constant potential technique, with varying applied potential. A, b and c correspond to an applied potential of 0.6, 0.9 and 1.2 V vs. Ag/AgCl. The middle row (d and e) are both films deposited using the potential pulsing technique. D corresponds to a film electroflocculated with an upper potential limit of 0.9 V vs. Ag/AgCl and a lower potential limit of 0.6 V vs. Ag/AgCl, while e was formed with an upper potential limit of 0.9 V vs. Ag/AgCl and lower potential limit of 0 V vs. Ag/AgCl. The bottom images (f, g and h) are of films flocculated via the potential cycling method, with upper and lower potential limits of 0.9 and 0 V vs. Ag/AgCl. Each letter corresponds to a different scan rate; 10 mV/s, 100 mV/s and 1 V/s are depicted in images f, g and h, respectively.

Looking at the images of the films formed via the constant potential technique, there is a distinct increase of film coverage with increase applied potential. The film formed at 0.6 V vs. Ag/AgCl is still quite sparse throughout the electrode surface, with only small islands of IrOₓ NP flocculates randomly space across the surface. It resembles a film formed at a higher potential over a short amount of time (< 5 min). For the films formed at 0.9 and 1.2 V vs Ag/AgCl, the entire electrode is covered with IrOₓ NPs. What started out as islands (as seen in Figure 2.6), has grown together to create a mesoporous film on the Au surface. Elemental analysis via Energy
Dispersive X-ray Spectroscopy (EDS) confirmed the presence of Ir throughout the surface, as well as the high atomic concentration (3-6%), indicating a fairly thick film on the electrode surface.

Images of the films electroflocculated with the potential pulsing method demonstrated that the films still form islands in the beginning stages of deposition. This indicates that there is similarity to the mechanism of electrofloculation compared to the constant potential technique. EDS confirmed that that the brighter spots in the images are the IrOx NP flocculates, based on the Ir atomic concentration (4-5%). The darker areas still had some Ir present, although the Ir

**Figure 2.21:** SEM images of electroflocculated IrOx NP films formed via different electrofloculation methods. (a) Constant potential with applied potential of 0.6 V. (b) Constant potential with applied potential of 0.9 V. (c) Constant potential with applied potential of 1.2 V. (d) Potential pulsing, 0.5 s pulse, upper potential limit of 0.9 V and lower potential limit of 0.6 V. (e) Potential pulsing, 0.5 s pulse, upper potential limit of 0.9 V and lower potential limit of 0 V. (f) Potential cycling, 10 mV/s scan rate, upper potential limit of 0.9 V and lower potential limit of 0 V. (g) Potential cycling, 100 mV/s scan rate, upper potential limit of 0.9 V and lower potential limit of 0 V. (h) Potential cycling, 1 V/s scan rate, upper potential limit of 0.9 V and lower potential limit of 0 V. All potentials are versus a Ag/AgCl reference electrode.
atomic concentration was low (< 2%). It is likely that if the pulsing method were performed for longer periods of time (> 10 total min more positive than the onset of water oxidation catalysis), the islands would eventually grow together to form films similar to those seen in Figure 2.21b and Figure 2.21c.

The films electroflocculated via potential cycling (Figure 2.21f, g and h) appear to also deposit in IrO$_x$ NP islands initially as well, particularly seen in the films formed at the faster scan rates (100 mV/s and 1 V/s). EDS ratified that the brighter areas in the images were IrO$_x$ NPs. For the film formed at 1 V/s, the darker areas of the electrode showed very little Ir concentration (< 1% Ir). The darker areas of the film flocculated at 100 mV/s exhibited higher concentrations of Ir (~2%), compared to the faster scan rate. At the slowest scan rate, the film morphology resembles that of a film formed via the constant potential method, where it’s starting to cover the entire electrode surface. EDS confirmed this with an atomic concentration ranging from 4-6% Ir.

2.3.3 Chemical Flocculation of Iridium Oxide Nanoparticles

For comparison, a chemical flocculation was attempted, using Ce(IV) as an oxidant. When a four-fold excess of Ce(IV) was added (i.e., four times the charge accumulated during the

![Figure 2.22: IrO$_x$ NP solution as-synthesized as pH 13 (left) and after the addition of CAN (right). The solution changes from a clear, purple solution to a colorless solution with a brown precipitate.](image-url)
induction phase of electroflocculation), the normally purple solution turned colorless and a brown precipitate formed at the bottom of the vessel, as seen in Figure 2.22.

In another test, a 1 mM solution of Ce(IV) oxidant was added gradually to the pH 13 IrOx NP solution. A color change was observed, first to a pale blue and then to a light brown, neither with any visible precipitate. However, addition of excess oxidant to the solution produced a brown precipitate; the solution remained brown as well. When left at room temperature for 15 hours, the solution turned colorless to resemble the resulting solution of the first chemical flocculation test.

X-ray Photoelectron Spectroscopy (XPS) performed on both precipitates reveal a similar spectrum for each. The spectrum for the precipitate formed in the second trial is seen in Figure 2.23. The expected signals for Ir, Ce, Na, O and Au were all present. The atomic ratio of Ce to Ir was roughly 2:1; this corresponds with the expected reaction, where two Ce(IV) would be needed to oxidize Ir^{IV} to Ir^{VI} which then flocculate. The precipitate included Ce due to the insolubility of Ce(OH)₃, as the NPs are synthesized in a pH 13 solution. Chemical flocculation by Ce(IV), therefore, is a less clean way to flocculate the IrOx NPs. The presence of Ir in the precipitate

![XPS spectrum](image-url)

**Figure 2.23**: XPS of the precipitate formed via “chemical flocculation” of the IrOx NPs with Ce(IV). The precipitate was drop-cast onto a Au coated glass slide.
precipitate is consistent with the precipitation mechanism of the electroflocculation discussed above, where enough charge must be passed in order for the NPs to flocculate and fall out of solution.

2.3.4 Direct pH Change for Iridium Oxide Nanoparticle Precipitation

From the hypothesis that a localized change in pH was triggering the flocculation and film formation of the IrO\textsubscript{X} NPs, directly changing the pH of the solution was explored as a means to deposit a film. A non-coordinating acid, HClO\textsubscript{4}, was chosen, as previous studies had shown that coordinating acids, such as H\textsubscript{3}PO\textsubscript{4}, can stabilize IrO\textsubscript{X} NPs in solution, which would defeat the purpose.\textsuperscript{1} A sufficient concentration of acid was added in order to neutralize the 0.1 M NaOH present in the as-synthesized IrO\textsubscript{X} NP solution and it was allowed to sit at RT for 24 hours in order to stabilize. Different electrode slides were then dipped into the pH adjusted solution. Films were successfully formed on nanoITO, TiO\textsubscript{2}, Au and nanoITO/TiO\textsubscript{2} core/shell electrodes, as well as on top of two different Ru polypyridal complexes. Film formation was unsuccessful for Au surfaces that were not previously cleaned via piranha solution and on a film comprised of a porphyrin based complex. This is likely due to the more hydrophobic nature of these surfaces, suggesting that the IrO\textsubscript{X} NP films are preferential to hydrophilic surfaces. More on this is discussed in Chapter 5. There does appear to be a time window of deposition where this dip-coating method works. Films will not form within the first 24 hours after adding the acid and after 72 hours of sitting on the benchtop, the IrO\textsubscript{X} NPs have completely precipitated out of solution onto the bottom of the vial. Once they have reached this phase, they are no longer viable to create films on other surfaces. The ideal window for this method is between 24 and 48 hours after acid addition.
2.4 CONCLUSIONS

The above results demonstrate how the electroflocculation of IrO\textsubscript{x} NPs is a precipitation process. The induction period observed via eQCM and AFM correlates to an amount of charge passed in order for the NPs to flocculate. The charge, in turn, is related to the acidification of the interface by the water oxidation process, initiating the NP flocculation. Electr
oflocculation in lower pH solutions yields significantly smaller films, suggesting that the mechanism has changed, possibly due to the change of surface of the IrO\textsubscript{x} NPs. The NPs precipitate onto whatever surface is present, creating a film.

Three different electroflocculation methods were explored: constant potential, potential pulsing and potential cycling. Based off of their electrochemistry and microscopy, the most ideal films were formed via the potential cycling and pulsing techniques. There appears to be a balance of H\textsuperscript{+} formation to induce flocculation and O\textsubscript{2} formation that inhibits film deposition onto the electrode surface that is met by varying the potential applied by the electrode.

Flocculation via chemical methods and direct pH change further endorses the localized pH change mechanism for electroflocculation. All of these methods create IrO\textsubscript{x} NP films without any stabilizing ligand, which could lead to an increase in catalytic activity. The data provide deeper insight into the creation of these films and how the structure could affect their catalytic properties for water oxidation.

2.5 ACKNOWLEDGEMENT

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of the SEM, AFM and XPS facilities at the Chapel Hill Analytical and Nanofabrication Laboratories. The exploration of different electroflocculation techniques was performed by Robert Kieber (undergraduate researcher), including the preparation and cyclic voltammetry of all of the films, as well as the integrations and conversions to coverage.
REFERENCES


CHAPTER 3: Characterization of Iridium Oxide Nanoparticles

3.1 INTRODUCTION

While the catalytic activity of iridium oxide nanoparticles has been thoroughly explored, little is known about the surface chemistry and why these nanoparticles are such efficient catalysts. There has been extensive research on the bulk counterpart, IrO$_2$, in terms of traditional characterization techniques, such as Raman, UV-Vis and X-ray photoelectron spectroscopy.$^{1-17}$ However, little of it has been applied to the IrO$_x$ NPs. Due to their very small size (< 2 nm in diameter), these nanoparticles have a high surface area to volume ratio. Because of this, understanding the surface chemistry and how it affects the catalytic ability of the IrO$_X$ NPs is paramount.

The bulk material IrO$_2$ has gained a lot of attention for use as a durable anode material.$^{1,4,5,7,13,17-21}$ It can also catalyze the water oxidation reaction, though at a higher overpotential compared to its high surface area nanoparticle counterpart.$^{22-28}$ These films can be prepared by a variety of methods, most involving the metallic Ir species undergoing oxidizing conditions. These materials have been extensively characterized using microscopy, spectroscopy and other methods, all with similar results.

Raman spectroscopy, in particular, has proven a useful tool for elucidating structural features of a material. Extensive research has been performed on various iridium oxide materials, including sputtered iridium oxide films (SIROF), electrodeposited iridium oxide films (EIROF), IrO$_2$ formed via thermochemical methods and single crystal IrO$_2$.$^{3,7,9,13-16,29}$ The large majority of these films exhibited tetragonal rutile structure, where the B$_{1g}$, E$_g$, A$_{1g}$ and B$_{2g}$ modes
are Raman active. These Raman shifts appear at 145, 561, 752 and 728 cm\(^{-1}\), respectively.

Additional Raman peaks have been observed at 366 and 456 cm\(^{-1}\), which correspond to the Ir=O and Ir-O stretching modes. In most Raman spectra collected of IrO\(_2\) films, the rutile structure is confirmed by the presence of two major peaks, corresponding to the E\(_g\) and combined A\(_{1g}\) and B\(_{2g}\) modes. These peaks are always present, though their exact peak position and full width half max can vary depending on the surface on which it has been deposited.\(^7,12\) The one exception to this is the EIROF, which exhibits multiple overlapping peaks from 445 to 744 cm\(^{-1}\).\(^8\) While some of these peaks overlap with the rutile peaks addressed above, the other peaks suggest that there is limited crystalline structure to these EIROFs.

IrO\(_2\) is tetragonal rutile in crystalline structure and it has long been assumed that the IrO\(_X\) NPs have chemical aspects similar to IrO\(_2\). There are some literature examples that refer to them as IrO\(_2\) NPs, though largely without any experimental justification.\(^25,30-32\) The NPs are typically synthesized using a Woehler method,\(^33\) where an Ir\(^{IV}\) chloride salt undergoes a basic hydrolysis to form IrO\(_X\) NPs at relatively low temperatures. Because of the lack of oxidative or reductive conditions, it was largely assumed that the Ir maintained its Ir\(^{IV}\) oxidation state. The research presented below sets out to compare the Raman spectra of these NPs to their bulk counterparts and determine whether the assumption is valid.

X-ray analysis methods, such as x-ray absorption spectroscopy (XAS), X-ray absorption near-edge structure (XANES), extended x-ray absorption fine structure (EXAFS) and x-ray photoelectron spectroscopy (XPS), have been used to further probe the structure of bulk IrO\(_2\) and, more recently, larger IrO\(_X\) NPs.\(^2,5,6,10,11,34,35\) X-ray techniques are popular for both elemental analysis and determining the oxidation states and surrounding environment of each element. In particular, XANES has been used to demonstrate a shift in the Ir L\(_3\)-edge towards higher energies
as it is electrochemically oxidized.\textsuperscript{2} Similarly, when the IrO\textsubscript{2} films are formed on other substrates, the Ir L\textsubscript{3}-edge can shift depending on whether the substrate acts as a reducing or oxidizing agent.\textsuperscript{10} EXAFS was also able to demonstrate structural disorder in electrodeposited bulk material IrO\textsubscript{2} films, as well as identify two different Ir-O bond lengths within the sample (1.995 and 1.959 Å). These bond lengths also changed with applied potential; as the IrO\textsubscript{2} films were oxidized, the Ir-O bond lengths shortened.\textsuperscript{2}

XPS, conversely, has largely been used to examine the oxidation states of various iridium oxide materials, focusing on thermally deposited and electrochemically deposited IrO\textsubscript{2} films.\textsuperscript{6,34} A doublet is usually observed at 62 and 65 eV, corresponding to the Ir 4f\textsubscript{7/2} and Ir 4f\textsubscript{5/2} orbital electrons. Tailing is also observed with these doublets, attributed to the 5d electron screening.\textsuperscript{6,36} More recently, the Nilsson laboratory developed an ambient-pressure XPS in order to incorporate electrochemical experiments.\textsuperscript{5} They applied this to the study of water oxidation catalysis via IrO\textsubscript{X} NPs (50-80 nm in diameter) and determined that the surfaces of the IrO\textsubscript{X} NP films was a mixture of both the oxide and hydroxide species. They also determined that water oxidation undergoes a deprotonation mechanism, where the hydroxide is oxidized to the oxide species on the surface of the catalyst.\textsuperscript{35} The research presented below aims to demonstrate how the small IrO\textsubscript{X} NPs (< 2 nm in diameter) compare to both the bulk IrO\textsubscript{2} and larger IrO\textsubscript{X} NPs using XPS, as well as demonstrate how the surrounding environment can deeply impact the spectra obtained.

Previous work by the Murray laboratory has focused on trying to characterize small IrO\textsubscript{X} NPs by altering their surface chemistry with capping ligands such as carboxylates.\textsuperscript{37} These capped NPs were then analyzed using techniques such as mass spectrometry and NMR. While the exchange into non-aqueous solvents was successful, the constant exchange of the capping
ligands resulted in difficult quantification. In the work presented below, the goal was to largely characterize them either in aqueous media, to remove the solvent entirely by electroflocculating the NPs into a film, or precipitating them using a variety of methods. Eliminating this uncertainty simplifies analysis of the IrOₓ NPs. Presented below are electrochemical, microscopic, spectroscopic and zeta potential investigations with the aim to better understand the surface chemistry behavior of small IrOₓ NPs.

3.2 EXPERIMENTAL

3.2.1 Aqueous Hydrolysis of IrOₓ NPs

The Ir⁴⁺Oₓ nanoparticles were synthesized using a Wohler method, in which a 2.5 mM solution of K₂IrCl₆ (99%, Strem Chemicals) in nanopure H₂O was adjusted to pH 13 with 25% w/w NaOH (50% w/w, Fisher Scientific). The solution was heated at 90 °C for 20 minutes and then allowed to cool to RT and to rest for at least 24 hours after the synthesis, before electroflocculation.

3.2.2 Electroflocculation of IrOₓ NP Films

For electroflocculations on Au coated glass slides, Au slides were first cleaned by exposure to piranha solution (3:1 concentrated H₂SO₄ (Fisher Scientific) to H₂O₂ (30% w/w, Fisher Scientific)), and then rinsed with nanopure H₂O and dried under a stream of Ar gas. Piranha solution is highly oxidizing and should therefore be handled with care.

The films were formed from unstirred pH 13 IrOₓ nanoparticle solutions by applying a potential bias of 0.9 V vs. Ag/AgCl for 10 minutes. The films were rinsed with nanopure H₂O and then cyclic voltammetry (CV) was performed in 0.1 M NaOH to verify the presence of a film.

3.2.3 Precipitation of Iridium Oxide Nanoparticles

Precipitation of the iridium oxide nanoparticles was induced using one of three methods:
direct lowering of the pH using a non-coordinating acid, addition of a chemical oxidation, and addition of isopropanol. The first two are previously discussed in Chapter 2, where the acidification of the IrO\(_x\) NPs with no coordinating ligand results in precipitation. The third method involves adding an excess of isopropanol (3:1 isopropanol:IrO\(_x\) NP solution), which in turn changes the polarity of the solution. This mixture is then centrifuged at 6000 rpm for 10 minutes, which results in precipitation of the nanoparticles.

### 3.2.4 Electrochemistry of Iridium Oxide Nanoparticles

Electrochemical measurements were performed using a three electrode set-up, with a Au coated glass slide as a working electrode, a Pt wire as an auxiliary electrode and a 3 M Ag/AgCl reference electrode. A CH Instruments 760c potentiostat was used for these experiments. All cyclic voltammetry was performed either in 0.1 M NaOH (from 50 % w/w NaOH, Fisher Scientific) or in various phosphate buffers that each had a constant phosphate concentration (0.1 M PO\(_4^{3-}\)).

### 3.2.5 UV-Vis Spectroelectrochemistry of Iridium Oxide Nanoparticles

IrO\(_x\) NP films were deposited on FTO\(\mid\)nanoITO conductive films using the pH adjusted dip-coating method discussed in Chapter 2. The as-synthesized pH 13 IrO\(_x\) NPs were adjusted to pH 1 using concentrated HClO\(_4\) (GSF Chemicals). After 24 hours, the FTO\(\mid\)nanoITO glass slides were dipped in the IrO\(_x\) NP solution for 1.5 hours, then rinsed thoroughly with nanopure H\(_2\)O and dried with Ar. The pH 5.8 buffers that were used in the aforementioned experiments were composed of 37.5 mM Na\(_2\)SiF\(_6\) (Aldrich) and 80 mM NaHCO\(_3\) (Aldrich) in nanopure water.

Spectroelectrochemical characterizations were conducted at pH 5.8 in a three electrode cell with a 1 cm path length cuvette by using a CHI 670 potentiostat, and an Agilent UV-Vis spectrometer. The potential was varied in 0.02 V increments from -0.2 to 1.2 V vs. Ag/AgCl.
with spectra recorded at each increment after holding the potential for 60 s. (The Ag/AgCl reference is +0.199V vs NHE.) The data were analyzed by using SpecFit.

3.2.6 Raman Spectroscopy of Iridium Oxide Nanoparticles

All Raman Spectra were obtained using a Renishaw Invia Raman Microscope, using a 633 nm laser. Spectra were obtained of the as-synthesized pH 13 IrO\textsubscript{x} NPs in solution, drop cast on a glass slide, the isopropanol precipitated IrO\textsubscript{x} NPs as a solid on a glass slide and the electroflocculated IrO\textsubscript{x} NPs on a Au coated glass slide.

3.2.7 Microscopy of Iridium Oxide Nanoparticle Films

Microscopic images of IrO\textsubscript{x} NP films were obtained from a Hitachi S-4700 Cold Cathode Field Emission Scanning Electron Microscope (SEM) and an Asylum Research MFP3D Atomic Force Microscope.

3.2.8 Zeta Potential Measurements of Iridium Oxide Nanoparticles

Zeta potential measurements were collected on a Malvern Zetasizer Nano-ZS. To resuspend the IrO\textsubscript{x} NPs in a solution with lower electrolyte concentration, an excess of isopropanol was added to the as-synthesized pH 13 IrO\textsubscript{x} NPs and the resulting solution was centrifuged using an Eppendorf 5810 centrifuge with a fixed angle rotator at 6000 rpm for 10 minutes. The excess liquid was decanted and the precipitate was then resuspended in 0.01 M phosphate solutions, which varied in pH.

3.2.9 X-Ray Photoelectron Spectroscopy of Iridium Oxide Nanoparticles

X-ray photoelectron spectra were obtained on a Kratos Axis Ultra DLD system with monochromatic Al K\textalpha\ x-ray source. High resolution scans were taken at pass energy of 20 eV and the spectral energy axis was aligned at the C 1s peak (284.6 eV). The IrO\textsubscript{x} NPs were prepared in four different ways for analysis via XPS. The first preparation involved drop-casting the as-synthesized IrO\textsubscript{x} NPs in 0.1 M NaOH onto a piranha cleaned (described in section 3.2.2)
Au coated glass slide. The second was electroflocculation onto a Au coated glass slide, as described above. The third preparation used a chemical oxidant (NH₄Ce(NO₃)₆), which resulted in precipitated IrOₓ NPs. This precipitate suspension was drop cast onto a piranha cleaned (as discussed in Section 3.2.2) Au coated glass slide. The fourth preparation involved exchanging the pH 13 IrOₓ NPs into dichloromethane (DCM), using valeric acid as a capping ligand. The exchanged NPs were then drop-cast onto a piranha cleaned (described above) Au coated glass slide.

3.3 RESULTS AND DISCUSSION

3.3.1 Electrochemistry of Iridium Oxide Nanoparticles

3.3.1.1 Electrochemical Behavior of IrOₓ NP Films at Different pH

As discussed in Chapter 2, there are three electrochemical areas of interest for the electroflocculated IrOₓ NP films, the Ir⁴⁺/³⁺ redox couple, the Ir⁵⁺/⁴⁺ redox couple and the water oxidation catalysis region, as seen in Figure 3.1. All of these regions are Nernstian behaved, shifting ca. 70 mV/pH.²⁴,²⁶-²⁸ Studying the electrochemical behavior of these NPs as
electroflocculated films also gives the added advantage of being able to integrate the charge under the \( \text{Ir}^{\text{IV}/\text{II}} \) and \( \text{Ir}^{\text{V}/\text{IV}} \) waves to find the coverage of Ir on the surface of the electrode.

During these studies, the apparent Ir coverage of the films was observed to change between phosphate buffers of different pH. When the same film was observed in a more acidic buffer (pH 2) and then in a more basic solution (pH 13), the coverage drastically changed by an order of magnitude, as seen in Table 3.1. The calculated coverage from the Ir IV/V wave was much larger at higher pH values and a trend was seen: as pH increased, the calculated coverage increased as well. Furthermore, when the same film (Film 3) was transferred back to the lower pH buffer, the coverage decreased back to a value comparable with the originally measured coverage at the same pH. This enormous change could be due to an increased resistance within the film itself at lower pH, resulting in a higher iR effect, and in turn, a lower apparent coverage, as discussed below.

**Table 3.1:** Examples of how the measured coverage of Ir of the same film can vary between different pH solutions. \( \Gamma_{\text{Ir}} \) is in mol Ir/cm\(^2\) and is determined by integrating the \( \text{Ir}^{\text{V}/\text{IV}} \) oxidation wave.

<table>
<thead>
<tr>
<th>Film</th>
<th>( \Gamma_{\text{Ir}} ) at pH 1.8</th>
<th>( \Gamma_{\text{Ir}} ) at pH 12.7</th>
<th>( \Gamma_{\text{Ir}} ) at pH 1.8</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( 7.99 \times 10^{-9} )</td>
<td>( 1.60 \times 10^{-8} )</td>
<td>----</td>
</tr>
<tr>
<td>2</td>
<td>( 3.19 \times 10^{-8} )</td>
<td>( 5.56 \times 10^{-8} )</td>
<td>----</td>
</tr>
<tr>
<td>3</td>
<td>( 1.77 \times 10^{-9} )</td>
<td>( 5.60 \times 10^{-8} )</td>
<td>( 3.58 \times 10^{-9} )</td>
</tr>
</tbody>
</table>

Because of this iR effect, the change in coverage with respect to potential scan rate was also studied and the results are listed in Table 3.2. In a system lacking resistance, the charge (Q) from the \( \text{Ir}^{\text{V}/\text{IV}} \) peak would remain constant with scan rate. However, as scan rate increased, the charge - and thus apparent coverage - of a given film decreased. Such an observation is indicative of a larger resistance in the film, preventing the flow of ions within. This iR effect,
therefore, hinders the oxidation of Ir sites that are not easily accessible by ions (i.e. those not on or near the surface of the NP film) at faster scan rates, resulting in a lower observed coverage.

Table 3.2: Change in charge (Q) of the Ir IV/V wave with varying scan rate (ν) at pH 3.

<table>
<thead>
<tr>
<th>Scan rate, ν</th>
<th>5 mV/s</th>
<th>20 mV/s</th>
<th>50 mV/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q of Ir IV/V wave</td>
<td>7.42 x 10^4 C</td>
<td>4.87 x 10^5 C</td>
<td>No peak observed</td>
</tr>
</tbody>
</table>

In all buffers, especially those at the lower pH values, an iR effect was apparent at higher overpotentials (η). As the overpotential increased, the turnover rate decreased, resulting in an almost non-existent change in current with respect to coverage at the highest measured overpotential, 0.6 V. Such results suggest there is a limiting factor at higher overpotentials where an increase in nanoparticle coverage no longer increases the overall catalytic activity. One might suspect the increased resistance in the films to be the limiting factor, as was observed with the change in coverage mentioned above because this would limit the amount of water accessing the active Ir sites within the film. While the driving force for the reaction increases with overpotential, the amount of water able to flow through the film would be limited by the resistance, resulting in little or no change in activity with increasing film coverage. Another possibility is that all of the films were too thick. In general, the dependence of catalytic reactivity on coverage follows a logarithmic trend, where at higher coverages of catalysts, the reactivity levels off. Thus, the films analyzed may have already reached their limit in reactivity and any slight difference seen in coverage was negligible.

To gain a better understanding of the iR effects, the conductivity of each phosphate buffer was measured and the results are shown in Table 3.3. All of the buffers had similar conductivities, ranging from 29 mS/cm to 52 mS/cm. Since the conductivities were all very similar, the solution resistance between the buffers must also be very similar. This demonstrates that while there is a significant iR drop in the lower pH buffers seen in the data, there is a
minimal effect from the actual solution regardless of buffer. This observation implies that the resistance is within the film, as opposed to in the solution.

**Table 3.3:** Conductivity measurements (mS/cm) of each of the phosphate buffers. pH 3 and 5 are both 1.0 M phosphate and pH 7.5, 10 and 12 are 0.1 M phosphate.

<table>
<thead>
<tr>
<th>Buffer</th>
<th>1.0 M pH 3</th>
<th>1.0 M pH 5</th>
<th>0.1 M pH 7.5</th>
<th>0.1 M pH 10</th>
<th>0.1 M pH 12</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conductivity (mS/cm)</td>
<td>39.0</td>
<td>27.0</td>
<td>42.8</td>
<td>45.0</td>
<td>52.8</td>
</tr>
</tbody>
</table>

3.3.1.2 Kinetic Studies of Water Oxidation Catalysis vis IrOx NP Films

The advantage of using a film in an electrochemical experiment is that it eliminates any solution mass transport effects on the kinetic activity of the redox species. This makes the kinetics, and the studies of them, much less complex compared to if the redox species were freely diffusing. In an unpublished message, Stephen Feldberg discussed the theory behind using an electrocatalyst as a film in order to determine the rate constant for a given reaction.

The equation that he derived is below:

**Equation 3-1**

\[ I_{SS} = nAFk_{cat}\Gamma_{cat}[S]_{bulk} \]

In this equation, the steady state current \( I_{SS} \) is proportional to the area of the electrode \( A \), the turnover rate constant of the catalyst \( k_{cat} \), the coverage of the catalyst \( \Gamma_{Ir} \), and the concentration of the substrate from the catalyzed reaction in the bulk solution \( [S]_{bulk} \). In order for this relationship to be true, it makes three major assumptions: \( k_{cat}[S]_{bulk} \) follows pseudo-first order kinetics, electron transfer (ET) is facile between the electrode surface and the redox species, and electron hopping is fast within the film. All of these conditions are assumed to be met with the IrOx nanoparticles when catalyzing water oxidation in an aqueous solution.
The films were created via electroflocculation, holding the potential of the electrode at 0.9 V in a solution of pH 13 nanoparticles. The length of time for the potential hold was varied from three to fifteen minutes in order to create a range of “coverages;” the process is not solely dependent on time, thus coverage may vary for films electroflocculated for equivalent times. The coverages themselves were determined from the charge ($Q$) of the Ir$^{V/IV}$ redox wave obtained using linear sweep voltammetry. In order to mimic the work of Nakagawa et al., the films were originally subjected to a linear sweep through the Ir$^{V/IV}$ wave out to water oxidation, where the potential was held for 200 seconds and then swept back through the Ir$^{V/IV}$ wave. It was observed that using this technique led to a drastic decrease in calculated coverage for the film, presumably due to loss of nanoparticles from O$_2$ gas formation (Table 3.4). From this, it was concluded that the coverage determined in the initial linear sweep was not representative of actual number of active Ir sites when the $I_{SS}$ was taken.

Table 3.4: Examples of how the coverage of Ir can change before and after potentials more positive the onset of water oxidation are applied. $\Gamma_{Ir}$ is in mol Ir/cm$^2$ and is determined by integrating the Ir$^{V/IV}$ oxidation wave.

<table>
<thead>
<tr>
<th>pH 13</th>
<th>pH 7</th>
<th>pH 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma_{Ir}$ Before</td>
<td>$\Gamma_{Ir}$ After</td>
<td>$\Gamma_{Ir}$ Before</td>
</tr>
<tr>
<td>6.8 x 10^{-9}</td>
<td>3.5 x 10^{-9}</td>
<td>1.7 x 10^{-9}</td>
</tr>
<tr>
<td>4.9 x 10^{-8}</td>
<td>1.8 x 10^{-8}</td>
<td>4.6 x 10^{-9}</td>
</tr>
<tr>
<td>2.7 x 10^{-7}</td>
<td>3.3 x 10^{-8}</td>
<td>2.8 x 10^{-8}</td>
</tr>
</tbody>
</table>

To ensure that the coverage determined by the Ir$^{V/IV}$ wave accurately represented the NPs that are catalytically involved in water oxidation, the current at different overpotentials ($\eta$) from a fast potential scan rate linear sweep were used as “$I_{SS}$” in lieu of a true steady state current. By limiting the time spent at the potentials where O$_2$ is produced, there is less time for the NP film to be disturbed, allowing the coverage measured at the IV/V wave to be a better representation of
the NPs present when water oxidation values are measured. Due to the observed change in coverage due to scan rate at low pH, the linear sweep of the IrV/IV couple was performed at a slower scan rate of 5 mV/s. This was then followed by a faster linear sweep (100 mV/s) into water oxidation to obtain the current values, “\( I_{SS} \)”, at different overpotentials (\( \eta \)).

**Figure 3.2:** \( j \) (A/cm²) vs. \( \Gamma_{Ir} \) (mol Ir/cm²) for four different overpotentials (\( \eta \)), indicated by the different symbols in each graph. a) Plot for IrO\(_x\) NP films in pH 3 phosphate buffer. b) Plot for IrO\(_x\) NP films in pH 5 phosphate buffer. c) Plot for IrO\(_x\) NP films in pH 7.5 phosphate buffer. d) Plot for IrO\(_x\) NP films in pH 10 phosphate buffer. e) Plot for IrO\(_x\) NP films in pH 12 phosphate buffer.
The results for the aforementioned experiments are seen in Figure 3.2, where current density, \( j \), at a given overpotential \( \eta \), is plotted versus the coverage in moles of Ir (\( \Gamma_{\text{Ir}} \)). The plots demonstrate a linear relationship where the slope is proportional to the rate constant of the catalytic reaction (\( k_{\text{cat}} \)), as per the equation mentioned above. However, at the higher overpotentials, the currents converge. Instead of showing the expected increase in rate with an increase in driving force, the apparent rate decreases and levels off at these higher potentials. This could be due to a number of reasons, including an iR effect, as previously mentioned, or a higher \( O_2 \) production, which in turn creates noise that distorts the values obtained. A third

<table>
<thead>
<tr>
<th>( \eta )</th>
<th>( \text{pH} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 0.3 )</td>
<td>( 3 )</td>
</tr>
</tbody>
</table>

\[
\text{Table 3.5 } k_{\text{cat}} \text{(s}^{-1}) \text{ of water oxidation catalysis for two different overpotentials in 0.1 M phosphate buffers of varying pH.}
\]

\[
\text{Figure 3.3: Distribution plot of the different phosphate species with respect to pH. The } k_{\text{cat}} \text{ values for the 5 different buffers are plotted, as well, for comparison.}
\]

75
reason that could cause the current to converge is that the buffers may not have the capacity to handle such high rates of water oxidation. If the buffer capacity is not sufficient, then the pH at the electrode surface may not be the same as that of the bulk solution. Because of this, the rates at lower overpotentials, such as $\eta = 0.3$ and 0.4, are a more accurate representation of the kinetics of water oxidation catalysis, where both the iR effect and water oxidation is minimal.

Using Figure 3.2, the turnover rate constants, $k_{cat}$ were determined at overpotentials of 0.3 and 0.4 V from the slopes, as shown in Table 3.5. Overall, the turnover rates from the lower pH buffers were much higher than that for the higher pH buffers, with an order of magnitude in change between pH 3 and pH 12, from 0.97 to 0.10 s$^{-1}$. A distribution diagram of phosphoric acid and its dissociated products is shown in Figure 3.3. The calculated $k_{cat}$ values are overlaid on this diagram. There does not appear to be a trend in the $k_{cat}$ values with respect to which phosphate anion is predominate in the buffer. Instead, there is a general decrease in rate with respect to pH. This trend, however, is not linear with respect to the concentration of H$^+$ or pH.

3.3.1.3 Catalytic Tafel Plots

The Tafel equation, shown below, is another way of analyzing irreversible electrochemical reactions and in this case, it overcomes the difficulty of analyzing higher overpotentials with $j$ vs. $I_R$ plots by extrapolating to smaller overpotentials.

**Equation 3-2**

$$\eta = \left(\frac{2.3RT}{\alpha nF}\right) \log\left(\frac{j}{j_0}\right)$$

It relates the overpotential, $\eta$, to the logarithm of the ratio of the current density, $j$, to the exchange current density, $j_0$. Catalytic Tafel plots, as discussed in a review by Nathan Lewis, use a simplified version of this equation, substituting $\left(\frac{2.3RT}{\alpha nF}\right)$ for a constant $b$. When plotted $\eta$
versus \( \log(j) \), the slope is \( b \) and the y-intercept is \( -b \log(j_0) \). This slope is a function of the rate of the reaction, in this case \( k_{cat} \), the iR drop experienced at high overpotentials, as well as the other parameters shown in the Tafel equation above. When compared with other catalysts, the slope can be a qualitative evaluation of whether the catalysts have similar mechanisms and if the solutions have similar resistances. The y-intercept, on the other hand, is related to the exchange current density, \( j_0 \), which is a measure of how the electrode surface behaves at zero overpotential.
is dependent on the electrode and catalyst material, the surface roughness of both, and the concentration of the reactants and products in the catalyzed reaction, in this case H₂O and O₂.

Figure 3.4 a through e are the catalytic Tafel plots for films of different electroflocculation times for a given pH. With the exception of pH 5, films exposed to the same buffer have similar slopes at higher overpotentials. This implies that they have similar iR effects and $k_{cat}$, which is expected considering they have the same parameters, with the exception of coverage. From this, it can be inferred that the mechanism of water oxidation doesn’t change with increased coverage at each specific pH. The $j_0$ for each of the pH buffers increases with electroflocculation time, or increased coverage, however, not significantly. This is due to the fact that the coverages of IrOₓ NPs are high enough that they may have reached their maximum catalytic potential, as discussed earlier. So while the exchange current density changes somewhat between the different coverages, they are essentially the same considering these values are extrapolated from higher overpotentials. The abnormality of the pH 5 Tafel plots (Figure 3.4b) could be due to the poor buffer capacity at this pH. This could greatly affect the

![Catalytic Tafel plot of similar coverage IrOₓ NP films in different pH phosphate buffers, represented by the different colors. The slope corresponds to the $k_{cat}$ and mechanism of catalysis, while the y-intercept corresponds to the exchange current density.](image)

**Figure 3.5:** Catalytic Tafel plot of similar coverage IrOₓ NP films in different pH phosphate buffers, represented by the different colors. The slope corresponds to the $k_{cat}$ and mechanism of catalysis, while the y-intercept corresponds to the exchange current density.
shape of the Tafel plot as the pH of the solution is more than likely changing with water oxidation.

**Table 3.6**: The slopes (b) and exchange current values (j₀) for the IrOx NP films at different pH values taken from the catalytic Tafel plot. Each film was electroflocculated for 10 minutes.

<table>
<thead>
<tr>
<th>pH</th>
<th>3</th>
<th>5</th>
<th>7.5</th>
<th>10</th>
<th>12</th>
</tr>
</thead>
<tbody>
<tr>
<td>slope (b)</td>
<td>0.7531</td>
<td>0.9053</td>
<td>0.802</td>
<td>0.8334</td>
<td>0.7343</td>
</tr>
<tr>
<td>j₀</td>
<td>0.0021</td>
<td>0.0025</td>
<td>0.0034</td>
<td>0.0027</td>
<td>0.0035</td>
</tr>
</tbody>
</table>

Figure 3.5 overlays the Tafel plots of films that have the same electroflocculation time (similar coverages) but were exposed to different pH buffers. The slopes of these are similar, however, the lines are not as parallel as the films compared in the same buffer. This suggests that there is a difference in either the $k_{cat}$ or the resistance within the film, as seen in Table 3.5. There is also an effect seen by the difference in conductivity of the solutions, referring back to Table 3.3. The less conductive buffers, pH 3 and pH 5, have steeper slopes because of the smaller change in current with applied potential, due to a higher resistance. The exchange current densities in all of the buffers, on the other hand, were very similar and clustered around 0.003 A/cm² (Table 3.6). They also followed no trend with respect to pH, inferring that a H⁺ is not involved in the rate determining step. This discovery suggests that while the measured coverages of Ir found from the integration of the Ir$^{V/IV}$ wave varied drastically, the active electrode area (or volume in this case with a permeable film) and roughness of the said film are fairly similar at $\eta = 0$. The variance between these values can be explained by non-uniformity of the films and also by the long extrapolation from a high overpotential back to zero.

### 3.3.2 UV-Vis Spectroelectrochemistry of Iridium Oxide Nanoparticles

UV-Vis difference spectra of the dip-coated IrOₓ NPs on FTO|nanoITO conductive films are presented in Figure 3.6 with respect to change in potential. The potential was held for 60 s, prior to each spectra being collected. The IrOₓ NP films were prepared by adjusting the pH of
the NP solution with a non-coordinating acid (HClO₄), as previously described in Chapter 2. The addition of a non-coordinating acid lowers the pH which induces precipitation of the IrOₓ NPs in the absence of a stabilizing ligand.

From the change in these spectra, a concentration gradient with respect to applied potential was created, as seen in Figure 3.7a. The intersects of each species corresponds to the E₁/₂ of each iridium redox couple. Difference spectra for each individual iridium oxidation species can be extrapolated from this information and that is seen in Figure 3.7b. Starting in the IrIII state, an absorbance peak at 600 nm grows in as the iridium is oxidized to the IrIV oxidation state. This peak continues to grow in intensity as the nanoparticles are oxidized to the IrV state. At more positive potentials, the IrOₓ NPs become black absorbers as they transition into the IrVI oxidation state, observed by the increase in absorbance at all wavelengths. These changes in absorbance correspond to the color of the nanoparticles in solution at each oxidation state: the reduced IrIII/Oₓ NPs are generally observed to have a yellow-green color, the as-synthesized

Figure 3.6: UV-Vis difference spectra for the precipitated IrOₓ NP films on a nanoITO buffer in pH 5.8 NaSiF₆ buffer. The potential was varied in 20 mV increments from -0.2 to 1.4 V vs. Ag/AgCl and was held for 60 s before each absorbance spectra was obtained.
Ir^{IV}\text{O}_x\text{NPs} are purple and as they are oxidized to higher oxidation states, they transition from a darker purple color to black. Also note that the Ir^{VI} oxidation state appears at potentials that are positive enough to induce water oxidation electrocatalysis, indicating that the Ir^{VI} species is an active participant in this reaction. Similar behavior has been reported for the bulk IrO$_2$ material, which has shown promise as an electrochromic sensor material.$^{130a, 130i}$

3.3.3 Zeta Potential Measurements of Iridium Oxide Nanoparticles

Zeta potential measurements were collected for IrO$_x$ NPs in different pH phosphate buffers. The method of adding 0.1 M H$_3$PO$_4$ and adjusting using NaOH to the as-synthesized pH 13 IrO$_x$ NPs proved to affect the zeta potential measurements due to the high electrolyte

![Figure 3.7: a) Distribution plot of each Ir oxidation state with respect to applied potential (V vs. Ag/AgCl), derived from the difference spectra in Figure 3.6. b) The difference spectra of each individual Ir oxidation state.](image-url)
concentration. In order to adjust the pH of the NPs with a decrease in electrolyte concentration, an excess of isopropanol was added to the pH 13 IrO\textsubscript{X} NPs and the resulting solution was centrifuged at 6000 rpm to induce precipitation. The precipitate was then resuspended in 0.01 M phosphate buffers of various pH. Presence of nanoparticles in the new solutions was confirmed via TEM, as seen in Figure 3.8.

The distributions of zeta potentials of the various pH IrO\textsubscript{X} NPs are presented in Figure 3.9 and the zeta potential values are in Table 3.7. At pH 2, the zeta potential is slightly positive, but centered ca. 0 mV. This is likely due to the species of phosphate present at pH 2, as previously presented in Figure 3.3. This is predominantly H\textsubscript{3}PO\textsubscript{4}, a neutral state. There is also a high concentration of H\textsuperscript{+}, which may explain the slightly positive zeta potential.
The IrO\textsubscript{X} NPs in pH 3.3 and 5.8 phosphate buffers have very similar zeta potentials at 
\(-44.9 \pm 2.7\) and \(-48.5 \pm 2.4\) mV, respectively. As both pH values are between the first and 
second pK\textsubscript{a}s of phosphoric acid, the dominant phosphate species is H\textsubscript{2}PO\textsubscript{4}\textsuperscript{−}. This would lead to a 
similar surface charge, and therefore zeta potential for these nanoparticles. This potential is 
negative due to the negative charge on the H\textsubscript{2}PO\textsubscript{4}\textsuperscript{−} species, which is likely the capping ligand 
present at these two pH values.

![Figure 3.9: Zeta potential distributions for the isopropanol precipitated IrO\textsubscript{X} NPs, resuspended in various phosphate buffers: a) pH 2  b) pH 3.3  c) pH 5.8  d) pH 7.7  e) pH 11 and f) pH 12.](image)

The IrO\textsubscript{X} NPs in pH 7.7 and 11 phosphate solutions also exhibited similar zeta potentials, 
at \(-31.3 \pm 4.2\) and \(-33.4 \pm 3.3\) mV. At both of these pH values, the predominant phosphate 
species is HPO\textsubscript{4}\textsuperscript{2−}, which is also negatively charged like H\textsubscript{2}PO\textsubscript{4}\textsuperscript{−}. While it is more negatively 
charged than H\textsubscript{2}PO\textsubscript{4}\textsuperscript{−}, the zeta potentials for these nanoparticles are more positive than the ones at 
the lower pH. This suggests that fewer of these capping ligands are required to stabilize the 
nanoparticles in solution, so a decrease in zeta potential is not observed.
Table 3.7: Zeta potentials for IrO$_X$ NPs, resuspended in 0.01 M Phosphate buffers of various pH.

<table>
<thead>
<tr>
<th>pH</th>
<th>Zeta Potential (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>8.2 ± 0.93</td>
</tr>
<tr>
<td>3.3</td>
<td>-44.9 ± 2.7</td>
</tr>
<tr>
<td>5.8</td>
<td>-48.5 ± 2.4</td>
</tr>
<tr>
<td>7.7</td>
<td>-31.3 ± 4.2</td>
</tr>
<tr>
<td>11</td>
<td>-33.4 ± 3.3</td>
</tr>
<tr>
<td>12</td>
<td>-6.5 ± 3.4</td>
</tr>
</tbody>
</table>

The zeta potential for the IrO$_X$ NPs at pH 12 shifts even further positive, but still remains negative. At this pH, the predominant phosphate species is PO$_4^{3-}$, however, there is also an abundance of OH$^-$ groups in solution as well. The OH$^-$ groups are presumed to be the stabilizing ligands method for the as-synthesized pH 13 IrO$_X$ NPs, so it is likely that they are also interacting with the NP surface in the phosphate buffers at this pH, as well. Looking at the distribution of the zeta potential measurements in Figure 3.9f, it no longer follows the Lorentzian distribution observed in the other pH solutions. Instead, there are two distinct distributions, a Lorentzian shaped one at -60 mV and an oddly shaped one centered ca. 0 mV. Because of this,

![Figure 3.10](image)

**Figure 3.10:** Raman spectra of the IrO$_X$ NPs in two different states. a) As-synthesized IrO$_X$ NPs in 0.1 M NaOH. b) Electrofloculated IrO$_X$ NP film on Au slide.
the overall zeta potential is -6.74 mV, however, it does appear that this value should be more negative. This may be explained by the nature of the experiment for measuring the zeta potential. For these measurements, a potential difference is applied across two electrodes to induce migration of the charged nanoparticles. However, it is known that when a potential is applied to the IrO\textsubscript{X} NPs in high pH solutions, the NPs will flocculate together. The peak at the more neutral potential may be due to the flocculated IrO\textsubscript{X} NPs, while the other peak at -60 mV is more representative of the IrO\textsubscript{X} NPs in pH 12 phosphate buffer.

### 3.3.4 Raman Spectroscopy of Iridium Oxide Nanoparticles

Raman spectra were obtained of the IrO\textsubscript{X} NPs in three different states, the as-synthesized pH 13 solution IrO\textsubscript{X} NPs, an electroflocculated IrO\textsubscript{X} NP film and the IrO\textsubscript{X} NPs precipitated via isopropanol. The spectra of the freely diffusing IrO\textsubscript{X} NPs and the electroflocculated IrO\textsubscript{X} NP film are shown in Figure 3.10. In the Raman spectrum of the pH 13 solution IrO\textsubscript{X} NPs, there is an abundance of peaks, some of which correlate to the rutile structure of bulk IrO\textsubscript{2} at ca.560 and 750 cm\textsuperscript{-1}.\textsuperscript{3,7,14,15} However, the presence of other Raman shifts suggests that the as synthesized

![Figure 3.11: Before (blue) and after (orange) Raman spectra of the same electroflocculated IrO\textsubscript{X} NP film, which presents a decrease in crystallinity over time.](image)

85
IrO$_x$ NPs are not the only Ir species present. It is likely that not all of the starting material (K$_2$IrCl$_6$) is converted to IrO$_x$ and there are some other Ir species, likely either Cl or OH salts, also in solution.

When the IrO$_x$ NPs are electroflocculated onto a Au plated glass slide, as seen in Figure 3.10b, there are two predominate Raman peaks observed at 550 and 720 cm$^{-1}$, both indicative of the tetragonal rutile structure of IrO$_2$. It appears that the act of electrofloculation avoids the addition of other Ir species that are present in solution and also increases the crystalline structure of the nanoparticles. This is also the first indication that these IrO$_x$ NPs have a crystalline structure and that it closely agrees with the rutile IrO$_2$ structure found in other bulk iridium oxide films.

Unfortunately, the rutile peaks are short lived in these films. Figure 3.11 shows the before and after of the same electroflocculated IrO$_x$ NP film. The before spectrum (in blue)

![Raman spectra and graph](image)

**Figure 3.12:** a) Raman spectra of an electroflocculated IrO$_x$ NP film over time as a 633 nm laser continuously illuminated the sample. b) % area of the spectra that is rutile over time, while the film is illuminated.
clearly exhibits the rutile peaks expected of an IrO\textsubscript{2} film. However, after laser exposure, these peaks decrease in intensity and other peaks overlap, resulting in the more blob like peak seen in orange of the same figure. This peak more closely resembles that of the EIROF discussed above in the introduction, which exhibits limited crystallinity.\textsuperscript{8,12} In order to determine what was causing this decrease in crystallinity, Raman spectra were collected every two minutes while the laser was continuously illuminated the sample. The results are displayed in Figure 3.12.

While the two rutile peaks are dominant in the initial spectrum in Figure 3.12a, they decrease in intensity overtime. To quantify this, the Raman spectra were fit to 5 different Gaussian peaks and the area of the two rutile peaks was compared to the area of the other three peaks over time. There is a distinct decrease in this value, as shown in Figure 3.12b, indicating that the film becomes less crystalline over time when illuminated by the 633 nm laser. It is possible that the high laser power (50\% power) could be changing the structure of the IrO\textsubscript{X} NP film to a more amorphous form over exposure time.

As a comparison, the Raman spectrum of the isopropanol precipitated IrO\textsubscript{X} NPs was also collected and is presented in Figure 3.13. There are significantly fewer Ir species present in this spectrum, compared to that of the pH 13 solution IrO\textsubscript{X} NPs, and the rutile peaks at 550 and 720

![Raman spectrum graph](image)

**Figure 3.13:** Raman spectrum of the isopropanol precipitated IrO\textsubscript{X} NPs.
cm\(^{-1}\) both appear to be present. There also appears to be a broader peak around 500 cm\(^{-1}\) which matches the Ir-O stretching mode reported by Mo et al for the EIROFs.\(^{12}\) We still observe the increase in crystallinity from the pH 13 solution IrO\(_x\) NPs, however, the two rutile peaks are

![SEM images](image)

**Figure 3.14:** SEM images at 30 and 35x magnification of electroflocculated IrO\(_x\) NP films after exposure to various phosphate buffers and electrochemical experiments. a) Immediately after electroflocculation, no phosphate buffer. b) After pH 12 phosphate buffer. c) After pH 10 phosphate buffer. d) After pH 7.5 phosphate buffer. e) After pH 5 phosphate buffer. f) After pH 3 phosphate buffer.
not as distinct as in the electroflocculated film. This suggests that there is an increase in crystalline order via electrofloculation that isn’t observed when the NPs are simply precipitated from solution.

**Figure 3.15:** SEM images at 80,000 and 90,000x magnification of electroflocculated IrO\textsubscript{X} NP films after exposure to various phosphate buffers and electrochemical experiments. a) Immediately after electrofloculation, no phosphate buffer. b) After pH 12 phosphate buffer. c) After pH 10 phosphate buffer. d) After pH 7.5 phosphate buffer. e) After pH 5 phosphate buffer. f) After pH 3 phosphate buffer.
3.3.5 Microscopy of Iridium Oxide Nanoparticles

Figure 3.14 is a collection of images of the IrOx NP films exposed to the different phosphate buffers taken via Scanning Electron Microscopy (SEM). Each film was electroflocculated for 10 minutes at 0.9 V and then placed in the specified buffer to perform the linear sweep program previously mentioned in Section 3.3.1.2. At 30x and 35x magnification, there are no apparent differences in the films based on the pH of the buffer. One difference, however, is that films that underwent the linear sweep program presented more bare spots than

Figure 3.16: Electroflocculated IrOx NP films after varying lengths of time. a) 3 minutes of electrofloculation. b) 5 minutes of electrofloculation. c) 12 minutes of electrofloculation. d) 15 minutes of electrofloculation.
films that did not. This is more than likely due to O₂ production knocking the NPs off of the electrode when potentials high enough to induce water oxidation catalysis were applied.

When magnified further to 80,000x and 90,000x, the morphology of the films is more apparent, as seen in Figure 3.15. The films exposed to the lower pH buffers closely resemble that of the freshly electroflocculated film. The films tested in buffers of pH 7.5 and higher, however, seem to take a different shape at this magnification. Instead of seeing smaller particles clustered together, the film appears more globular, as if the NPs fused together into an agglomeration. This could be due to the phosphate ions that are present in the buffer. At the higher pH values, the more deprotonated phosphate anions are present, specifically HPO₄²⁻ and PO₄³⁻, as shown in the distribution diagram in Figure 3.3. These could be interacting with the NPs differently as ligands and changing the nature of the NPs. Also, if NPs are fused together, it could explain the higher calculated coverages in the higher pH buffers as it would facilitate electron transfer throughout the film.

Figure 3.16 is the collection of images at 30 and 35x magnification of films exposed to the pH 3 phosphate buffer that each have different electroflocellation times. Though the contrast varies between the images, as the electroflocellation time increases, the film more

![Figure 3.17: Cross-section SEM images of an electroflocculated IrOₓ NP film on a Au coated glass slide. a) 600x magnification. b) 35,000x magnification.](image)
evenly covers the electrode. There are clusters of IrOx NPs with bare electrode in between, confirmed by energy dispersive x-ray spectroscopy (EDS). As electrofloculation time increases, the bare spaces become fewer and at 15 min, the darker areas in the image still contain high percentages of Ir, inferring that the NPs are close to fully covering the electrode. This implies that as electrofloculation time is increased, the coverage of the IrOx NPs also increases, as expected.

Figure 3.17 is a cross section of an IrOx NP film on a Au coated glass slide after electrofloculation for 1 hour. The IrOx NP film demonstrates complete coverage of the entire electrode, with a film thickness of ca. 1 µm. This corresponds to a thickness of about 500 IrOx NPs, as they are ca. 2 nm in diameter. The films still maintain their mesoporous structure and rough morphology and this confirms that the original IrOx NP islands formed at early

![Figure 3.17](image)

**Figure 3.18:** High resolution x-ray photoelectron spectra focused on the Ir 4f peak of IrOx NPs in four different states. a) As-synthesized IrOx NPs in 0.1 M NaOH (pH 13). b) Electroflocculated IrOx NP film on a Au coated glass slide. c) Valeric acid capped IrOx NPs in DCM. d) Chemically flocculated IrOx NPs, precipitated via \((\text{NH}_4)_2\text{Ce(NO}_3)_6\).
electroflocculation times grow together to form a more uniform film across the electrode surface when the electroflocculation process is extended to longer periods of time.

3.3.6 X-ray Photoelectron Spectroscopy of Iridium Oxide Nanoparticles

Full x-ray photoelectron spectra were gathered of IrO₅ NPs prepared in various ways and each spectra confirmed the presence of Ir and O, as expected. The samples that were analyzed were the as-synthesized pH 13 IrO₅ NPs, an electroflocculated IrO₅ NP on a Au coated glass slide, the valeric acid capped IrO₅ NPs, which are further discussed in Chapter 4, and the (NH₄)₂Ce(NO₃)₆ chemically flocculated IrO₅ NP precipitate. All samples were deposited onto Au coated glass slides for analysis either by drop-casting or electroflocculation. High resolution scans of the Ir 4f doublet peaks were performed to analyze the change in shape of the different forms of IrO₅ NPs. These spectra, along with their fits of various Ir doublets are featured in Figure 3.18.

The first thing to note is that the Ir 4f peak overlaps with that of the Na 2s orbital. For the as-synthesized IrO₅ NPs and the chemically flocculated IrO₅ NPs, this is accounted for with the addition of a Na 2s peak into the fit. Both of these spectra show the presence of Na in the elemental analysis. This is because these samples were drop cast while in solutions that contained 0.1 M NaOH. Neither the electroflocculated film nor the valeric acid capped IrO₅ NPs exhibited Na in the elemental analysis of the samples.

Each Ir 4f high resolution scan required at least two different Ir couples to fit the spectra. These doublets correspond to the Ir 4f₇/₂ and Ir 4f₅/₂ orbitals, with the Ir 4f₇/₂ appearing at a lower binding energy. The predicted ratio of the heights of Ir(4f₇/₂):Ir(4f₅/₂) is generally 4:3¹³⁰f and this is accounted for in all of the fittings. Table 3.8 presents the binding energies for the Ir 4f₇/₂ and Ir 4f₅/₂ orbitals of each Ir species present in the different IrO₅ NPs. The areas of each fitted peak
were also found, so as to find the percentage each Ir species is present in the IrO\(_x\) NPs. This percentage is listed in the final column of Table 3.8.

Beginning with the as-synthesized IrO\(_x\) NPs in 0.1 M NaOH, the Ir 4f doublet is apparent, although the ratio of the two peaks is much larger than the expected 4:3. This is due to the

<table>
<thead>
<tr>
<th>Ir Species</th>
<th>Ir 4f(_{7/2}) BE (eV)</th>
<th>Ir 4f(_{5/2}) BE (eV)</th>
<th>% Area of Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-synthesized</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>62.77</td>
<td>65.75</td>
<td>58.7</td>
</tr>
<tr>
<td>2</td>
<td>63.79</td>
<td>66.77</td>
<td>32.1</td>
</tr>
<tr>
<td>3</td>
<td>64.59</td>
<td>68</td>
<td>9.2</td>
</tr>
<tr>
<td>Electrofloculated</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>61.9</td>
<td>64.88</td>
<td>45.5</td>
</tr>
<tr>
<td>2</td>
<td>62.73</td>
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<td>27.5</td>
</tr>
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<td>3</td>
<td>63.91</td>
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<td>Valeric Acid Capped</td>
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<td>1</td>
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<tr>
<td>3</td>
<td>64.59</td>
<td>67.57</td>
<td>11.1</td>
</tr>
<tr>
<td>Chemically Flocculated</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>62.18</td>
<td>65.16</td>
<td>35</td>
</tr>
<tr>
<td>2</td>
<td>63.27</td>
<td>66.25</td>
<td>65</td>
</tr>
</tbody>
</table>

overwhelming concentration of Na, which overlaps the Ir 4f\(_{7/2}\) peaks. As a comparison, metallic Ir exhibits binding energies of 60.9 and 63.8 eV for the Ir 4f\(_{7/2}\) and 4f\(_{5/2}\) orbitals, respectively, while those of the bulk material IrO\(_2\) are 62.1 and 65.0 eV due to the oxidation of the iridium species. Three Ir species are required to fit the rest of the peak, where the lowest binding energy species makes up 58.7% of the Ir present in the nanoparticles. The other two species, combined, make up 43.1% of the nanoparticles. The lower binding energy species in the as-synthesized IrO\(_x\) NPs matches that of the bulk IrO\(_2\). The two other species have higher binding
energies than those observed in the bulk material, suggesting there are Ir species with higher oxidation states present in the nanomaterial. The difference between bulk materials and their nanoparticle counterparts is the vast difference in surface area to volume ratio. As there are a higher number of surface species present in the nanoparticles, we may be able to observe them more clearly in XPS, which has a relatively low analysis depth. The two Ir species at higher binding energies may correspond to these surface species and their higher binding energies suggests they are at higher oxidation states than those within the core of the nanoparticle.

The Ir 4f high resolution spectrum of the electroflocculated IrO\textsubscript{X} NP films can also be fit using three different Ir species. The tailing can also be explained by the difference in oxidation state of the surface and core Ir species in the film. The Ir species that mostly closely resembles bulk IrO\textsubscript{2} comprises 45.5\% of the Ir in the film. This is a slightly higher percentage of oxidized surface species, compared to the freely diffusing IrO\textsubscript{X} NP in 0.1 M NaOH. However, this appearance of a higher oxidization state Ir can be attributed to a phenomenon that occurs in bulk Ir materials. The overall shape, where there is significant tailing of the doublets, more closely matches that of the bulk IrO\textsubscript{2} films. Previous literature has attributed this to the screening response of the Ir 5d electrons in the bulk materials.\textsuperscript{6} As an electroflocculated film, the IrO\textsubscript{X} NPs appear to behave more like the bulk IrO\textsubscript{2}.

An attempt to manipulate the oxidation state of the electroflocculated IrO\textsubscript{X} NP film prior to XPS analysis and the results are shown in Figure 3.19. The potential of the electrode with the IrO\textsubscript{X} NP film was held at -0.3 V vs. Ag/AgCl for 10 minutes, at which point the slide was transported to another building on campus to run XPS on the film. Including the time to pump the x-ray photoelectron spectrometer down to vacuum, ca. 25 min elapsed between when the potential was held and when the spectrum was obtained. The potential that was applied was
negative enough to reduce the IrO\textsubscript{X} NP film to the Ir\textsuperscript{III} oxidation state. While there is a slight shift to lower binding energies of the Ir 4f electrons which could indicate a slightly more reduced Ir species, there is essentially no change to the peaks observed. Very similar results were observed when the potential was held at a more positive potential, in order to oxidize the IrO\textsubscript{X} NP film to the Ir\textsuperscript{V} oxidation state. This indicates that while we can reversibly reduce and oxidize these films electrochemically, the reduced and oxidized Ir species are short lived when the potential is no longer being applied.

When capped with valeric acid, the Ir 4f spectrum (Figure 3.18c) of the IrO\textsubscript{X} NPs exhibits a different shape than either the as-synthesized IrO\textsubscript{X} NPs or the electroflocculated NP film. There are two distinct Ir doublets in this spectrum, with minor tailing at the higher binding energies. The ratio of the area of these two doublets is near 1:1. The other IrO\textsubscript{X} NPs have ratios that are much closer to 2:1 and the third Ir species represents a much larger percentage of the Ir. This could indicate that the addition of the carboxylic acid as a capping ligand may create a more uniform surface species. The other two IrO\textsubscript{X} NP species mentioned above likely have a variety of different oxide and hydroxide species on the surface. By capping them with an excess of

![Figure 3.19: X-ray photoelectron spectra of an electroflocculated film before (red) and after (blue) holding the potential at -300 mV vs. Ag/AgCl.](image-url)
valeric acid, the surface becomes uniformly one oxidation state, controlled by the interaction with the carboxylic acid.

Figure 3.18d is the XPS spectrum of the chemically flocculated IrOₓ NPs. A chemical oxidant, (NH₄)₂Ce(NO₃)₆, was added to the as-synthesized IrOₓ NPs, which induced precipitation. Ce is also present in this precipitate (as explained in Chapter 2), due to the insolubility of Ce(OH)₃ in aqueous media. This is the only example of IrOₓ NPs where the higher binding energy couplet represents a higher percentage of the Ir species present, as seen in Table 3.8. This is likely due to the presence of Ce in the precipitate. The Ce can interact with the surface oxygen species of the IrOₓ NPs, pulling electron density away from the Ir sites, resulting in a higher observed binding energy. The presence of Ce appears to have a stronger oxidizing effect on the surface Ir sites, and possibly some of the core Ir species, than the carboxylic acid capping ligand.

From these experiments, it can be concluded that the IrOₓ NP environment greatly affects the binding energies of the Ir 4f electrons, especially those of the assumed surface species. We were able to shift these binding energies by replacing the capping ligand and changing the method of flocculation of the NPs.

3.4 CONCLUSIONS

From these characterization studies, much was learned about the IrOₓ NPs and their surface chemistry. The pH of the buffer which the film is exposed to can distinctly change the electrochemical behavior of the NP films, resulting in a higher resistance within the film. Catalytic Tafel plots established the similarity in water oxidation catalysis mechanisms for IrOₓ NP films in the same buffer, but different mechanisms for those obtained at different pH. UV-Vis spectroelectrochemistry demonstrated the spectral changes of the four different oxidation
states of Ir in the IrOₓ NPs and confirmed that the Ir⁶⁺ state is the active species in water oxidation catalysis. Zeta potential measurements demonstrated how the surface charge of the IrOₓ NPs changes depending on the buffer environment, when stabilized by phosphate species. Raman spectroscopy confirmed the short-lived rutile crystalline structure within the electroflocculated IrOₓ NPs, which further confirms that the ground state of these NPs is Ir⁴⁺. XPS confirmed that changing the environment of the IrOₓ NPs can change binding energy of the electrons, simply based on what is near the surface Ir species.

3.5 ACKNOWLEDGMENTS

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CHAPTER 4: Iridium Oxide Nanoparticles in Organic Media

4.1 INTRODUCTION

4.1.1 Electrochemistry of Iridium Oxide Nanoparticles

The electrochemistry of small (< 2 nm in diameter) iridium oxide nanoparticles (IrO\textsubscript{X} NPs) has been thoroughly explored in aqueous solutions by both the Murray and Mallouk laboratories.\textsuperscript{1-8} Both freely diffusing IrO\textsubscript{X} NPs and films deposited of the same NPs exhibit two Nernstian behaved proton coupled electron transfer (PCET) couples, Ir\textsuperscript{V/IV} and Ir\textsuperscript{IV/III}, before the onset of water oxidation. A figure (Figure 4.1) taken from an article published by the Murray lab depicts these shifts.\textsuperscript{1} Both couples for the IrO\textsubscript{X} NP films shift about 70 mV/pH, very close to the 60 mV/pH for a 1 e\textsuperscript{-}, 1 H\textsuperscript{+} process. The freely diffusing IrO\textsubscript{X} NPs also exhibit this behavior for the Ir\textsuperscript{V/IV} couple and the Ir\textsuperscript{IV/III} couple at in solutions below pH 6. Above pH 6, the formal potentials shift 116 mV/pH, which correlates more closely to a 1 e\textsuperscript{-}, 2 H\textsuperscript{+} reaction.

The expected Ir redox reactions for the electroflocculated IrO\textsubscript{X} NP films are presented in Scheme 4.1. The same reactions are expected for freely diffusing IrO\textsubscript{X} NPs in solutions below pH 6. For the freely diffusing IrO\textsubscript{X} NPs in solutions above pH 6, however, the expected reactions are shown in Scheme 4.2. This is based on the suspected 1 e\textsuperscript{-}, 2 H\textsuperscript{+} mechanism due to the Nernstian shift observed in Figure 4.1.
While these reactions are well defined, there has been little exploration into the IrO\textsubscript{X} NP behavior in organic and aprotic solvents. It is expected that these observed PCET changes would be greatly diminished in aprotic media. The research presented below in Sections 4.3.1 and 4.3.2 explores the electroflocculated IrO\textsubscript{X} NP behavior in completely aprotic media (DMSO). The addition of aqueous media and organic acids is also explored to observe how the electrochemical behavior changes as the films are changed from completely aprotic conditions to very low concentrations of protons and then to media that are a 50:50 mixture of aprotic and aqueous solutions.

### 4.1.2 Synthesis of Metal Oxide Nanoparticles with Organic Surfactant Shells

Iridium oxide nanoparticles are traditionally synthesized using a basic hydrolysis, based on the Woehler method.\cite{1-5,7-9} Hydrolytic synthetic methods can result in nanoparticles with poor monodispersity and crystallinity.\cite{10,11} As this could have significant effects on catalytic ability,
other synthetic methods were investigated to improve these qualities. Nanoparticles synthesized using a thermal degradation synthesis generally have both high crystallinity and good monodispersity.\textsuperscript{12-14} For these synthesis, a metal salt is refluxed in a high boiling point solvent in the presence of a surfactant, such as oleic acid or oleylamine. Surfactants are selected for their functional groups and their interactions with metal oxide surfaces; both long carbon chain carboxylic acids and amines have been favored in the literature.\textsuperscript{12-15} At these high temperatures, the metal salt decomposes and the nanoparticles start to nucleate. The surfactants form a shell around these nucleates and limit their growth; these syntheses rarely produce nanoparticles larger than 10 nm in diameter. The colloidal suspension that results from these syntheses can easily be precipitated with the addition of a polar solvent.

A wide variety of metal oxide nanoparticles have been successfully synthesized using this thermal degradation method, included ITO, ZrO\textsubscript{2}, Fe\textsubscript{2}O\textsubscript{3} and Fe\textsubscript{3}O\textsubscript{4}.\textsuperscript{10-21} The research presented in Section 4.3.3 extends this method to the synthesis of small IrO\textsubscript{X} NPs in an attempt to improve the monodispersity and crystallinity over the hydrolytic method mentioned above.

4.1.3 Ligand Modification of Metal Oxide Nanoparticles in Organic Media

Surface modification of metal oxide nanoparticles has been extensively studied, due to its wide variety of applications.\textsuperscript{1,22-25} Simply changing the capping ligand can change the solubility of the nanoparticles, increasing the applicability of a wider range of media.\textsuperscript{1} Many organic functional groups are known to interact with metal oxide surfaces, including carboxylic acids, amines, silanes, phosphates and phosphonates.\textsuperscript{26} Both amines and carboxylic acids interact via chemisorptive and physisorptive properties. There is an exchange equilibrium of these ligands on the surface of the nanoparticle and in solution. The Murray lab has previously shown exchange of the aqueous IrO\textsubscript{X} NPs into dichloromethane (DCM) using a variety of carboxylic acids, in excess.\textsuperscript{1,27} Silanes, phosphates and phosphonates form covalent bonds to metal oxide
surfaces, eradicating the equilibrium between surface bound and solvated ligands observed with carboxylic acids. These can then be used to quantify ligand attachment to the nanoparticle surface, using either an electrochemical or spectroscopic tag.\textsuperscript{26}

Ligands with phosphate functional groups are an attractive option due to their stable P-O-Metal bonds.\textsuperscript{26} There are limited phosphate functionalized compounds commercially available, so these ligands generally involve complex synthetic methods. One synthetic route which limits by-products and results in low hazard waste is to functionalize these ligands using click chemistry.\textsuperscript{28} The Turro laboratory\textsuperscript{29} developed an azide terminated phosphate ligand (5 in Scheme 4.3), which they were able to further functionalize using an azide alkyne Huisgen cycloaddition in the presence of a Cu(I) catalyst. Using the same concept, the Xian laboratory clicked ethynyl ferrocene onto the surface of iron oxide nanoparticles.\textsuperscript{16}

The research presented in Section 4.3.4 extends this method to valeric acid capped IrO\textsubscript{X} NPs, using the phosphate functional group’s affinity to metal oxide surface to electrochemically tag IrO\textsubscript{X} NPs with ferrocene (Fc). Previous surface modification of these aqueous IrO\textsubscript{X} NPs was successful with a wide variety of carboxylic acids. However, it was not quantifiable, due to the equilibrium and constant exchange of the ligands between the surface of the nanoparticles and solution. The use of a phosphate creates a covalent bond to the surface, eliminating this effect. The research presented below demonstrates the quantitative electrochemical analyses of these ferrocenated iridium oxide nanoparticles (FcIrO\textsubscript{x}), so as to determine the number of ligands present on the surface, as well as the NP diffusion coefficient in a non-aqueous solution.
4.2 Experimental

4.2.1 Aqueous Hydrolysis of IrOx NPs

The Ir$^{IV}$O$_X$ nanoparticles were synthesized using a Wohler method, in which a 2.5 mM solution of K$_2$IrCl$_6$ (99%, Strem Chemicals) in nanopure H$_2$O was adjusted to pH 13 with 25% w/w NaOH (50% w/w, Fisher Scientific). The solution was heated at 90 °C for 20 minutes and then allowed to cool to RT and to rest for at least 24 hours after the synthesis, before electroflocculation.

4.2.2 Electroflocculation of IrOx NP Films

For electroflocculations on Au coated glass slides, Au slides were first cleaned by exposure to piranha solution (3:1 concentrated H$_2$SO$_4$ (Fisher Scientific) to H$_2$O$_2$ (30% w/w, Fisher Scientific)), and then rinsed with nanopure H$_2$O and dried under a stream of Ar gas. Piranha solution is highly oxidizing and should therefore be handled with care.

For films formed on Pt disk electrodes, the Pt electrode was first prepared by polishing with varying sizes of silica, then sonicated to remove unwanted particles. The electrode was further cleaned by potential cycling in 0.1 H$_2$SO$_4$. For films formed on glassy carbon (GC) electrodes, the electrode was polished using 0.25 µm diamond spray and then sonicated to remove any excess diamond particles.

The films were formed from unstirred pH 13 IrOx nanoparticle solutions by applying a potential bias of 0.9 V vs. Ag/AgCl for 10 minutes. The films were rinsed with nanopure H$_2$O and then cyclic voltammetry (CV) was performed in 0.1 M NaOH to verify the presence of a film.

4.2.3 Non-Aqueous Electrochemistry of Iridium Oxide Nanoparticle Films

Electrochemical experiments were performed using a standard three electrode cell, where
an IrOx NP film atop a Au coated glass slide acted as a working electrode and Pt wire and Ag/AgCl (BASi) functioned as auxiliary and reference electrodes, respectively. Cyclic voltammetry of these films was performed in dimethyl sulfoxide (DMSO) (Fisher Scientific with 0.1 M tetrabutylammonium perchlorate (TBAP) (Sigma Aldrich) as supporting electrolyte. In the first experiment, nanopure water was added to the solution to gradually increase the H\(^+\) concentration. In the second, 0.1 M NaOH (Fisher Scientific) in nanopure water was added to the DMSO, so as to more accurately control the pH of the solution.

4.2.4 Addition of Carboxylic Acids and Carboxylates

Two different carboxylic acid/carboxylate, hexanoic acid and valeric acid (Both from Sigma Aldrich), were used to probe the electrocatalytic ability of IrOx NP films towards the Kolbe reaction. The conjugate bases were prepared from the corresponding carboxylic acid by titrating with tetrabutylammonium hydroxide (TBAOH) (Sigma). The product, which was in methanol, was rotovapped, yielding a liquid-like solid, suspected of being an ionic liquid. This product was then dissolved in acetonitrile (CH\(_3\)CN) (Fisher Scientific) with 0.1 M TBAP as supporting electrolyte. Cyclic voltammetry was performed to investigate the IrOx NP film’s ability to electrocatalytically oxidize each of the carboxylates.

In separate experiments, the carboxylic acids were dissolved in CH\(_3\)CN, along with 0.1 tetrabutylammonium hexafluorphosphate (TBAPF\(_6\)). Differential pulse voltammetry (DPV) was performed to examine how the IrOx NP Ir\(^{IV/III}\) wave shifted during a titration with 0.1 M TBAOH.

4.2.5 Hot Injection Thermal Degradation Synthesis of IrOx NPs

This procedure was developed in the Murray laboratory\(^{17,19}\) and was modified from a procedure published by the Fang laboratory.\(^{13,18}\) 0.2 mmol Iridium acetylacetonate (Ir(acac)\(_3\)) (Sigma) and 1.9 mmol oleic acid (Sigma) were dissolved in octadecene (Sigma) in a 50 mL 3-
neck round bottom flask equipped with a magnetic stir bar, thermocouple and condenser. The vessel was evacuated and heated for 1 hour at 120 °C while stirring. The temperature was rapidly increased to 295 °C. 2.4 mmol oleylamine (Sigma) in 0.2 mL octadecene was injected via syringe at this temperature, causing the solution to turn black. This solution was refluxed for an hour at 320 °C and then allowed to cool to RT. 40 mL of ethanol (Fisher Scientific) was added to the suspension, which was then centrifuged at 3000 RPM for 10 minutes to induce precipitation of the nanoparticles. The precipitate was then resuspended in 3 mL of hexanes (Fisher Scientific), producing a dark blue solution.

4.2.6 Valeric Acid Exchange of IrO$_X$ NPs to Organic Media

5 mL of the aqueous IrO$_X$ NPs in pH 13 as-synthesized solution (0.0192 mM) was exchanged using an excess of valeric acid (1 mmol) in dichloromethane (DCM). The solution was stirred overnight and the organic layer was decanted from the aqueous layer ca. 24 hours later. A change in color of the DCM layer from colorless to dark purple was indication of a successful exchange.

4.2.7 Ferrocenation of IrO$_X$ NPs

Following Scheme 4.3, IrO$_X$ NPs were ferrocenated from the valeric acid capped NPs discussed in Section 4.2.6. Synthesis of the azo terminated phosphate ligand (5) was from previous literature from the Turro laboratory$^{29}$ and the click synthesis attachment of the ethynyl ferrocene was reported by the Xian laboratory.$^{16}$ A 100 mL round bottom flask was flame-dried and Ar-purged. 55 mL of anhydrous ethylene glycol (2) (Sigma) was added along with a magnetic stir bar and cooled to 0 °C via icebath. 40.5 mmol of α-bromoisobutyryl bromide (1) (Sigma) was added dropwise via syringe and stirred vigorously for 3 hours. 100 mL of nanopure H$_2$O was added to quench the reaction and the product was extracted with chloroform (3 x 50
mL). The organic extract was dried over MgSO₄ (Sigma), filtered and concentrated via roto-vap to yield a viscous clear liquid (3).

9.5 mmol of 3 was dissolved in 15 mL of anhydrous dimethylformamide (DMF) (Fisher Scientific) in a flame-dried, Ar-purged 100 mL round bottom flask, equipped with a magnetic stir bar. 10.4 mmol of NaN₃ (Sigma) was added to the solution and stirred for 20 hours at RT. 20 mL of nanopure H₂O was added to quench the reaction and the product was extracted with chloroform (3 x 20 mL). The organic extract was again dried over MgSO₄, filtered and concentrated to yield a viscous clear liquid (4). This product was dried overnight en vacuo to remove excess DMF.

5.8 mmol of 4 was dissolved in 15 mL of anhydrous tetrahydrofuran (THF) (Fisher Scientific) in a flame-dried, Ar-purged round bottom flask, equipped with a magnetic stir bar. The solution was cooled to 0 °C via ice bath and 6.4 mmol triethyl amine (Sigma) was added. 6.4 mmol POCl₃ (Sigma) was added dropwise via syringe, forming a cloudy white solution. The

![Scheme 4.3: Synthetic route for the Click Ferrocenation of IrOₓ NPs. The purple circle represents the IrOₓ NPs, which begin the synthesis as valeric acid capped NPs.](image)
solution was warmed to RT and then stirred for an additional 3 hours. Over the course of stirring, the solution changed from a cloudy white suspension to a light yellow solution. 10 mL of nanopure H$_2$O was added to quench the reaction and the pH was adjusted to < 2. The product was then extracted with chloroform (Fisher Scientific) (3 x 15 mL), before being dried over MgSO$_4$, filtered and concentrated, resulting in a yellow, viscous oil (5).

A 1:1 ratio of 5:IrO$_x$ NPs by weight was added to 5 mL of chloroform. The solution was stirred for 24 hours. Hexanes were added and then the solution was centrifuged at 4000 RPM for 10 minutes. The precipitate (6) was collected after decanting off the excess liquid, and then washed three times with hexanes.

6 was dissolved in 4:1 DMSO:H$_2$O. 0.124 mmol of ethynyl ferrocene (7) (Sigma), 0.008 mmol of 3CuSO$_4$·5H$_2$O (Sigma) and 0.021 mmol sodium ascorbate (Sigma) were added to the solution. The reaction was stirred for 24 hours at RT. 1 mL each of CHCl$_3$, acetone and ethanol (All from Fisher Scientific) were added to the solution, which was then centrifuged at 4000 RPM for 10 minutes. The precipitate (8) was collected and washed three times with 4:1 DMSO:H$_2$O.

### 4.2.8 Instrumentation

#### 4.2.8.1 High Resolution Transmission Electron Microscopy (TEM)

TEM images were obtained on a JEOL 2010F FastTEM on copper grids (200 carbon mesh, carbon-coated Formvar, Ted Pella, Redding, CA).

#### 4.2.8.2 Energy-Dispersive X-Ray Spectroscopy (EDS)

EDS elemental analysis was performed using an Oxford INCA EnergyTEM 250 TEM microanalysis system within the JEOL 2010F FastTEM mentioned above.

#### 4.2.8.3 Centrifugation

Samples were centrifuged in an Eppendorf 5810 centrifuge with a fixed angle rotator at 3000-4000 RPM for 10 minutes.
4.2.8.4 X-Ray Photoelectron Spectroscopy (XPS)

A Kratos Axis Ultra DLD system with monochromatic Al Kα x-ray source was used to obtain XPS spectra. High resolution scans were taken at pass energy of 20 eV and the spectral energy axis was aligned at the C 1s peak (284.6 eV).

4.2.8.5 Electrochemistry

All electrochemical experiments were performed on a CH Instruments 760c potentiostat.

4.3 RESULTS AND DISCUSSION

4.3.1 Electrochemistry of Iridium Oxide Nanoparticle Film in Non-Aqueous Media

Cyclic voltammetry of electroflocculated IrOₓ NP films on Au coated glass slides were obtained in DMSO, a completely aprotic solvent. As all of the redox couples associated with the IrOₓ NP films (Ir^{IV/III}, Ir^{V/IV} and water oxidation catalysis) are proton coupled electron transfers (PCET), it was hypothesized that no electrochemically active species would be seen in the cyclic voltammetry under these conditions. This is largely true, as there are no distinct peaks within the window of -0.4 to 0.6 V vs. Ag/AgCl, as seen in Figure 4.2a. There is an increase in current around 0.6 V vs. Ag/AgCl, which may be water oxidation via IrOₓ NPs of the residual water left in the mesoporous film from electroflocculation. When the potential window was expanded to -1.0 V vs. Ag/AgCl, a quasi-reversible redox couple is observed with a E_{1/2} of -0.65 V vs.

![Cyclic voltammetry of an electroflocculated IrOₓ NP film in DMSO with 0.1 M TBAP. Three different scan rates are represented in each potential window, 50 mV/s in blue, 25 mV/s in orange and 10 mV/s in purple.](image)
Ag/AgCl and ΔE_p of 250 mV (Figure 4.2b). The i_p is linearly correlated with scan rate (ν), indicating that it is a surface species. However, it’s E_1/2 is much more negative than any Ir redox species that is generally observed for the IrO_x NP films.

It was hypothesized that this peak was the Ir^{IV/III} redox couple, shifted to more negative potentials due to the lack of protons available to undergo the expected PCET. In order to test this hypothesis, nanopure water was added to the solution of 0.1 M TBAP in DMSO in 1 mL increments (Figure 4.3a). The redox couple shifts positively with each respective addition of H_2O. When the solution is 50% aqueous, the final E_1/2 of the couple is -0.35 V. Because of the high aqueous character of the solution, however, the TBAP electrolyte is no longer soluble and

![Figure 4.3: a) Cyclic voltammetry of an electroflocculated IrO_x NP film in DMSO with additions of nanopure H_2O. b) Cyclic voltammetry of an electroflocculated IrO_x NP film in DMSO with additions of 0.1 M NaOH in nanopure H_2O. c) Final CV of an electroflocculated IrO_x NP film in 50% DMSO, 50% H_2O. d) Final CV of an electroflocculated IrO_x NP film in 50% DMSO, 50% 0.1 M NaOH. Scan rate is 10 mV/s for all figures. Black arrows indicated the direction in which the Ir redox waves are shifting.](image-url)
the high resistivity of solution results in a $\Delta E_p$ of 400 mV, instead of the near 0 mV expected $\Delta E_p$ for a reversible surface species.

In order to combat the decrease in solubility of the electrolyte, the same experiment was performed, but with additions of 0.1 M NaOH in nanopure H$_2$O instead (Figure 4.3b). The same shift in $E_{1/2}$ is observed, with the final $E_{1/2}$ at 50% 0.1 M NaOH being 0.45 V vs. Ag/AgCl. Because of the added supported electrolyte, the $\Delta E_p$ also decreases to 150 mV. The $E_{1/2}$ of this species shifts towards that of the Ir$^{IV/III}$ species in 0.1 M NaOH (ca. -0.3 V vs. Ag/AgCl).

Because it is not in a completely aqueous solution, the aprotic solvent that is still present results in a negative shift of the $E_{1/2}$. Also of note, the Ir$^{V/IV}$ redox wave is visible in these at -0.1 V vs. Ag/AgCl, as is the increase in current normally associated with water oxidation catalysis. The onset potential for what is presumed to be water oxidation catalysis is considerably lower than

![Figure 4.4: Cyclic voltammetry of various carboxylates in CH$_3$CN and 0.1 M TBAP. Various scan rates are shown, 200 mV/s in blue, 300 mV/s in orange and 400 mV/s in purple. a) 4 mmol tetrabutylammonium hexanoate with a GC working electrode. b) 4 mmol tetrabutylammonium hexanoate with an electroflocculated IrO$_x$ NP film. c) 4 mmol tetrabutylammonium valerate with a GC working electrode. d) 4 mmol tetrabutylammonium valerate with an electroflocculated IrO$_x$ NP film.](image)
those previously reported.\textsuperscript{2,4-8} At pH 13, the onset occurs at ca. 0.6 vs. Ag/AgCl. In the last CV of these 50% solutions, the onset is at ca. 0.2 V vs. Ag/AgCl. Due to the aprotic nature of DMSO, it is hard to quantify a pH of this solution, but it appears to make the solution more basic and shift all PCET reactions to more negative potentials. If this is indeed water oxidation catalysis, this is one of the lowest onset potentials reported for this reaction.

4.3.2 Addition of Carboxylic Acids and Carboxylates to Organic Media

In an effort to deduce whether the IrO\textsubscript{X} NPs could act as an electrocatalyst for the Kolbe reaction, cyclic voltammetry was performed in 0.1 M TBAPF\textsubscript{6} in CH\textsubscript{3}CN. CVs of the hexanoate and valerate with a GC working electrode and with an IrO\textsubscript{X} NP film on the working electrode are presented in Figure 4.4. The onset potentials for the oxidation of hexanoate are nearly identical for the two different electrode surfaces. For the hexanoate oxidation via IrO\textsubscript{X} NP film, there is no increase in current that suggests further catalysis of this reaction. For the valerate solution, in Figure 4.4d, the CV is largely dominated by the Ir\textsuperscript{IV/III} and Ir\textsuperscript{V/IV} waves of the film. If there is any current from valerate oxidation, it is indistinguishable from the film electrochemistry. While IrO\textsubscript{X} NPs may be able to oxidize carboxylates, such as hexanoate and valerate, GC carbon electrodes are also able to do so under the same conditions. Thus, there is no benefit in using such as expensive electrode material to perform this reaction.

The IrO\textsubscript{X} NP film electrochemical behavior in CH\textsubscript{3}CN, 0.1 M TBAP was explored with the addition of the same two carboxylic acids, as well as oxalic acid. Each carboxylic acid was titrated with 0.1 M TBAOH in order to observe the shifts of the IrO\textsubscript{X} NP redox couples. While the measurement of pH in organic media is a complicated concept, the titration of the carboxylic acid with TBAOH creates a more basic solution and the Ir redox couples shift accordingly. An
example of the shift of what is presumed to be the Ir$^{IV/III}$ redox couple with the titration of hexanoic acid is presented in Figure 4.5. The $E_p$ shifts from -0.075 to -0.25 V vs. Ag/AgCl. After the addition of 50 µL of 0.1 M TBAOH, however, the current drops significantly. At this point, the product of the titration, TBA hexanoate, is observed to precipitate, leading to a decrease in current.

$E_p$ vs. the addition of TBAOH is presented in Figure 4.6a for the hexanoic and valeric acid titrations and that of oxalic acid is in Figure 4.6b. The concentrations for these acids are 10 mM, 5 mM and 20 mM, respectively. The difference in concentration accounts for the variance in slopes in each titration; the slope for the valeric acid titration (ca. 0.0075 mV/µL) is about twice that of the hexanoic acid titration (0.0035 mV/µL), which is double the slope of the oxalic acid addition (0.0011 mV/µL). For a higher concentration analyte (carboxylic acid), there would be a smaller change in $E_p$ with each addition of titrant (TBAOH).
For the valeric acid and hexanoic acid titrations, the starting potential and final potential are very similar: -0.077 and -0.29 V vs Ag/AgCl for valeric acid and -0.076 and -0.26 V vs Ag/AgCl for hexanoic acid. However, the potentials for the oxalic acid titration are drastically different; the starting and final potentials are 0.60 and 0.48 V vs Ag/AgCl, respectively. This is a big shift in potential, which can be partially explained by the difference in pKₐ values of the various carboxylic acids. The pKₐ's of valeric acid (4.82) and hexanoic acid (4.88) are similar. Oxalic acid has two pKₐ's at 1.25 and 4.14, both lower than the other two acids. At the start of the titration, the relative pH in CH₃CN would be lower than the solutions of hexanoic and valeric acids. This would result in a shift of the IrOₓ redox waves toward more positive potentials. As only one redox wave is observed for each titration, it is difficult to know which Ir reduction is occurring. The Ir⁵⁺/⁴⁺ redox couple usually occurs at more positive potentials than the Ir⁴⁺/³⁺ redox couple, so part of the shift between the two acids could also be due to looking at two different electrochemical reactions.

### 4.3.3 High Boiling Point Solvent Synthesis of Iridium Oxide Nanoparticles

A thermal degradation synthesis was attempted to synthesize IrOₓ NPs in organic media in order to compare to those synthesized via a basic hydrolytic method, as previously discussed in this dissertation. This method results in IrOₓ NPs capped with oleic acid and oleylamine;
these ligands have long carbon chains (C_{18}) which act as a surfactant shell for metal oxide nanoparticles and control the size. Typically, these sort of syntheses result in more monodisperse nanoparticles, compared to hydrolytic methods.\textsuperscript{12-14}

Figure 4.7 is a TEM image of the IrO\textsubscript{X} NPs synthesized via the hot injection thermal degradation method. The average diameter of these nanoparticles are 1.78 ± 0.28 nm, very similar to the 1.8 ± 0.3 nm particles that result from the hydrolysis method. XPS and EDX both
Figure 4.9: EDS spectrum of the hot injection, thermal degradation synthesis IrO$_x$ NPs, demonstrating the presence of Ir in the NPs seen in the TEM images of Figure 4.6.

Figure 4.9: XPS of the hot injection, thermal degradation synthesis IrO$_x$ NPs. a) Full spectrum demonstrates a large C s1 peak at 300 eV due to the surfactant shell. b) High resolution spectrum of the Ir 4f double peak.
confirmed the presence of Ir and are featured in Figure 4.8 and Figure 4.9, respectively. The surfactant shell inhibits the signal of everything but the C 1s peak on the XPS spectra, but the Ir 4f peaks are visible via high resolution scans. As EDX has higher penetration depths, the Ir and O signals are much stronger. This reveals an Ir:O ratio of 0.43, very close to the expected 0.5 for a rutile structured IrO$_2$ species. However, there is no apparent increase in crystallinity or monodispersity from the aqueous pH 13 IrO$_x$ NPs. As the hydrolytic synthesis is much simpler

Figure 4.10: TEM images (a and b) of the valeric acid capped nanoparticles, as well as a histogram (c) of the nanoparticle diameter in nm.
and doesn’t result in an electrochemically inhibiting surfactant shell, all future research continued with that particular synthesis.

4.3.4 Ferrocenation of Iridium Oxide Nanoparticles

The as-synthesized pH 13 IrO$_x$ NPs were exchanged into dichloromethane (DCM) using valeric acid as a capping ligand. This capping ligand has a minor effect on the diameter of these

Figure 4.11: TEM images (a and b) of the N$_3$IrO$_x$ NPs and a histogram of the nanoparticle diameter (c).
nanoparticles, as seen in Figure 4.10. The valeric acid capped nanoparticles have a diameter of 1.86 ± 0.25 nm, slightly larger than the as-synthesized pH 13 diameter of 1.8 ± 0.3 nm.

Valeric acid capped IrOₓ NPs underwent a capping ligand exchange of valeric acid for 5, in Scheme 4.3. While it is presumed that carboxylic acids merely cap metal oxides with a chemisorptive association, phosphate ligands, such as 5, are suspected of forming covalent bonds with the metal oxide surface.²⁶ Compared to other covalently bonding ligands, such as silanes, they also have the added advantage of lack of polymerization, which would result in aggregated nanoparticles. With 5 has a capping ligand for the NPs, there was a significant change in polarity which resulted in successful separation of the products from the reactants via precipitation.

**Figure 4.12:** a) Full XPS spectrum of the N₃IrOₓ NPs. b) High resolution scan of the Ir 4f double peak. c) High resolution scan of the N 1s peak. A double peak at 399.5 and 406 eV indicates the presences of an N₃ species.
TEM of these N$_3$IrO$_x$ nanoparticles are shown in Figure 4.11. Their average diameter is 1.88 ± 0.19 nm, very similar to the valeric acid capped IrO$_x$. There is little change in size of these spherical NPs with the addition of this ligand. XPS of these nanoparticles (Figure 4.12a) confirms the presence of both Ir (Ir 4f peak in Figure 4.12b) and the azide terminated ligand (N 1p double peak in Figure 4.12c). Azides have a distinct XPS signal for their N 1s peak, instead of a single peak, it is split into two at 399.5 and 406 eV.

Figure 4.13: TEM images (a and b) of the FcIrO$_x$ NPs, as well as a histogram (c) of the nanoparticle diameters.
Figure 4.14: EDS of the FcIrO\textsubscript{X} NPs pictured in Figure 4.12, demonstrating the presence of both Ir and Fe.

Figure 4.15: a) Full x-ray photoelectron spectrum of FcIrO\textsubscript{X} NPs. b) High resolution scan of the Fe 2p peak. c) High resolution scan of the N s1 peak.
A click reaction was then performed with ethynyl ferrocene to form complex 8 in Scheme 4.3. Click reactions are convenient for their lack of side products and close to 100% completion.\textsuperscript{28} TEM images of these nanoparticles are in Figure 4.13. The capping ligand is substantially larger than the two previous capping ligands (azide terminated and valeric acid) with the addition of ferrocene and we observe an increase in average particle diameter to $2.08 \pm 0.29$ nm. XPS (Figure 4.15) and EDS (Figure 4.14) of the same nanoparticles confirmed the presence of both Ir and Fe. The azide double peak is no longer present in the XPS higher resolution scan of the N 1s peak, another indication of a successful click reaction. The Ir:Fe ratio was ca. 27:1 from the EDS elemental analysis. Assuming an average 130 Ir/NP based on the IrO\textsubscript{2} rutile structure, this corresponds on average to roughly 5 ferrocene ligands/NP.

Cyclic voltammetry of the FcIrO\textsubscript{X} NPs was performed in DMSO with 0.1 M TBAP supporting electrolyte. CVs of these diffusing species using both a Au coated slide and Au

![Cyclic voltammery plots](image)

**Figure 4.16:** a) Cyclic voltammetry of the FcIrO\textsubscript{X} NPs in 0.1 M TBAP DMSO using a Au coated glass slide as a working electrode. b) Cyclic voltammetry of the FcIrO\textsubscript{X} NPs in 0.1 M TBAP DMSO using a Au microdisk working electrode. c) Peak current ($i_p$) vs. the square root of scan rate ($\nu^{1/2}$) from the CVs presented in (a).
microelectrode are presented in Figure 4.16. One reversible redox couple is observed at 0.47 V vs. Ag/AgCl, with a ΔE_p of 95 mV, very close to the expected 90 mV of an ideal reversible couple. This is presumed to be the Fc/Fc^+ reaction, since the IrO_X redox couples are unlikely to be observed in an aprotic solvent (see discussion in section 4.3.1.). The ultimate goal of these experiments was to find the diffusion coefficient (D) of these nanoparticles with the Fc tag.

An estimate of the diffusion coefficient can be made with the Stokes-Einstein equation (Equation 4-1), where k is the Boltzman constant, T is temperature, η is the viscosity of DMSO and r is the hydrodynamic radius of the nanoparticles.

**Equation 4-1**

\[
D = \frac{kT}{6\pi\eta r}
\]

TEM of the FcIrO_X NPs estimated r to be ca. 2.08 nm, resulting in an estimated D of 1.03 x 10^{-6} cm^2/s. Previous studies with Au nanoparticles have shown this method of estimating the diffusion coefficient can be accurate within a factor of ca. two.149

A comparison of cyclic voltammetry using a macro and microelectrode can yield both the concentration of the analyte and the diffusion coefficient. The Randles-Sevcik equation (Equation 4-2) relates the peak current (i_p) to the square root of the scan rate (ν^{1/2}), where n is the number of electrons, A is the area of the electrode and C is the concentration of the analyte.

**Equation 4-2**

\[
i_p = 2.69 \times 10^5 n^{3/2}AD^{1/2}C^{1/2}ν^{1/2}
\]

If the analyte is a diffusing species, i_p will be linear with respect to ν^{1/2}. As seen in Figure 4.16c, the i_p of FcIrO_X correlates linearly with the square root of scan rate (ν^{1/2}), verifying that the
species is diffusing. From the equation mentioned above, we are able to obtain a $D^{1/2}C$ value of $3.83 \times 10^{-10}$ mol s$^{-1/2}$cm$^{-2}$.

The limiting current ($i_{lim}$) from the microdisk electrode cyclic voltammetry can be used to find DC using Equation 4-3, where $n$ is the number of electrons, $F$ is Faraday’s constant and $r_0$ is the microdisk electrode radius. A limiting current of $1.40 \times 10^{-10}$ A was found for the FcIrO$_X$ NPs at

$$i_{lim} = 4nFCr_0$$

$E_{1/2}$ of 0.49 V vs. Ag/AgCl, resulting in a DC of $7.23 \times 10^{-13}$ mol s$^{-1}$ cm$^{-1}$. A ratio of DC to the $D^{1/2}C$ obtained from the Randles-Sevcik equation yields the diffusion coefficient and concentration of the analyte, $3.56 \times 10^{-6}$ cm$^2$/s and 0.20 mM, respectively. The D is on the same order of magnitude of the Stokes-Einstein estimated diffusion coefficient. Assuming complete conversion of IrO$_X$ NPs from start to finish, the ratio of Fc:IrO$_X$ NP is ca. 0.5 ligands/NP.

However, TEM of each wash in the N$_3$IrO$_X$ NP synthesis and FcIrO$_X$ NP synthesis steps demonstrated the presence of IrO$_X$ NPs, suggested substantial loss of IrO$_X$ NPs with each step. The ligand:NP ratio is expected to be much higher, likely close to the ratio observed via EDS of 5:1.

### 4.4 CONCLUSIONS

The electrochemical behavior of IrO$_X$ NPs in organic media under a variety of conditions is presented. It is observed that a proton source, such as a protic solvent or carboxylic acid must be present for the NPs to be oxidized or reduced through the previously reported PCETs. In organic media, we are able to manipulate the $E_{1/2}$ of the IrO$_X$ redox couples with the addition of organic acids and bases.
IrO\textsubscript{x} NPs that are soluble in organic media can be synthesized with a surfactant shell, using a thermal degradation synthesis developed previously in the Murray lab.\textsuperscript{17} They do not differ in size and shape from the NPs synthesized via basic hydrolysis. There is also no observed improvement in crystallinity or monodispersity.

Aqueous IrO\textsubscript{x} NPs can be exchanged into organic media and then electrochemically tagged with ferrocene using a click reaction. These nanoparticles exhibit one reversible redox couple in DMSO, attributed to the Fc/Fc\textsuperscript{+} reaction. Using cyclic voltammetry from a macro and micro Au electrode, the diffusion coefficient and concentration of Fc in these solutions was determined to be 3.56 x 10\textsuperscript{-6} cm\textsuperscript{2}/s and 0.20 mM, respectively. This equates to a >0.5 ligand:NP ratio, likely closer to 5:1 from the EDS elemental analysis of the NPs.

4.5 ACKNOWLEDGEMENT

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CHAPTER 5: Chromophore Catalyst Assemblies of RuP₂ and Iridium Oxide Nanoparticles

5.1 INTRODUCTION

The use of dye-sensitized photoelectrosynthesis cells (DSPEC) for water splitting has evolved rapidly.¹⁻⁵ In a DSPEC for water splitting, a chromophore-catalyst assembly is used for light absorption and injection into the conduction band of a high band gap oxide semiconductor such as TiO₂ or SnO₂, which act as photoanodes for water oxidation to O₂. Reduction of H⁺/H₂O to H₂ occurs at an integrated cathode. Here we present a layer-by-layer assembly method for photocathodes of such cells, using a ruthenium chromophore and iridium oxide nanoparticles. This arrangement yields increases in photocurrent, relative to previous literature of similar assemblies that have utilized the surface chemistry of iridium oxide nanoparticles (IrOₓ NPs) to modify them with various ligands, including the chromophore itself.⁶⁻¹⁵ It is proposed here that the NPs should have a higher catalytic efficiency if they remain uncapped or as-synthesized at pH 13 capped with hydroxyl groups. In order to create a film without the addition of a deliberate ligand, a non-coordinating acid (perchloric acid) was added to adjust the pH of the as-synthesized IrOₓ NPs so as to induce precipitation.¹¹,¹⁶ The uncapped film should favor increased water oxidation catalysis.

Improved performance has been achieved by application of Atomic Layer Deposition (ALD) in two ways. This gas phase, conformal technique was first used to form a thin shell of TiO₂ on a core of transparent conducting oxide, indium tin oxide (ITO, Sn:In₂O₃) in mesoscopic, nanoparticle films (nanoITO). The assembly was subsequently formed on the surface of the
TiO$_2$ shell by first surface binding of the phosphonated Ru(II) polypyridyl derivative [Ru(4,4’-PO$_3$H$_2$Bpy)$_2$(Bpy)$_2$]$_2^{2+}$ (RuP$_2$). In earlier studies, it was shown that in core/shell structures with thin 1-4 nm outer shells of TiO$_2$ on nanoITO, excitation and injection into the TiO$_2$ shell was followed by rapid transfer of the injected electron into the conducting core for transport to the cathode where H$_2$ is produced.\textsuperscript{1,17} With an appended water oxidation catalyst, stepwise excitation-injection cycles build up multiple oxidative equivalents at the catalyst for oxidation of water to O$_2$.

![Figure 5.1](image)

**Figure 5.1:** Diagram of the dipcoated layer-by-layer assembly of RuP$_2$ and IrO$_x$ NPs on various electrodes. A) Assembly is seen on the mesoporous TiO$_2$ substrate atop FTO coated glass. B) Assembly is built upon the core/shell electrode with a nanoITO core coated with a thin TiO$_2$ shell, deposited via atomic layer deposition.

In a second step, ALD was used to stabilize surface binding of the chromophore by depositing an overlayer of TiO$_2$ to stabilize its binding to the surface (Figure 5.11). In previous studies it has been observed that, although phosphonate-to oxide surface binding is stable under acidic conditions, hydrolysis from the surface is rapid as the pH is increased to 7 and above. Use of ALD to deposit thin TiO$_2$ or Al$_2$O$_3$ overlayers has been shown to stabilize phosphonate derivatives of chromophores, catalysts, and assemblies even at high pH.\textsuperscript{18-26}

In this work, we describe the use of FTO|nanoITO|TiO$_2$ core/shell structures, derivatized by surface binding of RuP$_2$ followed by addition of IrO$_x$ NPs, to create photoanodes for DSPEC
water splitting. The stages in the formation of the photoanode are illustrated in Figure 5.1. The resulting surface-assembled structures on fluorine-doped tin oxide (FTO) optically transparent substrates – FTO[\text{TiO}_2]\text{RuP}_2\text{IrO}_X – and the core/shell analog – FTO[nanoITO][\text{TiO}_2\text{-RuP}_2\text{IrO}_X – have been evaluated as photoanodes for DSPEC visible light water splitting.

5.2 EXPERIMENTAL

5.2.1 Materials

The pH 5.8 buffers that were used in the aforementioned experiments were composed of 37.5 mM \(\text{Na}_2\text{SiF}_6\) (Aldrich) and 80 mM \(\text{NaHCO}_3\) (Aldrich) in nanopure water. 0.1 M \(\text{HClO}_4\) solutions were prepared from concentrated \(\text{HClO}_4\) (70%, GFS Chemicals) and nanopure water.

5.2.2 Synthesis of \(\text{IrO}_X\) NPs

Synthesis of the \(\text{IrO}_X\) NPs was based off of a Woehler method.\(^{28}\) A 2.5 mM \(\text{K}_2\text{IrCl}_6\) (Strem Chemicals) solution was adjusted to pH 13 using 50% w/w \(\text{NaOH}\) (Fisher Scientific). The resulting solution was heated at 90 °C for 20 minutes, then allowed to cool to RT.

5.2.3 Assembly of \(\text{RuP}_2\text{-IrO}_X\) NP systems

\(\text{RuP}_2\) ([\(\text{Ru}(4,4'-(\text{PO}_3\text{H}_2)\text{bpy})_2\text{bpy})^2\)] was dissolved into a 0.1 M \(\text{HClO}_4\) solution, so that the concentration was 0.1 mM \(\text{RuP}_2\). The as-synthesized \(\text{IrO}_X\) NPs were adjusted to pH 1 with 0.1 M \(\text{HClO}_4\). The electrodes were first soaked in 0.1 mM solutions of \(\text{RuP}_2\) in 0.1 M \(\text{HClO}_4\) for 1.5 h to bind the chromophore, followed by a second soaking in a solution of \(\text{IrO}_X\) NPs (2.5 mM in Ir) also in 0.1 M \(\text{HClO}_4\) for 1.5 h. Coverage of \(\text{RuP}_2\) after 1.5 hours of soaking is \(1 \times 10^8\) mol \(\text{RuP}_2/cm^2\), based on the geometric area.

5.2.4 Fabrication of \textit{nano}ITO-FTO substrates:

A 3 gram sample of \textit{nano}ITO (Lihochem, Inc.) powder was added to a mixture of acetic acid (3 g) and ethanol (10 mL), giving a 5 M solution/suspension (22 wt %). After brief shaking, this mixture was sonicated for 20 minutes. The colloidal suspension was further sonicated with a
Branson ultrasonic horn outfitted with a flat microtip (70% power, 50% duty cycle; 5 minutes). FTO glass substrates, 4 cm x 2.2 cm, were prepared and cleaned by sonication in EtOH for 20 min followed by acetone for 20 min. Kapton tape was applied to one edge to maintain a defined area (1 cm x 2.5 cm). The nanoITO colloidal suspension was coated on FTO glass substrates by a spin-coater (600 rpm, 10 s hold). nanoITO slides were annealed under air and then under 5% H₂ with a method described previously. Annealed films were measured to be 3.2 ± 0.5 μm thick by surface profilometry.

5.2.5 ALD deposition

Atomic layer deposition (ALD) was performed in a commercial reactor (Savannah S200, Cambridge Nanotech, Cambridge, MA). Titanium dioxide (TiO₂) was deposited using tetrakis(dimethylamido)titanium (TDMAT) (99.999%, Sigma-Aldrich) and water. The reactor temperature was 130°C. The TDMAT reservoir was kept at 75°C. The TDMAT was pulsed into the reactor for 0.3 s and then held for 10 s before opening the pump valve and purging for 10 s. Standard ALD coating conditions were 130°C and 20 Torr of N₂ carrier gas with a sequence of

![Figure 5.2: TEM images of A) the 50 cycles nanoITO/TiO₂ core/shell electrode and B) the 100 cycles nanoITO/TiO₂ electrode. The darker core represents the nanoITO coke and the surrounding layer is the TiO₂ shell, further pointed out by the bar lines.](image)
0.3 s metal precursor dose, 10 s hold, 20 s N₂ purge, 0.02 s H₂O dose, 10 s hold, 20 s N₂ purge. The growth rate under these conditions was 0.6 Å per cycle, as determined by ellipsometry on Si wafers. The quality of the outer TiO₂ outer layers with 50 and 100 cycles ALD TiO₂ on nanoITO are shown in the transmission electron micrograph (TEM) in Figure 5.2.

5.2.6 Spectroelectrochemical Characterization

Spectroelectrochemical characterizations were conducted in a three electrode cell with a 1 cm path length cuvette by using a CHI 670 potentiostat, and an Agilent UV-Vis spectrometer. The data were analyzed by using SpecFit. The potential was varied in 0.02 V increments from -0.2 to 1.2 V vs. Ag/AgCl with spectra recorded at each increment after holding the potential for 60 s. (The Ag/AgCl reference is +0.199V vs NHE.)

5.2.7 Photolysis Measurements

Photolysis experiments were conducted in a three electrode set-up, where the working electrode and auxiliary electrode were separated from the reference electrode via a fine frit. A Lumencor LED was used to back illuminate the working electrode at a 45° angle at 455 nm at different intensities. The current change was monitored using a CHI 670 potentiostat. The difference in current when the light was off and on was determined to be the photocurrent.

5.2.8 O₂ Detection

O₂ was detected using a four electrode set-up, where the two working electrodes were attached to each other in a thin cell-like arrangement via epoxy, separated by thin pieces of glass on either side. The two working electrodes were spaced 1 mm apart using glass spacers. Working electrode 1 (WE1) was a nanoITO/TiO₂ core/shell electrode on FTO with the RuP₂-IrOₓ NP assembly; working electrode 2 (WE2) was an FTO electrode. Pt wire and Ag/AgCl were used for the auxiliary and reference electrodes, respectively. WE1 was illuminated from behind while a potential of 400 mV vs. Ag/AgCl was held at that same electrode. The potential
at WE2 was held at -900 mV vs. Ag/AgCl in order to measure the reduction of O₂ produced at WE1.

5.3 RESULTS AND DISCUSSION

5.3.1 Dip-Coating Layer-by-Layer Synthesis of RuP₂ and IrOₓ NP Assemblies

The surface-bound chromophore-catalyst assemblies were synthesized using a simple layer-by-layer method. Preparation of the chromophore, RuP₂, is described elsewhere.₁⁶ The chromophore RuP₂ becomes bound to the metal oxide electrode through the phosphonic acid linkers, a previously studied and reported process.²⁷ IrOₓ NPs were synthesized based on a

![Figure 5.3](image-url)

**Figure 5.3:** (a) UV-Vis absorbance spectrum of RuP₂-IrOₓ NP assembly on a nanoITO electrode. (b) UV-Vis difference spectra of RuP₂ – IrOₓ NP assembly on nanoITO in a pH 5.8 NaSiF₆ buffer, as the applied potential is varied (bottom to top) from -0.2 V to 1.2 V vs. Ag/AgCl. Two features are observed: A) increase in absorbance due to oxidation of Ir from Ir³⁺ to Ir⁶⁺ where it becomes a black absorber and B) photobleaching of RuP₂ as it is oxidized from Ru²⁺ to Ru³⁺.
Wohler method. The NP synthesis was carried out at pH 13, resulting in nanoparticles capped with hydroxyl groups. In order to form the assembly overlayer without adding a capping ligand, solutions were acidified with 0.1 M HClO₄, which yields a non-coordinating perchlorate anion, to induce precipitation-binding to the surface-bound layer. By adding the non-coordinating acid as mentioned above, the IrOX NPs precipitate and form an overlayer atop the RuP₂ layer.

5.3.2 UV-Vis Spectroelectrochemistry of RuP₂ and Iridium Oxide Nanoparticles on nanoITO

The resulting RuP₂/IrOₓ assemblies were characterized by UV-Vis spectroelectrochemistry at pH 5.8 in a NaSiF₆ buffer on nanoITO electrodes. Spectroelectrochemical difference spectra for the assembly FTO[nanoITO]-RuP₂,IrOₓ is shown in Figure 5.3, along with the absorbance spectra for the ground state assembly for reference. Spectroelectrochemical data for RuP₂ is shown in Figure 5.4 and that of the IrOₓ NPs was previously discussed in Chapter 3. In Figure 5.3, two spectral features are present, the first (A) assigned to the oxidation of Ir³⁺ to Ir⁶⁺ and the second (B) assigned to the oxidation of Ru²⁺ to Ru³⁺. As the IrOₓ NPs are oxidized through their various oxidation states, they change color from green to purple to black. This is seen spectrally in the increase of absorbance at 540 nm as the Ir sites are oxidized to the IV and V oxidation states. As the assembly is further oxidized, the

![Figure 5.4: UV-Vis difference spectra of RuP2 on nanoITO/FTO coated glass with varying potential in a pH 5.8 NaSiF₆ buffer, as the applied potential is varied (bottom to top) from -0.2 V to 1.2 V vs. Ag/AgCl. Photobleaching of the chromophore as it is oxidized from Ru²⁺ to Ru³⁺ is observed at 455 nm.](image-url)
NPs become black absorbers, observed as the increase in absorbance at all wavelengths. This change happens around the electrochemical onset of water oxidation catalysis, indicating $\text{Ir}^{\text{VI}}$ as a participant in the process. When the RuP$_2$ chromophore is oxidized, there is a bleaching seen at 450 nm. The individual difference spectra of each species is featured in Figure 5.5, along with a concentration gradient of each species. The intercepts of each species in Figure 5.5a correspond to the redox potentials of $\text{Ir}^{\text{IV/III}}$, $\text{Ir}^{\text{V/IV}}$, $\text{Ir}^{\text{VI/V}}$ and $\text{Ru}^{\text{III/II}}$.

The UV-Vis difference spectra of the assembly are summations of the spectra of the individual species. The electrochemical redox potentials obtained from the concentration gradients derived from these spectra match those from the literature. Both spectral and electrochemical integrity are maintained through the dip-coating process. This indicates that the

![Figure 5.5](image)

**Figure 5.5:** (Top): Concentration gradients of each redox species present from -0.2 to 1.4 V vs. Ag/AgCl at pH 5.8. (Bottom): Individual difference spectra of each oxidation species. The first four changes in spectra correspond to different oxidation states of Ir. The last change corresponds to the oxidation of the RuP$_2$. 


two species remain unchanged in the assembly making process and furthermore, the IrO\textsubscript{X} NPs remain uncapped – the overall goal of this synthesis.

### 5.3.3 Photolysis of RuP\textsubscript{2} and Iridium Oxide Nanoparticle Assemblies at pH 1

While the UV-Vis spectra are additive, the photocurrents obtained from the assembly on a mesoporous TiO\textsubscript{2} electrode are significantly larger than the sum of the individual components, suggesting that water oxidation was occurring. Photolysis experiments were performed on three different electrode types at pH 1, featured in Figure 5.6. In these experiments, a potential bias of 0 V vs. Ag/AgCl was held and the current was measured with a 455 nm LED light on and off at various intensities. The difference between the light and dark current was considered the photocurrent at that potential bias.

**Table 5.1:** Photocurrent (\(\mu\text{A/cm}^2\)) of the RuP\textsubscript{2}-IrO\textsubscript{X} NP assemblies on three different electrodes in pH 5.8 NaSiF\textsubscript{6} solution, illuminated at 450 nm at 14.5 mW/cm\textsuperscript{2} with an applied potential bias of 0 V. The core/shell electrode has an ALD TiO\textsubscript{2} layer that is 3.7 nm in thickness.

<table>
<thead>
<tr>
<th>Electrode Configuration</th>
<th>RuP\textsubscript{2}</th>
<th>IrO\textsubscript{X} NPs</th>
<th>RuP\textsubscript{2} + IrO\textsubscript{X} NPs</th>
</tr>
</thead>
<tbody>
<tr>
<td>FTO</td>
<td>nanoITO</td>
<td>-0.98</td>
<td>-1.42</td>
</tr>
<tr>
<td>FTO</td>
<td>TiO\textsubscript{2}</td>
<td>8.56</td>
<td>2.92</td>
</tr>
<tr>
<td>FTO</td>
<td>nanoITO</td>
<td>TiO\textsubscript{2}</td>
<td>4.62</td>
</tr>
</tbody>
</table>

Figure 5.6a features the current of the individual components (RuP\textsubscript{2} and IrO\textsubscript{X} NPs) and that of the assemblies on an FTO|nanoITO electrode. Despite the initial spikes of current when the light is turned on, there is very little difference in current between when the light is on and off after 10 s of decay for all three photoanodes. These figures are reported in Table 5.1. In the case of the RuP\textsubscript{2} and IrO\textsubscript{X} NPs, individually, the photocurrent is negative. There is some photocurrent observed (10.5 \(\mu\text{A/cm}^2\)) for the assembly, though it is not as high as the assemblies on the other two electrodes, discussed below. The assembly on FTO|nanoITO also exhibits a
background current which slopes upward. This falsely gives the impression of higher photocurrents. The lack of photocurrent for assemblies on this electrode can be accounted for based on the conductivity of the electrode. \textit{nano}ITO is a very conductive surface and lacks the charge separation feature observed in semiconductors, such as TiO$_2$. Because of this, when the chromophore (RuP$_2$) is excited, back electron transfer to RuP$_2$ is very common at the electrode surface. There is a very low level of electron injection into the circuit for these photoanodes.

Figure 5.6b depicts the same components as Figure 5.6a, but on an FTO|TiO$_2$ semiconductor electrode, as seen in Figure 5.1a. Compared to the assemblies on FTO|\textit{nano}ITO, there is measureable photocurrent. These values are found in Table 5.1. As TiO$_2$ is a semiconductor material, there is sufficient charge separation within the material and the excited electrons from the chromophore are injected into the circuit. Also of note, the photocurrent for the assembly of -RuP$_2$, IrO$_x$ is greater than that of the sum of the individual components. This is an indication that water oxidation catalysis is occurring at this low applied bias (0 V vs. Ag/AgCl).

The photocurrents in Figure 5.6c represent those of the individual components and the chromophore catalyst assembly on FTO|\textit{nano}ITO|TiO$_2$ core/shell electrodes, depicted in Figure 5.1b. These particular electrodes underwent 50 cycles of atomic layer deposition and had a TiO$_2$ shell thickness of 3.7 nm, as seen in Figure 5.2a. The photocurrents for these anodes decay less quickly than those of the TiO$_2$ photoanodes, signifying more efficient electron injection. Within 10 s, a steady state current is reached, as opposed to the TiO$_2$ assemblies which continued to decay. Also of note, the photocurrents are greater for the core/shell electrodes. This is due to the thin semiconductor layer of TiO$_2$, which allows for charge separation and then injection into the conductive electrode material. Back electron transfer to the chromophore is sufficiently decreased in these electrodes, as previously reported by the Meyer lab.$^{17}$
A potential bias study was performed using the FTO|nanoITO, |TiO$_2$|RuP$_2$,IrO$_X$ photoanodes with a 6.7 nm TiO$_2$ thickness; the results are featured in Figure 5.7. The potential bias ranged from 0 to 0.86 V vs. Ag/AgCl and the potentials are shifted from those discussed in the next section in Figure 5.10 using the Nernst Equation (60 mV/pH). With this photoanode, there is an increase in photocurrent with respect to applied potential, indicating fast electron transfer through the assembly. The potentials reported are all below the onset of water oxidation electrocatalysis via IrO$_X$ NPs, which occurs at ca. 1.35 V vs. Ag/AgCl at pH 1.
5.3.4 Photolysis of RuP2 and Iridium Oxide Nanoparticle Assemblies at pH 5.8

Photolysis experiments of the individual components and assemblies on various electrodes were also performed in a pH 5.8 solution, comprised of a NaSiF$_6$ and HCO$_3$ buffer. Photocurrents were significantly higher at this pH, at a potential bias of 0 V vs. Ag/AgCl, due to the Nernstian behavior of the water oxidation reaction. Current-time traces as a function of incident light intensity for a FTO|TiO$_2$|-RuP$_2$,IrO$_x$ photoanode are shown in Figure 5.8a at an applied bias of 0 V vs. Ag/AgCl, compared to the individual components. Photocurrent data are summarized in Table 5.2. The current comparisons in Figure 5.8a demonstrate significantly enhanced photocurrents for the -RuP$_2$/IrO$_x$ assembly on TiO$_2$ compared to -RuP$_2$ or IrO$_x$ by

Table 5.2: Photocurrent (µA/cm$^2$) of the RuP$_2$-IrO$_x$ NP assemblies on three different electrodes in pH 5.8 NaSiF$_6$ solution, illuminated at 450 nm at 14.5 mW/cm$^2$ with an applied potential bias of 0 V. 50 cycles and 100 cycles refer to 3.7 nm and 6.6 nm thickness of the TiO$_2$ shell.

|                | FTO|TiO$_2$ | FTO|nanoITO/TiO$_2$ Core/Shell, 50 cycles | FTO|nanoITO/TiO$_2$ Core/Shell, 100 cycles |
|----------------|---------|---------------------------------|----------------------------------|
| IrO$_x$ NPs    | 0.27    | 22                              | 37                               |
| RuP$_2$        | 6.9     | 53                              | 27                               |
| RuP$_2$ + IrO$_x$ NPs | 37      | 88                              | 100                              |
themselves. These data are reported at 0 V vs. Ag/AgCl applied bias as the photocurrent after 10 seconds of photolysis. The photocurrent produced by these assemblies on the mesoporous TiO₂ electrodes is ~3 x that reported in previous literature, largely due to the uncapped nature of the iridium oxide nanoparticles.⁵-⁷,¹⁰,¹¹,¹⁵

Water oxidation catalysis was confirmed using a two electrode, generator-collector, pseudo-thin cell system (see Figure 5.9). The electrode set-up is described in the experimental section. Using Fe/Fc⁺ as a model generator-collector reaction, collection efficiencies of 60-65% were observed. For the FTO|nanoITO|TiO₂|RuP₂,IrOX generator and FTO collector set-up, collection efficiencies of O₂ were between 20-25%, similar to those previously reported.⁷,⁸,¹⁰,¹¹,¹⁵ Some loss of O₂ between the generator and collector electrodes is expected, as the space between the two electrodes is not sealed at the top and the bottom of the electrodes. As water oxidation catalysis is occurring at a rate where visible bubbles are produced, it is likely that some of these will dislodge and escape through the top of the apparatus before reaching the collector electrode. This would result in a decrease of collection efficiency.

**Figure 5.8:** Photocurrent measurements of the RuP₂-IrOX assembly, as well as the individual components. Photocurrents on a TiO₂ mesoporous electrode are featured on the left in (a) and photocurrents on a 100 cycle nanoITO/TiO₂ core/shell electrode are on the right in (b). Three different light intensities. 10%, 50% and 100% correspond to 3.4, 14.5 and 23.1 mW/cm² at 455 nm, respectively. A potential bias of 0 V vs. Ag/AgCl was applied.
When the RuP₂-IrOₓ NP assemblies were combined with a nanoITO/TiO₂ core/shell electrode, the photocurrent was significantly increased, as seen in Figure 5.8b. This increase in photocurrent is due to the decrease in back electron transfer of the core/shell electrodes, as previously reported.¹⁷ Comparison of these values to that of the undecorated TiO₂ mesoporous structure is made in Table 5.2. The increase in photocurrents for the core/shell electrodes is notable, reinforcing related observations in both DSPEC and DSSC applications.¹,¹⁷ The origin of the “core/shell” effect is dynamic. Following excitation and injection by the surface bound chromophore – FTO|nanoITO|TiO₂|-RuP₂²⁺ → FTO|nanoITO|TiO₂|-RuP₂²⁺* → FTO|nanoITO|TiO₂(e⁻)|-RuP₂³⁺ – rapid transport through the thin TiO₂ shell to the conducting nanoITO shell provides a basis for electron transfer to the cathode allowing the accumulation of four oxidative equivalents at the catalyst for water oxidation.

Two different TiO₂ shell thicknesses were studied at various potentials vs. Ag/AgCl, as reported in Figure 5.10. Significant photocurrent is produced at an applied potential of 0 V vs. Ag/AgCl, with substantial further increases incited by increased applied potential through 0.5 V
This increase in catalysis with applied potential suggests fast electron transfer throughout the system. As found earlier for related cells, the photocurrent output is dependent on applied bias with the dependence arising, at least in part, from meeting the driving force requirements for H\textsubscript{2} evolution at the cathode.\textsuperscript{4} It is important to note, at the pH value reported, that these applied potentials are less positive than those producing the onset of direct electrocatalytic water oxidation of the IrO\textsubscript{X} NPs (\textasciitilde 0.9 V vs. Ag/AgCl), i.e., direct electrolysis of water does not occur.

A shell thickness effect is also apparent in the data in Figure 5.10, with enhanced photocurrents observed for the TiO\textsubscript{2} shell thickness of 6.7 nm. The extent of photocurrent enhancement is bias dependent, increasing with applied bias, reaching a current enhancement of \textasciitilde 4 at 0.5 V vs. Ag/AgCl. Shell thickness effects in core/shell DSPEC and dye sensitized solar cells (DSSC) have been reported in previous studies.\textsuperscript{17,23,25}

The data presented above were obtained on slides that were dipped in the chromophore and catalyst solutions for 1.5 hours each. In order to optimize these assemblies, the dipping time was varied in both the RuP\textsubscript{2} and IrO\textsubscript{X} NP solutions. Increasing the loading time for RuP\textsubscript{2} yielded

![Figure 5.10: Photocurrent density of the RuP\textsubscript{2}-IrO\textsubscript{X} NP assemblies on two different core/shell electrodes at pH 5.8 with varied applied potential. These values are taken after 90 s of photolysis when illuminated by the Lumencor at 455 nm and 14.5 mW/cm\textsuperscript{2}. (The photocurrent density is based on the geometric area of the electrode.)](image-url)
positive results, as there was a significant increase in photocurrent. The photocurrents measured at different applied biases for an assembly where the loading time for RuP₂ is 24 hours are listed in Table 5.3. Photocurrents up to 655 µA/cm² are reported for this assembly. As a comparison, the same assemblies with a 1.5 hr RuP₂ loading time only produced up to ~200 µA/cm².

Table 5.3: Photocurrent (µA/cm²) of the RuP₂-IrOₓ NP assemblies, with a 24 hour loading time for RuP₂, in pH 5.8 NaSiF₆ solution, illuminated at 455 nm with various light intensities and applied biases. The core/shell electrode has an ALD TiO₂ layer that is 6.2 nm in diameter.

<table>
<thead>
<tr>
<th>Applied Bias (V vs. Ag/AgCl)</th>
<th>Light Intensities (mW/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.4</td>
</tr>
<tr>
<td>0.3</td>
<td>77.9</td>
</tr>
<tr>
<td>0.6</td>
<td>120</td>
</tr>
<tr>
<td></td>
<td>119</td>
</tr>
</tbody>
</table>

Extending the loading time of the IrOₓ NPs, however, resulted in a decrease in photocurrent. An assembly with an IrOₓ NP loading time of 17 hours yielded photocurrent that was 50% of the photocurrent from an assembly with an IrOₓ NP loading time of 1.5 hours. This is likely due to the competing light absorbance from the IrOₓ NPs at 455 nm. A smaller percentage of the light is being absorbed by the chromophore, which results in a decrease in photocurrent. Electroflocculation was also explored as a film formation technique for the IrOₓ NPs in these assemblies. However, since this technique requires basic solutions as discussed in Chapter 2 and the RuP₂ chromophore detaches from the metal oxide surface as the pH approaches 7, electroflocculation was performed before the addition of the chromophore.

For the initial 10 s photolyses, the photocurrent of the electroflocculated assemblies is much less than that of the dip-coated assemblies (2.0 and -2.8 µA/cm² compared to 37 µA/cm²). This indicates that the order of assembly plays a large role in the amount of photocurrent that is produced. When the chromophore is loaded onto the slide first, it is positioned at the metal
oxide semiconductor surface where it can more easily inject excited electrons. If the catalyst is loaded.

**Table 5.4:** Photocurrent (µA/cm²) over time from assemblies of electrofloculated IrOₓ NPs and RuP₂, where the arrangement of the photoanode is FTO|TiO₂|IrOₓ,RuP₂. Two different electrofloculation times were explored, 10 and 20 minutes. The photoanodes were backlit at a 45° angle with a 455 nm LED at 14.5 mW/cm². A 0 V vs. Ag/AgCl potential bias was applied in pH 5.8 NaSiF₆ buffer.

<table>
<thead>
<tr>
<th>Photolysis Time (s)</th>
<th>10 min Electrofloculation + RuP</th>
<th>20 min Electrofloculation + RuP</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>2.0</td>
<td>-2.8</td>
</tr>
<tr>
<td>30</td>
<td>0.52</td>
<td>-0.34</td>
</tr>
<tr>
<td>60</td>
<td>0.36</td>
<td>-0.21</td>
</tr>
<tr>
<td>90</td>
<td>0.33</td>
<td>-0.18</td>
</tr>
</tbody>
</table>

first, such as in the electrofloculated assemblies, it blocks the chromophore from the semiconductor surface and inhibits electron injection. The decrease in photocurrent from 20 minutes of IrOₓ NP electrofloculation compared to 10 minutes of electrofloculation further demonstrates this effect. Electrofloculating for longer periods of time results in higher coverage of the semiconductor electrode surface; this further inhibits electron injection from the chromophore, resulting in a decrease in observed photocurrent.

### 5.3.5 Atomic Layer Deposition of TiO₂ as Stabilization Technique

Long term photolysis of the FTO|nanoITO|TiO₂|RuP₂,IrOₓ assemblies demonstrated a significant decrease in photocurrent over time. This is suspected to reflect the instability of the RuP₂ chromophore’s immobilization at the higher pH of the NaSiF₆ buffer used in these experiments. As observed earlier for phosphonate-derivatized assemblies on TiO₂, surface binding is unstable as the pH is increased toward 7 leading to rapid loss from the surface by
Further evidence of this is the loss in color of the slide and the increase in color of the solution after prolonged photolysis. The Meyer and Hupp laboratories have previously reported on atomic layer deposition (ALD) as a means to stabilize the chromophores on metal oxide surfaces.\textsuperscript{21,24,26,30,31} A cartoon of this ALD stabilization layer on the assembly is depicted in Figure 5.11. Figure 5.12 presents results that support this finding on the core/shell electrode with 6.6 nm TiO$_2$ thickness. The effect of an added 10 cycle TiO$_2$ overlayer (less than 1 nm in thickness) added to stabilize -RuP$_2$ before addition of the IrO$_x$ NPs is also shown in Figure 5.12. After two hours of photolysis with a 300 mV applied bias vs. Ag/AgCl, the photocurrent from the unstabilized assembly has fallen appreciably, to a level that is well below that of the dark current (\(\sim 97 \, \mu A/cm^2\)). The stabilized electrode sustains a photocurrent of 110 \(\mu A/cm^2\) over the photolysis period, indicating significant improvement in stability. Compared to the photocurrent obtained from 90 s photolysis at the same potential bias (150 \(\mu A/cm^2\)), the loss is significantly decreased with ALD stabilization.

\textbf{Figure 5.11:} A cartoon of the assembly after an additional ALD of \(\sim 1\) nm of TiO$_2$, represented by the light blue edge of the nanoparticles. This ALD layer is added after the chromophore (RuP$_2$) is adsorbed to the surface, but before the IrO$_x$ NPs are deposited. This creates a protective layer of TiO$_2$ around the phosphonic acid groups of the chromophore, which anchor the complex to the metal oxide surface.
A conductive polymer, poly(methacrylic acid) (PMAA), was also tested as a means to stabilize the RuP$_2$ chromophore in higher pH solutions. A solution of 3% PMAA was applied to the photoanode after RuP$_2$ loading, but before the slide was dipped in the IrO$_x$ NP solution to load the catalyst. This was then allowed to air dry to form a protective layer. After loading the IrO$_x$ NPs via the dip-coating method, there was no apparent purple color that usually accompanies these films. This suggested that the IrO$_x$ NP did not precipitate onto the PMAA surface. Figure 5.13 is the 10 minute photolysis experiment performed with this assembly. The light was turned on at 60 s, as indicated by the black arrow. There is a slight spike in current when the light is turned on, but no apparent water oxidation catalysis occurs (as indicated by the lack of O$_2$ detection at the collector electrode). This further supports the theory that the IrO$_x$ NPs do not deposit onto the PMAA surface. This is likely due to the more hydrophobic nature of the polymer, compared to that of TiO$_2$ and RuP$_2$.
CONCLUSIONS

The results described here are important in building on the earlier results of Mallouk and coworkers on the use of Ru(II) polypyridyl-IrO₅ assemblies on semiconductor oxides to achieve visible light water splitting.⁷,⁸,¹⁰,¹¹,¹⁵ The use of nanoITO|TiO₂ core/shell structures results in impressive gains in photocurrent efficiency which increase with applied bias. Long term instability arising from hydrolysis and loss of the chromophore from the surface has been addressed by use of ALD overlayers of TiO₂. With the combination of enhanced efficiencies and surface stabilization this approach to self-assembly based on IrO₅ nanoparticles offers promise as a platform for achieving relatively high efficiencies with extensions to chromophores and combinations of chromophores for extending light absorption further into the visible with surface stabilization by ALD.

**Figure 5.13**: Photolysis of PMAA stabilized FTO|nanoITO|TiO₂|RuP₂, IrO₅ assembly. The light (455 nm, 14.6 mW/cm²) is turned on at 60 s, indicated by the arrow. A potential bias of 0.4 V vs. Ag/AgCl was applied in a pH 5.8 NaSiF₆ buffer.
5.5 ACKNOWLEDGEMENT

This research is based upon work supported as part of the UNC EFRC: Center for Solar Fuels, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number DE-SC0001011. Atomic layer deposition and syntheses of the FTO/nanoITO, FTO/TiO$_2$ and core/shell electrodes were performed by Leila, Alibabei. Synthesis of the RuP$_2$ chromophore was performed by Dennis Ashford. Assembly of the collector/receptor electrode set-up for O$_2$ detection was performed by Ben Sherman. We would also like to thank Alessa Gambardella for her help with starting this project and Robert Binstead for writing the SpecFit program and his assistance with using the program.
REFERENCES


CHAPTER 6: Electrochemical Characterization of Quaterpyridine Ruthenium Complexes for Benzyl Alcohol Oxidation Catalysis

6.1 INTRODUCTION

6.1.1 Molecular Water Oxidation Catalysts

While heterogenous catalysts generally are easier to synthesize, molecular water oxidation catalysts (WOC) have the advantage when it comes to analysis of the mechanism. Furthermore, there are more possibilities for modification of molecular complexes to enhance and promote facile catalysis. As discussed in the introduction, the original catalysts for water oxidation were based upon Photosystem II (PSII), the protein complex responsible for producing oxygen gas (O₂) in photosynthesis. The water is oxidized by manganese ions that are within the complex and are bonded together by µ-oxo bridges. Various mono-, di-, tri- and tetrametallic complexes have been synthesized as catalysts trying to mimic its behavior using ruthenium, manganese, rhodium, osmium and iridium metal centers. They have polypyridal ligands, such as bipyridine, tripyridine, and phenanthraline which are good oxidizers, due to their ability to accept electrons in the conjugated π system.

Although the majority of WOCs consist of one or two polypyridyl ligands bound to a ruthenium(II) centre with one coordination site free for a water molecule, coordinatively saturated ruthenium WOCs are being discovered. Recently Thummel and coworkers reported the complex [Ru(dpp)(pic)₂] (dpp = 2,0-di(pyrid-2'-yl)-1,10-phenanthroline), which is active as a WOC in the presence of Ce⁴⁺. Studies with a related complex were reported by Lau et al. who demonstrated that the complex [Ru(qpy)(pic)₂] (qpy = 2,2':6',2''-quaterpyridine) was oxidized in the presence of Ce⁴⁺ to form a qpy-N,N'-dioxide complex, which acted as a
water oxidation catalyst. The bis-aqua form of this complex had previously been reported by Che et al. and its properties as an alcohol oxidation catalyst were tested. The three complexes presented in this chapter are derivatives of this [Ru(qpy)(L)₂] complex, as seen in Figure 6.1, where the L groups in 1 are a chloro (Cl) and acetonitrile (MeCN), in 2, both L groups are MeCN and in 3, the ligands are vinyl pyridine (VP). Their electrochemistry is presented in the results and discussion below, which shows their potential as water oxidation catalysts.

6.1.2 Benzyl Alcohol Oxidation Catalysis

![Figure 6.1: Structures of the three quaterpyridine complexes studied. In 1, L = Cl, MeCN. In 2, L = MeCN. In 3, L = vinyl pyridine (VP).](image)

One way of probing the mechanism for water oxidation via a homogeneous, molecular catalyst is to investigate its properties as a benzyl alcohol oxidation catalyst. Benzyl alcohol (BnOH) is a readily oxidized compound that can undergo a two electron, two proton oxidation to benzaldehyde. There is also the possibility of over-oxidizing the substrate to benzoic acid, which would require another two electron, two proton reaction. This is analogous to water oxidation, another four electron, four proton reaction. Many research groups, in particular the Meyer and Hill laboratories, have used this reaction as a probe to study the intermediates of water oxidation.
catalysts, largely polypyridal Ru based complexes.\textsuperscript{25-29} Polypyridal Ru complexes have shown to be effective catalysts for the oxidation of alcohols, aldehydes, ketones, diols and aromatics hydrocarbons.\textsuperscript{29-41} The extensive use of these complexes in mechanistic studies is largely due to their coordinative stability and their formation of stable intermediates at high oxidation states.\textsuperscript{40}

These oxidations were found to be predominately second order and this rate constant, $k_{\text{cat}}$, dependent on a wide variety of factors, including solvent, electrolyte and ligand substitution on the catalyst.\textsuperscript{27,35,36} Depending on conditions, the mechanism of BnOH oxidation catalysis varies, undergoing either a 1 or 2 electron (e\textsuperscript{-}) pathway. In water, the mechanism is believed to be a 2 e\textsuperscript{-} process, involving a hydride transfer step, seen in Scheme 6.4. There is no trend correlated between redox couple of the catalyst and rate of benzyl alcohol oxidation.\textsuperscript{26} Additionally, derivitizing the aromatic ring of the benzyl alcohol substrates demonstrated little change in rate.\textsuperscript{27} The Hill group found that there is a steric effect on rate of oxidation of benzylic alcohols via $[^\text{Ru(trpy)}(4,4'\text{-Me}_2\text{dppi})(\text{OH}_2)]^{2+}$ [4,4\textsuperscript{'-}dppi = 3,6-dimethylpyrid-2-yl] pyridazine], as adding carbon substituents on the benzylic carbon resulted in a decreased catalytic rate. This suggests that the rate determining step is the pre-association of the alcohol with the catalyst, as opposed to electron transfer.\textsuperscript{26,27} A general mechanism for this reaction with a Ru polypyridal complex is presented below in Scheme 6.4.

\textbf{Scheme 6.4}

\[
\begin{align*}
\text{Ru}^{\text{IV}}=&\text{O}^{2+} + \text{HC(OH)Ph} \rightarrow \text{Ru}^{\text{IV}}=&\text{O}^{2+}, \text{HC(OH)Ph} \\
\text{Ru}^{\text{IV}}=&\text{O}^{2+}, \text{HC(OH)Ph} \rightarrow [\text{Ru}^{\text{IV}}=&\text{O}\cdots\text{H}\cdots\text{C(OH)Ph}]^{2+} \rightarrow \text{Ru}^{\text{II}}=&\text{OH}^{+}, \text{PhCOH}^{+} \\
\text{Ru}^{\text{II}}=&\text{OH}^{+}, \text{PhCOH}^{+} \rightarrow \text{Ru}^{\text{II}}=&\text{OH}_2 + \text{PhC}=\text{O}
\end{align*}
\]
The Meyer lab has also demonstrated that BnOH oxidation can occur with [Ru(Mebimpy)(bpy)(OH$_2$)]$^{2+}$ (Mebimpy = 2,6-bis(1-methylbenziidazol-2-yl)-pyridine; bpy = 2,2’-bipyridine) via four different intermediates, Ru$^{IV}$=O$^{2+}$, Ru$^{IV}$(OH)$^{3+}$, Ru$^V$=O$^{2+}$ and Ru$^V$(OO)$^{3+}$. The Ru$^{IV}$=O$^{2+}$ mechanism is accessible in higher pH solutions and undergoes a similar mechanism to Scheme 6.4. The Ru$^{IV}$(OH)$^{3+}$ and Ru$^V$(OO)$^{3+}$ pathways are accessible in lower pH solutions (pH 5, compared to > pH 9), with the Ru$^V$(OO)$^{3+}$ pathway yielding a higher rate by a factor of two. The Ru$^V$(OO)$^{3+}$ intermediate would be reduced to Ru$^{III}$(OOH)$^{2+}$ upon oxidation of BnOH, as seen in Scheme 6.5. It is hypothesized that it also undergoes a hydride transfer mechanism, as with the Ru$^{IV}$=O$^{2+}$ intermediates. BnOH oxidation catalysis occurring from four different pathways of the same catalyst is important to note as it indicates that mechanistic and kinetic studies may not be as simple as expected. This is especially true when dealing with chemical oxidants, such as cerium ammonium nitrate (CAN), rather than direct electrolysis, where multiple oxidation states of the catalyst may be coexisting.

Scheme 6.5

\[ \text{Ru}^V\text{(OO)}^{3+} + \text{PhCHOH} \rightarrow \text{Ru}^{III}\text{(OOH)}^{2+} + \text{PhCHO} + \text{H}^+ \]

Work also performed by the Meyer lab has recently proposed a base-catalyzed pathway for BnOH oxidation catalysis using [Ru(Mebimpy)(bpy)(OH$_2$)]$^{2+}$, after exploring the effect of the concentration of the buffer present on the rate of catalysis. As opposed to proton coupled electron transfers (PCET) noted above, this mechanism suggests concerted hydride proton transfer (HPT) is occurring with the help of the base present in solution. This suggests that performing these oxidations in solutions with higher pH may facilitate catalysis.
Initial BnOH oxidation catalysis studies for the three complexes in Figure 6.1 are presented in this chapter, as well as kinetic studies of BnOH oxidation catalysis via complex 1 and long term bulk electrolyses.

6.2 EXPERIMENTAL

6.2.1 Synthesis of the ruthenium quaterpyridine ligand and [Ru(qpy)2(Cl)2] complex

The ligand qpy\textsuperscript{42} and the complex [Ru(qpy)\textsubscript{2}(Cl)\textsubscript{2}]\textsuperscript{43} were prepared according to literature procedures. [RuCl\textsubscript{3}], dry solvents from Sigma Aldrich and chromatography solvents from Fisher Chemicals were all used as received. Size exclusion chromatography was carried out using Sephadex LH-20.

6.2.2 Synthesis of Complex 1

[Ru(qpy)(CH\textsubscript{3}CN)Cl][BF\textsubscript{4}] (1). Sixty mg (0.12 mmol) of [Ru(qpy)\textsubscript{2}(Cl)\textsubscript{2}] and 24.2 mg (1 eq., 0.12 mmol) of AgBF\textsubscript{4} were put into a flask, equipped with a stir bar, and evacuated and refilled with N\textsubscript{2} three times. Following addition of 15 mL dry acetonitrile the reaction was heated at reflux overnight. The solution was cooled to room temperature, filtered and the solvent removed \textit{in vacuo}. The complex was purified using size exclusion chromatography with 1:1 acetonitrile:H\textsubscript{2}O as eluent. The purple fraction was collected and dried yielding a purple powder. Yield: 35 mg, 49.0 %.

6.2.3 Synthesis of Complex 2

[Ru(qpy)(CH\textsubscript{3}CN)\textsubscript{2}][BF\textsubscript{4}]\textsubscript{2} (2). Sixty mg (0.12 mmol) [Ru(qpy)\textsubscript{2}(Cl)\textsubscript{2}] and 55 mg (excess, 0.28 mmol) AgBF\textsubscript{4} were put into a flask equipped with a stir bar, and evacuated and refilled with N\textsubscript{2} three times. Following addition of 15 mL of dry acetonitrile, the reaction was heated at reflux overnight. The solution was cooled to room temperature, filtered and the solvent removed \textit{in vacuo}. The complex was purified using size exclusion chromatography with 1:1 acetonitrile:H\textsubscript{2}O
as eluent. The second fraction from the column was collected and the solvent removed *in vacuo* affording a dark red powder. Yield: 53.0 mg, 83.2 %

### 6.2.4 Synthesis of Complex 3

\[\text{[Ru(qpy)(VP)_2][Cl]}_2 (3)\]. Sixty mg (0.12 mmol) \([\text{Ru(qpy)}_2(\text{Cl})_2]\) and 0.65 mL (50 eq., 6.0 mmol, 654 mg) vinyl pyridine were heated at reflux in 10 mL ethanol and 3 mL H\textsubscript{2}O for 2 days. The reaction was then allowed to cool to room temperature and the solvent removed *in vacuo*. The resulting solid was dissolved in 1:1 methanol:H\textsubscript{2}O and purified using size exclusion chromatography with 1:1 methanol:H\textsubscript{2}O as the eluent. The dark purple fraction was collected and the solvent removed *in vacuo* affording a dark purple powder. Yield: 60.0 mg, 73.4%

### 6.2.5 Electrochemical experimental setup

Cyclic voltammetry was performed on a CH Instruments 660a potentiostat, using a conventional three electrode setup consisting of either a glassy carbon (GC) or boron doped diamond (BDD) working electrode, platinum wire auxiliary electrode and 3 M Ag/AgCl (BASi) reference electrode. 1 mM solutions of each complex in acetonitrile were used for these experiments, with 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF\textsubscript{6}) as supporting electrolyte. For the aqueous electrochemical measurements, a 1 mM solution of each complex was prepared in 0.1 M trifluoroacetic acid (TFA).

For the kinetic studies of benzyl alcohol oxidation, cyclic voltammetry was performed on 0.1 M TFA solutions with low concentrations of the catalyst (1 mM, 0.5 mM, 250 \(\mu\)M, 125 \(\mu\)M, 67.5 \(\mu\)M and 33.8 \(\mu\)M) and 20 mM benzyl alcohol in order to achieve a limiting current.

Bulk electrolyses were originally performed in 0.1 M TFA solutions, with 0.5 mM of each catalyst and 20 mM benzyl alcohol. A three electrode setup was used, where the working electrode (nanoITO on a FTO coated glass slide) was separated from the auxiliary electrode (Pt
wire) and reference electrode (3 M Ag/AgCl) via a fine frit. The electrolyte was later switched to 0.1 M HClO$_4$ when it was discovered that the TFA electrochemically etched the nanoITO surface when the potential was held oxidatively. Each bulk electrolysis lasted 13 hours and the concentrations of the reactant (benzyl alcohol) and product (benzaldehyde) were detected using gas chromatography.

![Figure 6.2: Heating program for GC detection of benzyl alcohol and benzaldehyde.](image)

6.2.6 Detection of benzyl alcohol and benzaldehyde via Gas Chromatography

A Shimadzu GC-2014 gas chromatograph was used to detect the reactant and product of the bulk electrolyses. The program used is shown in Figure 6.2, where the temperature is paused twice just below the boiling point of benzaldehyde and benzyl alcohol. Two peaks are observed in the typical gas chromatograph, one at 39 min and one at 60 min, corresponding to benzaldehyde and benzyl alcohol, respectively.

6.3 RESULTS AND DISCUSSION

6.3.1 Electrochemistry of Ru(qpy)L$_2$ in Acetonitrile

As expected, all three complexes exhibited a Ru$^{II/III}$ redox couple in acetonitrile; the data
is summarized in Table 6.1 and depicted in Figure 6.3. For complexes 1 and 2 the redox wave was fully reversible and the potential of 1 was more negative than that of 2 due to the electron withdrawing nature of the chloride ligand.

Table 6.1: Formal potential of each of Complexes 1, 2 and 3 in 0.1 M TBAPF$_6$ and MeCN.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Auxiliary Ligands</th>
<th>$E_{1/2}$ (V vs. Ag/AgCl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>MeCN, Cl</td>
<td>0.898</td>
</tr>
<tr>
<td>2</td>
<td>MeCN</td>
<td>1.333</td>
</tr>
<tr>
<td>3</td>
<td>VP</td>
<td>0.956</td>
</tr>
</tbody>
</table>

Complex 3 exhibited behavior of an EC' reaction, where after the electrochemical oxidation of 3, a chemical reaction, likely the polymerization of the vinyl ligands, immediately follows. Because of this, the voltammetry of 3 is irreversible, particularly at slower scan rates. A film is also observed on the electrode surface after multiple scans, which is further indication of polymerization on the electrode surface.

![Figure 6.3: Cyclic voltammetry of complexes 1 (orange), 2 (blue) and 3 (green) in 0.1 M TBAPF$_6$ and MeCN, at 10 mV/s.](image)
6.3.2 Electrochemistry of Ru(qpy)L₂ in Aqueous Media

Upon dissolution of 1 in 0.1M TFA solution three redox couples were observed in the cyclic voltammogram, Figure 6.4, which is evidence for the exchange of the acetonitrile ligand for an aquo ligand. These couples were assigned to Ru^{II/III}, Ru^{III/IV} and Ru^{IV/V} and the $E_{1/2}$ values are reported in Table 6.2. The potential for the Ru^{II/III} couple has decreased by 320 mV compared to the measurement in acetonitrile. The exchange of the acetonitrile ligand for the aquo, combined with the low Ru^{IV/V} redox potential indicates that this complex has the potential to act as a water oxidation catalyst.

Table 6.2: $E_{1/2}$ values for the aqueous electrochemistry of Complexes 1, 2, and 3 in 0.1 M TFA.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$E_{1/2}$ (V vs. Ag/AgCl)</th>
<th>Vinyl Polymerization</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ru^{II/III}</td>
<td>Ru^{III/IV}</td>
</tr>
<tr>
<td>1</td>
<td>0.578</td>
<td>0.874</td>
</tr>
<tr>
<td>2</td>
<td>0.586</td>
<td>0.816</td>
</tr>
<tr>
<td>3</td>
<td>0.975</td>
<td></td>
</tr>
</tbody>
</table>

Figure 6.4: Cyclic voltammetry of 1 in 0.1 M TFA at 25 mV/s.
Three redox couples are also observed for 2 in 0.1 M TFA solution, as seen in Figure 6.5. However, the cyclic voltammogram of the complex changes with each scan, with a shift in the Ru\(^{V/IV}\) redox couple. In the return reduction of this couple, \(E_{peak}\) shifts more negative over time, likely due to the difficulty in exchanging two acetonitrile ligands for two water ligands. We propose that with each sequential scan a small amount of the bis-acetonitrile complex is converted into the bis-aquo complex and it is this that causes the CVs to look different with each scan. After 20 scans, the CV of 2 in 0.1 M TFA closely resembles the CV of Che et al.’s reported [Ru(qpy)(OH\(_2\))\(_2\)] complex\(^{44}\), which gives confidence to this hypothesis.

The \(E_{1/2}\) of 3 in 0.1 M TFA shows no change in aqueous media, when compared to the CV measured in MeCN. However, the peak appears more reversible than that of the complex in MeCN. This indicates that the MeCN is a likely co-participant in the polymerization of the vinyl ligand. Some polymerization is still observed in aqueous media, as observed by the peak that appears at 0.54 V vs Ag/AgCl in Figure 6.6. To try to reduce the polymerization on the GC electrode, a boron doped diamond (BDD) electrode was implemented as a working electrode (Figure 6.6). This effectively eliminated the appearance of the peak at 0.5 V and also reduced

![Graph](image)

**Figure 6.5:** Cyclic voltammetry of Complex 2 in 0.1 M TFA at 25 mV/s. Scan 1 is in blue and scan 12 is in orange. The CVs change over time due to MeCN exchange with H\(_2\)O.
the non-faradaic current observed. This is largely due to the nature of the surface of a BDD electrode, compared to that of GC. While the surface of a GC electrode contains functional groups ready for polymerization, that of the BDD electrode is considered to be benign.\textsuperscript{45} However, as it is not possible to observe any oxidation states higher than the Ru\textsuperscript{III}, we do not expect this complex to be an active catalyst for water oxidation or benzyl alcohol oxidation.

![Graph](image)

**Figure 6.6**: Cyclic voltammetry of Complex 3 in 0.1 M TFA. The blue curve corresponds to the GC working electrode, where higher rates of polymerization are observed (the peak formation at 0.5 V). The orange curve corresponds to the BDD working electrode, which observes no polymerization of the catalyst.

### 6.3.3 Addition of Benzyl Alcohol to Aqueous Ru(qpy)L\textsubscript{2} Solutions

20 mM benzyl alcohol was added to the aqueous solutions of each complex; the results can be seen in Figure 6.7. Both Complex 1 Figure 6.7(a) and Complex 2 Figure 6.7(b) exhibit a significant increase in oxidative current, with an onset potential of 1.2 V vs. Ag/AgCl. This is an indication that catalysis of benzyl alcohol oxidation is occurring. For Complex 1, the catalytic current is saturated at 20 mM BnOH with 1 mM 1, likely due to the saturation of the alcohol-complex association. There is virtually no change in the CV of Complex 3 with the addition of BnOH, supporting the hypothesis that the lack of access to higher oxidation states of Ru inhibits
catalysis. Due to the changing nature of the cyclic voltammetry of Complex 2, kinetic studies were only explored on Complex 1.

The first approach for determining the rate constant of benzyl alcohol oxidation catalysis was to explore the relationship of $i_c/i_p$ with respect to scan rate, as has been done frequently in the literature.\textsuperscript{25,28} This is based on Equation 6-1, below, and the results are shown in Figure 6.8.

**Equation 6-1**

$$\frac{i_c}{i_p} = 2.24 \frac{n_c}{n_p} \sqrt{\frac{RT}{n_pF}} \sqrt{\frac{1}{v}} \sqrt{k_{obs}}$$

In this equation, $i_c$, $i_p$, $n_c$, $n_p$, $R$, $T$, $F$, $v$ and $k_{obs}$ correspond to the catalytic current, the peak current for a particular redox couple, the number of electrons for the catalytic reaction, the number of electrons for the redox couple mentioned for $i_p$, the gas constant, temperature, Faraday’s constant, scan rate and the observed rate constant. The relationship between $i_c/i_p$ and $v^{-1/2}$ is clearly not linear, as seen in Figure 6.8, largely due to the lack of steady state current in catalysis. This exponential relationship also suggests that the reaction is not first order. Three different applied potentials (1.3, 1.4 and 1.5 V vs. Ag/AgCl) were explored using this method. $k_{obs}$ values of 320, 3800 and 7500 s$^{-1}$ were found for each potential, respectively. While the higher potentials saw significantly higher rates of catalysis, it is likely that a competing reaction, water oxidation catalysis, is also occurring at this potentials, resulting in a falsely increased rate.

In order to compensate for the second order nature of the catalysis, Equation 6.2 was utilized, which takes the concentration of both the catalyst ($C_o$) and analyte ($C_s$) into consideration. In this equation, $n$, $F$, $A$, $C_o$, $D$, $k_{cat}$ and $C_s$ correspond to the number of electrons, Faraday’s constant, the area of the electrode, concentration of the catalyst, diffusion coefficient of the catalyst, catalytic rate constant and concentration of the analyte, respectively. The catalytic rate
**Figure 6.7:** Cyclic voltammetry of Complexes 1 (a), 2 (b) and 3 (c) in 0.1 M TFA, without (blue) and with (orange) benzyl alcohol.
Figure 6.8: Plot of $i_c/i_p$ vs. $\nu^{-1/2}$ for Complex 1 in 0.1 M TFA with 20 mM benzyl alcohol. CVs were performed using a BDD working electrode, Pt auxiliary electrode and Ag/AgCl reference electrode. Three different potentials were reported, each vs. Ag/AgCl. The $k_{obs}$ derived from each potential was 320 s$^{-1}$, 3800 s$^{-1}$ and 7500 s$^{-1}$, respectively.

A constant ($k_{cat}$) derived from this equation is a second order rate constant with units of M$^{-1}$s$^{-1}$, provided that $C_O$ is expressed in units of mol/cm$^3$ and $C_S$ in M.

**Equation 6-2**

$$i_L = nFAC_O(Dk_{cat}C_S)^{1/2}$$

To find $k_{cat}$, a limiting current ($i_L$) for the catalysis reaction was needed. In order to obtain this information, very low concentrations of catalyst (discussed earlier in the experimental section) and slow scan rates (5 mV/s) were implemented. CVs of the low concentrations of catalyst with 20 mM benzyl alcohol are seen in Figure 5.9a. The ca. linear relationship between concentration of Complex 1 ($C_O$) and the limiting current ($i_L$) is depicted in Figure 5.9b. Linearity ceases at concentrations higher than 0.25 M Complex 1, due to the lack of observed limiting current. The rate constant ($k_{cat}$) determined using Equation 6.2 was 470 M$^{-1}$s$^{-1}$. This is significantly higher.
than previous literature, where most catalytic rate constants were one to two orders of magnitude smaller. 24-26,28,29,36

6.3.4 **Bulk Electrolysis of Ru(qpy)(CH$_3$CN)(Cl) with Benzyl Alcohol**

Bulk electrolyses of Complex 1 with 20 mM benzyl alcohol were performed in order to determine the efficiency of this process. Originally, the bulk electrolyses were performed under the same conditions as the voltammetry reported above (0.1 M TFA), with the substitution of a high surface area *nano*ITO electrode for the working electrode. However, low current efficiencies were observed (2-4%). It was determined that the source of current was the electrochemical etching of the *nano*ITO by the TFA electrolyte. The electrolyte was then switched to 0.1 M HClO$_4$, which resulted in a decrease in solubility of Complex 1. To compensate for this, 20% MeCN was added to the solution. A bulk electrolysis at 1.25 V vs. Ag/AgCl yielded 1.8 * 10$^{-5}$ mol of benzaldehyde with faradaic efficiency of 98%. As this is around the onset potential of catalysis, low turnover is expected, but the high faradaic efficiency is promising that the primary reaction occurring at this potential is the oxidation of benzyl alcohol.

![Figure 6.9: (a) Cyclic voltammetry of low concentrations of Complex 1 and 20 mM benzyl alcohol. (b) The linear relationship between the concentration of the catalyst, Complex 1, and the limiting current.](image)
However, bulk electrolyses at higher potentials (> 1.3 V), seem to pose a dilemma in terms of current efficiency. As seen in Table 6.3, the calculated current efficiencies for the bulk electrolyses at 1.3 and 1.4 V were 136 and 182%, respectively. The gas chromatographs for these electrolyses showed complete conversion of benzyl alcohol to benzaldehyde and/or other products, such as benzoic acid. However, the charge from the bulk electrolyses suggested much lower yields of product. At these potentials, it appears that the benzyl alcohol was oxidized via non-electrochemical methods. One hypothesis for this might be oxidation via the electrolyte HClO₄, which is a known oxidant of organic compounds.¹⁶⁹

Upon further inspection of the chronoamperograms such as in Figure 6.10, the current for the higher potential bulk electrolyses follows a unique pattern. There is a sudden increase in current for a short period of time and then the current decays away. This suggests that the electrode is becoming passivated in some way. Comparing the solutions before and after electrolysis, the color changes from pink to orange, indicating possible decomposition of the catalyst during the bulk electrolysis. Furthermore, the nanoITO electrode has an orange film deposited onto the

![Chronoampergram of a bulk electrolyses of Complex 1 and benzyl alcohol in 0.1 M HClO₄ and 20% MeCN, where the potential was held at 1.4 V vs. Ag/AgCl for 13 hours. nanoITO on FTO coated glass was used as a working electrode, with a Pt auxiliary electrode and 3 M Ag/AgCl reference electrode.](image)
Table 6.3: Current efficiencies of bulk electrolyses at various potentials.

<table>
<thead>
<tr>
<th>Potential Applied vs. Ag/AgCl</th>
<th>1.25 V</th>
<th>1.3 V</th>
<th>1.4 V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current Efficiency</td>
<td>98%</td>
<td>136%</td>
<td>182%</td>
</tr>
</tbody>
</table>

surface, presumably the product of this reaction. This film deposition could explain the passivation of the electrode during electrolysis.

6.4 CONCLUSION

The electrochemical characterization of three [Ru(qpy)L₂]^{2+} complexes is reported as well as the initial kinetic studies of benzyl alcohol oxidation via [Ru(qpy)(MeCN)(Cl)]⁺. In MeCN, one redox couple is observed for each complex, corresponding to the Ru^{III/II} couple. Under acidic aqueous conditions, the MeCN ligands are exchanged for aqua groups, resulting in the accessibility of higher oxidation states of Ru, suggesting a possible water oxidation catalyst. Benzyl alcohol oxidation catalysis was observed for [Ru(qpy)(MeCN)(Cl)]⁺, with a high rate constant of 470 M⁻¹ s⁻¹. At low potentials, high selectivity for this reaction is observed. At high

Figure 6.11: Complex 1 in 0.1 M HClO₄ and 20% MeCN before (left) and after (right) bulk electrolysis. The complex undergoes a color change from pink to orange, indicating the catalyst may be decomposing.
potentials, the catalyst may experience decay and other methods of benzyl alcohol oxidation may also occur.

6.5 ACKNOWLEDGEMENT

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