

DISSERTATION

ENGINEERING PHTHALOCYANINES AND CARBON COMPOSITES FOR USE IN SENSING,
MICROFLUIDICS AND DYE SENSITIZED SOLAR CELLS

Submitted by

Kevin Jay Klunder

Department of Chemistry

In partial fulfillment of the requirements

For the Degree of Doctor of Philosophy

Colorado State University

Fort Collins, Colorado

Summer 2018

Doctoral Committee:

Advisor: Charles Henry

Amy Prieto

Melissa Reynolds

George Barisas

Shantanu Jathar

Copyright by Kevin Jay Klunder 2018

All Rights Reserved

ABSTRACT

ENGINEERING PHTHALOCYANINES AND CARBON COMPOSITES FOR USE IN SENSING, MICROFLUIDICS AND DYE SENSITIZED SOLAR CELLS

The focus of this thesis is on fundamental and applied electrochemistry in the areas of photovoltaics, sensors, and microfluidics. Photovoltaics are important as they are needed to reduce the amount of greenhouse gases, pollution, and reliance on finite energy sources that are currently associated with energy production. A thin film photovoltaic device known as a dye sensitized solar cell (DSSC) is studied in his work. Specifically the cathode of the DSSC is studied in detail. A new method to create a highly transparent and catalytic DSSC cathode coating is proposed. The phthalocyanine based coatings have $\sim 97\%$ transmittance at 550 nm and low charge transfer resistance of $\sim 1.3 \Omega \text{ cm}^2$, representing one of the best cathode coatings in terms of transparency and charge transfer resistance to date.

Electrochemical sensors and electrochemical microfluidics can be used to monitor air, water and soil pollution, both of which can occur from anthropogenic and/or natural sources. Quantifying this pollution is vital for human and animal safety. Electrochemical sensors are also used for health diagnostics and are commonly applied in blood glucose monitoring. It is projected that wearable forms of electrochemical sensors will emerge as a vital class of real-time point-of-care sensors to monitor health indicators in the near future. To advance the field of electrochemical sensors and electrochemical microfluidics low cost, easily miniaturized, patterned, and shaped electrodes are needed. The work here

introduces a new fabrication method for carbon composites which enables electrodes to be patterned and made into micron features in a facile manner through solvent or melt processing. The composites are also shown to be easily integrated into microfluidic devices, demonstrated with the assembly of electrochemical droplet microfluidics. The ease of fabrication of the new composites represents a milestone for the widespread use of low cost carbon composites in complex electrochemical systems. Within this thesis, Raman, SEM, XRF, and a wide range of electrochemical redox species and techniques are used to determine what factors affect the electrochemical activity, capacitance, and conductivity of the carbon composites.

Finally, phthalocyanines for uses in electrochemical catalysis are a recurring theme throughout the thesis. Chapter 4 is dedicated to creating new types of electropolymerizable phthalocyanines. Cobalt phthalocyanine is integrated into the carbon composites from Chapter 2 for uses in thiol oxidation and the sensing of thiols. The thiol of interest was dithiothreitol (DTT) which is used in the “DTT assay”. The DTT assay is a chemical measure of oxidative potential of particulate matter, and is commonly used to try and understand health effects relating to air pollution. Here, low volume disposable cells, as well as flow based sensors are developed for the detection of DTT.

ACKNOWLEDGMENTS

I would like to thank my parents, as well as my academic parents for all of their many contributions to my success. I would like to thank the chemistry professors at GRCC, Dr. Niels, William Faber, and Jennifer Batten for the time and energy they invested in me. Jennifer's organic class was a main reason I chose chemistry as a major. I am also grateful for the energetic atmosphere within the chemistry department at Hope College and my undergraduate advisors Graham Peaslee, Ken Brown, as well as Fred Heckman (Tennent). I must also acknowledge the MSU Bioeconomy institute and Tom Guarr for letting me run loose in the lab and providing me with a highly rewarding research experience.

I would like to acknowledge Mike Elliott. Upon meeting Mike initially I was attracted to his passion for science, no BS attitude, and general saltiness. He is a main reason why I came to CSU and my first year working side by side with him in the lab was something I will always remember. I would like to thank Rick Finke and the members of the Finke group. Rick and the group helped immensely throughout my graduate school progression.

Finally, I would like to thank Charles Henry, who has broadened my education in a number of unique ways. Chuck has been a cheerleader for my research, even when I didn't think it is all that good. Despite his crazy schedule he still managed to be actively involved in my work, was responsive and engaged, and for this I am grateful.

TABLE OF CONTENTS

Abstract	ii
Acknowledgments	iv
Chapter 1: INTRODUCTION	1
Chapter 2: DEVELOPMENT AND CHARACTERIZATION OF THERMOPLASTIC CARBON COMPOSITE ELECTRODES.....	5
2.1 Introduction.....	5
Overview	5
Background on graphite and its electrochemistry	5
Background on carbon composite electrodes.....	8
2.2 Results and Discussion	11
Fabrication, Templating, and Patterning of ThermoPlastic Electrodes (TPE).....	11
Conductivity measurements.....	13
Electrochemical characterization of TPE	16
Capacitance of TPE.....	17
Comparison to commercial electrodes.....	19
Surface insensitive probe.....	21
Oxide sensitive probe	22
Surface sensitive probe	24
Surface adsorption dependent	25
SEM characterization of TPE surface treatment.....	26
Raman characterization of TPE.....	28
Investigation into electrochemical reactivity of some commercial carbons ..	33
Solvent window of TPE electrodes in acid and base.....	36
Metal and oxide sensitive redox probes	45
2.3 Conclusion and Future Work.....	49

Overview	49
Future work.....	50
2.4 Materials and Methods	53
Reagents	53
Fabrication of TPE-Step 1 Electrode Fabrication-Solution Preparation.....	53
Fabrication of TPE-Step 2 Electrode Fabrication-	
Templating characterization	54
Conductivity measurements.....	55
Electrochemical measurements and surface treatment	56
Capacitance Measurements	57
Spectroscopy	58
REFERENCES	60
CHAPTER 3: APPLICATIONS OF TPEs WITHIN FLOW CELLS, MICROFLUIDICS, AND SENSORS	68
3.1 Introduction.....	68
Overview	68
Introduction to electrochemical microfluidics.....	69
3.2 Results and discussion.....	71
Fabrication of melt processed PCL patterned electrodes	71
Conductivity and capacitance of PCL based electrodes	73
Fabrication of PCL sealed microfluidics with integrated carbon composites	75
Electrochemistry of PCL composites integrated into droplet generators.....	79
Summary of PCL sealed carbon composite integrated microfluidic devices ..	85
Future work for droplet microfluidics.....	85
Quantification of oxidative potential of particulate matter.....	87
Development of electrochemical TPE sensors for the DTT assay	94
Future work.....	101

3.3 Conclusion	103
Future work	
3.4 Materials and Methods	104
Methods PCL section	104
Electrochemistry and conductivity measurements	105
DTT assay chemicals and materials	105
Chelex treatment.....	106
DTT Assay protocol.....	106
REFERENCES	108
CHAPTER 4: SUBSTITUTED PHTHALOCYANINES- SYNTHESIS, CHARACTERIZATION AND ELECTROCHEMISTRY.....	117
4.1 Introduction.....	117
Overview	117
General synthesis of phthalocyanines (Pc) and substituted Pcs.....	118
Overview on the functionalization of Pcs.....	121
Overview & background on the catalytic nature of phthalocyanines	122
Strategy for the synthesis of new electropolymerizable Pc derivatives	127
4.2 Results and Discussion	130
Characterization of thiophene appended Pcs	133
Electrochemistry of thiophene Pc derivatives.....	134
Possible reasons for failed electropolymerization	136
Synthesis of nickel 4-(2-methoxythienyl) phthalocyanine.....	139
Synthesis of 4-(diphenylamino)-phthalonitrile	143
Synthesis and characterization of 4-(diphenylamine)-phthalocyanines.....	145
Electrochemistry of copper 4-(diphenylamino)-Pc	146
4.3 Conclusion and Future Work.....	148
Future work.....	149

4.4 Materials and Methods	153
Electrochemistry	153
Chemicals	153
REFERENCES	154
CHAPTER 5: PHTHALOCYANINE MODIFIED ELECTRODES FOR DSSC CATHODES	164
5.1 Introduction	164
Overview	164
Cathode development for DSSCs	168
5.2 Results and Discussion	170
Electropolymerization of NiTAPc	170
Charge transfer resistance to Co(Bipy)	172
Optical transmittance and charge transfer resistance to Co(Bipy)	178
Effect of 4-tert-Butylpyridine on R_{ct} to Co(bipy)	180
Stability of NiTAPc in Co(Bipy) mediator solutions	182
XPS analysis of NiTAPc coated electrodes	184
5.3 Conclusion and Future Work	188
Overview	188
Future work	188
5.4 Materials and Methods	189
Electrochemistry in symmetric cells and UV-Vis measurements	189
XPS measurements	191
Mass determination with EQCM	190
Calculation of diffusion coefficients of Co(Bipy)	190
Synthesis of nickel tetranitrophthalocyanine (NiTNPc)	192
Synthesis of nickel tetraaminophthalocyanine (NiTAPc)	193
REFERENCES	198

APPENDIX I-Supporting information for Chapter 2: DEVELOPMENT AND CHARACTERIZATION OF THERMOPLASTIC CARBON COMPOSITE ELECTRODES.....	207
APPENDIX II-Supporting information for Chapter 4: SUBSTITUTED PHTHALOCYANINES- SYNTHESIS, CHARACTERIZATION AND ELECTROCHEMISTRY	216

CHAPTER 1: INTRODUCTION

The thesis is written in a “journal format” for manuscripts that have been, are in the process of being submitted, or have been accepted. To form a uniform document that adheres to thesis guidelines, some sections of the manuscripts have been rearranged and some of the supplementary information has been added to the body of the thesis document. It was also necessary to add additional background information on some sections. As the work presented here is quite diverse there is not a unifying introduction, conclusion and future work chapters. Instead, the background is reported at the beginning of each new chapter, similar to that of a normal journal publication. Each chapter contains a conclusion and future work section.

In Chapter 2 the development and characterization of thermoplastic carbon composite electrodes is introduced. This work focuses on the development of a generic electrode substrate to perform electrochemistry for a wide range of platforms and techniques. Electrochemistry is entering nearly a 100 year history, and the range of electrode geometries and cell types are incredibly diverse. It is often difficult, however, to pattern and shape carbon electrodes for applications such as microfluidics or small scale voltammetry. The work in this chapter proposes a new method to pattern, shape and manipulated carbon composite electrodes. It was found that these new electrodes had excellent electrochemical activity and were highly conductive with only the use of simple graphite. Because of its low cost, graphite is a focus of study in terms of electrochemical performance. Graphite is a highly complex material and can be full of oxides and metallic impurities and these issues are discussed and tested in this chapter. The thesis chapter

largely consist of the content from a publication in the *Journal of the American Chemical Society* titled “Patternable Solvent-Processed Thermoplastic Graphite Electrodes”.

Chapter 3 continues the work of Chapter 2, demonstrating the integration of the newly proposed carbon composites into microfluidics. A new binder material is proposed (poly-caprolactone) which enables electrodes to be melt-processed. This is yet again a new strategy to fabricate the new class of carbon composite electrodes. Poly-caprolactone (PCL) is also used to seal microfluidic devices. Methods and methodology are presented to ease the process of both microfluidic fabrication and carbon electrode integration into microfluidic devices. Electrochemical sensing within droplet microfluidics are demonstrated as a high level application of the new devices. The work with PCL microfluidics is tentatively aimed for submission to the journal *Lab-on-a-Chip*.

Also contained in Chapter 3 is the application of the carbon composites for use as thiol sensors. Specifically, the composites are used for the sensing of the dithiol dithiothreitol (DTT). dithiothreitol is frequently used to gauge oxidative potential of particulate matter through the use of a chemical assay. The assay is known as the “DTT assay” and investigates the catalytic reaction of aerosol particulate matter (PM) with dithiothreitol (DTT). In the assay the free thiol DTT is oxidized into a disulfide, the oxidation of DTT is proposed as a mimic of the biological response of PM in the human body. To perform the assay, quantitatively knowing the concentration of the thiol is required, which is then correlated to the rate that the PM and the thiol are reacting. In this chapter section fluidic devices as well as small scale electrochemical devices are proposed for the quantitative detection of DTT. Initial results indicate that the composite electrode

devices are promising for automation of the DTT assay, as well as low volume single container experiments.

Chapter 4 begins with the synthesis of various phthalocyanine (Pc) derivatives. Pcs are a historically important class of molecules for a variety of electrochemical applications, including thiol sensors. The goal of this work was to produce stable electropolymerized thin films of phthalocyanines. Electropolymerization enables the tunable growth of polymeric films on the electrode surface. Thiophene, and diphenylamino appended phthalocyanines were chosen as synthetic targets. Electropolymerization of thiophene Pcs was relatively unsuccessful, and ultimately the diphenylamino-Pc was found to be the most promising electrode coating. The diphenylamino-Pc derivatives are a completely new class of polymerizable Pcs and have potential applications in electrochromics, sensors, energy storage, or electrochemical catalysis.

Finally, Chapter 5 introduces electropolymerized tetraaminophthalocyanines as a new cathode material in DSSCs. The work compliments and validates the need and value of electropolymerization to produce catalytic electrode coatings, highlighting the work in Chapter 4. These DSSC cathode coatings are tested for the key parameters of charge transfer resistance, optical transparency, and stability. It was found that the films are one of the more catalytic and transparent to be reported in the current DSSC cathode literature. This work was published in the *Journal of Materials Chemistry A* titled “Highly transparent DSSC cathodes based on tetraamino phthalocyanine polymer films”.

To summarize, the efforts of the work contained within this thesis provide new methodologies for working with carbon composites as well as phthalocyanines. The new

methodologies were developed through an extensive review of the literature, which often was wide in scope, greatly extending past the immediate field of study. It is through the scavenging and adapting of ideas and concepts from the literature that the research efforts within this thesis have found any success. The impact of this work is then dually rooted in both new chemistries and materials and utilizing and recognizing past research efforts.

CHAPTER 2: DEVELOPMENT AND CHARACTERIZATION OF THERMOPLASTIC CARBON COMPOSITE ELECTRODES

2.1 Introduction

Overview

This chapter highlights the electrochemistry and fabrication of carbon composite electrodes. Most of the content is taken from a publication in the *Journal of the American Chemical Society* titled “Solvent Processed Thermoplastic Graphite Composite Electrodes”. Follow up work to this initial paper is also contained within this chapter which highlights the aqueous solvent window of the composite electrodes. Metallic impurities and surface oxides of the commercial graphite source are discussed as they pertain to the electrochemical activity of the composites. Overall, this chapter proposes a new methodology for fabricating carbon composites and presents multiple characterization techniques of these materials. The fundamental work lays a foundation for Chapter 3 which details the integration of the composite electrodes into flow cells, microfluidics, and sensors.

Background on graphite and its electrochemistry

To begin, it is worthwhile to briefly discuss the structure of graphite, which is made of stacked layers of graphene. The layers are composed of a large conjugated network of sp^2 carbon sheets. The sheets are held together with weak interactions from the delocalized π bonded conjugated network.¹ In Figure 2.1 (left) an idealized example of the stacked structure of graphite is shown, the layers have a spacing of 0.335 nm. However, the

layer spacing can vary significantly by thermal treatment, graphite oxidation, intercalation or exfoliation of the graphene sheets.²⁻³ On the edges, graphite has either of two chemical environments which are often called zip-zag or arm chair edges. Other useful nomenclature is the term edge and basal planes, which are shown in Figure 2.1. The terms are often used in an electrochemical context, as the different planes have dramatic effects on the electrochemistry of graphitic materials.

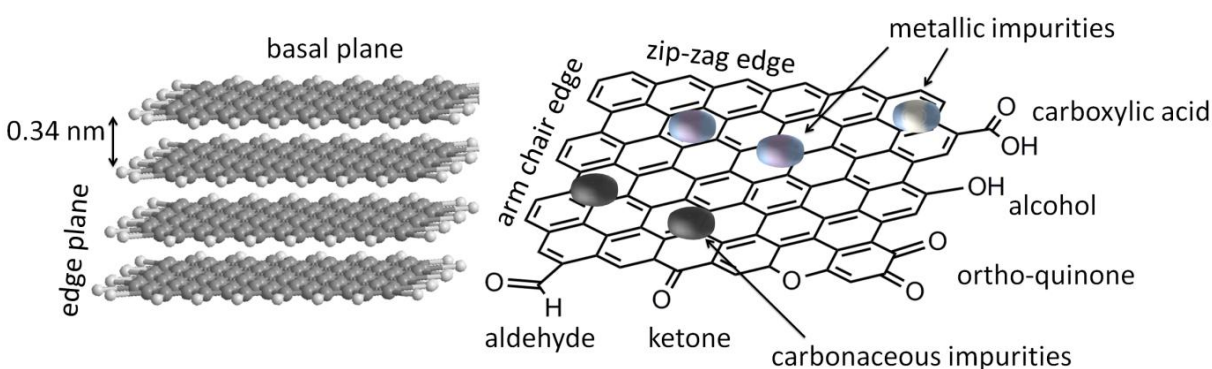


Figure 2.1 (left) Stacked graphene sheets representing a layered graphitic material. (right) Quasi-realistic depiction of chemical environments found in typical graphitic carbon materials.

In reality, the graphite used in this work (and most studies in general) is polycrystalline with crystalline domains that range from about a micrometer to just a few nanometers. Commercial graphite is often ball milled or broken up mechanically cleaving the sp^2 structure which then can react with oxygen in the air.⁴⁻⁶ This can leave a myriad of oxygen functional groups on the surface of the graphite, some of which are shown in Figure 2.1 (right). The processing can also leave a variety of defects in the graphite structure including vacancies as well as dangling sp^3 moieties.^{4, 7} What are also present in commercial and natural graphite are carbonaceous and metallic impurities.⁸

The diverse chemical environments depicted in Figure 2.1 can greatly impact the electrochemical properties. One of the biggest effects is seen between the edge and the basal planes. For quite some time it was thought the basal plane was inactive.⁹ However, recent work from the Unwin group has demonstrated that if the carbon surface is clean, the basal plane is nearly as active as the edge plane.¹⁰⁻¹¹ In practice, the basal plane fouls fairly quickly from adsorbed adventitious carbon, and this fouling is nearly unavoidable. A high density of edge sites have then been a recent focus in electrochemical research, involving the use of graphene, carbon nanotubes, and edge plane highly ordered pyrolytic graphite.¹² Under normal lab conditions edge plane graphite is highly electrochemically active and isn't nearly as prone to fouling as the basal plane.

Oxides drastically affect the electrochemistry of graphite based electrodes. McCreery, who is arguably a foremost pioneer in the understanding of the electrochemistry of graphitic carbon, has an excellent review which covers the interactions with oxides.⁹ As an example, molecules like dopamine are thought to adsorb to oxygen groups, which can facilitate electron transfer. The electrochemistry of aqueous iron almost entirely disappears when the surface is devoid of oxides.¹³

Besides oxides, certain types of impurities can impact the electrochemistry at a carbon electrode. Two common impurities are carbonaceous and metallic debris. Carbonaceous impurities can take the form of small highly oxidized clusters. A recent paper highlights the removal, isolation, and the catalytic nature these particles.¹⁴ The small particles can be highly electrochemically active and confuse the apparent source of

catalysis. This has been an issue with the characterization of carbon nanotubes and graphene.

Small amounts of metallic impurities such as iron or manganese can also dominate the electrochemistry of a carbon material. Related, metal impurities within carbon materials have been shown to be extremely difficult to remove.¹⁵⁻¹⁶ Later in the chapter, metallic impurities are discussed in more detail and the data suggest they may play a role in significantly decreasing the solvent window of commercial graphite.

Background on carbon composite electrodes

Carbon electrodes have been widely used because of their favorable electroactivity, biocompatibility, chemical stability, high conductivity, wide potential window, and low cost. Common carbon electrodes include glassy carbon, screen-printed carbon (SPE), carbon paste (CPE), boron doped diamond (BDD), carbon black, pyrolytic graphite, carbon nanotubes, and graphene.⁹ The breadth of applications of carbon based electrodes is diverse and includes batteries,¹⁷ fuel cells,¹⁸ waste water treatment,¹⁹⁻²⁰ supercapacitors,²¹ anti-static applications,²² and chemical sensors,²³⁻²⁴ just to name a few.

One challenge with carbon electrodes, however, is the trade-off between ease of fabrication and electrochemical performance. Composite carbon electrodes (CEs), as first demonstrated by Adams, tackle the issue of ease of fabrication.²⁵ CE are made from carbon particles held together with a binder and are among the easiest carbon electrodes to make and pattern. To assemble CE a broad range of binders including wax,²⁶ ionic liquids,²⁷ epoxy,²⁸ and plastics such as poly(methyl methacrylate),²⁹⁻³¹ Teflon,³²⁻³³ and polyethylene³⁴⁻³⁶ have been used. While carbon CE are easy to fabricate, they generally

suffer from low conductivity and slow electron transfer kinetics. As a result, there remains significant interest in developing CEs that are easy to fabricate, low cost, highly conductive, and have high electrochemical performance.

Among binder materials, poly(methyl methacrylate) (PMMA) has been largely ignored and only a handful of unique reports exist on its use as a binding medium for CE. The lack of use of PMMA as a binder is odd considering its low cost, ready availability, solubility in a variety of solvents, and popular use in analytical devices.³⁷ Methacrylate thermoplastic CEs have been known for several decades,³⁸ but have largely relied on either tedious fabrication methods,²⁹⁻³⁰ or methods that limit patterning.³⁹ More recently, an *in-situ* polymerization method for making PMMA:carbon nanotube electrochemical devices was developed,^{31, 40} as well as a single example of an impregnation technique to fabricate PMMA:graphite electrodes.⁴¹ While these reports provide a basis for the current studies in this chapter, it is generally unclear how CE processing conditions such as surface treatment, particle size, carbon source, and binder:carbon composition can be used to improve electrode fabrication, patterning, conductivity, and electrochemical performance.

In this chapter, a new solvent assisted fabrication technique generating electrodes referred to as ThermoPlastic Electrodes (TPE) is reported. TPEs can be easily patterned via template printing, embossing, and laser cutting, into a variety complex geometries, including flow channel and pillar arrays with micron-sized features. As expected the electrode conductivity increased with an increase of carbon in the TPE, but the conductivity varies by nearly an order of magnitude as a function of carbon type.

Following conductivity measurements, electrochemical characterization using cyclic voltammetry and electrochemical impedance spectroscopy in comparison to glassy carbon, screen-printed carbon, and Pt electrodes was carried out. The TPE outperforms both commercial carbon electrode types and performed similarly to Pt with ferricyanide as the redox probe. A variety of inner and outer sphere redox probes designed to test different electron transfer processes were then evaluated.

Surface treatments, including polishing, sanding, and plasma exposure, provide the ability to tune the reactivity, activating and deactivating the electrode for certain chemical systems. Remarkably, with surface treatments, the TPE gives comparable electrochemistry towards the highly surface sensitive redox probes of dopamine and ascorbic acid to that of the more difficult to prepare electrode materials of graphene, carbon nanotube and/or highly ordered pyrolyzed graphite.

Finally, the electrodes were characterized through scanning electron microscopy (SEM) and Raman spectroscopy to elucidate changes in the electrode composition from the surface treatments. Major structural changes of the TPE surface are seen in the SEM images for each treatment. Interestingly, the Raman spectra suggest that the quantity of edge type defects (crystallite domain size) did not drastically change, with no vacancy or sp^3 defects being introduced upon surface treatment. Overall, the TPEs provide a significant stepping stone for future advancement in the fabrication and integration of composite carbon electrodes into high end electrochemical systems.

2.2. Results and Discussion

Fabrication, templating, and patterning of ThermoPlastic Electrodes (TPE)

To address the key problem of ease of fabrication and templating, reported is a simple and low cost solvent assisted fabrication method as an alternative to air-free *in-situ* synthetic conditions commonly used with PMMA composite electrodes.⁴²⁻⁴³ Templating TPEs to make complex electrode geometries is straightforward as illustrated in Figure 2.2A. To make the electrodes a PMMA template is cut or etched with the CO₂ laser, and a semi-solid TPE material is pressed into the PMMA template. Applying pressure (~50 psi) to the TPE while drying was found to be crucial to achieve a defect free and uniform electrode material. Additional details can be found in the methods section on the process. The gum-like consistency of the partially dried TPE material allowed for easy fabrication of electrodes with micron-scale dimensions.

The ~150 μm spot size of the CO₂ laser defined the lower size limit of attainable features within the PMMA templates. Figure 2.2B shows 150 μm band electrodes, as well as an individually addressable disk electrode array containing nine 150 μm electrodes. The electrode arrays would be challenging to fabricate with traditional carbon materials, but can be readily fabricated with the solvent assisted TPE system shown in Figure 2.2A. For patterning based on cutting methods, 1 to 2 mm thick TPE sheets were made by pouring the mixture into a small mold. Once fully dried, the TPE sheets were cut using a CO₂ laser to create electrodes with complex geometric shapes, demonstrated in the top of Figure 2.2C. The CO₂ laser TPE cutouts, when heated slightly above the T_g (~121 °C from Plaskolite) with applied pressure (~50 psi), were readily moldable into premade PMMA templates.

The entire process is shown chronologically moving from the top to the bottom in Figure 2.2C.

Despite the mass loading in the TPE being comprised largely of graphite, it was envisioned that embossing could be used to create intricate patterns into the TPE material. Figure 2.2D shows a series of structures embossed directly into the TPE, including microfluidic channels and a pillar microarray. Creation of unique structures like the pillar array are particularly attractive for applications where high electrode surface areas are needed to maximize faradaic or non-faradaic currents.⁴⁴⁻⁴⁵ At low carbon content for all particle sizes, the TPE retains PMMA-like character and is easily embossed, while at a higher carbon content the TPE cannot be shaped into micron sized features due to the reduced PMMA binder content. We found a rough upper limit for carbon content to generate well resolved embossed features to be 1:2 (PMMA:carbon) for the 11 and 20 μm particles, and 1:0.6 for ≤ 500 nm particles.

The ≤ 500 nm particles were the most versatile for embossing intricate features, perhaps owing to the small particle size which potentially allowed for facile rearrangement of the carbon polymer matrix. The difference in the quality of embossed features can be seen in Figure 2.2 (D1 & D2), where the 1:2 11 μm TPE has rounded edges, and the ≤ 500 nm TPE was nearly a perfect negative of the template. It should be noted that the embossing parameters were not optimized, and this initial embossing work represents a starting point for more in-depth studies. The next sections explore how mass loading impact electrode conductivity and electrochemical performance.

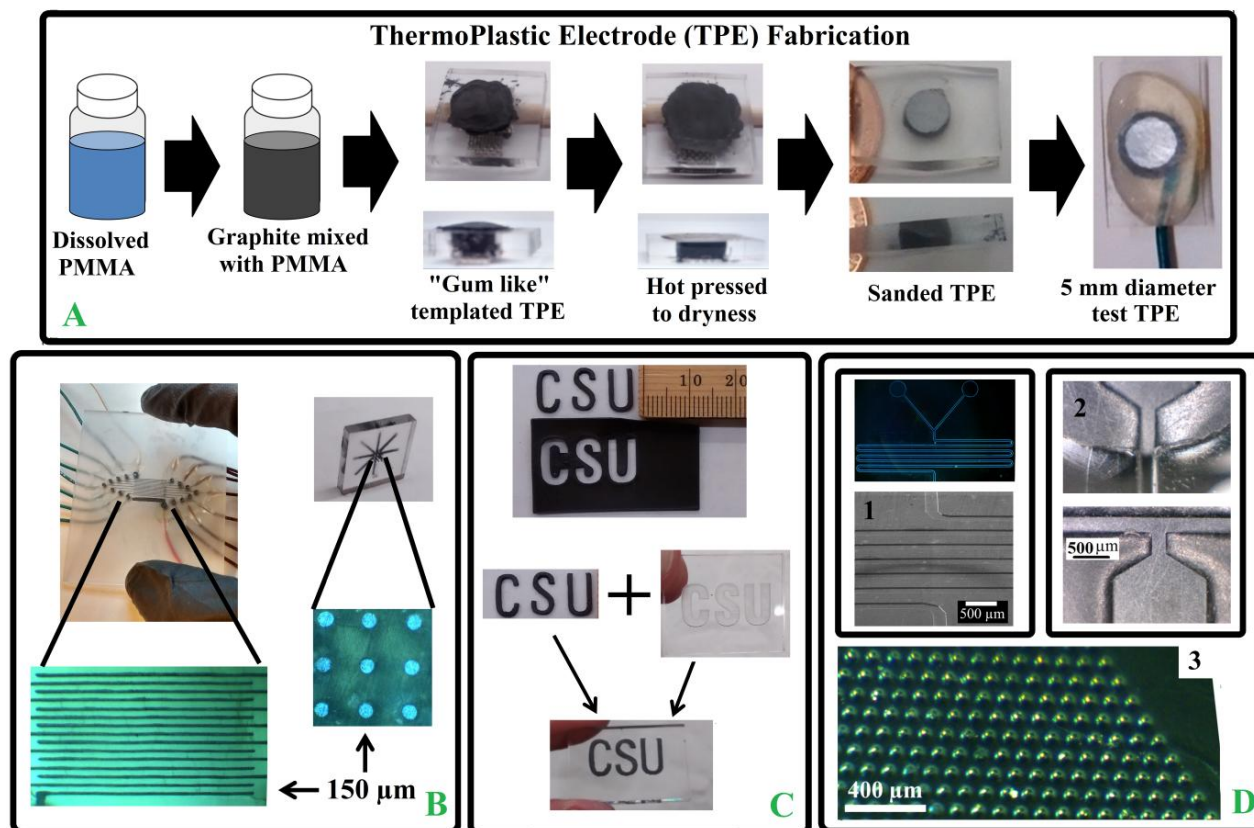


Figure 2.2 (A) General fabrication method for making templated TPEs. (B) 1:2 11 μm TPE with 14 individually addressable 150 μm wide bands, and an array of 150 μm diameter individually addressable TPE. (C) Laser cut TPE letters, which were hot pressed into a premade matching templated. (D1) Serpentine micro-channel SU-8 template (top) and the negative embossed image into a 1:0.3 ≤ 500 nm TPE. (D2) channels embossed in a 1:2 11 μm TPE. (D3) Hot embossed pillar array using 1:0.3 ≤ 500 nm TPE.

Conductivity measurements

High electrode conductivity is critical to minimize ohmic drop and improve electrochemical performance of composite electrodes. Figure 2.3 shows a comparison of conductivity as a function of electrode composition. As expected, TPE conductivity increased with increasing carbon content. The conductivity of the ≤ 500 nm TPEs did not reach saturation and was limited by physical electrode integrity. This trend was also

observed for the carbon black particles (50 nm). The conductivity of the 11 μm TPEs increased initially but then decreased at higher loadings. The decrease may be due to particle agglomeration at higher mass loadings, which could limit the total number of conductive pathways. A similar conductivity trend to that of the 11 μm TPE was previously observed for a carbon nanotube/graphite/epoxy composite.⁴⁶ Similar to the 11 μm particles, the conductivity of the 20 μm TPE increases until reaching a saturation point at a 1:3 PMMA:carbon ratio. The conductivities in Figure 2.3 are consistent with the literature on carbon composites with similar carbon mass loadings, while the values of the 11 μm TPEs are considered high.⁴⁶⁻⁴⁸ A recent report on a graphene screen printed electrode proposed an “extremely high” conductivity of 11.2 S m^{-1} .²³ By comparison, the best performing 11 μm TPE reported in this section exhibited an average conductivity of nearly 700 S m^{-1} .

The high conductivity of TPE arises most likely from increased numbers of low resistance particle-to-particle contacts.⁴⁹ The contact resistance (quality of contact) between particles, as well as the number of contact points determines the conductivity of composite materials. In the proposed TPE system the contact quality and number of contacts will invariably be affected by the particle size, processing technique (pressure), particle shape, and polymer-particle wettability.⁴⁹⁻⁵⁴ Therefore, given the complexity of the TPE system the relationship between electrode composition and the exact mechanism that governs a low or a high conductivity isn't completely clear. It is clear, however, that the particle source has a profound effect on the resulting conductivity.

Besides providing conductivity information, the data in Figure 2.3 can also be used to define lower and upper PMMA:carbon mass loading thresholds that allow for a usable electrode. Here, the low carbon mass loading range is defined by a conductivity of $\sim 10 \text{ S m}^{-1}$, below this threshold significant contributions to ohmic drop are observed in an electrochemical cell. The upper limit of mass loading is defined by mechanical instability of the electrode caused by lack of binder. Figure 2.3 is also useful for defining the minimum carbon loading required to achieve the maximum electrode conductivity. Higher binder content (low carbon loading) yields electrodes that are more robust and easier to emboss. Given the broad applicability of the TPE system, the construction of this plot is then highly recommended and invaluable when working with new particle types or new polymer binders.

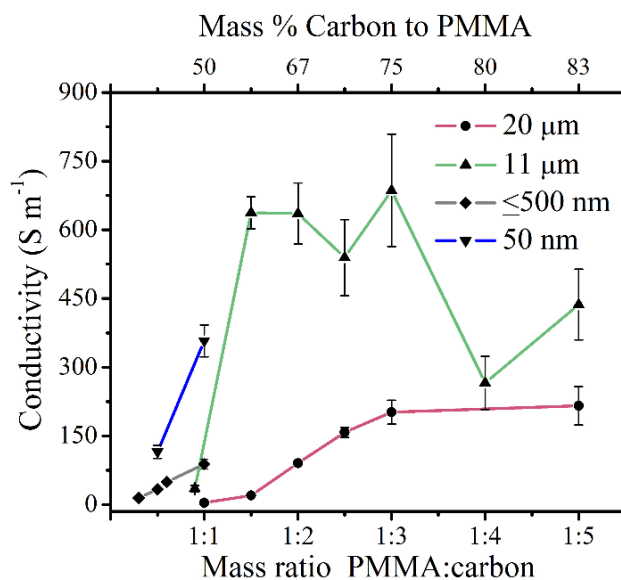


Figure 2.3 Conductivity as a function of various ratios of PMMA:carbon with differing particle type and size. The 20 μm , 11 μm and $\leq 500 \text{ nm}$ were graphitized carbon and the 50 nm particles were acetylene carbon black.

Electrochemical characterization of TPE

Electrochemical experiments were selected in order to highlight the range of electroactivity of the carbon based TPEs. Initially, the capacitance of various TPE compositions was quantified, as it is a major contributor to background signal and negatively affects the sensitivity and detection limits in electrochemical sensing measurements. Additionally, cyclic voltammetry and electrochemical impedance spectroscopy (EIS) were used with a variety of redox probes to inform on the electrocatalytic activity. The redox probes were chosen as to understand the impact of surface treatment (polishing, sanding with 600 grit paper, and plasma exposure) on the electrochemical properties of the TPEs.

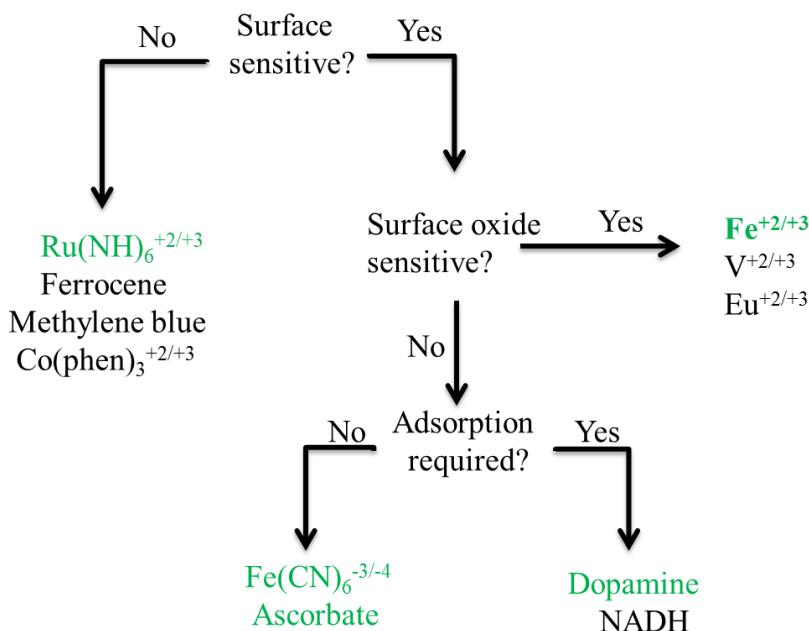


Figure 2.4. Flow chart for describing electrode surface sensitivity towards various analytes proposed by McCreery. The analytes in green were tested in this work.

As proposed by McCreery (Figure 2.4), species such as ferricyanide, ascorbic acid, dopamine, and $\text{Fe}^{2+}/\text{Fe}^{3+}$ have electrochemical responses which are heavily reliant on the chemical composition at the carbon electrode surface.^{13, 55-56} For brevity, the 11 μm particles in a PMMA to carbon ratio of 1:2 are highlighted in the main text due to their favorable embossing characteristics, high conductivity, electrochemical stability, and lower capacitance. Similar data for TPE fabricated with 1:3 20 μm and 1:0.55 ≤ 500 nm particles can be found in Appendix I (Figure S2.1) in this chapter.

Capacitance of TPE

Electric double layer (EDL) values of TPEs were calculated from cyclic voltammetry (Figure 2.5) using a 0.5 M KCl solution. The current from the cyclic voltammograms is directly related to the capacitance via Equation 2.2 in the methods section. Figure 2.5 shows increasing capacitance with increasing carbon content for all electrodes. For all ratios, the capacitances of the 11 μm and 20 μm TPEs were higher than common planar electrodes. Typical capacitance values for planar metal (platinum, gold) electrodes are 20 $\mu\text{F cm}^{-2}$, glassy carbon electrodes are 24-36 $\mu\text{F cm}^{-2}$, and basal and edge plane graphitic carbon electrodes are ≤ 2 $\mu\text{F cm}^{-2}$ and ~ 60 $\mu\text{F cm}^{-2}$, respectively.⁹ The 2x to 20x increased capacitance of the 11 μm and 20 μm TPEs above what is expected for planar edge or basal graphite points towards an electrode that contains some porosity and surface roughness, especially in the higher carbon to PMMA ratios. The ≤ 500 nm had capacitance of 35 ± 15 $\mu\text{F cm}^{-2}$, which is more consistent with a planar carbon electrode, and similar to a commercial DropSens CPE (average capacitance of 37 $\mu\text{F cm}^{-2}$).

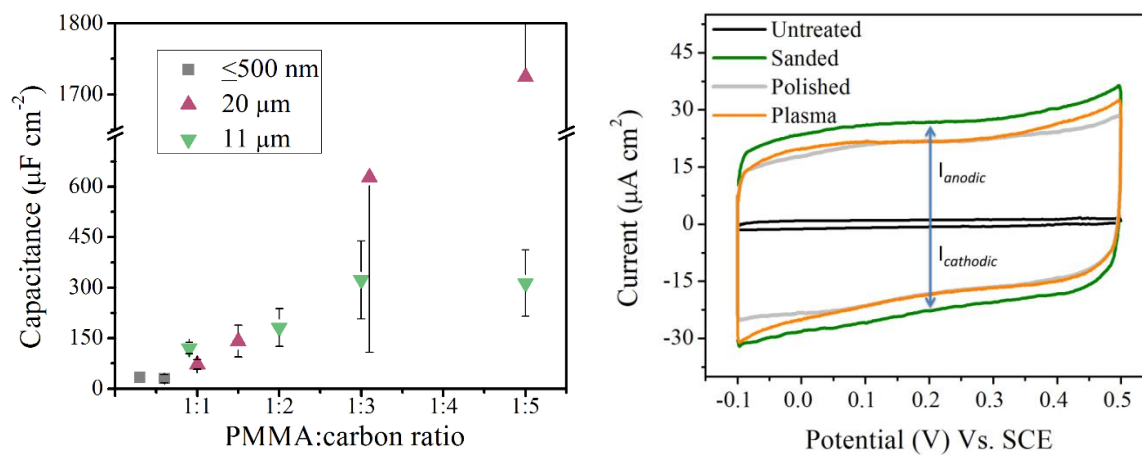


Figure 2.5 (left) Averaged cyclic voltammograms (N=3) from the various surface treatments performed on a 1:2 11 μm TPE. (right) Geometric area normalized capacitance as a function of PMMA:carbon mass loading and particle size with sanded electrode surfaces. For clarity a break was placed in the Y-axis, causing truncated error bars for the 20 μm data.

Lastly, it was found that the surface treatments did not greatly affect the capacitance (Figure 2.5), however, the untreated electrodes had a large decrease in capacitance ($\sim 8 \mu\text{F cm}^{-2}$), most likely from surface deactivation caused by excess plastic binder coating the graphite particles. The surface deactivation is also consistent with the following sections which examine electrochemical properties with different redox probes as well as the electron microscopy of the TPE surface.

Comparison to commercial electrodes

A comparative study of TPEs to commercially available carbon and Pt electrodes was performed using cyclic voltammetry and EIS (Figure 2.6). Ferricyanide was used as the redox probe because it is surface sensitive and a popular molecule for initial electrode characterization.⁹ DropSens CE have been reported to have a more favorable electroactivity compared with other commercially available composite electrodes and make for a suitable comparison to TPEs.⁵⁷ The cyclic voltammograms show peak separations of 140 mV, 90 mV, 400 mV, and 110 mV for glassy carbon, Pt, screen printed carbon, and TPE electrodes, respectively.

The 10 mM concentration and 500 mV s⁻¹ scan rate induce high current densities, which can be difficult for an electrode to meet. However, using these conditions the TPE had a peak current of 500 $\mu\text{A cm}^{-2}$, close to the ideal peak current density (510 $\mu\text{A cm}^{-2}$) as calculated from the Randles-Sevcik equation (Equation 2.4), and the highest of all electrodes tested. Peak separation is often used for extracting kinetic information, however, in this instance cell resistance/ohmic drop cannot be ruled out as a contributing factor to peak separation. Therefore, EIS was used to gain insight into electrode kinetics as it can decouple cell resistance/ohmic drop from charge transfer resistance. It is noteworthy that the peak separation with the TPE is more like glassy carbon and platinum, most likely from the intrinsic high conductivity.

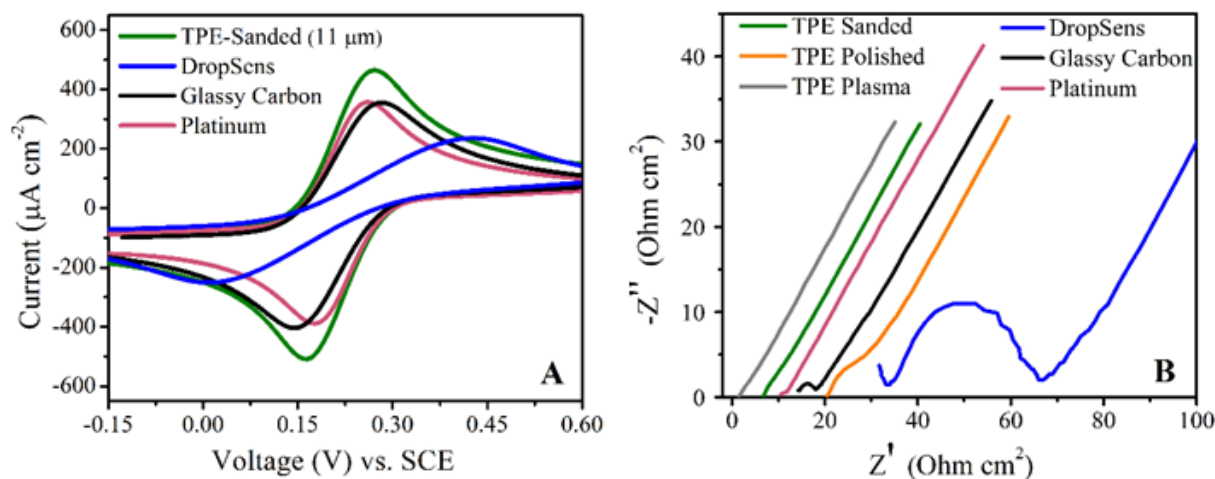


Figure 2.6. (A) Cyclic voltammetry of a 1:2 $11 \mu\text{m}$ sanded TPE, Pt, GC, and DropSens electrodes with potassium ferricyanide redox couple (10 mM), Scan rate was 500 mV s^{-1} , (B) impedance spectra (Nyquist plot) taken directly after the cyclic voltammograms. Note, the spectra are manually shifted on the x-axis for clarity.

In Figure 2.6B the TPE with surface treatments are compared with screen-printed carbon, Pt, and GC electrodes. The spectra are shown in apparent decreasing charge transfer resistance (diameter of semi-circle) with the spectra manually shifted on the x-axis for clarity. The impedance spectra for the sanded and plasma treated TPEs have no discernible charge transfer resistance. Under these conditions, TPEs appear kinetically similar to Pt and seemingly are outperforming glassy carbon and screen-printed carbon with the ferricyanide redox probe. Attempts were made to sand and plasma treat the screen-printed carbon electrode similar to the TPE, but in both cases electrode performance did not improve. Interestingly, polishing the TPE had a detrimental effect on charge transfer resistance. The SEM images in the following section show that graphite

particles are significantly rearranged with polishing and may give a clue into the origin of the increased charge transfer resistance.

Finally, the stability of the TPEs was tested over the course of 3 days with ferricyanide using the simplest surface treatment (sanded). The electrodes were tested, rinsed with Millipore water, then left in ambient air. The cyclic voltammograms in Figure S2.2 show a 14% and 1% loss of peak current after the first day, which is unchanged on day 3, for the 11 and 20 μm TPEs, respectively. Through cycling and aging both the 11 and 20 μm particles saw nearly a 10 mV increase in peak separation. In contrast, the ≤ 500 nm TPE saw a 30% and 50% decrease in peak current after the first and second days, with nearly a 200 mV increase in peak separation after 3 days of aging. It seems likely that the freshly sanded/cleaved surface of the TPE is picking up contamination slowly from the ambient conditions, and the fouling mechanism is heavily dependent on the particles used in the TPE. Similar fouling characteristic have been seen with freshly cleaved HOPG under ultra-pure and ambient conditions.⁵⁸

Surface insensitive probe

$\text{Ru}(\text{NH}_3)_6^{2+/3+}$ was used to establish Nerstian voltammetric responses from the TPE and to gauge the non-surface reliant activity of the electrode (Figure 2.7A). $\text{Ru}(\text{NH}_3)_6^{2+/3+}$ is well known to be insensitive to the electronic and/or chemical structure of the electrode surface and has been used to calculate electrochemically active surface area.⁵⁹ It was observed that untreated TPE gave a lower current density ($140 \pm 50 \mu\text{A cm}^{-2}$) than theoretically predicted ($240 \mu\text{A cm}^{-2}$), suggesting surface deactivation. Interestingly, the untreated electrode appears to display microelectrode behavior, evident from the quasi-

sigmoidal shape of the voltammogram, most likely arising from “active islands” of graphite on the TPE surface. Microelectrode behavior is a well-known characteristic of some composite electrodes.⁶⁰ When TPEs are sanded, polished, or plasma treated, the electrochemical activity is substantially higher. At a 100 mV s⁻¹ scan rate, peak separation for the TPEs are close to Nernstian at 61 ± 2 mV. Since the peak currents are close to theoretically predicted, large amounts of nano- or microscopic porosity are not expected. Porosity can cause an increase in peak current in a cyclic voltammogram from thin layer effects within the porous electrode material, which can be problematic with electrochemical characterization of small carbon particles like carbon nanotubes, graphene and potentially composite electrodes.⁶¹⁻⁶² The increased surface area can make an electrode material appear more catalytic than it actually is.

Oxide sensitive probe

The Fe^{2+/3+} redox couple is known to be highly sensitive to surface oxides.^{55,63} The cyclic voltammograms in Figure 2.7B show a drastic difference in peak separation with the various surface treatments. After plasma exposure, the TPEs exhibit well defined reversible peaks, implying the addition of quinone functionality. The peak separation for a plasma treated surface is 150 mV, which is comparable to an electrochemically heavily oxidized highly oriented pyrolytic graphite (HOPG) electrode, that was held at an oxidation potential of 2.2 V vs. Ag/AgCl (3M KCl).¹³

Sanded and polished surfaces have peak separations nearing 400 mV, more akin with GC electrodes polished under ambient conditions. Plasma generation of oxides on graphite is well known and is most likely the cause of the peak separation decrease.⁶⁴

Oxygen groups generated from milling or sheering by the manufacture of the micron sized carbon particles could explain the partial activity of the sanded and polished electrodes towards $\text{Fe}^{2+/3+}$.⁶⁵ It can thus be concluded that the graphite most likely contains quinone functionalities with all surface treatments, with plasma treatment yielding the highest population of oxygen moieties on the carbon surface.

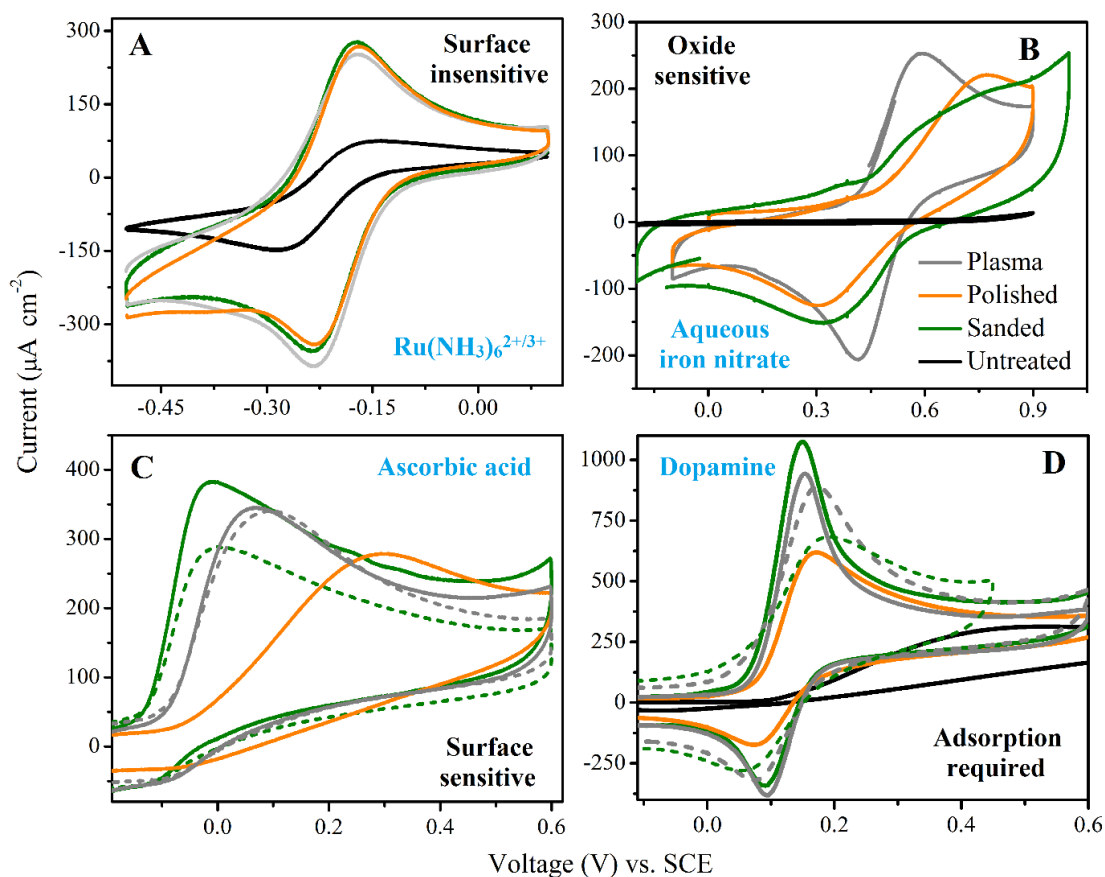


Figure 2.7 Cyclic voltammograms of a 1:2 11 μm TPE with $\text{Ru}(\text{NH}_3)_6^{2+/3+}$, 1 mM ascorbic acid (AA), 1 mM dopamine (DA) in 0.1M phosphate buffer at pH 7.4. The electrolyte for $\text{Ru}(\text{NH}_3)_6^{2+/3+}$ was 0.5 M KCl. Dashed lines represent cyclic voltammograms after the electrode has been cycled in the respective solution for 25 cycles.

Surface sensitive probe

The oxidation of ascorbic acid (AA) is an irreversible two electron, two proton process, that is highly surface sensitive.⁶⁶ The electrochemical oxidation of AA can be problematic and numerous electrode modifications have been proposed to enhance electrode kinetics.⁶⁷⁻⁶⁸ The voltammetry of AA at TPEs (Figure 2.7C) appeared to have no pre-concentration effects, in agreement with predicted responses and aligned relatively well with predicted peak currents. Calculation of theoretical peak current ($343 \mu\text{A cm}^{-2}$) requires a different equation than the previously used Randles-Sevcik equation as detailed in the methods section (Equation 2.3). The polished electrode gave a lower peak current and a ~ 400 mV positive shift in the peak potential relative to the sanding condition, demonstrating the extreme surface sensitivity of AA oxidation. The onset potential of the sanded TPE (-0.05 V vs. SCE) is similar to or better than that of electrodes composed of carbon nanotubes or graphene,⁶⁹⁻⁷⁰ and lower than edge plane HOPG (0.2 V vs. SCE).⁷¹⁻⁷²

With the sanded TPE, the peak does not shift to higher potentials with repetitive cycling, although the peak current decreases by 26% after 25 cycles. The current for the plasma treated TPE had excellent stability and remained essentially constant through repetitive cycling. One explanation for the stability may be from the introduction of additional oxygen moieties on the plasma treated TPE, which have been shown to give an enhanced and stable electrochemical response for AA, DA and uric acid.⁷³ The appendix (Figure S2.1) contains cyclic voltammograms for TPEs with $20 \mu\text{m}$ and the ≤ 500 nm particles with AA. The $20 \mu\text{m}$ particles had similar voltammetry to the $11 \mu\text{m}$ TPE, while the

≤500 nm based TPE typically had lower peak currents and increased overpotentials with sanding and polishing conditions.

Lastly, the reproducibility of the 11 μm TPE was examined with AA; representative data are shown in Figure S2.3. For two separate TPEs, repeatedly sanded (n = 6), peak current RSDs of 5.1% and 8.0% were observed. The RSD of peak current across 8 individual electrodes was 15.4%. In addition, the oxidative peak location was quite sensitive to sanding with an average across all eight electrodes of -0.023 ± 0.016 V vs. SCE.

Surface adsorption dependent

The electrochemistry of dopamine is known to be variable on different types of graphitic surfaces. For example with HOPG, there are accounts of low activity on the basal plane compared to edge plane sites.⁷⁴ It is also known that the cleanliness of the surface and preparation of basal plane HOPG greatly affects the voltammetry of dopamine.⁷⁵ Figure 2.7D shows that the peak locations are in general agreement for clean graphitic surfaces, with the oxidative peak current occurring at 0.18 V vs. SCE.⁷⁵ It was found that the peak currents with TPEs and dopamine do not follow the Randels-Sevick equation for a two electron oxidation ($490 \mu\text{A cm}^{-2}$). The observed current was closer to a four electron process, arising most likely from dopamine pre-concentration (adsorption) on the surface as seen for other composites.⁷⁶ Similar trends were also seen for 20 μm TPE, and the ≤500 nm based electrodes (Figure S2.1).

Dopamine fouling (at 1 mM) is reportedly different for edge plane and basal plane graphite. For HOPG, the oxidation peak potential shifts only slightly with edge plane fouling, while the peak current is reduced to roughly 50%, before becoming relatively

stable.⁷⁵ With TPEs, the fouling appears to be edge-plane dominated for sanded and polished electrodes. Remarkably, the peak current and peak location for plasma treated electrodes at 1 mM remains stable with cycling. Similar to the cycling stability of AA, the enhanced stability towards DA may again be related to an increase in oxygen functionalities.⁷³

The reproducibility of the 11 μm electrodes was tested with the same conditions as in Figure 2.7D using DA. For three individual TPEs, which were each repetitively sanded ($n = 6$) to expose a fresh surface, the RSDs for oxidative peak current were 6.0%, 4.7%, and 11.7%, for an average of 7.5%. The RSD for oxidative peak current across eight different individual TPEs was 11.8%, implying that reproducibility is dominated by the surface treatment. The oxidative peak location had an RSD of 4.5% for the eight individual TPEs, and an average RSD of 1.7% for three individual electrodes repetitively sanded. Unlike AA the reproducibility of DA in terms of peak location seems more favorable across different electrodes with a standard deviation of 0.007 vs. 0.016 V for DA and AA, respectively. Overall, considering the highly surface sensitive nature of DA and AA, the general reproducibility of TPEs is promising.

SEM Characterization of TPE surface treatment

The electrochemistry of TPEs is profoundly affected by surface treatment. SEM and Raman spectroscopy were used to gain insight into structural or chemical changes following the surface treatments. The SEM images in Figure 2.8 show a significant difference in the TPE surface as a function of treatment method. First, the untreated surfaces (top left) appear to be coated with a polymer film. The lack of charging implies

that the polymer film is thin, given that electrons can efficiently migrate to conductive networks in the TPE. Second, relative to the untreated electrode, the sanded electrode (top right) has large jagged domains of exposed graphite. The sanded surface is highly complex and undoubtedly contains a myriad of unique carbon chemical environments, including edge planes, ideal for facilitating electrochemical charge transfer.

Third, the polished TPE (bottom left) has a drastically altered surface containing clumps or islands where individual graphite sheets are almost unobservable, which may explain the significantly diminished electrochemical response. Finally, the plasma treated electrode (bottom right) is seemingly devoid of polymer binder on the surface, and the removal of binder has exposed thin (semi-transparent) sheets of graphite (inset). One hypothesis as to the origin of the thin graphite sheets is that sheer force from sanding is exfoliating the graphite. The excess PMMA is then removed from the exfoliated graphite via the plasma treatment, which ultimately creates graphene-like regions on the surface of the TPE. Sheer force has been reported to produce high quality graphene in large quantities.⁷⁷ Additionally, the plasma treated and sanded 11 μm electrode are strikingly similar to a graphene film mechanically pressed onto a plastic substrate.⁷⁸ TPEs made with the 20 μm particles had morphologies similar to the 11 μm particles for the respective surface treatments (Figure S2.4). The ≤ 500 nm TPE, while appearing nothing like the 11 μm and 20 μm , also had much less diversity than the 11 μm electrodes as a function of electrode treatment (Figure S2.5).

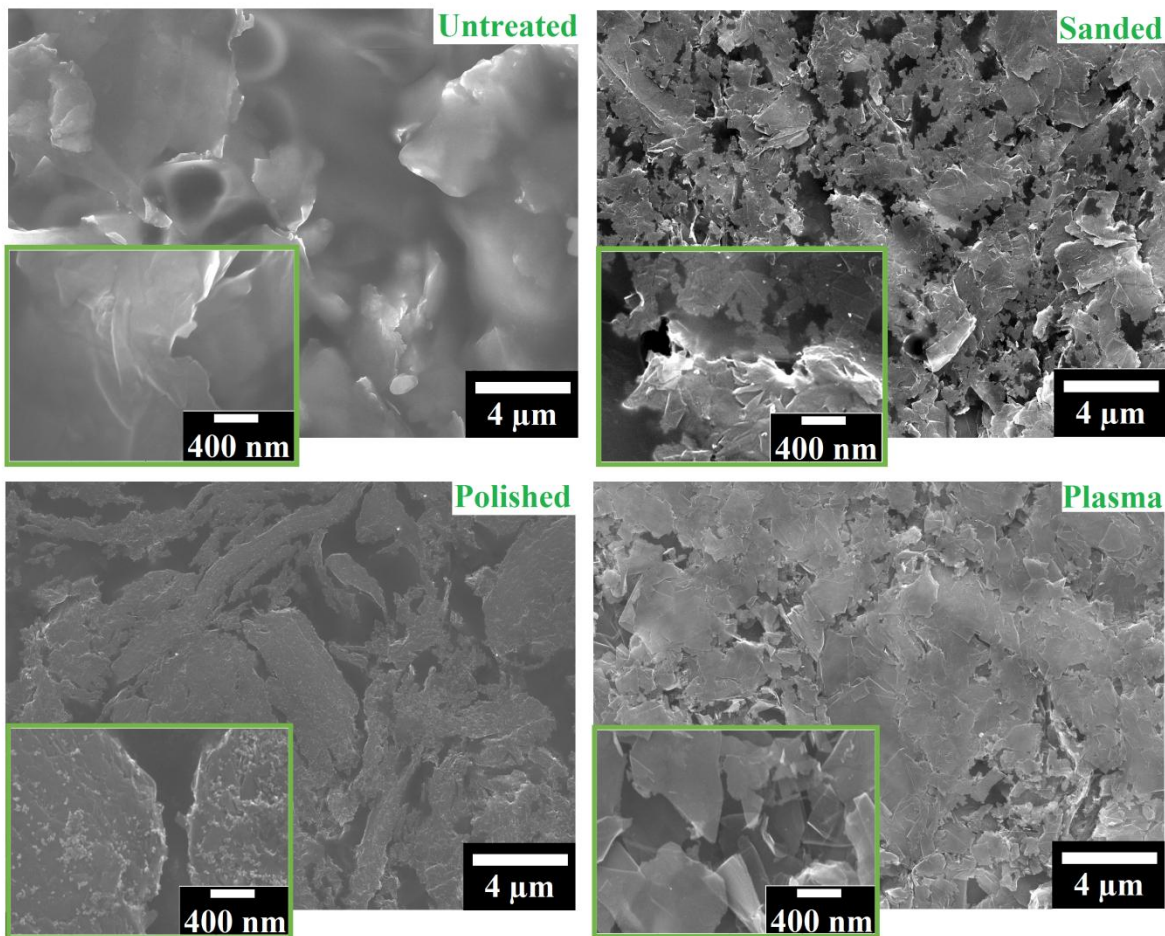


Figure 2.8 SEM images at 5,000x of a 1:2 11 μm TPE subjected to the various surface treatments. The insets are at 50,000x magnification of the surface.

Raman characterization of TPE

Finally, the TPEs were characterized with Raman spectroscopy to observe chemical changes occurring on the electrode surface which could impact electrochemical performance (Figure 2.9 & S2.6). The spectra in Figure 2.9 represent the average of 49 individual spectra. For all treatments, peaks associated with polycrystalline sp^2 carbon are clearly present (Lorentzian peak fitting results are shown in Table S2.1).⁷⁹ Although mechanical exfoliation of the graphite via sanding or polishing might shift the G' peak

position towards lower wavenumber from thinning of the graphite sheets, no significant peak shift between different surface treatments was seen.⁸⁰ Additionally, changes in the number of sp^3 defects from treatments would increase the width of the D and G peaks, which was also not observed.⁸¹

Considering mechanical abrasion, plasma treatment, and sheer are known to introduce defects and drastically change graphite composition, it seems unlikely that these processes are not happening in some amount at the TPE surface.^{7, 82-83} The lack of changes seen in the spectra are perhaps from the Raman laser probing sub-surface within the TPE, rather than Raman scattering from the outermost electrode surface. The similarities between the untreated sample and other treatments seems to support this hypothesis. It is also possible that graphite particles are not changing in a sufficiently large enough quantity as to largely affect the Raman signal. A combination of these two points is also logical.

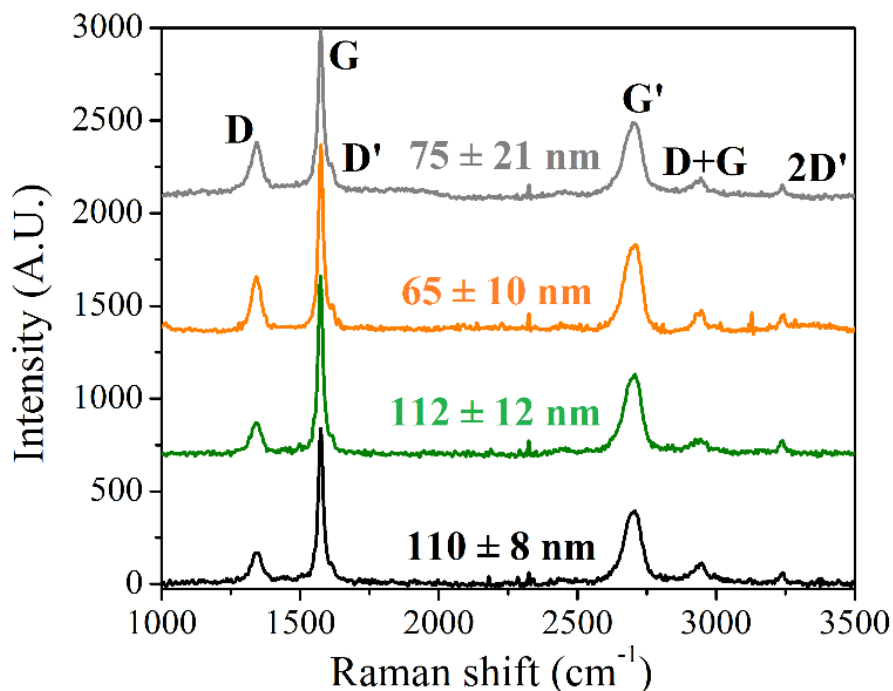


Figure 2.9. Raman spectra of a 1:2 11 μm TPE subjected to various surface treatments. Graphite crystallite domain sizes are listed above each spectra and based on calculations provided in the appendix taken from the data in Table S2.1. Color code is the same as Figure 2.7.

The Lorentzian peak fitting of the spectra can be used to elucidate small changes. The D/G peak intensity ratio can be used to gauge the amount of disorder in a graphite sample.⁸⁴ Related to the amount of disorder is the crystallite domain, and a general equation based on the D/G ratio can be used to estimate the crystallite domain size (Equation 2.5 in methods section).⁸⁵ The calculated domain sizes are listed in Figure 2.9 above the spectra and indicate there is a slightly larger crystallite domain in the untreated and sanded samples, with polishing having the smallest crystallite domain. A similar trend was seen with the 20 μm based TPE (Figure S2.6). The ≤ 500 nm TPE had essentially no crystallite domain size changes among surface treatments. The smaller domain size, seen

with the 11 μm & 20 μm particles is reasonable since plasma treatment and polishing are secondary, coming after an initial sanding step. The values in Figure 2.9 imply that the changes in crystallite domain size are small, but give evidence towards polishing and plasma treatment chemically altering the carbon particles or removing larger particles.

The plasma treated TPE had the largest standard deviation associated with the crystallite domain (27 nm), as well as the largest relative standard deviation (28%). The larger standard deviation would suggest a more heterogeneous surface, qualitatively consistent with the SEM images. Finally, while it is clear that the surface treatments can induce some effect upon the carbon at the TPE surface, at this time, relating these differences to changes in the electrochemistry is not straight forward.

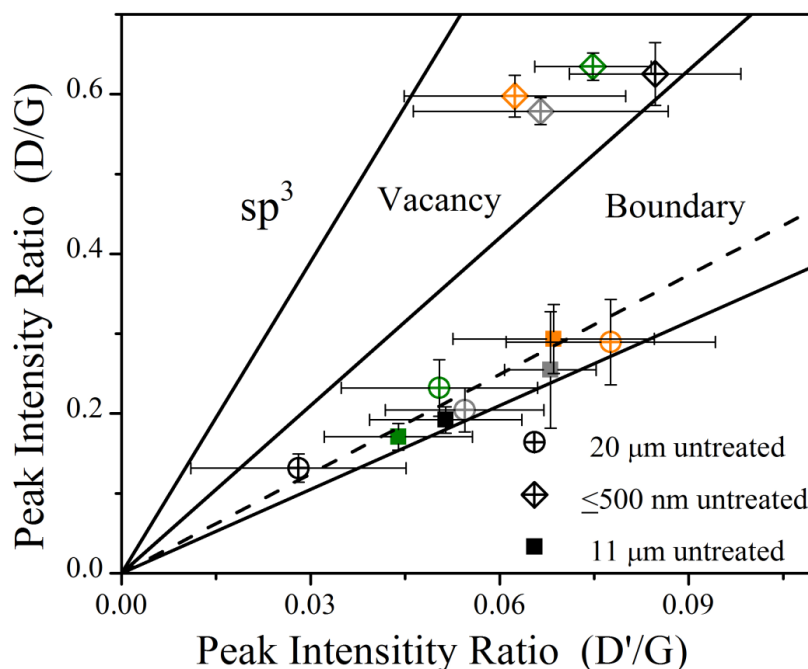


Figure 2.10 Plot of D/G versus D'/G ratio of a 1:2 11 μm , 1:0.6 ≤ 500 nm, and 1:2 20 μm TPE with various surface treatments. The color scheme is the same used for Figure 2.7.

Finally, within the literature on Raman spectroscopy of sp^2 carbon the type of defects that are most present in a sample can be estimated. By comparing the D/G ratio with the D'/G ratio, the type of defects can also be inferred.⁸⁶ The lines in Figure 2.10 are slopes (D/D' ratio) which represent specific defects, where a slope of ~ 13 indicates sp^3 defects, ~ 7 indicates lattice vacancy, and 3.5 indicates boundary or edge defects.⁸⁶ A separate study on the exfoliation of graphite proposed a slope of 4.2 for edge defects, and is represented as a dotted line in Figure 2.10.⁸⁷ Both the 11 μm and 20 μm particles fall into the region of edge defects, labeled as 'Boundary' in Figure 4. The ≤ 500 nm particles have the highest D/G ratio and are in a region having vacancy defects. Changes in the D/D' ratio among particle sizes is negligible upon surface treatment, supporting that within the resolution of this technique no new defects are introduced into a specific carbon type.

Investigation into electrochemical reactivity of some commercial carbons

The next section highlights the electrochemical reactivity of four new commercially sourced carbons. In the previously discussed sections the voltammetry is mainly studied as a function of surface treatment, with only 3 different carbons being compared. In this section the new carbons as well as the previously explored 11 μm carbon are examined for their aqueous solvent window. The aqueous solvent window is defined as the potential at which the electrode oxidizes or reduces the solvent. The solvent window is important for aqueous sensor development, in that a decreased solvent window can hinder the usefulness of an electrode. The currents from oxidizing or reducing water can overlap with the analyte of interest and completely overwhelm the signal from the analyte.

The new carbons are labeled 3569 which is from Asbury carbon and is -100 mesh, meaning the carbon contains particles that passed through a mesh size of 150 μm . MG is from Great Lakes Graphite and is reported as a 15 μm particle. The Alfa-HP is a ~ 4 μm particle which has a reported high purity of 99.9995% trace metals, supplied from Alfa Aesar. The 2299 particles (Asbury) are 3-4 μm in size, are low cost, and a lower purity carbon (97.5%). Since the 11 μm particles used earlier performed well they were chosen for study in this section also.

Table 2.1 has information on the metallic impurities of these samples, as it was expected that these impurities may affect the solvent window of the various carbons. The data was collected by X-ray fluorescence spectroscopy (XRF) and details can be found in the methods section. The table shows that there is a wide range of metallic content depending on the carbon type. Somewhat as expected, the less pure 2299 particles had the

highest amount of metal impurities, with 10,740 ppm of iron, a common metallic impurity in graphite. The 11 μm and MG particles also have higher iron content, which is also consistent with their reported purities of 99%.

M. Pumera is heavily active in the study of metallic impurities within carbon and their effects on electrochemical catalysis.⁵ In one example study the voltammetry to hydrogen peroxide and hydrazine was tested with carbon nanotubes having various iron concentrations. It was found that as little as 10 ppm could contribute significantly to the electrochemical catalysis to peroxide and hydrazine.¹⁶ Clearly seen in Table 2.1 the concentrations of many metals greatly exceed 10 ppm and, relying on Pumera's conclusions, may impact the electrochemistry of the TPE system. It should be noted that the data in Table 2.1 will be validated in the future with inductively coupled mass spectrometry (ICP-MS) as this is a more accurate metal quantification method. A motivation to validate the XRF data is that the purity of the Alfa-HP sample does not align with the manufacturers claims. The Alfa-HP sample should have low ppm or sub-ppm metal content.

Table 2.1 Values are in ppm for metal content in commercial graphite determined by XRF.

Sample ID	Bi	Cu	Fe	Mn	Ni	S	Ti	W	Specific area m^2g^{-1}	Size μm	purity
3569	0	83	536	91	< LOD	< LOD	249	301	5	≤ 150	99.9
2299	65	1186	10740	93	49	2870	66	na	405	~ 3	97.5
Fisher 11 μm	30	307	2042	< LOD	< LOD	< LOD	71	na	na	7-11	99
Alfa-HP	27.84	22.84	985.3	44.2	82.25	< LOD	< LOD	322.6	na	~ 4	99.9995
MG	22.44	12.94	4267	26.09	10.7	na	< LOD	192	na	~ 15	99

Initially the conductivity of the particles was tested as this is invaluable in finding the working ranges for carbon loadings and also quantifying the peak conductivity. Somewhat surprisingly the conductivities vary by nearly an order of magnitude with different particle types, this is demonstrated with the 2299 vs. Alfa-HP particles. The Raman data (Figure 2.11) suggest that particles that have a higher degree of crystallinity may have a higher conductivity. Low crystallinity in carbon materials can induce defects which hinder electron transport and diminish conductivity.⁸⁸ This is in agreement also with the carbon black and ≤ 500 nm conductivities shown earlier in Figure 2.3, which are smaller and less crystalline particles. The max conductivity was 1500 S m^{-1} which is high for a through-plane measurement, as well as double that of the previously best particle (11 μm) tested.

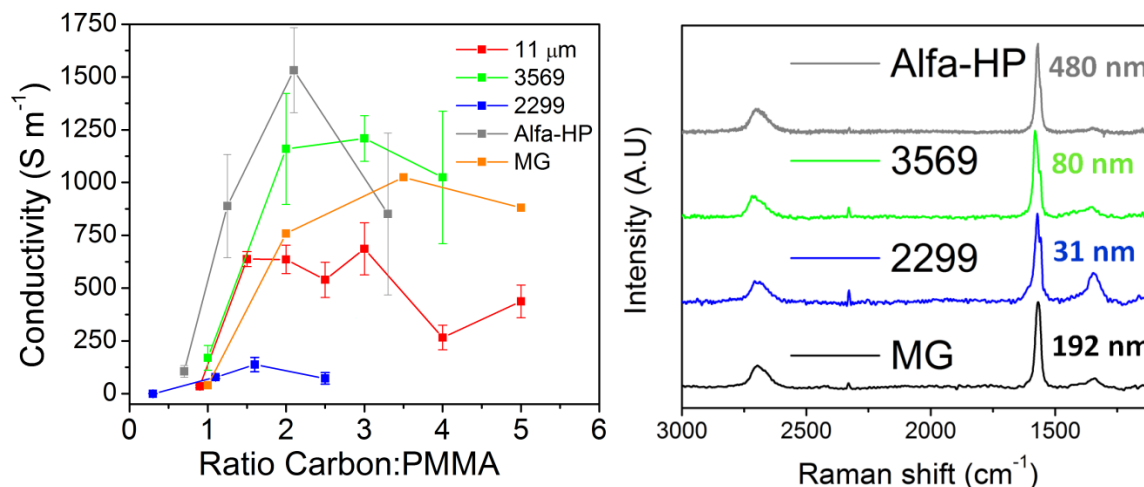


Figure 2.11. (left) Conductivity of various commercial graphite powders in TPEs. (right) Raman spectra of individual graphite powders, inset values are the crystal domain sizes.

Solvent window of TPE electrodes in acid and base

In this section the solvent window was explored in solutions of 0.5 M H₂SO₄ and in 0.1 M pH 7.4 phosphate buffer. The mechanisms shown in Scheme 2.1 and Scheme 2.2 represent water splitting at an electrode surface. At the negative electrode water or protons are reduced upon adsorption to the electrode surface to create hydrogen gas. The process is often referred to as the hydrogen evolution reaction (HER). At the positive electrode water or hydroxide is oxidized in a four electron process which creates oxygen gas.

HER is a multi-electron process, and in general is difficult to perform with a carbon electrode. The suppression of this reaction on carbon electrodes makes carbon ideal for performing generic electrochemistry, because of the larger solvent window. Platinum which is often used in electrochemistry is one of the most active HER catalyst,⁸⁹ which limits its uses in aqueous media as a sensor. The search for non-noble metal catalyst is a topic of intense research in the field of HER, typically transition metals and their alloys are found in the literature. Nickel is one of the best HER catalyst, however, other metals found in Table 2.1 such as copper, iron, manganese are also active for HER.⁸⁹⁻⁹³

Acid		Alkaline
Volmer step-	$\text{H}_3\text{O}^+ + \text{e}^- \rightarrow \text{H}_{\text{ad}} + \text{H}_2\text{O}$	$\text{H}_2\text{O} + \text{e}^- \rightarrow \text{OH}^- + \text{H}_{\text{ad}}$
Heyrovsky step-	$\text{H}_{\text{ad}} + \text{H}_3\text{O}^+ + \text{e}^- \rightarrow \text{H}_2 + \text{H}_2\text{O}$	$\text{H}_{\text{ad}} + \text{H}_2\text{O} + \text{e}^- \rightarrow \text{OH}^- + \text{H}_2$
Tafel step-	$\text{H}_{\text{ad}} + \text{H}_{\text{ad}} \rightarrow \text{H}_2$	$\text{H}_{\text{ad}} + \text{H}_{\text{ad}} \rightarrow \text{H}_2$

Scheme 2.1 Elemental reaction steps for hydrogen evolution reaction (HER) in acidic and basic conditions. H_{ad} designates an adsorbed proton to electrode or catalyst surface.

Oxygen evolution reaction (OER) is arguably more difficult than HER, involving multiple adsorption steps and the transfer of four electrons. Platinum is less catalytic for OER, but the expensive metals of iridium and ruthenium are highly active.⁹⁴ As with HER, there are massive research efforts dedicated to finding new catalyst for OER. Cobalt based catalyst are well studied which began with what is known as Nocerita's catalyst.⁹⁵ Besides cobalt metal catalyst, Ni, Mn, and Fe are also active for OER, however these are typically in the form of mixed metal oxides.⁹⁶ To conclude, both HER and OER are catalyzed in the presence of transition metals, it then seems within the realm of possibility that these impurities may impact the solvent window the TPEs.

Acid	Alkaline
$\text{H}_2\text{O} + \text{b} \rightarrow \text{H}^+ + \text{e}^- + \text{OH-b}$	$\text{HO}^- + \text{b} \rightarrow \text{OH-b} + \text{e}^-$
$\text{OH-b} \rightarrow \text{O-b} + \text{H}^+ + \text{e}^-$	$\text{HO}^- + \text{OH-b} \rightarrow \text{O-b} + \text{H}_2\text{O} + \text{e}^-$
$\text{H}_2\text{O} + \text{O-b} \rightarrow \text{H}^+ + \text{e}^- + \text{OOH-b}$	$\text{O-b} + \text{OH}^- \rightarrow \text{e}^- + \text{OOH-b}$
$\text{OOH-b} \rightarrow \text{b} + \text{O}_2 + \text{H}^+ + \text{e}^-$	$\text{OOH-b} + \text{OH}^- \rightarrow \text{b} + \text{O}_2 + \text{H}_2\text{O} + \text{e}^-$

Scheme 2.2 Elemental reaction steps for oxygen evolution reaction (OER) in acidic and basic conditions. The -b designates adsorbed species to the electrode or catalyst surface.

The solvent window of the 11 μm particles is shown in Figure 2.12 and it is apparent that there is a substantial difference in the solvent window which changes with carbon loading. The solvent window decreases significantly with increased carbon ratio to PMMA in the composite. There also seems to be an apparent decrease in the current related to

oxygen reduction, this is demonstrated with the dotted lines representing a N₂ degassed solution.

The solvent window for the 1:3 11 μm particles is roughly from -0.25 V to 0.9 V (1.15 V total). In stark contrast, when the particle mass ratio is 1:0.9 the solvent window extends to -1.3 V to 1.2 volts (2.5 V total). The solvent window with the lower ratio is over twice that of the higher ratio. As shown in the previous figures, cyclic voltammograms in this chapter of a one electron process at 1 mM, have peak currents that are in the range of 250 $\mu\text{A cm}^{-2}$. In the case of the 1:3 ratio the background current is approaching this current. The high background current is highly undesirable for performing analytical electrochemistry, since electrochemical signals from μM concentrations of analytes are often needed.

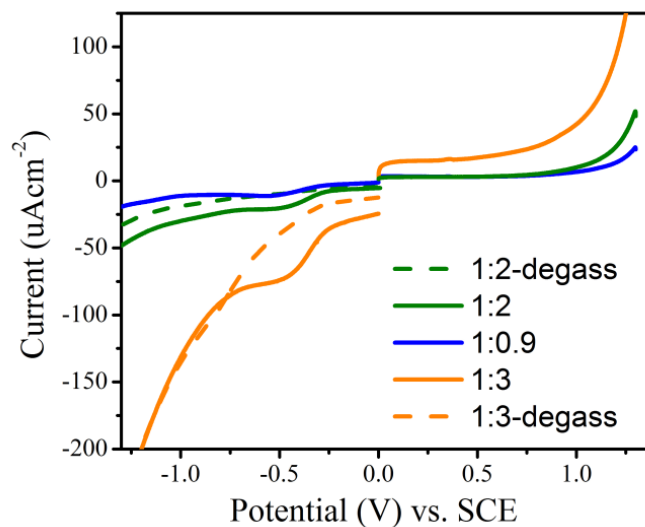


Figure 2.12 Solvent window of the 11 μm particles with different carbon loadings. Voltammetry is aqueous 0.1 M phosphate buffer at pH 7.4 with a scan rate of 100 mV s^{-1} .

It should be noted that in Figure 2.12 the scan rate is 100 mV s^{-1} , a common scan rate for performing generic electrochemistry. This scan rate is not often used to study HER or OER reactions. Instead slower scan rates are used which help to negate some effects from capacitive charging, and surface redox chemistries. Slower scan rates also keep the currents lower which in turn reduces ohmic drop. To further study the carbon materials in this section a scan rate of 5 mV s^{-1} was chosen, which should give a more accurate depiction of the catalytic nature of the various TPE for OER and HER.

Figure 2.13 shows voltammetry in the same solution as Figure 2.12, and it appears that there are wildly different activities for HER and OER with the various commercial carbons. As in Figure 2.12 there is difference between the high carbon content and low carbon content 11 μm TPE, however, the major difference now only appears around -1.5 V vs. SCE. The real onset of HER is roughly -1.4 V vs. SCE, and this is the same for the low and high mass loading of the 11 μm TPEs. The only difference is the magnitude of the current, which can be partially explained by the increase in surface area of the TPE with the 1:4 11 μm TPE.

Noteworthy, the scale of the graphs in Figure 2.13 have changed which highlight current densities that are more relevant to studying HER. Catalysis of water splitting is often reported and quantified at 10 mA cm^{-2} . It is very interesting that at 10 mA cm^{-2} the high carbon content 2299 particles have a lower over potential than platinum. It is unclear whether this is still a surface phenomenon where moieties are being reduced on the 2299 particles or whether it is the Volmer step in Scheme 2.1 in alkaline media. A somewhat recent paper has shown that transition metal hydroxides can initiate the Volmer step in

alkaline solutions to a higher degree than Pt. However, these transition metal hydroxides were poor at initiating the Tafel step, so it was found that a bi-functional catalyst of Pt and metal hydroxides was the most efficient at HER.⁹⁷ Perhaps the 2299 particles are initiating the Volmer step through metal content or on the carbon surface, which may explain the large drawn out currents.

Interestingly, the 2299 particles in a low carbon to binder ratio are almost completely deactivated for HER. The dependence on ratio is consistent with the 11 μm particles. In the bottom left of Figure 2.13 the higher purity carbons are shown, as well as a highly ordered pyrolytic graphite (HOPG) electrode, which was oriented to have the edge planes exposed. The HOPG electrode is meant to serve as a control for the other high purity graphites. The HOPG seems to be the most active of the electrodes, with the Alpha-HP being the most deactivated. It should be noted that the HOPG electrode had high capacitance values of over $2000\text{ }\mu\text{F cm}^{-2}$ (rough surface) which may be inflating the apparent catalytic activity of the electrode. In general, for HER there appears to be a trend that the less crystalline and more metal rich electrodes have increased currents.

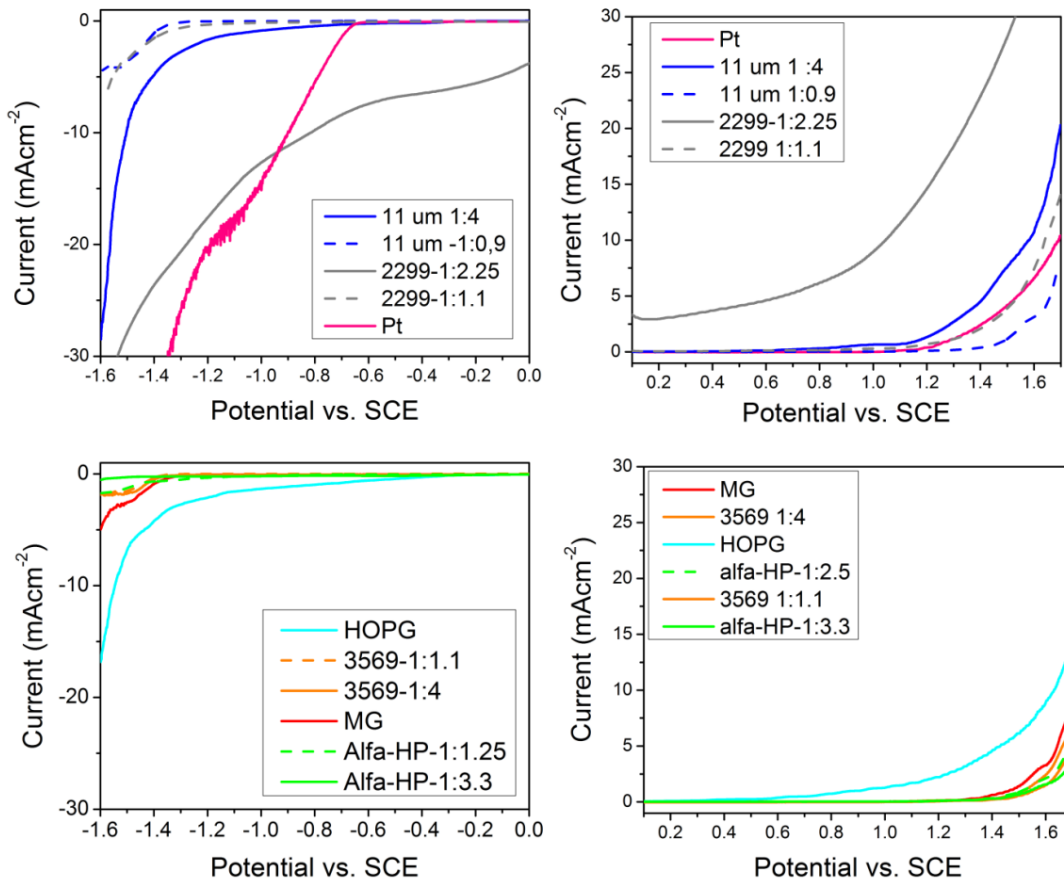


Figure 2.13 Solvent window of TPEs in 0.1 M phosphate buffer at pH 7.4, scan rate of 5 mV s⁻¹. All solutions were purged with N₂.

The trends for OER in Figure 2.13 are nearly the same as with HER. For the 11 μm particles the 1:4 ratio is the second highest in current density followed by the high ratio 2299 particles. Again for both the 11 μm and the 2299 particles the lower ratio is significantly deactivated. As mentioned earlier Pt is not highly active for OER, which may explain the lower current densities. The higher purity increased crystallinity graphites were largely inactive for OER, with HOPG again having the largest current densities. At the present, it is somewhat unclear if the current past 1.4 V vs. SCE is from OER or from oxidation of the electrode surface.

Briefly, the same electrodes in Figure 2.14 were tested in acidic media as the mechanism of HER and OER is quite different and should potentially have differing current responses between the various carbon sources. In acidic media the rate limiting step is typically the Tafel step. This rate limiting step leads to sharp drops in current that are seen with both the platinum and graphite electrodes. In contrast to the voltammetry at pH ~7 the voltammetry in acid was nearly the same for both low purity and high purity graphites, as well as for HOPG. It can be tentatively concluded that the voltammetry in acid for HER with the carbon electrodes is mainly dominated by the graphitic carbon. For OER at the various electrodes in acid they appear to again follow the same trends as in Figure 2.13. The high ratio 2299 and 11 μm particles are the most active with the higher purity electrodes being almost inactive for OER.

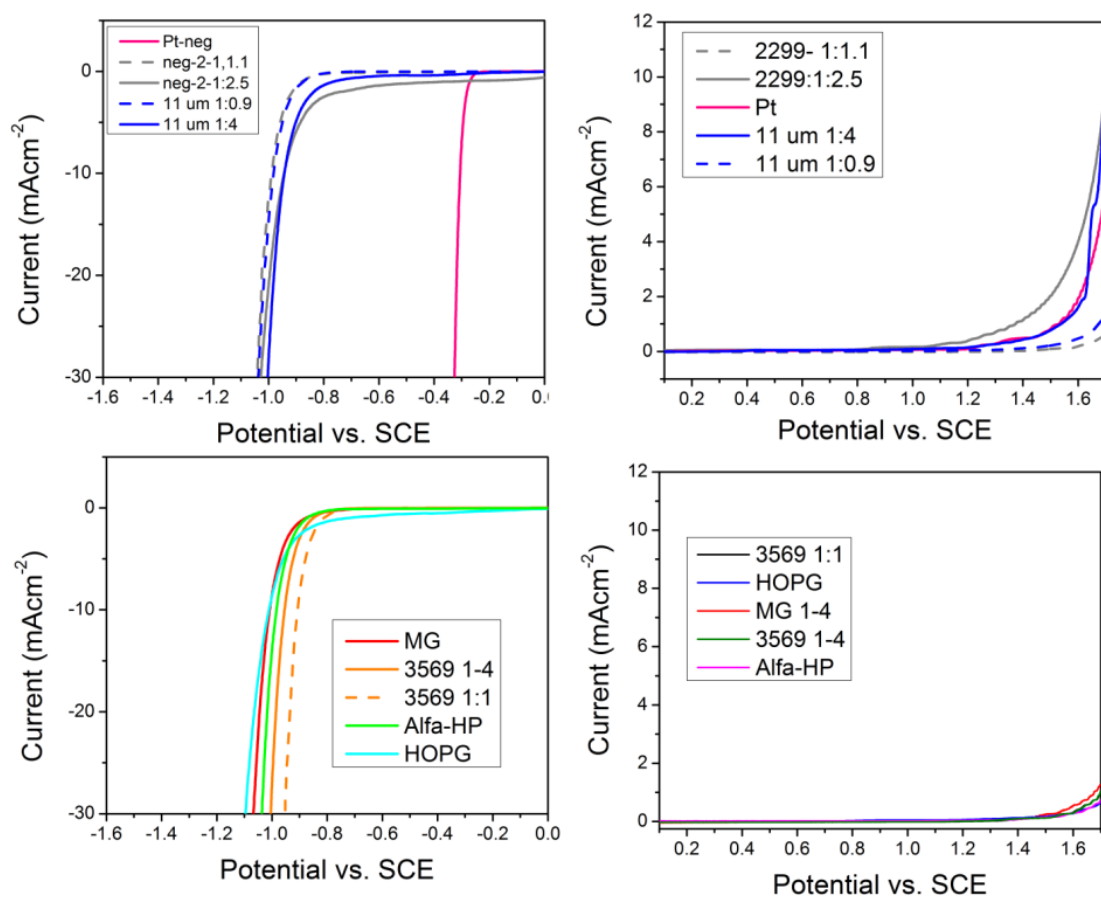


Figure 2.14 (Top) edge plane HOPG platinum and various commercial carbons in 0.5 M H_2SO_4 . All solutions were purged with N_2 .

One continuing theme for increased current density related to OER and HER is that an increase in particle to binder ratio causes increases in current. To investigate the surface of different ratios of carbon SEM images were acquired for the electrodes tested in Figures 2.13 and 2.14. The images are located in Figure 2.15 and show that the 2299 particles look drastically different from the other carbons. The 2299 particles appear much smaller and devoid of the large jagged sheet-like structures seen for the 11 μm , Alfa-HP, and 3569 particles. One other noticeable feature is that the higher ratios of the 2299 and also the 11

μm particles have a rougher surface that contain pockets or pitting. This roughness should increase the surface area of the electrode and therefore increase the number of catalytic sites. Increased numbers of catalytic sites would be consistent with the observed voltammetry thus far.

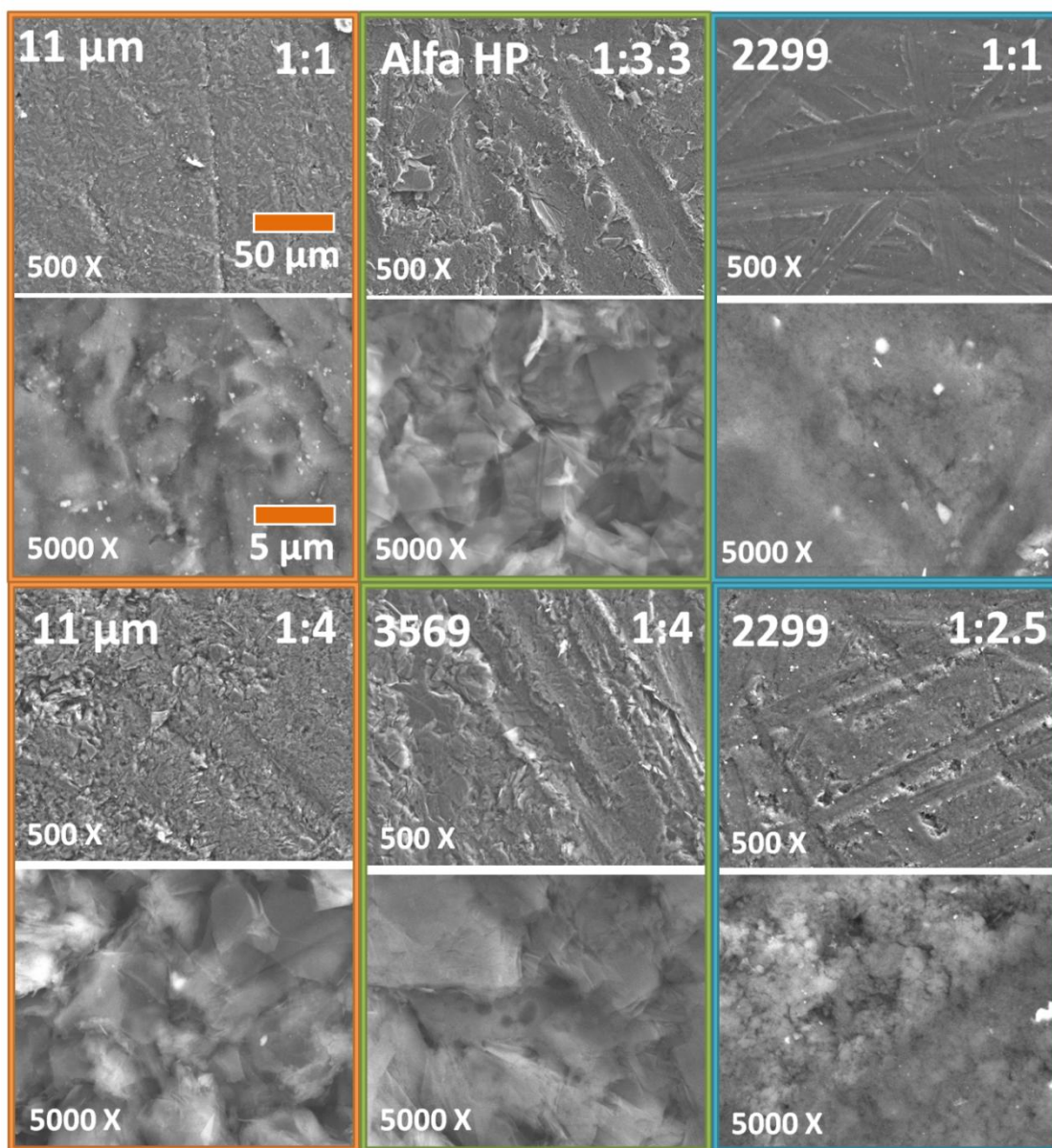


Figure 2.15 SEM images of TPE electrodes with various commercial carbons and ratios of PMMA:carbon.

Metal and oxide sensitive redox probes

While the data on HER and OER is useful, there is little information gained on where the catalysis originates from. It seems possible that there may be non-graphitic sources of catalysis given the vastly different electrochemical responses. To try and further elucidate the source of catalysis, the electrodes tested for HER and OER were tested with hydrazine and hydrogen peroxide. Both of these molecules are proposed to be sensitive to metallic impurities within carbon materials. Metals such as iron can drastically lower the oxidation over-potential of hydrazine and the reduction of peroxide.¹⁶

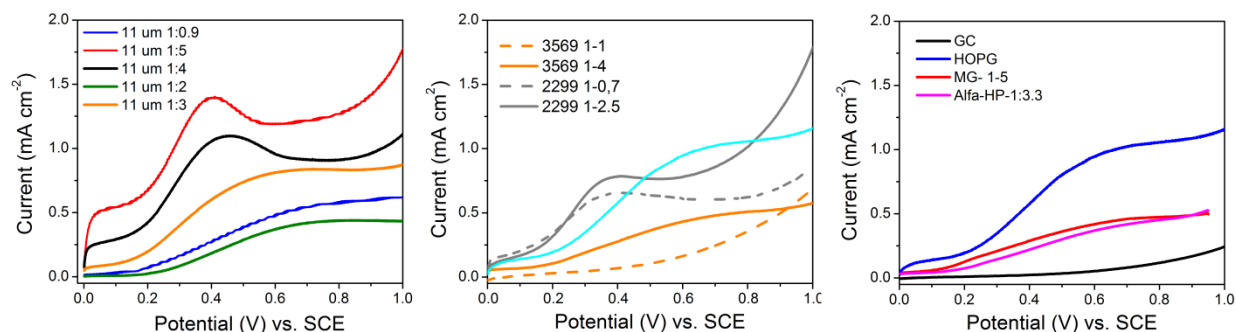


Figure 2.16 Hydrazine oxidation at various TPEs. Scan rates were 100 mV s^{-1} with 1 mM hydrazine in 0.1 M phosphate buffer pH 7.4.

In Figure 2.16 similar trends to that seen for OER and HER are observed. The trend of higher mass loadings of carbon enhancing electrochemical activity is again a theme. This is further demonstrated by not just testing a high and low concentration of the $11 \mu\text{m}$ particles but five different ratios. It appears that after the 1:2 ratio the $11 \mu\text{m}$ electrode becomes increasingly activated for hydrazine oxidation. Again this is most likely to a higher surface coverage of catalytic sites arising from the increased carbon content. The high purity 3569, MG, and Alfa-HP carbons are highly deactivated, showing large over-potentials

along with decreased current densities. The most deactivated electrode was glassy carbon which is a form of amorphous graphitic carbon.

Finally, in contrast to the OER and HER of the composites, the 2299 particles were quite active in both the high and low ratio for hydrazine oxidation, meaning whatever is driving the catalysis is in large quantity within the particles. Caution should be taken in relating hydrazine electrochemical activity to metal impurities. This discretion is often not taken in many examples within the current literature. P. Unwin has shown with scanning electrochemical microscopy that defect and oxide rich cavities within graphite can greatly enhance the electrochemical signal to hydrazine.⁹⁸ Also, a recent paper has highlighted that metals, defect sites, or oxide groups can all be catalytic for hydrazine oxidation.⁹⁹

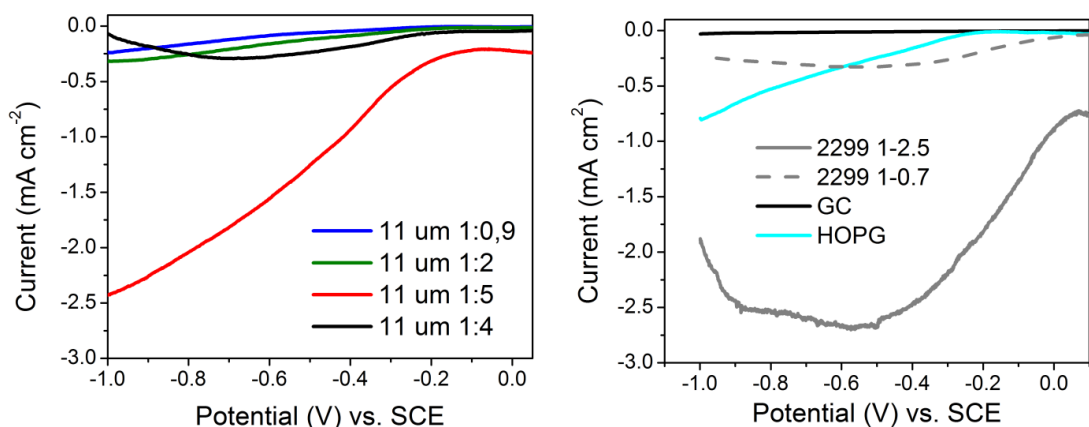


Figure 2.17 Hydrogen peroxide reduction at various TPEs. Scan rates were 100 mV s⁻¹ with 2 mM hydrogen peroxide in 0.1 M phosphate buffer pH 7.4. The spectra have been background subtracted. All solutions were purged with N₂.

Peroxide was also briefly tested with a few select electrodes to further confirm the trends of electrochemical reactivity seen with hydrazine and the OER and HER experiments. Like hydrazine, electrochemical activity towards hydrogen peroxide and other peroxides are supposedly indicators of metallic contamination. Indeed, the general trends for reactivity are consistent, in that the higher mass loadings of the 11 μm and 2299 particle are much more active than the lower mass loadings of the same particles.

In general, none of the TPE are extraordinarily catalytic for hydrogen peroxide reduction. When the equation for an irreversible electrochemical reaction (Equation 2.3) is used for the conditions in Figure 2.17, a peak current of 2 mA cm^{-2} is predicted. Only the most active 11 μm and 2299 particles are close to this current density, and both electrodes have wide or non-existent peaks. The wide drawn out peaks are indicative of slow kinetics.

Finally, as discussed earlier oxygen moieties have previously been reported to catalyze reactions such as the oxidation of hydrazine. To investigate these moieties aqueous iron was used. The use of this molecule to test for the presence of oxides was discussed earlier in the chapter. The cyclic voltammograms for this redox indicator are shown in Figure 2.18 for a few specific examples of the TPEs.

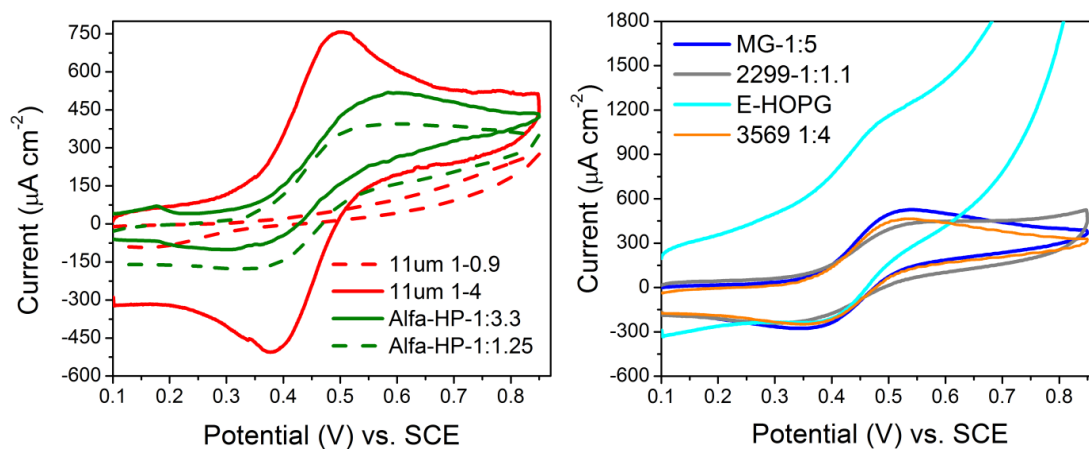


Figure 2.18 Electrochemistry of 6 mM aqueous iron sulfate in 1 M KCl at 50 mV s⁻¹.

The hypothesis of increased exposure of catalytic sites at higher carbon mass loadings seems to be again confirmed with the 11 μm particles. The particles had nearly a non-existent signal towards aqueous iron when in the 1:0.9 ratio. The voltammetry transforms into the largest peak heights and smallest peak separation at high 11 μm carbon to PMMA ratios. The data suggest that the 11 μm particles most likely contain a higher content of oxygen groups than the MG, 3569, and Alfa-HP particles. The 2299 particles in the high ratio had no discernable peaks due to a high background current. However, it is interesting that the low ratio 2299 TPE had well defined peaks, which indicated that there are potentially a large number of oxides present.

2.3 Conclusion and Future Work

Overview

In general, the work in the last section investigating the electrochemical reactivity of commercial carbons may raise more questions than it answers. While it could be easy to quickly relate the increased activity of the less pure carbons to metallic impurities, this may not be accurate. The catalysis may arise from oxides, metals, edge plains, carbonaceous debris, or possibly some unknown chemical species. Pores within an electrode have also been shown to greatly enhance catalysis in a few applications.¹⁰⁰⁻¹⁰¹ The SEM images of TPEs suggest that there may be a significant amount of porosity in the high ratio TPEs. The removal of bubbles from the surface is also proposed to catalyze reactions that evolve gas such as OER, HER, and hydrazine oxidation.¹⁰² Perhaps efficient gas removal is playing a role in TPE catalysis as well. In the future work section there are some proposed methods to further characterize the oxides present on these carbons as oxides seem like a possible source of enhanced catalysis.

To summarize the chapter, the work presented highlights the fabrication of solvent processed thermoplastic electrodes and their resulting physical, Raman, and electrochemical characterization. The unique fabrication method enabled an electrode material which demonstrates easy fabrication, high conductivity, and excellent electrochemistry. Through judicious selection of the particle type, particle-to-binder ratio, and surface treatment, the electrochemical and physical properties can be varied greatly. The electrode material also adds the ability to create micron size features using an array of common fabrication methods, including embossing. Of significant importance is that these

new low cost graphite electrodes can realize high electrochemical activity when properly activated, similar to that of more exotic carbons like carbon nanotubes, graphene or HOPG.

Future work

Future work of these carbon composites could be quite diverse, the ability to pattern electrodes, tune the reactivity, as well as couple or mix in catalyst opens many opportunities for electrochemical applications. Applications that include coupling patterned TPEs to paper based microfluidics, flow cells, small volume electrochemical cells, bipolar electrodes, biosensors, disposable electrodes, and integration into microfluidics.

Besides new devices, the carbon within TPEs should be further characterized. The work presented in this chapter does little to quantify the type of oxide groups found on the surface of the electrode. Characterizing these oxides could help with predicting and troubleshooting the electrochemical performance of TPEs. Oxides are well known to effect sensor performance as well as the electrochemistry to charged electrochemically active species. The oxides could also be used to covalently graft molecules onto carbon for sensing applications.¹⁰³

Titration is a proposed method to determine various forms of oxides. The technique involves a simple acid base titration which is known as a Boehm titration.¹⁰⁴⁻¹⁰⁵ It has been reported that the titration can be used to quantify alcohol, quinone, and carboxylic acid groups on the carbon surface. One down fall is that it doesn't specifically tell you the type of quinone. In general the technique requires a high level of analytical chemistry skills but conversely doesn't require expensive equipment or chemicals.

Ideally multiple techniques should be used to determine the identity of oxides. X-ray photoelectron spectroscopy (XPS) could also be used to compliment the Boehm titration. Practically though, fitting of the peaks as well as adventitious carbon may bring doubt to the actual amount, type and identity of the oxide present on the surface. Infrared spectroscopy (IR) could also be tried; however, the low concentration of oxides relative to the carbon can make obtaining a signal difficult. IR was tested extensively for the 11 μm particles used in this chapter. The particles should possess a fair amount of oxides but no real discernable spectra could be obtained.

To aid with obtaining a spectroscopic signal, tagging of the oxide groups could be explored. A review by the well-known electrochemist R. Compton,¹⁰⁶ highlights various methods to tag and probe the type of oxides on graphitic surfaces. Quinones can be tagged with 2,4-dinitrophenylhydrazine, which then is electrochemically active as well as Raman active. To determine ortho-quinone concentration, ortho-phenylenediamines can be used which specifically react with ortho-quinones. The ortho-phenylenediamine molecules can be made to be electrochemically active which can then be used to quantify ortho-quinone concentration by exploiting the surface contained redox electrochemical signal. Carboxylic acids can be tagged using acyl chloride chemistry, through the reaction with 4-nitrophenol. The nitro-derivatized carbon provides an electrochemically active moiety which can then be used to quantify the carboxylic acid content.

Now that a relative base line for electrochemical performance, processability, and conductivity has been established with graphite, other carbons should also be tested within TPEs. A logical next step is to use graphene, carbon nanotubes as well as carbon fiber.

There are a number of reasons to test these carbon types, in the case of carbon nanotubes or carbon fiber, the increased aspect ratio of these carbons should significantly enhance the conductivity.¹⁸ Mixtures of particle types and sizes like carbon black mixed with graphite can also be used to increase conductivity.¹⁰⁷ Graphene and CNT are also widely used as sensors and their electrochemical response to various analytes using TPEs would be a valuable comparison to the graphite based TPE.

The integration of these materials into TPE may bring significant difficulties, and a firm understanding of dispersing the particles within a thermoplastic matrix that is well founded in the literature is advised. One such technique maybe be through the use of shear, where a kitchen blender is used to exfoliate graphite in the presence of a stabilizer.¹⁰⁸ In this case, the stabilizer would be the thermoplastic binder material used to make the TPE. Sonication is also a tried and true method of dispersing graphene and carbon nanotubes.¹⁰⁹

Finally, the TPEs could be used for the sensing of a variety of molecules. Carbon often fouls less than platinum and is quite active for the electrochemistry of biomolecules. There are a number of reports of carbon based electrodes for sensing of dopamine, norephedrine, ascorbic acid, uric acid, and many others. The carbon type, the plastic or the surface treatment may significantly impact the voltammetry for sensing. This chapter has already shown that the electrochemistry is greatly affected by the particle type as well as the binder to graphite ratios. When developing a sensor, judicious choice of the composition of the electrode will most likely be necessary. The ability to pattern the TPE into microelectrodes also enables their use for high level sensing applications such as tissue on a chip, gas sensors, or embedded within microfluidic devices. The low cost of the

TPEs makes them a candidate for disposable sensing applications for use in point-of-care health diagnostics as well. Preliminary work on TPE sensor development will be discussed in Chapter 3 titled “Applications of TPEs within flow cells, microfluidics, and sensors” which also deals with future applications and directions of TPEs.

2.4 Materials and Methods

Reagents

Poly(methyl methacrylate) PMMA was Optix from Plaskolite, and was used as the TPE binder and the template material. Carbon sources were synthetic graphite powder 7-11 micron 99% (Alfa Aesar), acetylene carbon black 100% compressed (STREM Chemicals), synthetic graphite powder <20 micron (Sigma-Aldrich), and carbon nanopowder ≤ 500 nm 99.95% trace metal basis (Sigma-Aldrich). Chemicals were potassium ferricyanide 99% (Sigma-Aldrich), potassium phosphate monobasic 99.8% (Sigma-Aldrich), potassium phosphate dibasic (98%) EMD chemicals, potassium chloride 99-100.5% (Sigma-Aldrich), hexaammineruthenium(III) chloride (Sigma-Aldrich), ascorbic acid 99% (Sigma-Aldrich), dopamine hydrochloride (Sigma-Aldrich), iron (III) nitrate nonahydrate (Fisher), 1,2 dichloroethane (Fisher).

Fabrication of TPE-Step 1 Electrode Fabrication- Solution preparation

Scrap centimeter sized PMMA sheet (Optix, Plaskolite) were massed and placed in a vial, then mixed with dichloroethane typically in a ratio of ~5 mL solvent to 1 gram of PMMA, and kept for a period of months as stock solutions. When using dichloroethane the

small pieces of PMMA dissolved in about 24 hours depending on the size. Dichloroethane and chloroform were found to be aggressive solvents for dissolving PMMA, acetone, ethyl acetate, and DMF were also effective solvents. Toluene, xylenes, and propylene carbonate (PC) could dissolve the PMMA, however the process took much longer requiring a week or many weeks to fully dissolve. Once fully dissolved, carbon was added and the solvent level was then adjusted to achieve a uniform mixture. A consistency of viscous oil was found to be desirable for the Solvent/PMMA/Carbon mixtures. Before use the mixture was vortex mixed for ~ 3 minutes, typically in a 20 mL scintillator vial. If the mixture is too viscous efficient mixing will not occur. Sonication was not used in order to avoid any alteration to the chemical structure of the particles or the binder. The resulting mixtures were kept as stock solutions and were seemingly indefinitely stable and only required remixing by vortex before use.

Fabrication of TPE-Step 2 Electrode Fabrication- Templating

The electrode mixture was poured onto silicon wafers, which served as an inert non-stick surface. The solvent loaded electrode mixture was constantly worked with a small wooden stick on the wafer sheet to facilitate solvent evaporation while in a fume hood. Once the material could be formed into a ball of stiff chewing gum like consistency, then it was firmly hand pressed into the PMMA template. A CO₂ laser (Epilog) was used to cut and etch PMMA electrode templates from stock PMMA sheets. The electrode was then placed into a heat press consisting of two brass plates, a piece of PDMS was placed on one side of the electrode. A temperature of ~ 60 Celsius with a pressure of ~ 50 psi was used. If the TPE mixture is too full of solvent, or too high of a temperature or pressure is used, the

finished electrode may be deformed or the template may be disfigured. In most cases the electrode was left overnight under pressure and heat. However, after a few hours it appears almost all of the solvent is removed. The dried electrode was then sanded with 200 or 300 grit sand paper to remove the excess TPE material, then finished with 600 grit sand paper for a smoother surface. The electrode and the template can be further smoothed by following sanding with polishing with alumina. To finish the electrode, a wire was attached to one side of the TPE using silver paint, and covered with two part epoxy. The entire process is shown schematically in Figure 2.2A.

Conductivity measurements

Resistivity (inverse of conductivity) was measured by a two point probe (Fluke 187 Multimeter, accuracy of 0.01 Ω) placed on two opposing faces of a TPE cylinder. The faces of the cylinder were coated with a thin layer of silver paint to compensate for contact resistance. Typical dimensions were in the range of a diameter 5-2 mm and 3 mm length. In the cases of very low resistivity, longer cylinder lengths and smaller diameters can be used. The dimensions of the cylinder were adjusted to try to keep measured resistances above 1 Ω to minimize error. It was also found important to subtract background resistance inherent with a metal to metal contact, which was variable and typically around 0.3 Ω .

$$\rho = R * \frac{\pi(0.5D)^2}{L} \quad \text{and} \quad \sigma = 1/\rho \quad \text{Equation 2.1.}$$

Equation 2.1 describes conductivity and resistivity, where ρ is resistivity, R (Ω) is resistance, D is diameter of disk (m) and is related to the cross-sectional area, L (m) is length, and σ (S/m) is conductivity.

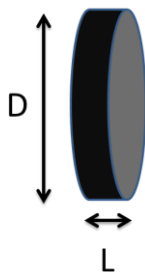


Figure 2.19 Example of a templated cylinder TPE used for conductivity measurements.

Electrochemical measurements and surface treatment

Electrochemistry was performed with a CHI 660 potentiostat, using a calomel reference saturated with KCl (SCE). The counter electrode was a 1:3 PMMA:carbon TPE plate made using 20 μm particles with an area that exceeded the working electrode by at least 10-fold. Potassium ferricyanide solutions were 10 mM, using a 0.5 M KCl solution. Impedance measurements were done at the $E^{1/2}$ of the ferricyanide redox couple taken from cyclic voltammetry at 100 mV s^{-1} , perturbation voltage was 10 mV, with a frequency range from 100,000 Hz to 0.1 Hz. Dopamine, ascorbic acid, iron nitrate solutions were in a 0.1 M phosphate buffer solution at pH 7.4. Hexaammineruthenium(III) chloride experiments were at 1 mM in a 0.5 M KCl solution. The platinum electrode had a diameter of 1.8 mm, TPE electrodes were 5 mm diameter, glassy carbon was 3 mm diameter, and the DropSens electrode was 4 mm in diameter. The surface treatments were plasma exposure

(after sanding) for 3 min at 35 W in ambient air, wet sanding with 600 grit paper, and polishing with 0.05 micron alumina for ~ 1 minute with firm pressure.

Capacitance Measurements

The capacitance was measured with cyclic voltammetry using the current response at 0.2 V vs. SCE, with a totaled sampled region of -0.1 to 0.5 V vs. SCE, and a scan rate of 100 mV s⁻¹. Capacitance was calculated using Equation 2.2, where C_{area} is the geometric area normalized capacitance, V is the scan rate (V s⁻¹), $I_{anodic} + I_{cathodic}$ is the width of the cyclic voltammogram at 0.2 V vs. SCE.¹¹⁰

$$C_{area} = \left(\frac{|I_{anodic}| + |I_{cathodic}|}{2 V} \right) \quad \text{Equation 2.2}$$

Irreversible peak current calculation

$$I_p = 3.01 \times 10^5 n [(1-\alpha)n_a]^{1/2} A C D^{1/2} \nu^{1/2} \quad \text{Equation 2.3}$$

Where I_p is the peak current, n is the number of electrons, α electron transfer coefficient, A is area, C is concentration, D diffusion coefficient, ν is the scan rate.¹¹¹ The electron transfer coefficient used here was 0.5, and the ascorbic acid diffusion coefficient was 6.5E⁻⁶ cm/s.¹¹²

Reversible peak current calculation

Equation S3 is a simplified version of the Randles-Sevcik equation assuming a temperature of 25 °C. Where I_p is the peak current, n is the number of electrons, A area, C concentration, D diffusion coefficient, v is the scan rate. Dopamine coefficient of 4.15E^{-6} cm/s taken from previous literature,¹¹³ ferricyanide 6.67E^{-6} cm/s,¹¹⁴ and hexaammineruthenium (III) chloride 7.9E^{-6} cm/s.⁵⁸

$$I_p = 2.69 \times 10^5 n^{3/2} A C D^{1/2} v^{1/2} \quad \text{Equation 2.4}$$

Spectroscopy

The Raman spectra were obtained by Zack Nilsson and the data was processed by Justin Sambur. A JEOL JSM-6500F field emission scanning electron microscope was used at a 15 keV accelerating voltage to capture images. Raman spectroscopy was performed on an Olympus IX-73 optical microscope with an Ondax THz-Raman laser source (5 mW, 532 nm laser with a 1.2 μm spot size). The Raman signal was collected in a backscattering geometry, passed through a Horiba iHR-550 Imaging Spectrometer, and detected on a Synapse Back-Illuminated Deep Depletion CCD. Individual spectra were acquired for 60 s across a 1 mm by 1 mm sample area. The crystallite domain size was calculated using Equation 2, where L_a is the domain size in nm, λ_l is the wavelength of the laser, $\left(\frac{I_D}{I_G}\right)$ is the ratio of the peak intensity of the D and G bands.

$$L_a \text{ (nm)} = (2.4 \times 10^{-10}) \lambda_l^4 \left(\frac{I_D}{I_G} \right)^{-1} \quad \text{Equation 2.5}$$

The XRF data was collected at the University of Notre Dame in the Peaslee lab. The instrument used was a SciAps X100 series XRF, it used a 40kV Au anode to produce the x-rays, and has a 20 mm² SDD detector to measure the resultant fluorescence. External calibration with NIST SRM-2586 was performed, which was found to be quantitative within 5% for the dominant trace elements.

REFERENCES

1. Xiao, H.; Zongyou, Y.; Shixin, W.; Xiaoying, Q.; Qiyuan, H.; Qichun, Z.; Qingyu, Y.; Freddy, B.; Hua, Z., Graphene - Based Materials: Synthesis, Characterization, Properties, and Applications. *Small* **2011**, *7* (14), 1876-1902.
2. Yan, Q.-L.; Gozin, M.; Zhao, F.-Q.; Cohen, A.; Pang, S.-P., Highly energetic compositions based on functionalized carbon nanomaterials. *Nanoscale* **2016**, *8* (9), 4799-4851.
3. Martinez, U.; Dumont, J. H.; Holby, E. F.; Artyushkova, K.; Purdy, G. M.; Singh, A.; Mack, N. H.; Atanassov, P.; Cullen, D. A.; More, K. L.; Chhowalla, M.; Zelenay, P.; Dattelbaum, A. M.; Mohite, A. D.; Gupta, G., Critical role of intercalated water for electrocatalytically active nitrogen-doped graphitic systems. *Science Advances* **2016**, *2* (3).
4. Milev, A. S.; Tran, N. H.; Kannangara, G. S. K.; Wilson, M. A., Unoccupied electronic structure of ball-milled graphite. *Phys. Chem. Chem. Phys.* **2010**, *12* (25), 6685-6691.
5. Chua, C. K.; Sofer, Z.; Khezri, B.; Webster, R. D.; Pumera, M., Ball-milled sulfur-doped graphene materials contain metallic impurities originating from ball-milling apparatus: their influence on the catalytic properties. *Phys. Chem. Chem. Phys.* **2016**, *18* (27), 17875-17880.
6. Ong, T. S.; Yang, H., Effect of atmosphere on the mechanical milling of natural graphite. *Carbon* **2000**, *38* (15), 2077-2085.
7. Yue, X.; Wang, H.; Wang, S.; Zhang, F.; Zhang, R., In-plane defects produced by ball-milling of expanded graphite. *J. Alloy. Comp.* **2010**, *505*, 286-290.
8. Ma, D.; Dong, L.; Zhou, M.; Zhu, L., The influence of oxidation debris containing in graphene oxide on the adsorption and electrochemical properties of 1,10-phenanthroline-5,6-dione. *Analyst* **2016**, *141* (9), 2761-2766.
9. McCreery, R. L., Advanced Carbon Electrode Materials for Molecular Electrochemistry. *Chem. Rev.* **2008**, *108*, 2646-2687.
10. Patel, A. N.; Collignon, M. G.; O'Connell, M. A.; Hung, W. O. Y.; McKelvey, K.; Macpherson, J. V.; Unwin, P. R., A New View of Electrochemistry at Highly Oriented Pyrolytic Graphite. *J. Am. Chem. Soc.* **2012**, *134* (49), 20117-20130.
11. Lai, S. C. S.; Patel, A. N.; McKelvey, K.; Unwin, P. R., Definitive Evidence for Fast Electron Transfer at Pristine Basal Plane Graphite from High-Resolution Electrochemical Imaging. *Angew. Chem. Int. Edit.* **2012**, *51* (22), 5405-5408.
12. Dryfe, R.; Chen, G. Z.; Bayer, D.; Jonsson-Niedziolka, M.; McCreery, R.; Macpherson, J.; Abruna, H.; Gogotsi, Y.; Hu, C.-C.; Beguin, F.; Hardwick, L.; Foord, J.; Duca, M.; Howe, E.; Holt, K.; Alvarez-Guerra, M.; Unwin, P. R.; Rabbow, T.; Shaffer, M.; Lee, J.-S.; Frackowiak, E.; Qiu, F.; Dyatkin, B.; Ash, P. A.; Stevenson, K.; Guldi, D.; Bergonzo, P., The many faces of carbon in electrochemistry: general discussion. *Faraday Discussions* **2014**, *172* (0), 117-137.

13. McDermott, C. A.; Kneten, K. R.; McCreery, R. L., Electron Transfer Kinetics of Aqueated $\text{Fe}^{3+}/\text{Fe}^{2+}$, $\text{Eu}^{3+}/\text{Eu}^{2+}$, and $\text{V}^{3+}/\text{V}^{2+}$ at Carbon Electrodes: Inner Sphere Catalysis by Surface Oxides. *J. Electrochem. Soc.* **1993**, *140*, 2593-2599.
14. Ambrosi, A.; Pumera, M., Amorphous Carbon Impurities Play an Active Role in Redox Processes of Carbon Nanotubes. *J. Phys. Chem. C* **2011**, *115* (51), 25281-25284.
15. Chua, C. K.; Pumera, M., Carbocatalysis: The State of “Metal-Free” Catalysis. *Chem-Eur. J.* **2015**, *21* (36), 12550-12562.
16. Pumera, M.; Miyahara, Y., What amount of metallic impurities in carbon nanotubes is small enough not to dominate their redox properties? *Nanoscale* **2009**, *1* (2), 260-265.
17. Goriparti, S.; Miele, E.; De Angelis, F.; Di Fabrizio, E.; Proietti Zaccaria, R.; Capiglia, C., Review on recent progress of nanostructured anode materials for Li-ion batteries. *J. Power Sources* **2014**, *257*, 421-443.
18. Antunes, R. A.; de Oliveira, M. C. L.; Ett, G.; Ett, V., Carbon materials in composite bipolar plates for polymer electrolyte membrane fuel cells: A review of the main challenges to improve electrical performance. *J. Power Sources* **2011**, *196*, 2945-2961.
19. Mussa, Z. H.; Othman, M. R.; Abdullah, M. P., Electrochemical Oxidation of Landfill Leachate: Investigation of Operational Parameters and Kinetics Using Graphite-PVC Composite Electrode as Anode. *J. Brazil. Chem. Soc.* **2015**, *26*, 939-948.
20. Duan, F.; Li, Y.; Cao, H.; Wang, Y.; Crittenden, J. C.; Zhang, Y., Activated carbon electrodes: Electrochemical oxidation coupled with desalination for wastewater treatment. *Chemosphere* **2015**, *125*, 205-211.
21. Li, X.; Wei, B., Supercapacitors based on nanostructured carbon. *Nano Energy* **2013**, *2*, 159-173.
22. Lee, B.-L., Electrically conductive polymer composites and blends. *Polym. Eng. Sci.* **1992**, *32*, 36-42.
23. Randviir, E. P.; Brownson, D. A. C.; Metters, J. P.; Kadara, R. O.; Banks, C. E., The fabrication, characterisation and electrochemical investigation of screen-printed graphene electrodes. *Phys. Chem. Chem. Phys.* **2014**, *16*, 4598-4611.
24. Hayat, A.; Marty, J. L., Disposable Screen Printed Electrochemical Sensors: Tools for Environmental Monitoring. *sensors* **2014**, *14*, 10432-10453.
25. Adams, R. N., Carbon Paste Electrodes. *Anal. Chem.* **1958**, *30*, 1576-1576.
26. Wang, J.; Naser, N., Modified carbon-wax composite electrodes. *Anal. Chim. Acta* **1995**, *316*, 253-259.
27. Opallo, M.; Lesniewski, A., A review on electrodes modified with ionic liquids. *J. Electroanal. Chem.* **2011**, *656*, 2-16.

28. Henriques, H. P.; Fogg, A. G., Preparation of graphite-loaded epoxy-based voltammetric electrodes using a multi-layer coating and hardening technique. *Analyst* **1984**, *109*, 1195-1199.
29. Clem, R. G.; Sciamanna, A. F., Styrene impregnated, cobalt-60 irradiated, graphite electrode for anodic stripping analysis. *Anal. Chem.* **1975**, *47*, 276-280.
30. McLaren, K. G.; Batley, G. E., Radiation-cured polymer-impregnated graphite electrodes for anodic stripping voltammetry. *J. Electroanal. Chem. Interfac. Electrochem.* **1977**, *79*, 169-178.
31. Yao, X.; Xu, X.; Yang, P.; Chen, G., Carbon nanotube/poly(methyl methacrylate) composite electrode for capillary electrophoretic measurement of honokiol and magnolol in Cortex Magnoliae Officinalis. *Electrophoresis* **2006**, *27*, 3233-3242.
32. Klatt, L. N.; Connell, D. R.; Adams, R. E.; Honigberg, I. L.; Price, J. C., Voltammetric characterization of a graphite-teflon electrode. *Anal. Chem.* **1975**, *47*, 2470-2472.
33. Wang, J.; Musameh, M., Carbon Nanotube/Teflon Composite Electrochemical Sensors and Biosensors. *Anal. Chem.* **2003**, *75*, 2075-2079.
34. Mascini, M.; Liberti, A., Preparation and some analytical applications of a new sulfide-selective heterogeneous membrane electrode. *Anal. Chim. Acta.* **1970**, *51*, 231-237.
35. Liberti, A.; Morgia, C.; Mascini, M., Graphitized carbon black in polyethylene as an electrochemical sensor. *Anal. Chim. Acta* **1985**, *173*, 157-164.
36. Zhong, S.; Kazacos, M.; Burford, R. P.; Skyllas-Kazacos, M., Fabrication and activation studies of conducting plastic composite electrodes for redox cells. *J. Power Sources* **1991**, *36*, 29-43.
37. Becker, H.; Locascio, L. E., Polymer microfluidic devices. *Talanta* **2002**, *56* (2), 267-287.
38. Mascini, M.; Liberti, A., An analytical study of a new type of halide-sensitive electrode prepared from silver halides and thermoplastic polymers. *Anal. Chim. Acta* **1969**, *47*, 339-345.
39. Kauffmann, J. M.; Laudet, A.; Patriarche, G. J., L'electrode a Pate de Carbone Modifiee Son Utilisation en Voltammetrie par Redissolution Anodique a Impulsions Differentielles en Presence d'Un Film de Mercure. *Anal. Lett.* **1982**, *15*, 763-774.
40. Yao, X.; Wu, H.; Wang, J.; Qu, S.; Chen, G., Carbon Nanotube/Poly(methyl methacrylate) (CNT/PMMA) Composite Electrode Fabricated by In Situ Polymerization for Microchip Capillary Electrophoresis. *Chem-Eur. J.* **2007**, *13*, 846-853.
41. Regel, A.; Lunte, S., Integration of a graphite/poly(methyl-methacrylate) composite electrode into a poly(methylmethacrylate) substrate for electrochemical detection in microchips. *Electrophoresis* **2013**, *34*, 2101-2106.
42. Staudinger, U.; Krause, B.; Steinbach, C.; Pötschke, P.; Voit, B., Dispersability of multiwalled carbon nanotubes in polycarbonate-chloroform solutions. *Polymer* **2014**, *55*, 6335-6344.
43. Ou, R.; Gupta, S.; Parker, C. A.; Gerhardt, R. A., Fabrication and Electrical Conductivity of Poly(methyl methacrylate) (PMMA)/Carbon Black (CB) Composites: Comparison between an

Ordered Carbon Black Nanowire-Like Segregated Structure and a Randomly Dispersed Carbon Black Nanostructure. *J. Phys. Chem. B* **2006**, *110*, 22365-22373.

44. Anandan, V.; Rao, Y. L.; Zhang, G., Nanopillar array structures for enhancing biosensing performance. *Int. J. Nanomed.* **2006**, *1*, 73-79.
45. Anandan, V.; Yang, X.; Kim, E.; Rao, Y. L.; Zhang, G., Role of reaction kinetics and mass transport in glucose sensing with nanopillar array electrodes. *J. Biol. Eng.* **2007**, *1*, 5-5.
46. H. Suherman, J. S., A. B. Sulong,, "Electrical Properties of Carbon Nanotubes-Based Epoxy Nanocomposites for High Electrical Conductive Plate". *Advanced Materials Research* **2011**, Vols. 264-265, pp. 559-564, .
47. Pham, V. H.; Dang, T. T.; Hur, S. H.; Kim, E. J.; Chung, J. S., Highly Conductive Poly(methyl methacrylate) (PMMA)-Reduced Graphene Oxide Composite Prepared by Self-Assembly of PMMA Latex and Graphene Oxide through Electrostatic Interaction. *ACS Appl. Mater. Inter.* **2012**, *4*, 2630-2636.
48. Wu, C.; Huang, X.; Wang, G.; Lv, L.; Chen, G.; Li, G.; Jiang, P., Highly Conductive Nanocomposites with Three-Dimensional, Compactly Interconnected Graphene Networks via a Self-Assembly Process. *Adv. Funct. Mater.* **2013**, *23*, 506-513.
49. Arenhart, R. G.; Barra, G. M. O.; Fernandes, C. P., Simulation of percolation threshold and electrical conductivity in composites filled with conductive particles: Effect of polydisperse particle size distribution. *Polymer Composites* **2016**, *37* (1), 61-69.
50. Pandolfo, A. G.; Wilson, G. J.; Huynh, T. D.; Hollenkamp, A. F., The Influence of Conductive Additives and Inter-Particle Voids in Carbon EDLC Electrodes. *Fuel Cells* **2010**, *10*, 856-864.
51. Bârsan, O. A.; Hoffmann, G. G.; van der Ven, L. G. J.; de With, G., Single-Walled Carbon Nanotube Networks: The Influence of Individual Tube–Tube Contacts on the Large-Scale Conductivity of Polymer Composites. *Adv. Funct. Mater.* **2016**, *26*, 4377-4385.
52. Deng, H.; Lin, L.; Ji, M.; Zhang, S.; Yang, M.; Fu, Q., Progress on the morphological control of conductive network in conductive polymer composites and the use as electroactive multifunctional materials. *Prog. Polym. Sci.* **2014**, *39*, 627-655.
53. Gautam, R. K.; Kar, K. K., Synergistic Effects of Carbon Fillers of Phenolic Resin Based Composite Bipolar Plates on the Performance of PEM Fuel Cell. *Fuel Cells* **2016**, *16*, 179-192.
54. Balazs, A. C.; Emrick, T.; Russell, T. P., Nanoparticle Polymer Composites: Where Two Small Worlds Meet. *Science* **2006**, *314*, 1107-1110.
55. Chen, P.; McCreery, R. L., Control of Electron Transfer Kinetics at Glassy Carbon Electrodes by Specific Surface Modification. *Anal. Chem.* **1996**, *68*, 3958-3965.
56. DuVall, S. H.; McCreery, R. L., Control of Catechol and Hydroquinone Electron-Transfer Kinetics on Native and Modified Glassy Carbon Electrodes. *Anal. Chem.* **1999**, *71*, 4594-4602.
57. Kadara, R. O.; Jenkinson, N.; Banks, C. E., Characterisation of commercially available electrochemical sensing platforms. *Sensor. Actuat. B-Chem.* **2009**, *138*, 556-562.

58. Kozbial, A.; Zhou, F.; Li, Z.; Liu, H.; Li, L., Are Graphitic Surfaces Hydrophobic? *Acc. Chem. Res.* **2016**, *49*, 2765-2773.
59. Hallam, P. M.; Banks, C. E., Quantifying the electron transfer sites of graphene. *Electrochem. Commun.* **2011**, *13*, 8-11.
60. O'Hare, D.; Macpherson, J. V.; Willows, A., On the microelectrode behaviour of graphite-epoxy composite electrodes. *Electrochem. Commun.* **2002**, *4*, 245-250.
61. Guo, S.-X.; Zhao, S.-F.; Bond, A. M.; Zhang, J., Simplifying the Evaluation of Graphene Modified Electrode Performance Using Rotating Disk Electrode Voltammetry. *Langmuir* **2012**, *28*, 5275-5285.
62. Streeter, I.; Wildgoose, G. G.; Shao, L.; Compton, R. G., Cyclic voltammetry on electrode surfaces covered with porous layers: An analysis of electron transfer kinetics at single-walled carbon nanotube modified electrodes. *Sensor. Actuat. B-Chem.* **2008**, *133*, 462-466.
63. Kuo, T.-C.; McCreery, R. L., Surface Chemistry and Electron-Transfer Kinetics of Hydrogen-Modified Glassy Carbon Electrodes. *Anal. Chem.* **1999**, *71*, 1553-1560.
64. Cvelbar, U.; Markoli, B.; Poberaj, I.; Zalar, A.; Kosec, L.; Spaić, S., Formation of functional groups on graphite during oxygen plasma treatment. *Appl. Surf. Sci.* **2006**, *253*, 1861-1865.
65. Huang, J. Y., HRTEM and EELS studies of defects structure and amorphous-like graphite induced by ball-milling. *Acta. Mater.* **1999**, *47*, 1801-1808.
66. Chethana, B. K.; Arthoba Naik, Y., Electrochemical oxidation and determination of ascorbic acid present in natural fruit juices using a methionine modified carbon paste electrode. *Anal. Methods* **2012**, *4*, 3754-3759.
67. Sudhakara Prasad, K.; Muthuraman, G.; Zen, J.-M., The role of oxygen functionalities and edge plane sites on screen-printed carbon electrodes for simultaneous determination of dopamine, uric acid and ascorbic acid. *Electrochem. Commun.* **2008**, *10*, 559-563.
68. Falat, L.; Cheng, H. Y., Voltammetric differentiation of ascorbic acid and dopamine at an electrochemically treated graphite/epoxy electrode. *Anal. Chem.* **1982**, *54*, 2108-2111.
69. Zhu, S.; Li, H.; Niu, W.; Xu, G., Simultaneous electrochemical determination of uric acid, dopamine, and ascorbic acid at single-walled carbon nanohorn modified glassy carbon electrode. *Biosens. Bioelectron.* **2009**, *25*, 940-943.
70. Raoof, J. B.; Ojani, R.; Baghayeri, M., A selective sensor based on a glassy carbon electrode modified with carbon nanotubes and ruthenium oxide/hexacyanoferrate film for simultaneous determination of ascorbic acid, epinephrine and uric acid. *Anal. Methods* **2011**, *3*, 2367-2373.
71. Kachoosangi, R. T.; Banks, C. E.; Compton, R. G., Simultaneous Determination of Uric Acid and Ascorbic Acid Using Edge Plane Pyrolytic Graphite Electrodes. *Electroanal.* **2006**, *18*, 741-747.
72. Wantz, F.; Banks, C. E.; Compton, R. G., Direct Oxidation of Ascorbic Acid at an Edge Plane Pyrolytic Graphite Electrode: A Comparison of the Electroanalytical Response with Other Carbon Electrodes. *Electroanal.* **2005**, *17*, 1529-1533.

73. Hadi, M.; Rouhollahi, A., Simultaneous electrochemical sensing of ascorbic acid, dopamine and uric acid at anodized nanocrystalline graphite-like pyrolytic carbon film electrode. *Anal. Chim. Acta* **2012**, *721*, 55-60.
74. Brownson, D. A. C.; Foster, C. W.; Banks, C. E., The electrochemical performance of graphene modified electrodes: An analytical perspective. *Analyst* **2012**, *137*, 1815-1823.
75. Patel, A. N.; Tan, S.-y.; Miller, T. S.; Macpherson, J. V.; Unwin, P. R., Comparison and Reappraisal of Carbon Electrodes for the Voltammetric Detection of Dopamine. *Anal. Chem.* **2013**, *85*, 11755-11764.
76. Wang, J.; Walcarius, A., Zeolite-modified carbon paste electrode for selective monitoring of dopamine. *J. Electroanal. Chem.* **1996**, *407*, 183-187.
77. Yi, M.; Shen, Z., A review on mechanical exfoliation for the scalable production of graphene. *J. Mater. Chem. A* **2015**, *3*, 11700-11715.
78. Malekpour, H.; Chang, K. H.; Chen, J. C.; Lu, C. Y.; Nika, D. L.; Novoselov, K. S.; Balandin, A. A., Thermal Conductivity of Graphene Laminate. *Nano Lett.* **2014**, *14*, 5155-5161.
79. Couzi, M.; Bruneel, J.-L.; Talaga, D.; Bokobza, L., A multi wavelength Raman scattering study of defective graphitic carbon materials: The first order Raman spectra revisited. *Carbon* **2016**, *107*, 388-394.
80. Cançado, L. G.; Takai, K.; Enoki, T.; Endo, M.; Kim, Y. A.; Mizusaki, H.; Speziali, N. L.; Jorio, A.; Pimenta, M. A., Measuring the degree of stacking order in graphite by Raman spectroscopy. *Carbon* **2008**, *46*, 272-275.
81. Dresselhaus, M. S.; Jorio, A.; Cançado, L. G.; Dresselhaus, G.; Saito, R., Raman Spectroscopy: *Characterization of Edges, Defects, and the Fermi Energy of Graphene and sp² Carbons*. Raza, H., Ed. Springer: Berlin Heidelberg, 2012; pp 15-55.
82. Schäfer, H.; Hess, C.; Tobergte, H.; Volf, A.; Ichilmann, S.; Eickmeier, H.; Voss, B.; Kashaev, N.; Nordmann, J.; Akram, W.; Hartmann-Azanza, B.; Steinhart, M., Ultrafine Sanding Paper: A Simple Tool for Creating Small Particles. *Small* **2015**, *11*, 931-935.
83. Pattammattel, A.; Kumar, C. V., Kitchen Chemistry 101: Multigram Production of High Quality Biographene in a Blender with Edible Proteins. *Adv. Funct. Mater.* **2015**, *25*, 7088-7098.
84. Jorio, A.; Ferreira, E. H. M.; Moutinho, M. V. O.; Stavale, F.; Achete, C. A.; Capaz, R. B., Measuring disorder in graphene with the G and D bands. *Phys. Status Solidi B* **2010**, *247*, 2980-2982.
85. Cançado, L. G.; Takai, K.; Enoki, T.; Endo, M.; Kim, Y. A.; Mizusaki, H.; Jorio, A.; Coelho, L. N.; Magalhães-Paniago, R.; Pimenta, M. A., General equation for the determination of the crystallite size La of nanographite by Raman spectroscopy. *Appl. Phys. Lett.* **2006**, *88*, 163106.
86. Eckmann, A.; Felten, A.; Mishchenko, A.; Britnell, L.; Krupke, R.; Novoselov, K. S.; Casiraghi, C., Probing the Nature of Defects in Graphene by Raman Spectroscopy. *Nano Lett.* **2012**, *12* (8), 3925-3930.

87. Paton, K. R.; Varrla, E.; Backes, C.; Smith, R. J.; Khan, U.; O'Neill, A.; Boland, C.; Lotya, M.; Istrate, O. M.; King, P.; Higgins, T.; Barwich, S.; May, P.; Puczkarski, P.; Ahmed, I.; Moebius, M.; Pettersson, H.; Long, E.; Coelho, J.; O'Brien, S. E.; McGuire, E. K.; Sanchez, B. M.; Duesberg, G. S.; McEvoy, N.; Pennycook, T. J.; Downing, C.; Crossley, A.; Nicolosi, V.; Coleman, J. N., Scalable production of large quantities of defect-free few-layer graphene by shear exfoliation in liquids. *Nat Mater* **2014**, *13* (6), 624-630.
88. Shimoi, N., Effect of increased crystallinity of single-walled carbon nanotubes used as field emitters on their electrical properties. *Journal of Applied Physics* **2015**, *118* (21), 214304.
89. Daniel, E.; Sean, H.; Alan, S.; Kevin, D.; Brian, M.; Robert, B.; Jingguang, C., Low - Cost Hydrogen - Evolution Catalysts Based on Monolayer Platinum on Tungsten Monocarbide Substrates. *Angew. Chem. Int. Edit.* **2010**, *49* (51), 9859-9862.
90. Eftekhari, A., Electrocatalysts for hydrogen evolution reaction. *International Journal of Hydrogen Energy* **2017**, *42* (16), 11053-11077.
91. Lu, Q.; Hutchings, G. S.; Yu, W.; Zhou, Y.; Forest, R. V.; Tao, R.; Rosen, J.; Yonemoto, B. T.; Cao, Z.; Zheng, H.; Xiao, J. Q.; Jiao, F.; Chen, J. G., Highly porous non-precious bimetallic electrocatalysts for efficient hydrogen evolution. **2015**, *6*, 6567.
92. Du, J.; Wang, J.; Ji, L.; Xu, X.; Chen, Z., A Highly Active and Robust Copper-Based Electrocatalyst toward Hydrogen Evolution Reaction with Low Overpotential in Neutral Solution. *ACS Appl. Mater. Inter.* **2016**, *8* (44), 30205-30211.
93. Zhou, W.; Jia, J.; Lu, J.; Yang, L.; Hou, D.; Li, G.; Chen, S., Recent developments of carbon-based electrocatalysts for hydrogen evolution reaction. *Nano Energy* **2016**, *28* (Supplement C), 29-43.
94. McCrory, C. C. L.; Jung, S.; Peters, J. C.; Jaramillo, T. F., Benchmarking Heterogeneous Electrocatalysts for the Oxygen Evolution Reaction. *J. Am. Chem. Soc.* **2013**, *135* (45), 16977-16987.
95. Kanan, M. W.; Nocera, D. G., In Situ Formation of an Oxygen-Evolving Catalyst in Neutral Water Containing Phosphate and Co²⁺. *Science* **2008**, *321* (5892), 1072-1075.
96. Fabbri, E.; Haberer, A.; Walzer, K.; Kotz, R.; Schmidt, T. J., Developments and perspectives of oxide-based catalysts for the oxygen evolution reaction. *Catalysis Science & Technology* **2014**, *4* (11), 3800-3821.
97. Subbaraman, R.; Tripkovic, D.; Strmcnik, D.; Chang, K.-C.; Uchimura, M.; Paulikas, A. P.; Stamenkovic, V.; Markovic, N. M., Enhancing Hydrogen Evolution Activity in Water Splitting by Tailoring Li-Ni(OH)-Pt Interfaces. *Science* **2011**, *334* (6060), 1256-1260.
98. E, S. P.; Kim, Y.-R.; Perry, D.; Bentley, C. L.; Unwin, P. R., Nanoscale Electrocatalysis of Hydrazine Electro-Oxidation at Blistered Graphite Electrodes. *ACS Appl. Mater. Inter.* **2016**, *8* (44), 30458-30466.
99. Sánchez Arribas, A.; Moreno, M.; Martínez-Fernández, M.; Bermejo, E.; Zapardiel, A.; Chicharro, M., Effect of edge plane sites, oxygenated species and metallic impurities upon the electroactivity of carbon nanotube-modified electrodes toward hydrazine. *Sensor. Actuat. B-Chem.* **2013**, *182*, 31-39.

100. Banerjee, S.; Shim, J.; Rivera, J.; Jin, X.; Estrada, D.; Solovyeva, V.; You, X.; Pak, J.; Pop, E.; Aluru, N.; Bashir, R., Electrochemistry at Edge of Single Graphene Layer in a Nanopore. *ACS nano* **2013**, *7* (1), 834-843.
101. Wang, Y.; Narayanan, S. R.; Wu, W., Field-Assisted Splitting of Pure Water Based on Deep-Sub-Debye-Length Nanogap Electrochemical Cells. *ACS Nano* **2017**, *11* (8), 8421-8428.
102. Akbar, K.; Kim, J. H.; Lee, Z.; Kim, M.; Yi, Y.; Chun, S.-H., Superaerophobic graphene nano-hills for direct hydrazine fuel cells. *Npg Asia Materials* **2017**, *9*, e378.
103. Sassolas, A.; Blum, L. J.; Leca-Bouvier, B. D., Immobilization strategies to develop enzymatic biosensors. *Biotechnology Advances* **2012**, *30* (3), 489-511.
104. Nekahi, A.; Marashi, P.; Fatmesari, H., Modified structure of graphene oxide by investigation of structure evolution. *Bulletin of Materials Science* **2015**, *38* (7), 1717-1722.
105. Goertzen, S. L.; Thériault, K. D.; Oickle, A. M.; Tarasuk, A. C.; Andreas, H. A., Standardization of the Boehm titration. Part I. CO₂ expulsion and endpoint determination. *Carbon* **2010**, *48* (4), 1252-1261.
106. Wildgoose, G. G.; Abiman, P.; Compton, R. G., Characterising chemical functionality on carbon surfaces. *J. Mater. Chem.* **2009**, *19* (28), 4875-4886.
107. Arenhart, R. G.; Barra, G. M. O.; Fernandes, C. P., Simulation of percolation threshold and electrical conductivity in composites filled with conductive particles: Effect of polydisperse particle size distribution. *Polym. Compos.* **2016**, *37*, 61-69.
108. Yi, M.; Shen, Z., Kitchen blender for producing high-quality few-layer graphene. *Carbon* **2014**, *78*, 622-626.
109. Yu, H.; Hermann, S.; Schulz, S. E.; Gessner, T.; Dong, Z.; Li, W. J., Optimizing sonication parameters for dispersion of single-walled carbon nanotubes. *Chemical Physics* **2012**, *408*, 11-16.
110. Hou, C.-H.; Liang, C.; Yiacoumi, S.; Dai, S.; Tsouris, C., Electrosorption capacitance of nanostructured carbon-based materials. *J. Colloid. Interf. Sci.* **2006**, *302*, 54-61.
111. Yu, D.; Wei, L.; Jiang, W.; Wang, H.; Sun, B.; Zhang, Q.; Goh, K.; Si, R.; Chen, Y., Nitrogen doped holey graphene as an efficient metal-free multifunctional electrochemical catalyst for hydrazine oxidation and oxygen reduction. *Nanoscale* **2013**, *5*, 3457-3464.
112. Raoof, J.-B.; Ojani, R.; Hosseinzadeh, R.; Ghasemi, V., Electrocatalytic Characteristics of a 1-[4-(Ferrocenyl ethynyl)phenyl]-1-ethanone Modified Carbon-Paste Electrode in the Oxidation of Ascorbic Acid. *Anal. Sci.* **2003**, *19*, 1251-1258.
113. Wang, Q.; Li, N.; Wang, W., Electrocatalytic Response of Dopamine at a Metallothioneins Self-Assembled Gold Electrode. *Anal. Sci.* **2002**, *18*, 635-639.
114. Moldenhauer, J.; Meier, M.; Paul, D. W., Rapid and Direct Determination of Diffusion Coefficients Using Microelectrode Arrays. *J. Electrochem. Soc* **2016**, *163*, 672-678.

CHAPTER 3: APPLICATIONS OF TPEs WITHIN FLOW CELLS, MICROFLUIDICS, AND SENSORS

3.1 Introduction

Overview

The chapter is segmented into two separate sections focusing on different applications of the TPE system developed in Chapter 2. The first application discussed is the development of a new melt processed TPE which uses poly-caprolactone as the binder material. Droplet microfluidic devices are demonstrated with a novel method of fabricating poly-caprolactone sealed microfluidics. The methods proposed enable microfluidics with integrated electrodes to be rapidly fabricated using simple tools in a non-laborious way.

The second section details methods for quantifying aerosol toxicity through the dithiothreitol assay (DTT assay). Initially spectroscopic methods are used to perform the DTT assay for a pilot study involving personal air sampling. Later, electrochemical methods are introduced that demonstrate sensing DTT in both static solution and in flow. A focus for the device design was ease of fabrication that doesn't sacrifice quality. O-ring based flow cells are described which are extremely versatile and can be coupled to microfluidics or used as standalone devices. Band electrodes, tubular flow-through cells, and wall-jet electrodes are demonstrated.

Introduction to electrochemical microfluidics

The work presented in this section entails the coupling of electrochemistry with microfluidics. Microfluidic devices, often referred to as “lab on a chip”, enable the ability to perform chemical separations, complex sequential mixing, and chemical reactions all within a small platform.¹ Microfluidics enable high throughput sample analysis as well as low analyte and reagent volumes. Molecular detection within microfluidic devices is performed with a variety of techniques including spectroscopic, conductance, or electrochemically.² While it is highly desirable to couple electrochemistry with a microfluidic chip it is often difficult. Most often platinum or gold electrodes are used, the electrodes are created by vapour deposition or lithography.³ However, Pt and Au electrodes are expensive, can be prone to fouling, and typically are not fully integrated into the microfluidic substrate.

Pyrolyzed carbon is one alternative to noble metal electrodes. Pyrolyzed carbon electrodes are made by thermally annealing a carbon precursor such as photo-resist at 1000 °C in a reducing atmosphere. The pyrolyzed electrodes enable the ability to create intricate micron features with favorable conductivity and electrochemical activity.⁴⁻⁵ The high heat needed to pyrolyze the carbon is however troublesome, making the integration into solely thermoplastic based microfluidics impossible.⁶

An alternative to noble metals and pyrolyzed carbon electrodes are carbon composite electrodes. Carbon composites are an attractive electrode material because they are low cost and allow for sensing moieties or catalyst to be integrated into the electrode.⁷⁻⁸

However, carbon composite electrodes are often poorly integrated into microfluidics because they have raised features (printing) and/or have limited physical stability.⁹⁻¹¹ Methods of integration are also often tedious which involve micro-molding using harsh chemicals,¹² or are painstakingly inserted after the device is sealed.¹³ Overall, the difficulty in carbon composite electrode integration can lead researchers to place electrodes in the waste area of the microfluidic device, diminishing their response.¹⁴

PDMS-based carbon composite electrodes have been proposed, but are limited to this single type of material. The PDMS composites also suffer from low conductivity and an apparent diminished electrochemical activity.¹⁵ In general, only a handful of reports exist on full integration of carbon composite electrodes into thermoplastic substrates. The electrodes are typically made with epoxy as the binder material.¹⁶⁻¹⁷ One drawback of epoxy electrodes is that once hardened the electrode can not be manipulated. Depending on hardening time of the epoxy, the graphite must be mixed and placed in the template under a time constraint.¹⁸

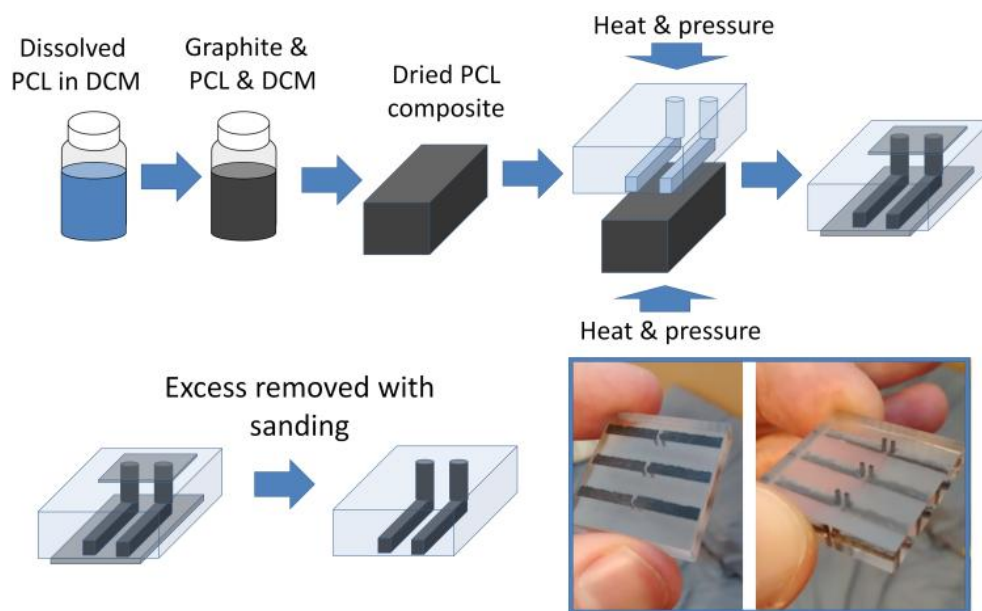
Herein, a new type of binder material (poly-caprolactone) is proposed which allows for the easy integration of carbon composites into traditional thermoplastic substrates used in microfluidics. The use of poly-caprolactone (PCL) as a binder overcomes the issues encountered with epoxy electrodes, where the electrodes need to be mixed and integrated into the substrate under a time constraint. The PCL based composites are also seamlessly integrated into the substrate, with no raised features. As of yet, PCL composite electrodes have not been demonstrated in the literature, despite PCL's nearly ideal properties for

making composite electrodes. The key properties being that PCL melts at 60 °C, is resistant to many common organic solvents,¹⁹ biocompatibility, and is low cost and readily available.

3.2 Results and Discussion

Fabrication of melt processed PCL patterned electrodes

To fabricate microfluidics with integrated electrodes it requires patterning of the electrode material onto or into a substrate. Patterned PCL and graphite electrodes were assembled via Scheme 3.1. These electrodes can be used as a substrate for electrochemical microfluidics or can be used as standalone electrodes. The process is simple and begins with dissolving PCL in dichloromethane (DCM) followed by mixing graphite powder with the dissolved plastic. The graphite, solvent, and plastic mixture is then poured out onto a silicon wafer and mixed until it becomes a semi-solid. The semi-solid is then left in air to fully dry. The dried material can be stored and is seemingly indefinitely reusable. The dried material could also be shaped or ground up and stored as a powder, pellets, sheets, or blocks.



Scheme 3.1 Generic fabrication of melt processed PCL composite electrodes.

To make patterned electrodes, the dried composite is heated above the melting point of PCL and then hot pressed into templates. The templates shown in Figure 3.1 were generated with a CO₂ laser. Any technique which delivers pressure and heat could be used to make the electrodes, such as a hot plate and large weight, or clamps and an oven. In this work a heated press was used. The excess material is then removed with a razor blade (while still pliable), followed by smoothing the surface with sand paper.

The roughness of the electrode is determined by the sand paper used to remove the excess electrode material. Upon sanding with 600 grit sand paper the roughness of the electrode is estimated to be 1 μm or less as determined by the resolution limit of the optical profilometry instrument used. A smooth well integrated surface is important for sealing microfluidics and is a major advantage of this new fabrication method. As shown in Scheme

3.1, the electrodes can be patterned in 3 dimensions. Patterning in 3 dimensions allows for a well-defined electrode area and the ability to make contact pads for backside connections to the potentiostat.

Conductivity and capacitance of PCL based electrodes

Cell resistances within microfluidics can be quite high arising from the small solution volumes and micron channel dimensions.²⁰ Conductivity is therefore important for the performance of a microfluidic integrated electrode system. If the composite electrode materials are highly conductive they can be made into very small or thin geometries, without exacerbating cell resistances.

The conductivity of different carbons were tested at various ratios of graphite to PCL. The carbons chosen were the MG, 11 μm , 3569, and carbon black. These carbons had higher conductivities and solvent windows, which was described in Chapter 2. Figure 3.1A shows the conductivity as a function of the carbon:PCL ratios. As expected, conductivity increases with increasing carbon content, but the conductivities were lower than the PMMA-based electrodes. As an example, the maximum conductivity for the MG particles was 1000 S m^{-1} with the use of PMMA and with PCL it is about half of that value. The exact reason for this unknown, but it could be from the graphite particles being encased or coated to a higher extent with PCL, diminishing particle-particle contact.

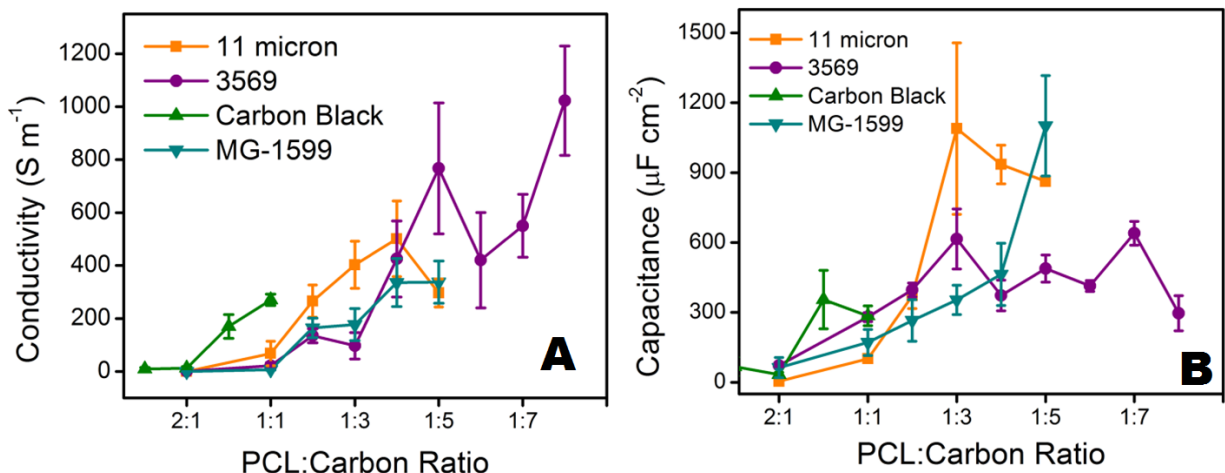


Figure 3.1 Conductivity (A) and capacitance (B) of various carbon ratios and carbon types with PCL as the binder material. The electrodes used in this figure were fabricated by Kaylee Clark, she also collected the electrochemical data and plots.

The capacitance of the PCL composites was measured with the same method as in Chapter 2 and is shown in Figure 3.1B. The composites using PCL had similar capacitance values to the composite made with PMMA as the binder. However, it does appear that with the higher ratios, the capacitance values with PCL are somewhat larger. The 11 μm particles in a 1:3 ratio highlight this trend where the PCL electrodes have about three times the capacitance as the PMMA based electrodes. With PMMA the 1:3 11 μm particles had $\sim 300 \mu\text{F cm}^{-2}$ vs. $\sim 1000 \mu\text{F cm}^{-2}$ with the use of PCL. The exact cause of the increased capacitance is not known at this time. Most of the electrodes had capacitance values much larger than $60 \mu\text{F cm}^{-2}$, which is the value of a planar edge plane HOPG electrode. The increased capacitance indicates that the electrodes have significantly increased surface roughness over a planar electrode. Taking into account the capacitance and conductivity data, moving forward the MG particles in a 1:2 ratio were chosen to integrate into microfluidics. This composite composition has adequate conductivity, a lower capacitance,

and a lower carbon content that allows the electrodes to be easily melt-processed. Lower carbon ratios are typically easier to use when fabricating templated electrodes, the composites retain more of the thermoplastic character. The MG particles also had a larger solvent window which was measured and discussed in Chapter 2.

Fabrication of PCL sealed microfluidics with integrated carbon composites

PMMA was chosen as the microfluidics substrate, as well as the use of a CO₂ laser to create the microfluidic features. Devices are fabricated by cutting channels into one piece of PMMA followed by sealing this to a second, typically unpatterned, piece of PMMA. PMMA is reported to be one of the best plastics for use with a laser cutter/engraver in regards to quality of cut.²¹⁻²² When heated with the laser PMMA depolymerizes back to methyl methacrylate, which then is vaporized; these qualities may explain the better cut quality over other plastics that decompose or melt.²³ PMMA also strongly adsorbs the energy (mid infrared) from a CO₂ laser, has low thermal conductivity, a low heat capacity, which are all excellent traits to create well resolved micron features.²⁴

Sealing of microfluidics can be a difficult task and there are many different proposed methods. PMMA-based microfluidics can be sealed with a variety of techniques,²⁵ which include thermally,²⁶ plasma treatment,²⁷ plasticizers,²⁸ microwave treatment,²⁹ ultrasonic assisted bonding,³⁰ or solvent bonding/welding.³¹⁻³³ Another common technique is the use of a thin adhesive layer to join the two halves, the adhesive can be commercially sourced or made in house.³⁴⁻³⁶ There are pros and cons to all sealing methods and in practice it was found that the popular methods of thermal and solvent sealing are quite difficult, inconsistent, and often lead to clogged or deformed channels, or devices that leak.

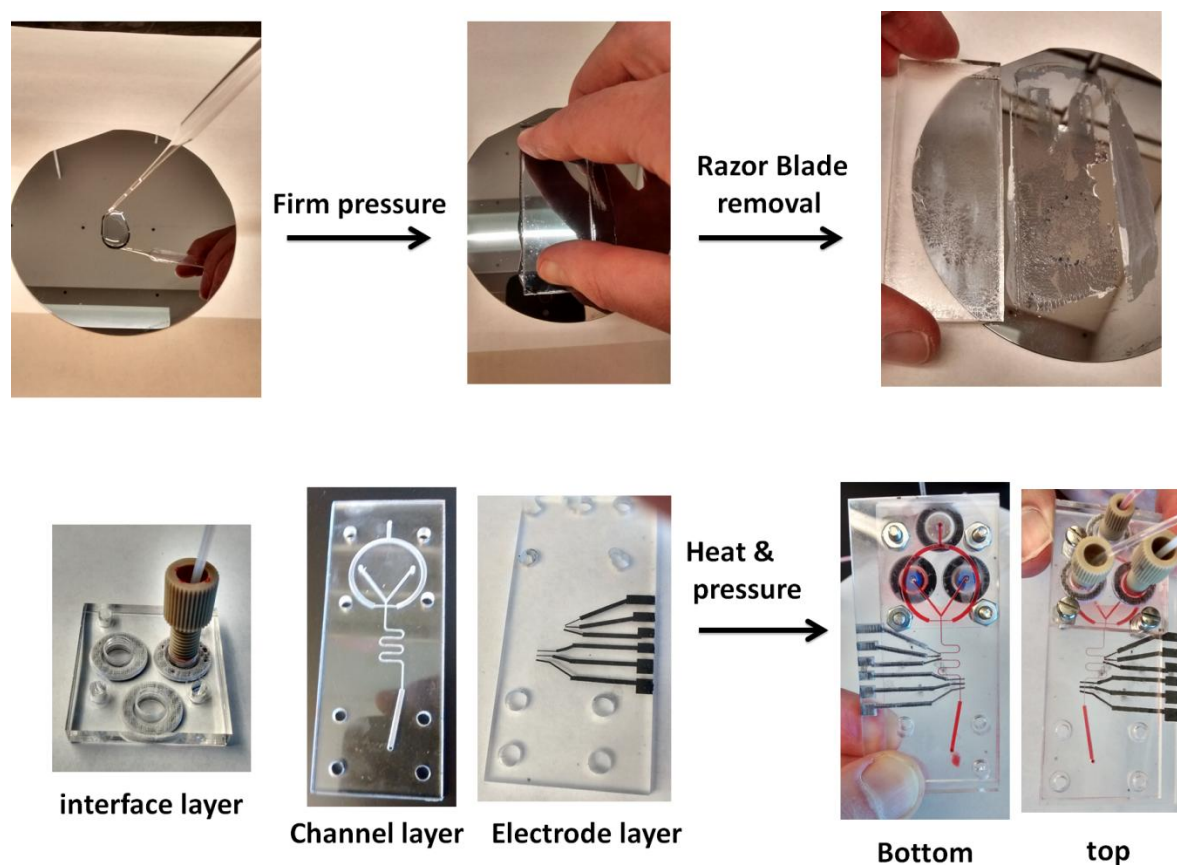
Another method to seal the microfluidics is to apply a thin layer coating of a lower melting point thermoplastic such as poly-caprolactone (PCL) or polylactic acid (PLA) to the PMMA surface. The thin polymer coating has a lower T_{melt} than PMMA, PMMA begins soften $\sim 121^{\circ}\text{C}$, where PCL completely melts at 60°C . When heated under pressure, the PCL coating allows the two pieces to be bonded without deforming the PMMA.³⁷ There is currently just a single report on the use of PCL to bond microfluidics,³⁸ which used a spin-coater to create the PCL thin layer.

To make the coating process easier a “push coating” method was developed. Push coating was recently proposed as a simple method to create thin uniform coatings.³⁹ Scheme 3.2 shows the process of applying a thin PCL coating, as well as the sealing of the microfluidic device. It was found that DCM in a ratio of 1 part (grams) PCL to 100 parts (grams) of DCM provided a coating thickness of $3 \pm 1 \mu\text{m}$. The thickness of $3 \mu\text{m}$ was chosen as to not interfere or clog the channels, but also to supply a sufficient layer of PCL to facilitate sealing.

In contrast to the other report of PCL sealed microfluidics,³⁸ the work herein was constrained to put the PCL film on the channel layer. Scheme 3.2 shows that after the thin layer is applied a CO_2 laser is used to ablate a channel into the PMMA. We chose the rastering setting to create the channel. With settings of 25 speed and 30 power (30 W laser) it provided about $150 \mu\text{m}$ deep channel that was $\sim 200 \mu\text{m}$ wide at the top. Full optimization of these parameters was not explored for this initial proof of concept study. Related to this, there are many literature reports on CO_2 laser ablation of PMMA for

optimizing the shape, width, depth and quality of channels for microfluidic applications.⁴⁰⁻

42



Scheme 3.2 (top) Process for “push coating” to create a thin PCL layer onto PMMA. (bottom) Fabrication of PCL bonded electrochemical microfluidic droplet generator. The Channel is filled with a red dye.

Creating a fluidic connection to the microchip can be problematic and often the connections are permanently glued in place.²⁵ Here, the connections to the chips were made with a unique laser cut PMMA and O-ring reversible interface, which is shown in Figure 3.2 (interface layer). PMMA was etched to accommodate an O-ring and then tapped to accept threaded standard microfluidic fittings. The interface piece is simply bolted to the

sealed chip. The interfaces were leak free and provided a fast and easy way to interface to the microfluidic chip.

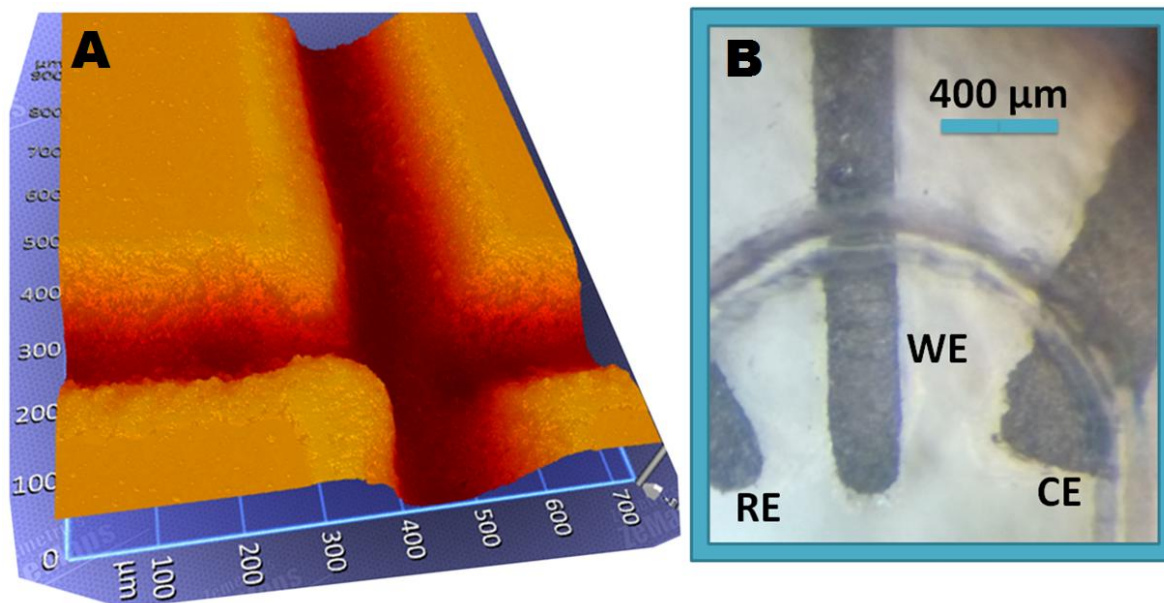


Figure 3.3 (left) Optical profilometry characterization of the pinching architecture used for droplet generation. (right) Image of electrodes interfaced to a channel in a sealed device.

Figure 3.3B shows that the electrodes are both apparently well integrated into the substrate as well as sealed to the channel layer. Since the electrodes are made with PCL they formed a leak free bond to the other half of the microfluidic chip. Like the channels, the width of the electrode is around ~200 microns which is approximately the resolution of the laser cutter.

Overall the new method for creating microfluidic devices proposed in Scheme 3.2 is ideal for rapid prototyping. The interface piece can be left as a constant and the channel

designs can be iterated as needed. While it isn't difficult to make electrodes, it was also found that the electrode layer was reusable many times over. Prying the chip apart with a razorblade and sanding the electrode provided a fresh electrode layer that could be repeatedly reused.

Electrochemistry of PCL composites integrated into droplet generators

Droplet microfluidics are a unique analytical tool.⁴³ One of the main advantages of droplet microfluidics is the ability to rapidly mix reagents in nanoliter to picoliter volumes. In droplet microfluidics mixing can occur nearly three orders of magnitude faster than in laminar flow microfluidics. The increased mixing arises from the small volume of the droplets as well as recirculating flow within the droplet.⁴⁴ Droplet microfluidics are an exciting tool which enable applications such as single cell analysis, droplet-based chemical synthesis, drug screening, nano-particle fabrication, and small-scale cell cultures.⁴³

Electrochemistry of droplets was first reported in 2008. The initial work used electrochemistry to determine the droplet frequency, droplet size, and droplet velocity.⁴⁵ A follow up publication from the Crooks lab used a novel squeeze-zone to pinch the droplet, greatly enhancing the reproducibility of the electrochemical sensing of droplets.⁴⁶ Droplet-based electrochemistry has also been demonstrated for a hand full of applications including cancer cell recognition,⁴⁷ 4-aminophenol detection,⁴⁸ glucose sensing,⁴⁹ and others.⁵⁰⁻⁵¹ Very recently it has been proposed that internal recirculating convection within droplets can enhance an electrochemical signal from increased mass transfer to the electrode surface.⁵²

Electrochemical signal enhancement is not always easily obtained and this property of droplet microfluidics is promising for the development of their use in electrochemical sensors. In general, there are not a large number of reports that demonstrate electrochemically probing the redox properties within droplets and the field is arguably in its infancy. A possible reason for the lack of publications in this field is a difficulty in the fabrication of electrochemical microfluidics.

In this work pinching droplet generators were chosen for the microfluidic design. It was found that this design more easily generated droplets than the T-junction prototypes tested. There are a variety of ways to generate droplets and this useful review highlights the various geometries that can be used.⁵³ Figure 3.4 demonstrates droplets being generated in the newly proposed PMMA microfluidic devices. On the left oil droplets are being generated. The devices used to generate oil droplets were simply plasma treated, ~ 1 minute ambient air, before heat sealing to ensure a hydrophilic surface and good wetting of the surface by water.⁵⁴ In practice, the PMMA devices worked well both with plasma treatment and without for the generation of oil droplets, however, they performed quite poorly for generating water droplets.

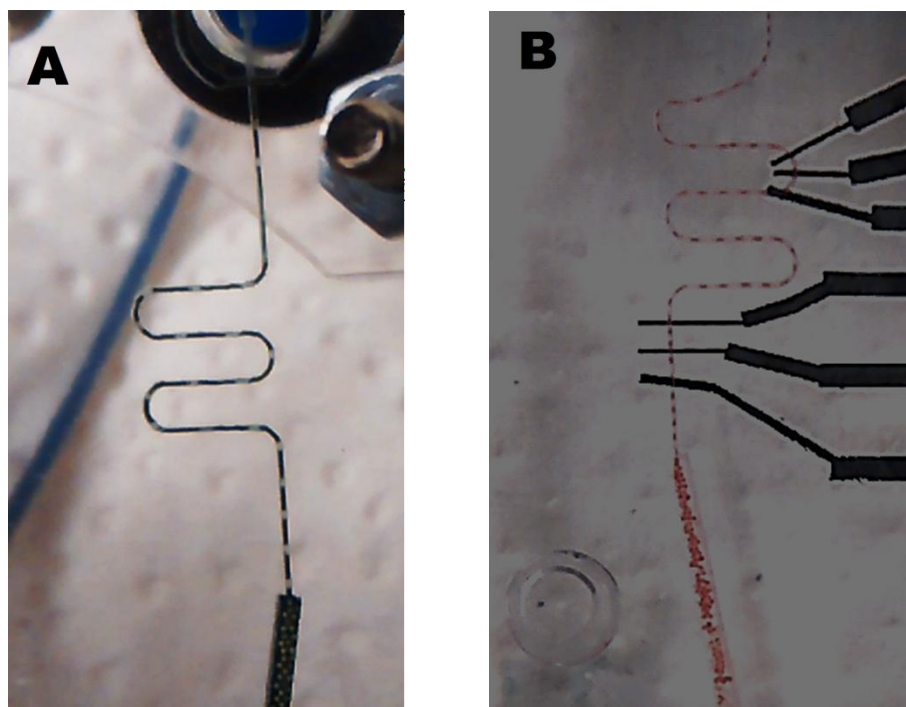


Figure 3.4 Demonstration of droplet generation in PCL sealed microfluidics. The left device (A) shows oil droplets in water with a green dyed aqueous carrier phase, and the right device (B) contains water droplets (red dye) in oil.

Making water droplets requires the surface of the channel be fully hydrophobic. Difficulty in making water droplets with PMMA has been addressed previously, and surface modification was needed to create a sufficiently hydrophobic layer.⁵⁵⁻⁵⁷ To make the channels hydrophobic the device was first plasma treated after assembly following literature precedent.⁵⁷ The channel was then exposed to light-weight mineral oil and salinizing agent solution for 3 hours. The mineral oil is the same used as a carrier phase in Figure 3.4. The reactive species generated on the surface of PMMA during the plasma treatment reactant with the salinizing agent and form covalent bonds with the surface of the channel.⁵⁷ Once treated the microfluidic chips could generate aqueous droplets for hours.

The electrochemistry within the droplet generator is shown in Figure 3.5. 15 mM ferricyanide was used to generate an electrochemical signal, this solution was then mixed in flow to create differing concentrations. When the data is shown for a total of 1 minute of sampling, peaks are not observable. At the total flow rate of $8\ \mu\text{L min}^{-1}$ the aqueous space between the oil droplets are generating electrochemical signals at a rate of ~ 4 per second. The plugs of green aqueous solution can be seen in Figure 3.4. Overall, the peak shapes are somewhat as expected and are logical for a plug of solution flowing over an electrode. The peaks also appear to be quite uniform. It is interesting that the baseline current increases with increasing concentrations of ferricyanide. It may be possible that thin layers of aqueous carrier phase may be in contact with the electrode at all times, which are providing this background current.

In Figure 3.5C a calibration curve created from the peaks in Figure 3.5A is shown. The calibration shows good agreement between changes in flow rates and the analyte concentration changes. Overall, as an initial proof of concept the device is shown to be capable of electrochemical sensing of aqueous carrier phase plugs, the chips were stable to oil for a period of days, and had consistent droplet generation and electrochemical signal.

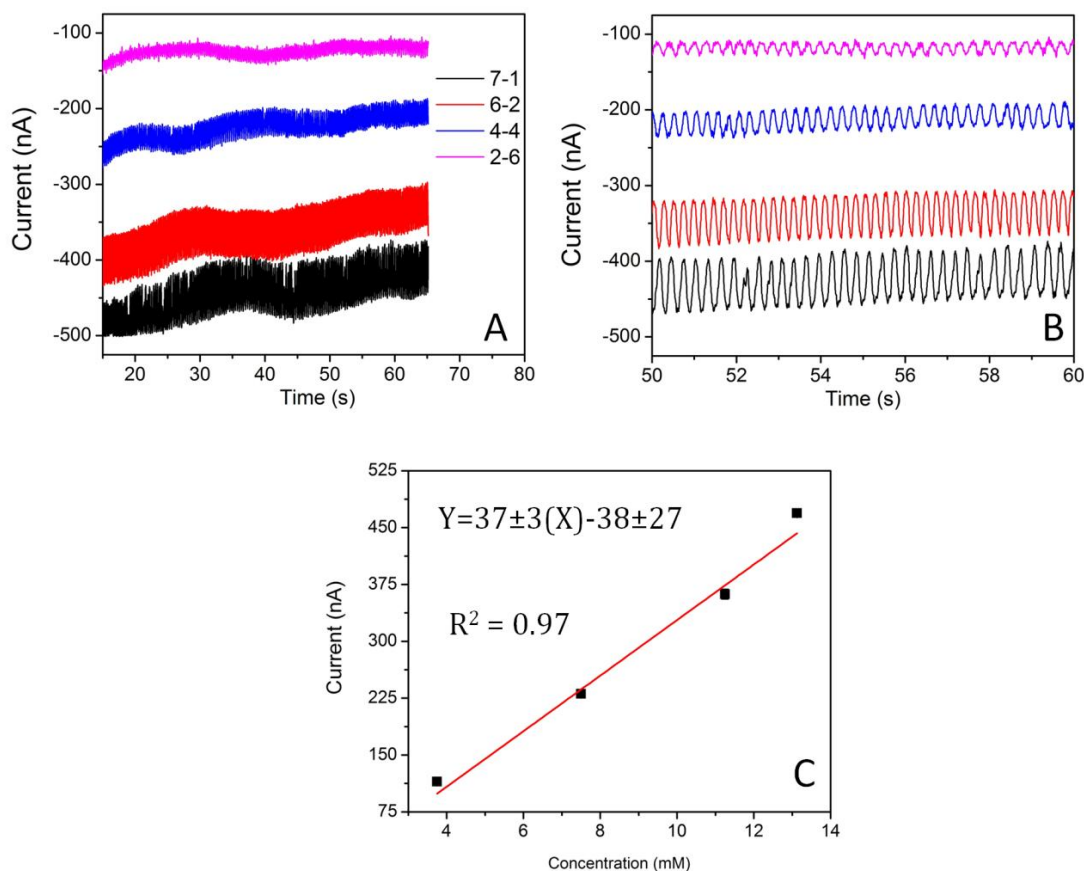


Figure 3.5 (A) Electrochemistry of PCL enable electrochemical microfluidics for droplet generation and electrochemical detection. The values in the legend are the flow rates ($\mu\text{L min}^{-1}$) of the 15 mM ferricyanide-Blank electrolyte. (B) Zoomed in region of Figure 3.5A. (C) Calibration curve for randomly selected peaks from Figure 3.5A ($n=6$), error bars are present but are too small to be visible.

The electrochemistry of water droplets stabilized in an oil carrier phase are shown in Figure 3.6. There are a few contrasts to the electrochemical data obtained for the oil in water droplets. One main difference is that the background current is quite low, which is most likely caused by the oil carrier phase being non-conductive. The non-conductive nature of the oil should completely shut off capacitive and faradaic currents between aqueous droplets.

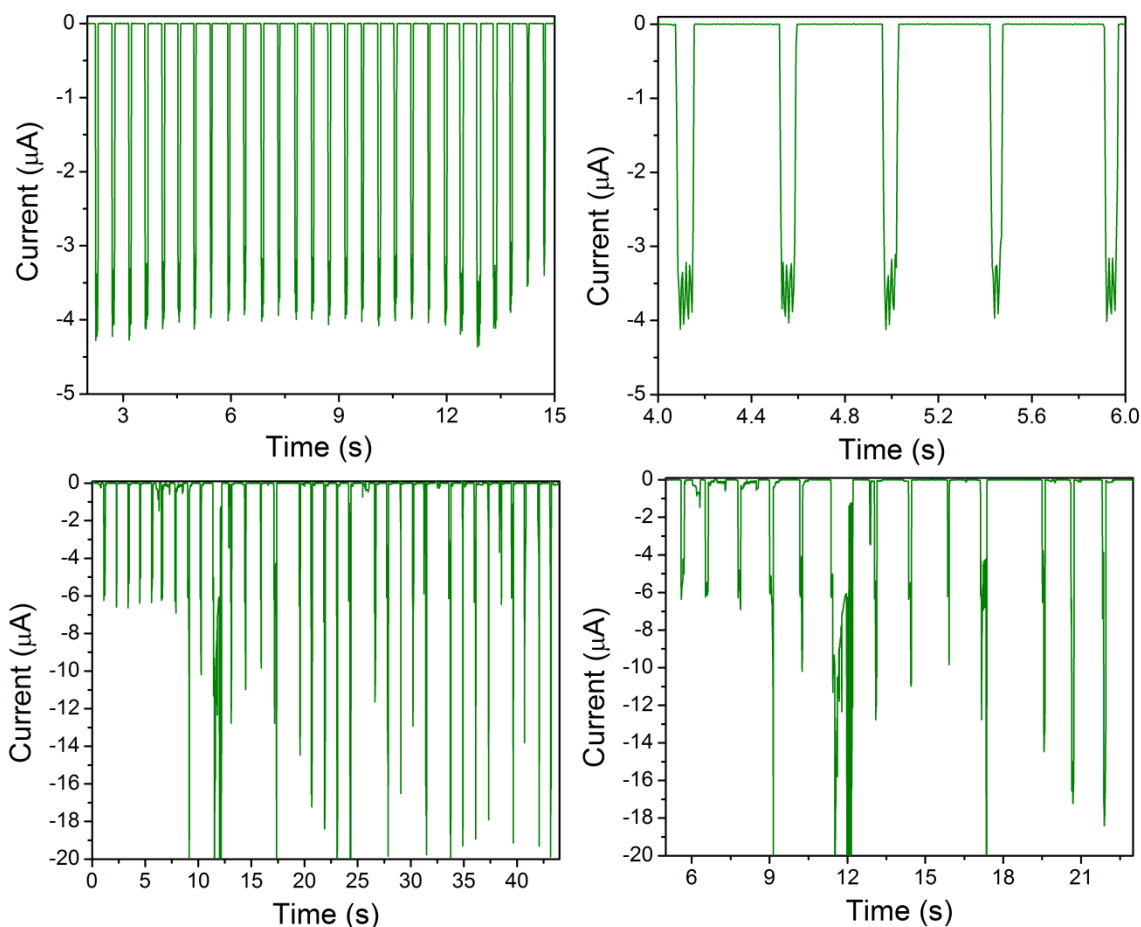


Figure 3.6 Water droplet generation within a PMMA PCL sealed device. (top) Initial run measuring 1 mM ferricyanide aqueous droplets. (bottom) Current response after 30 minutes of droplet generation measuring 1 mM ferricyanide aqueous droplets.

At the bottom of Figure 3.6 the current response after 30 minutes of electrochemical testing is shown. After the device was continuously used for 30 minutes the peaks became completely erratic. It is unclear as to the cause for the inconsistencies, but it may stem from the devices becoming less hydrophobic over time, causing streaking or smearing of the droplets over the electrode surface. It may also be that the droplets are not making good contact with the electrode. Throughout all of the testing, the device was still visually making stable droplets, so the later hypothesis may be the most likely. Overall, it is highly

promising that aqueous droplets could be created and sustained over the course of a few hours, as well as periodic intervals of consistent electrochemical signals from the droplets.

Summary of PCL sealed carbon composite integrated microfluidic devices

To conclude this section, a new method for fabricating patterned electrodes was introduced using a novel PCL melt based technique. Through the use of an adapted PCL bonding method, electrochemical microfluidics could be easily fabricated. Electrochemical detection within droplet microfluidics was demonstrated for both water in oil and oil in water droplets. The methods proposed here should directly apply to any number of microfluidic application requiring integrated electrodes. This new system represents a fast, simple, low cost method to make high-end microfluidic devices with integrated carbon composite electrodes.

Future work for droplet microfluidics

A logical next choice for future work is to try and stabilize the signal of aqueous droplets. This may be achieved by increasing the size of the channel in the zone of droplet generation. This would increase the size of the droplet. The droplet would then be passed over a smaller channel which contains the electrodes. The squeezing of the droplet should help to make better contact with the electrode and hopefully create a reproducible sensing environment.

Droplet sorting within microfluidics is now a common practice,⁵⁸ and devices to perform sorting should be easily fabricated with the methods proposed in this section. The sorting is accomplished with an electric field which is generated by two electrodes

embedded in the microfluidic device. The electrodes used for sorting are not in contact with solution. Depending on the analyte/contents within a droplet, the droplet can be directed into side channels, where the analyte can then be electrochemically probed (Figure 3.7 left).⁵⁸ The charged particles are directed in the presence of an electric field.

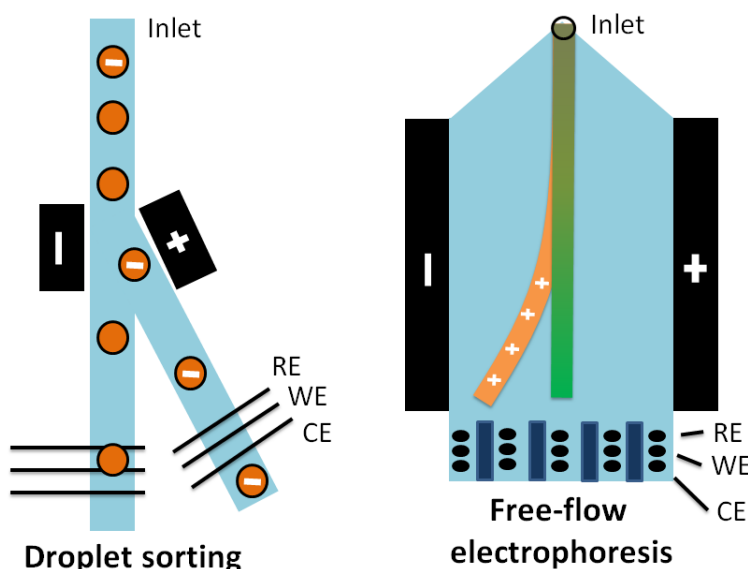


Figure 3.7 (left) Channel design for electric field sorting of charged droplets. (right) Schematic for a free flow electrophoretic (FFE) device with integrated electrodes.

Besides sorting, the new PCL based system of making microfluidics with integrated electrodes could be used to create devices for electrophoresis. A lesser used type of electrophoresis called free-flow electrophoresis (FFE) would be an interesting design to study.⁵⁹ With FFE solution is passed between two polarized plates, depending on the charge of the analytes within the solution, the analyte will begin to separate within the electric field. One advantage of free flow electrophoresis is that the separated analytes of

interest can be collected and stored for off chip analysis. Shown in Figure 3.7(right) the separated analytes can also be electrochemically probed as they pass into the segmented collection zone.

One major issue with constructing FFE devices is the need to get the electrode inside of the separation zone without actually contacting the solution.⁶⁰ Ideally the electrode is separated from the solution by a very thin layer of insulating material. If the electrode is too far from the solution the electric field is greatly diminished. Conversely, if the electrode is inside of the separation zone and exposed to the solution, large amounts of gas and electrolysis by-products are formed from solvent decomposition. The decomposition products can interfere with detection. Given the ease and ability to elegantly pattern electrodes in 3-dimensions with the PCL system, FFE would be a perfect example to show the utility of the melt-based fabrication method.

Quantification of oxidative potential of particulate matter

The second part of this chapter focuses on conducting measurements and developing sensors for determining the oxidative potential (OP) of particulate matter (PM). Indoor and outdoor pollutants in the form of small particulate matter (PM) are a major source of respiratory illness and early mortality.⁶¹⁻⁶⁶ It has been reported that cities with higher PM levels have higher incidents of morbidity that scales linearly with increases in PM.³ Related, anthropogenic increases in fine particulate matter are expected to cause premature deaths of an estimated 3 million people.⁶⁷

A large fraction of PM consist of secondary organic aerosols (SOA) created in the atmosphere from a combination of sunlight, man-made and natural volatile organics and

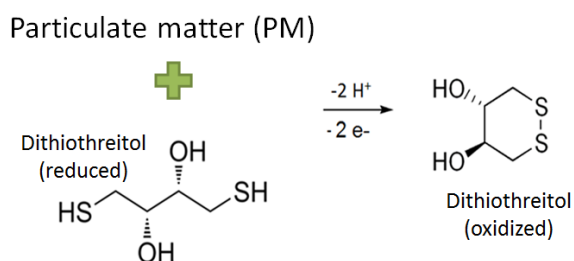
small molecules.⁶⁸ A major source of toxicity from PM is thought to be from the generation of reactive oxygen species (ROS) in the human body leading to cellular oxidative stress. PM also contains redox active metal species such as iron, and copper, as well as quinones, and amorphous carbons, which can all generate ROS within the human body.⁶⁹⁻⁷¹ The generated ROS is typically in the form of hydroxyl radicals ($\cdot\text{OH}$), superoxide (O_2^-), hydroperoxyl (HO_2) and hydrogen peroxide (H_2O_2).⁷²⁻⁷³ Overall, the mechanism of ROS generation in the human body is complex and remains a topic of intense study.⁷⁴

Particles that are $2.5\text{ }\mu\text{m}$ or smaller in aerodynamic diameter, which are designated as $\text{PM}_{2.5}$, are considered more dangerous since these particles can travel deep into the lung and infiltrate into the circulatory system.⁷⁵⁻⁷⁶ Once in the circulatory system, PM can affect bodily systems and cellular functions.⁷⁷ While ROS is continuously made in the body as part of normal cellular function, antioxidants can be overwhelmed with excess ROS generation from PM and lead to cellular damage.

Often, only $\text{PM}_{2.5}$ mass or particle numbers are used as an indicator of health risk of so called “bad air days”.⁷⁸ The $\text{PM}_{2.5}$ measurement devices are typically positioned around cities, for example China has 946 monitoring stations in 190 cities. These monitoring stations can also measure SO_2 , NO_2 , $\text{PM}_{2.5}$, PM_{10} , CO, and O_3 at a resolution of minutes or hours.⁷⁹ While the chemical sensor information is useful to track air quality, these sensors do not provide any information on the actual toxicity of the air or its OP.

There are a number of ways to test air quality and toxicity towards humans which include the use of living organisms,⁸⁰ in vitro cell culture,⁸¹ or chemical methods.⁸² The work in this thesis section measures oxidative potential (OP) of PM through a chemical

method. The method utilizes the chemistry seen in Scheme 3.3. The molecule dithiothreitol (DTT) is used as a surrogate to mimic the reaction happening between antioxidants within the human body and PM. The seminal paper by Cho et al,⁸³ introduced the DTT assay and correlated the method to human health outcomes. Now common practice, the DTT assay is used in the presence of PM as an indicator of ROS human health risk.^{82, 84} Recently, hospital visits have been positively correlated to increased DTT assay activity of sampled air.⁸⁵ Overall, the DTT assay is proposed as a method of mimicking glutathione chemistry within the body. DTT is more reactive than glutathione which can speed up the time scale of measuring the toxicity of airborne PM. However, since DTT is not found in the human body and has different reactivity rates with PM than glutathione, it does call into question the validity of the assay.⁸⁶



Scheme 3.3 Simplified reaction scheme for the reaction of particulate matter (PM) with dithiothreitol (DTT).

In Figure 3.8 the generic mechanism typically used to measure DTT is shown. The mechanism involves the use of Ellman's reagent (5,5'-dithiobis-(2-nitrobenzoic acid) which rapidly reacts with a thiol (DTT in this case) at slightly basic conditions. The product of the

reaction is 2-nitro-5-thiobenzoate, often referred to as TNB. TNB has a main adsorption at 412 nm which is readily detectable with UV-Vis spectroscopy. On the right of Figure 3.8 the UV-Vis spectra of the DTT assay is shown. The spectra show the absorption signal from TNB diminishes over time if DTT is exposed to particulate matter, when compared with a non-PM loaded control solution. In simple terms, the more DTT that is consumed in the presence of PM, the more the UV-Vis signal of TNB will decrease, which indicates increased oxidative potential of the PM.

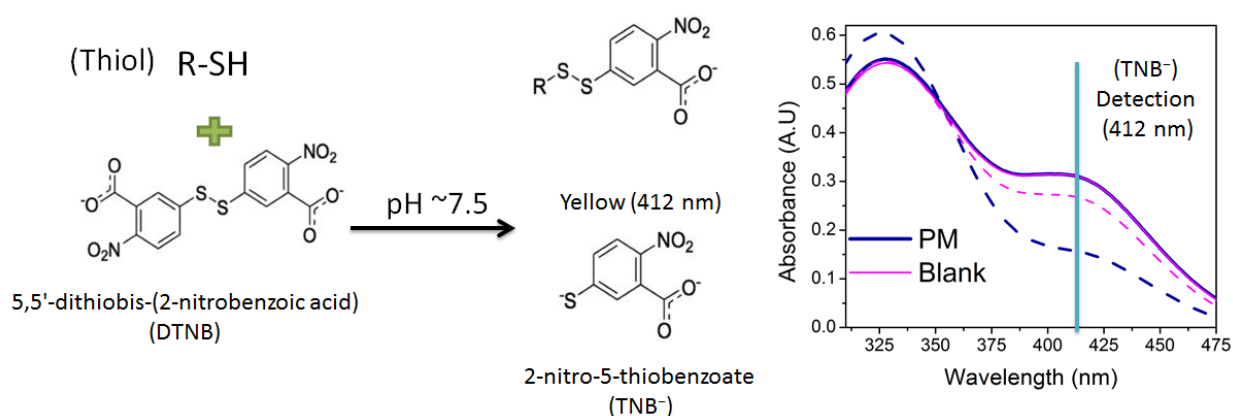


Figure 3.8 (left) reaction scheme for the colorimetric detection of thiols using Ellman's reagent. On the right is the UV-Vis spectra of the DTT assay. The dotted lines are the signal after 50 minutes in the DTT assay.

Working off the hypothesis that DTT consumption correlates to oxidative potential within humans, a study was performed which collects PM onto filters. The work developing the air sampler to collect PM onto filters was largely orchestrated by Casey Quinn and the Volkens group and has been submitted for publication.⁸⁷ To collect the PM a wearable

Automated Microenvironmental Aerosol Sampler (AMAS) was used (manuscript pending). The AMAS active aerosol sampling device contained four separate filter channels that sampled PM_{2.5} from microenvironments. The exposure microenvironments were home, school, and other. The “other” microenvironment designated any environment that was not home or school. An algorithm using GPS switched the device to sample air from specific environments onto individual filters. The pilot study was conducted with high-school-aged children in the Fresno, California area. The AMAS collected PM_{2.5} filter samples (n=126 microenvironments) were evaluated for both black carbon,⁸⁸⁻⁸⁹ and oxidative potential.⁹⁰⁻⁹² The black carbon data will not be discussed in the thesis section. The PM loaded filters were then used in the DTT assay to gauge OP.

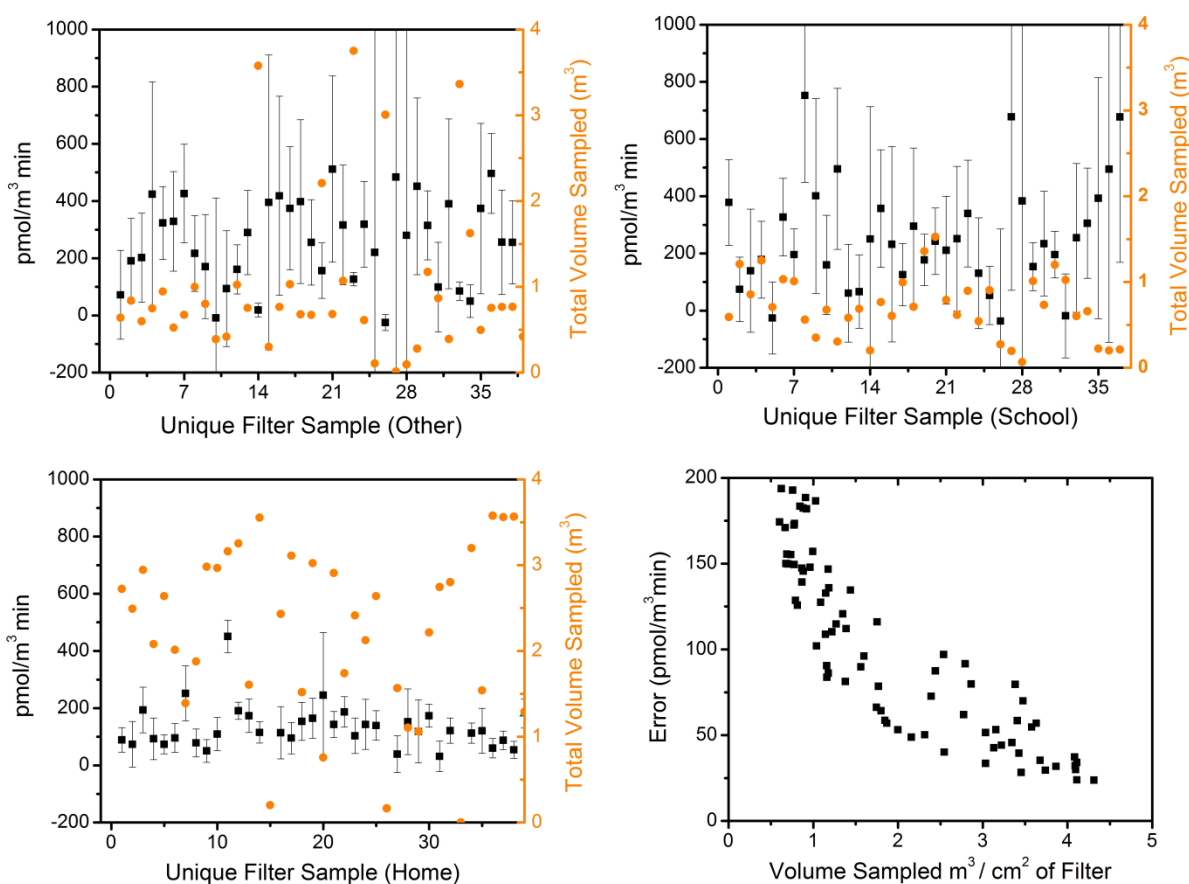


Figure 3.9 Personal oxidative potential exposure measured through the DTT assay from high-school-aged children in Fresno, California. The bottom right graph plots error as a function of volume of air sample for a specific filter.

The data in Figure 3.9 show the OP values measured from the filter samples from the AMAS sampler. As is typical for this field, the reactivity of the filter in the DTT assay was normalized by the amount of air that passed through the filter. More often used to normalize the reactivity is the PM mass, however, in this work the PM mass was not measured because it was very small. Many of the filters were estimated to contain less than 10 μg of PM which can be quite difficult to measure accurately. When normalized to sampled

air volume the OP values are similar to those previously reported for urban, rural, or roadside PM.⁹²

The most notable aspect of these results is the error within the measurements. The errors are correlated to the volume of air sampled. When the volume sampled is less than 2 m³ large amounts of uncertainty are introduced. The dependence of air sampled on uncertainty is demonstrated in all the graphs in Figure 3.9, and is highlighted in the lower right hand graph. Future sample collection should then be aimed at collecting a minimum sampled mass equal to the black carbon LOD (0.49 µg), this would equate to 11.2 µg PM mL⁻¹ in the DTT assay (based on an estimated ambient BC:PM ratio of 0.04 and a 500 µL dilution volume for the DTT assay). The filters and the resulting solution in the DTT assay would then be loaded with a mass to volume ratio that is near 10 µg mL⁻¹, which has previously been recommended for the DTT assay.⁹¹

Overall, the “home” OP data appears to be the most reliable which is where the students spent a majority of their time and the highest volume of air was sampled. The unique property of the AMAS system was that it draws in air over the filter that the subject was actually breathing in. When looking at the data for “home” in Figure 3.9 sample 3, 7, and 11 had elevated DTT consumption rates, and samples 9, 26 and 31 had lower rates than the other samples. While these are only single data points, this information could be beneficial to understand what factors determine high or low OP in certain environments. If these factors are better understood, strategies could then be put in place to limit the OP for a given environment.

The work for the Fresno student pilot study used spectroscopic methods for conducting the DTT assay. Some issues encountered with the method were tedious amounts of pipetting when mixing the reagents for the process shown in Figure 3.8. The large amount of pipetting limited the number of samples that could be run at one time ($n=10$). The minimum volume that could be used was also 500 μL , since aliquots from the sample needed to be withdrawn and tested at periodic time points. In the Henry lab, electrochemistry has been proposed as a way to simplify measuring the concentration of DTT.⁹⁰ However, for the Fresno study electrochemical methods were not used since the electrochemical microfluidics used previously were somewhat tedious to make, and at the time of the study were not optimized to use smaller sample volumes. The work in the next section uses the TPE system to build new devices for flow based concentration measurements of DTT as well as static based detection methods.

Development of electrochemical TPE sensors for the DTT assay

This section introduces TPE modified with cobalt phthalocyanine (CoPc) for the detection of DTT. CoPc is a common sensing moiety for electrochemical detection of thiols.⁹³ Chapter 4 goes into detail on the nature of the catalysis of phthalocyanines as well as the general synthesis of the molecules describes here. In Figure 3.10, the structure of a phthalocyanine coordinated to a thiol is shown. It is through this coordination that the oxidation of thiols, including DTT is catalyzed.

Cobalt tetraaminophthalocyanine (CoTAPc) can be electrochemically polymerized as shown in Figure 3.10B. When the electrode is cycled to a potential above 0.7 V vs. SCE a polymer film grows on the electrode surface. A chemical reaction for this film growth is

proposed in next chapter, which deals with this type of polymer more in-depth. The film thickness can also be tuned by repeated cycling.⁹⁴ The polymerized film provides a high surface area electrode coating, with an increased density of the active cobalt centers. The basic amine groups on CoTAPc may also provide a unique catalytic environment. Thiol oxidation is catalyzed in the presence of base because it involves the loss of a proton (Scheme 3.3). A recent report with a porphyrin complex containing pendant amine groups greatly enhanced the reduction of CO₂ by having the basic nitrogens close to the metal center.⁹⁵ It is possible with CoTAPc free amines could hydrogen bond with the thiol and help to facilitate proton loss.

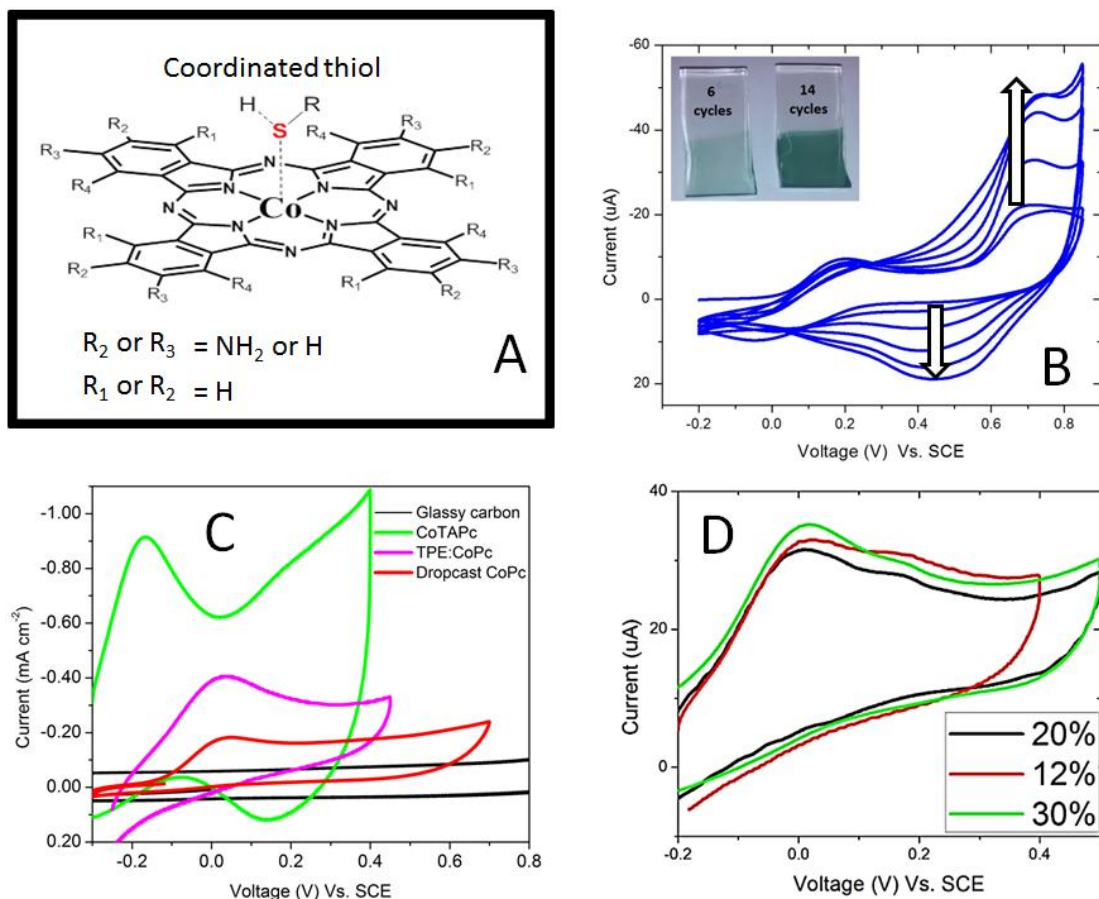


Figure 3.10 (A) Cobalt phthalocyanine (CoPc) and cobalt tetraaminophthalocyanine (CoTAPc) coordinated to a thiol. (B) Electropolymerization of CoTAPc, inset show FTO coated with CoTAPc. (C) Various forms of electrodes modified with CoPc and CoTAPc in the presence of 1 mM DTT at pH of 7.4. (D) TPE electrodes with differing carbon:CoPc ratios in the presence of 1 mM DTT at pH of 7.4.

Figure 3.10C has three different electrode modifications with phthalocyanines. The CV of the bare glassy carbon electrode demonstrates the need for a catalyst modified electrode. The glassy carbon electrode is completely inactive towards the oxidation of DTT. When CoPc is dropcasted onto the glassy carbon surface a clear DTT oxidation peak forms at a voltage of ~ 0.02 V vs. SCE. When CoPc (12%) was mixed directly into TPE material there was an increase in the current response over dropcasting. Increases in current

typically correlate to increased catalysis. The CoTAPc had the highest peak current as well as a decrease in the over-potential needed to oxidize DTT. The peak for oxidation of DTT occurs at -0.22 V vs. SCE on the CoTAPc modified electrode, which is nearly 200 mV lower than CoPc. The amine moieties as discussed earlier may be causing the increased catalytic properties of CoTAPc. Of note, the CoTAPc electropolymerization process requires the electrode be immersed in DMF, this solvent dissolves TPE that are made with PMMA. At the present it is unclear how dissolving of the electrode material will affect catalysis. The CoTAPc coating also needs to be applied before a day of testing of DTT, which is then an added step. Finally, it was found that CoTAPc was not stable in the solid state, and the usability of the material is around a month. The lack of stability limits the utility of CoTAPc as sensing medium.

Since the TPE modified with CoPc is the easiest to create, it was tested via CV in Figure 3.10D to determine the effect of increased amounts of catalyst within the TPE matrix. Based on the current responses seen in Figure 3.10D there appears to be no major signal enhancement with increased catalyst loading. It is advantageous that the CoPc catalyst is effective at a meager 12% carbon:CoPc mass percentage. While CoPc is low cost (~\$15/g Sigma), it still is the highest cost per gram material within the TPE.

The DTT assay which was performed for the Fresno study was carried out in 1.5 mL centrifuge tubes. The tubes were used once and thrown away for concerns over contamination. The DTT assay is also performed at 37 °C with the vials nearly fully submerged in a temperature controlled water bath. Ideally then, the assay could be performed in the vial without the need to remove aliquots for spectroscopic sampling and

multiple pipetting steps. In Figure 3.11, a cap TPE is proposed which was used for seemingly invasive free DTT sensing within the 1.5 mL centrifuge tube.

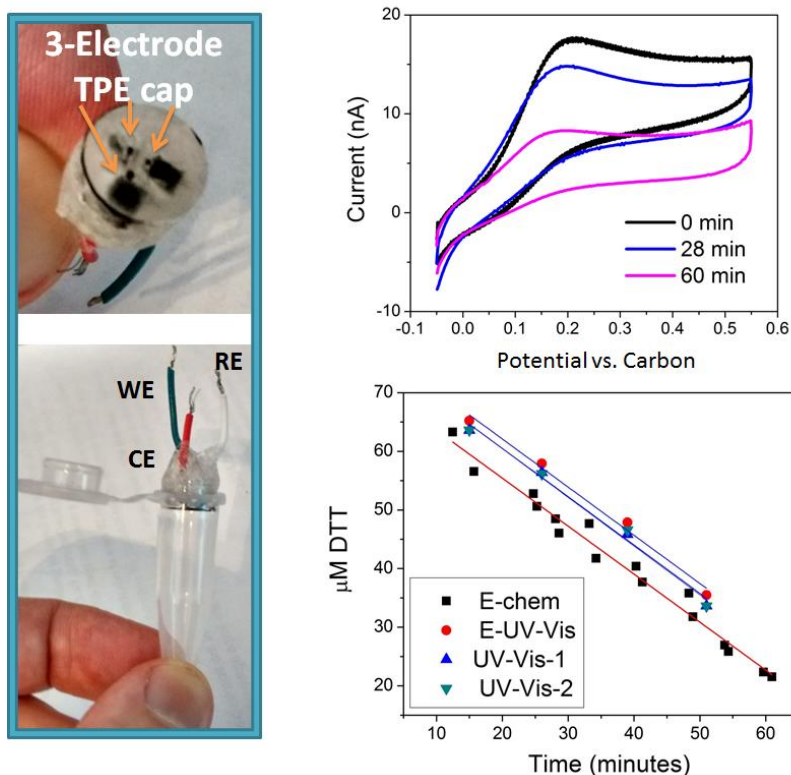


Figure 3.11 Photographs of a cap sensor containing TPE electrodes for the sensing of DTT within a 1.5 mL centrifuge tube. (right) graphs of cyclic voltammograms of DTT consumption in the presence of 2 μM of the model oxidant 1,4-naphthoquinone. DTT starting concentration was 75 μM , with a reaction temperature of 37 $^{\circ}\text{C}$.

The cap sensor utilized a CoPc-modified (12%) TPE made with PMMA and carbon black (CB) in a PMMA:CB ratio of 1:0.3. From previous chapters, carbon black had low capacitance values, which is why it was chosen here. The cap fits snugly into the centrifuge tube and is leak free. The upper right graph in Figure 3.11 shows the loss of peak current relating to the oxidation of DTT over the course of 60 minutes. A major advantage

of using electrochemistry to monitor DTT concentration is that data points can be collected as fast as once a minute. This system was not without flaws; in practice it was found to be difficult to take an initial measurement at $t=0$, and this data point was left out of Figure 3.11. The initial heating of the vial and the solution seemed to affect the peak current of the initial measurement. However, once the sensor and the solution were heated the measurements stabilized. Preheating the vial and sensor may help to overcome this issue.

Overall, good agreement between the spectroscopic method and the e-chem cap sensor was observed. The data labeled UV-Vis-1 and UV-Vis-2 used the same stock solutions as that in the e-chem vial. The E-UV-Vis vial had solution directly removed from the cap sensor and tested spectroscopically as an additional control. As expected all of the UV-Vis measurements were nearly identical. While the data from the e-chem method is slightly shifted from the UV-Vis measurements, the slope is nearly the same. This proof of concept is quite encouraging for the development of a static electrochemical method to perform the DTT assay. Overall, the TPE CoPc modified electrodes do not appear to be fouling and they have a sufficient current response to measure as little as 20 μM DTT. The cap sensor is also sandable, which enables it to be reused many times over.

Previous work in the Henry lab utilized electrochemical flow cells to measure DTT concentration for the DTT assay.⁹⁶ The flow cells can be coupled to instruments like an auto sampler and potentially enable high throughput automation of the DTT assay. Therefore, the new TPE based electrodes are of interest for use in flow cells. Many methods to make flow cells with TPEs were attempted, these consisted of sealing microfluidics with solvent,

or with double sided adhesive. In general these devices did not perform well, were of a low quality, and had issues with obtaining a reproducible functioning device.

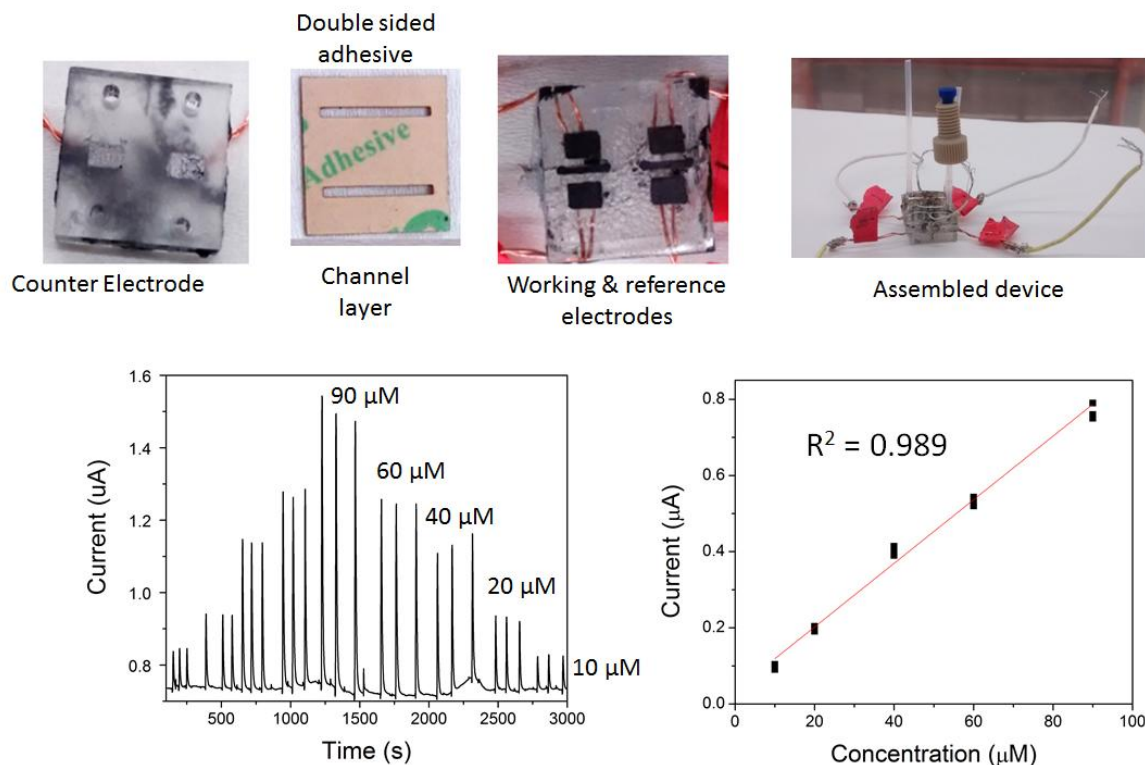


Figure 3.12 (top) Double sided adhesive (50 μm thick) based fluidic cell for the detection of DTT. (bottom) Flow injection analysis using the adhesive based flow cell. Injection volume was 20 μL , with a flow rate of 200 $\mu\text{L min}^{-1}$, and applied voltage of 0.3 V vs. carbon reference. The calibration plot was constructed with the peaks shown in this figure.

Figure 3.12 demonstrates flow injection analysis from a double sided adhesive sealed fluidic TPE. The top of Figure 3.12 shows the pieces used for assembly, microfluidic tubing was glued into the counter electrode layer and sealed with epoxy. In general this specific device had reproducible oxidation of DTT and functioned as a sensor in the concentration ranges used in the DTT assay. In practice, the flow sensor was not stable over the course of days or even hours. The sensor does however show that with TPEs, DTT can be detected in flow. Ideally, the TPEs would be integrated into a flow system that does

not require epoxy to glue in fittings, could use a commercial reference electrode, and allows for quick regeneration of the electrode surface. In the future work section flow cells are proposed which meet all of these requirements.

Future work

O-ring based fluidic devices are shown in Figure 3.12. The devices have many improved features over the adhesive based devices discussed earlier. The devices are simple and rely on stacking of layers. There are two interface layers which use standard threaded microfluidic fittings (top and bottom layer). The body of the fluidic cell then consists of a layer to form a channel or well which allow for solution to flow over an electrode layer. The orange arrows in Figure 3.12 show the direction of flow for the various electrode designs. The ability to interchange electrode designs is also an advantage of these O-ring based devices. Band electrodes, wall-jet and tubular flow through devices are all easily made and assembled. As with the microfluidic devices discussed in this chapter these O-ring devices were fabricated entirely with the CO₂ laser cutter.

The devices in Figure 3.12 were briefly tested with ferrocenylmethyl-trimethylammonium (FCTMA). The oxidation of FCTMA is a one electron process which is fairly insensitive to the surface of the electrode. The three electrode designs were tested with low concentration of FCTMA for a rough idea of the limit of detection. The data suggest that the wall-jet configuration has the best signal to noise, followed by the band electrodes, and lastly the tubular electrodes. The tubular electrodes had the highest background current and were unable to resolve a signal from 1 μ m FCTMA. In contrast the wall-jet electrode had well defined peaks for injections of 1 μ m FCTMA.

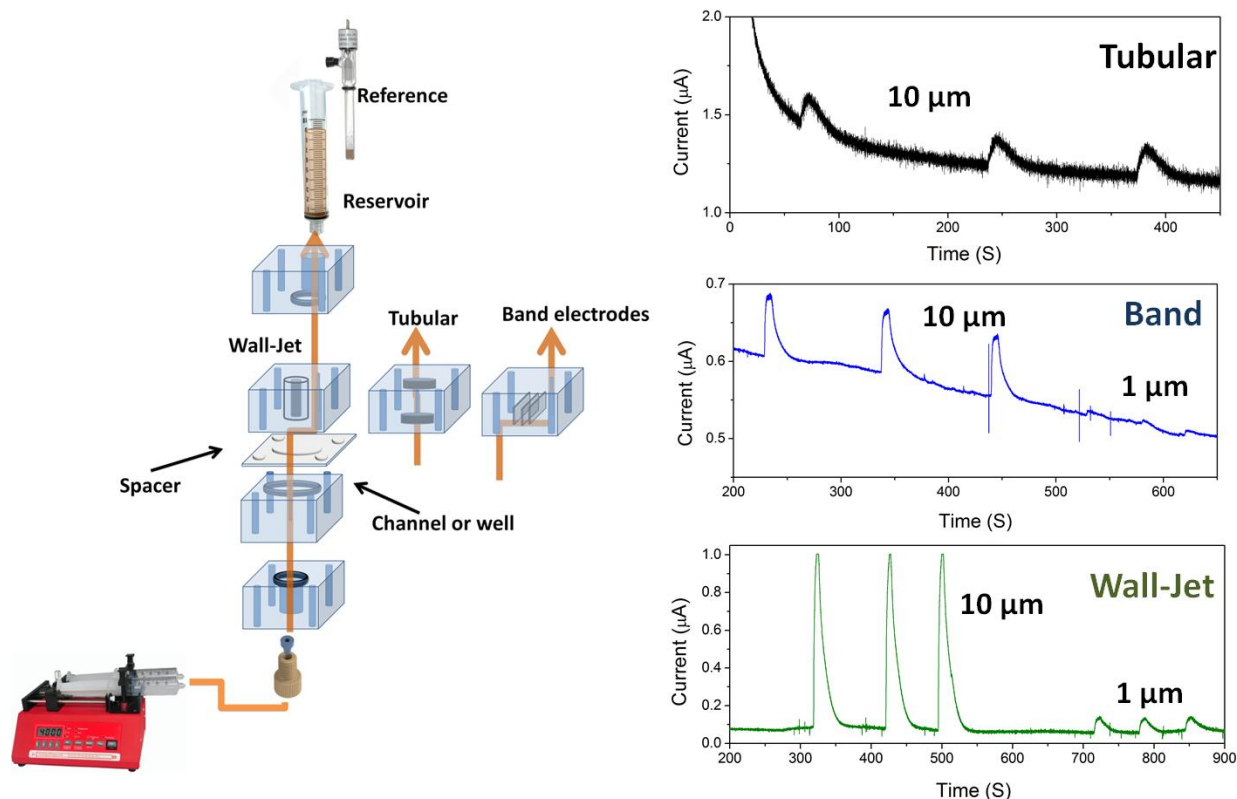


Figure 3.12 Exploded view of O-ring based fluidic device with interchangeable TPE electrodes.(right) electrochemistry from injections of ferrocenylmethyltrimethylammonium (FCTMA) within the O-ring fluidic devices. The TPE used was 3569 in a 1:3 Carbon:PMMA ratio. Flow rate for all cells was 300 $\mu\text{L min}$. Band electrode had a channel width of ~ 1 mm. The channel/tube for the tubular electrode was created with a 150 μm drill bit. The spacer was CO₂ laser cut from copy paper.

The work with the O-ring base flow cells is quite promising as an initial proof of concept. Because the cells are bolted together they are highly robust and leak free. They can easily utilize a commercial reference electrode. Conveniently, the waste is neatly contained within an attached reservoir. The electrode layer is sandable, making it reusable many times over. Also, the spacer layer can be made of materials of various thicknesses, which can change the volume of liquid the electrode sees. The electrode layers are also easy

to fabricate with the TPE system, and the carbon type, amount of carbon in the TPE, or catalyst type within the electrode layer could be changed and iterated rapidly.

Work is already underway to utilize the wall-jet configuration for use in the automation of the DTT assay. Kathleen Berg (Henry lab) is using the wall-jet coupled to an HPLC auto sampler. The aim is to try and fully automate the DTT assay, greatly increasing sample throughput. Initial results indicate that CoPc/TPE O-ring flow cells are stable enough to sense DTT over the course of hours or days. The flow cells are not just useful for the DTT assay and should have use for a plethora of flow based analytical electrochemical applications. The cells could also be used to measure and investigate electrochemical kinetics. Crooks has shown that band electrodes in laminar flow cells like the ones shown in Figure 3.12 are analogous to rotating ring disk electrochemistry.⁵ The O-ring layered structure could also work well for prototyping redox flow batteries or microbial fuel cells.

3.3 Conclusion

In conclusion, PCL has enabled the integration of carbon composite electrodes into complex microfluidics. PCL has also enabled fast and highly robust sealing of electrochemical microfluidics. The general approach to fabrication is universal and could apply to any thermoplastic type with only minor modification of the fabrication method. This work has significant impact for electrophoresis applications, droplet microfluidics, bipolar electrodes, tissue on a chip, or any other application requiring small well integrated electrodes.

Finally, oxidative potential through the use of the DTT assay was measured both spectroscopically and with electrochemistry. A pilot study using a novel AMAS unit to collect PM on filters exposed the need to decrease the volume of solution used in the DTT assay, or increase the volume of air sampled. The large error associated with low sampled air volumes made many of the OP measurements unusable. Systems like the TPE cap sensor may help with lowering the error associated with filters that have low PM loading. The demonstrated cap sensor should be able to operate with 100 μ L or less, where the spectroscopic method required 500 μ L. In theory this should increase the signal from the DTT assay by a factor of 5, and in the case of the Fresno study would have made most or all of the OP measurements statistically significant. Lastly, flow based electrochemical cells were created for use in the measure of DTT. Overall, it was found that the TPE material modified with CoPc was useful for sensing DTT within flow cells. However, the flow cells lacked stability and were tedious and difficult to fabricate in a reproducible manner. The future work addresses these issues with new O-ring sealed fluidic devices.

3.4 Materials and Methods

Methods PCL section

The PCL was from a commercial source called Thermorph. The devices were sealed by placing a PCL coated piece (containing a laser cut channel) of PMMA and a non-coated piece between two aluminum plates. Two pieces of rubber were placed between the metal plate and the PMMA. Screw type C-clamps were then used to applied pressure on the plates. The screw clamps were tightened to near the maximum amount of turns (this could

be tuned as needed). Often many clamps were used to maximize pressure per area. The assembly was then placed in a circulating oven for ~10 minutes at 80 °C (might be longer depending on oven). The assembly is left to cool either in air or placed in a refrigerator to speed the cooling process. The plates must be cooled under pressure to seal. If efficient sealing is not seen, the process can be repeated, repositioning of the clamps may be needed.

Electrochemistry and conductivity measurements

Electrochemistry was performed with a CH Instruments 660 potentiostat. A SCE reference was used for all experiments except in adhesive based flow cells which used a carbon reference. Conductivity measurements were conducted in the same manner as Chapter 2, using through-plane conductivity measurements as previously reported.⁹⁷ The disks used for conductivity were 2 mm, which had ~3 mm thickness. Electrochemistry chemicals were provided as follows, Potassium chloride (Sigma), potassium phosphate (Sigma or Fisher) ferricyanide (Sigma). All aqueous solutions used 18 Ω Millipore water.

DTT assay chemicals and materials

Ultrapure water (18.2 MΩcm) from a Mill-Q system was used for the preparation of solutions and cleaning of supplies and equipment (Merck Millipore, Darmstadt, Germany). Phosphoric acid (EMD), potassium phosphate monobasic 100.1% purity (Sigma), potassium phosphate dibasic 100.1% purity (Baker), copper sulphate pentahydrate (Sigma), dithiothreitol (DTT) (Acros), Ellman's reagent (DTNB) 5,5'-dithiobis-(2-nitrobenzoic acid) (Pierce), 2,2,2-Trifluoroethanol (Sigma), Chelex® 200-400 mesh sodium form (BIO-RAD).

Chelex treatment

As a one-time pretreatment, the Chelex was washed with 3 liters of deionized water to remove any slightly soluble Chelex moieties, and then treated with washing (a few liters) with high purity 0.1 M phosphate buffer to adjust to pH to 7.4. To make buffer solution for use in the DTT assay, high purity potassium dibasic and monobasic phosphate buffer was made into 0.1 M individual solutions. The solutions were then combined incrementally until a pH of 7.4 was reached. Roughly 200 mL of the pH 7.4 phosphate solution was then added to ~50 grams of the pretreated Chelex in a Nalgene bottle, which was shaken periodically for a period of 1 to 3 weeks while being stored in a 3 °C refrigerator. After the 1 to 3 weeks time lapse the buffer solution was placed in a plastic syringe and filtered through a 0.22 µm PVDF filter (CELLTREAT). The filtered Chelex treated buffer was then stored in a Nalgene container and typically used within a few weeks.

DTT Assay protocol

The 15 mm filters were cut in half and the 25 mm filters were quartered with ceramic scissors (Kyocera); one filter half or quarter was used for the DTT assay. The DTT assay was performed similar to the traditional method.⁸³ However, quenching with acid was not necessary as the samples were run immediately after DTNB addition, eliminating two pipetting/dilution steps in the process. The reaction of DTNB and DTT is near instantaneous at pH 7.5, and we found a 1.5 molar excess (3 moles DTNB: 1 moles DTT) was sufficient for quenching, this then prevents the UV-Vis peak from DTNB interfering with the peak TNB peak at 412 nm.

To run the DTT assay, filters were placed in 1.5 mL centrifuge tubes (Eppendorf) and wet with 15 μ L of 50/50 2,2,2-trifluoroethanol and MilliPore water. Trifluoroethanol has been reported to aid in wetting the surface of the filter and has been used previously in similar studies.⁹⁸ 500 μ L of buffered 75 μ M DTT solution was then added to the vials, which was made fresh minutes before running the assay. Stock 0.001 M phosphoric acid with a concentration of 4.5 mM of DTT, diluted by the Chelex buffer, was used to make the 75 μ M DTT solution. The dilute acid stabilizes the DTT and enables the stock 4.5 mM DTT solution to be used through a day of testing, these solutions were remade fresh after 24 hours.

The vials were placed in a 37 $^{\circ}$ C water bath. At time points 0, ~15, ~30, and ~45 minutes 100 μ L aliquots were removed from the vials and added to 400 μ L of stock DTNB solution. DTNB was ~56 μ M in 0.1 M phosphate buffer at pH of ~7.5. The DTNB stock solution was stable for at least a month with storage in a 3 $^{\circ}$ C refrigerator. Spectra were measured within 15 minutes of reacting DTT with DTNB and absorbance at 412 nm was used to measure concentration. The concentration was calculated with Beer's law using a molar extinction coefficient of 14150 $\text{M}^{-1} \text{cm}^{-2}$. For all trials two blank DTT decay rates were measured, blank rates were also recorded in the presence on non-PM loaded filters as a control for any filter related activity.

REFERENCES

1. Rackus, D. G.; Shamsi, M. H.; Wheeler, A. R., Electrochemistry, biosensors and microfluidics: a convergence of fields. *Chemical Society Reviews* **2015**, *44* (15), 5320-5340.
2. Zhu, Y.; Fang, Q., Analytical detection techniques for droplet microfluidics—A review. *Anal. Chim. Acta* **2013**, *787*, 24-35.
3. B., M. K.; Henning, K.; P., K. J., Recent developments in detection for microfluidic systems. *Electrophoresis* **2004**, *25* (21-22), 3498-3512.
4. Martinez-Duarte, R.; Gorkin Iii, R. A.; Abi-Samra, K.; Madou, M. J., The integration of 3D carbon-electrode dielectrophoresis on a CD-like centrifugal microfluidic platform. *Lab on a Chip* **2010**, *10* (8), 1030-1043.
5. Dumitrescu, I.; Yancey, D. F.; Crooks, R. M., Dual-electrode microfluidic cell for characterizing electrocatalysts. *Lab on a Chip* **2012**, *12* (5), 986-993.
6. Fischer, D. J.; Vandaveer, W. R.; Grigsby, R. J.; Lunte, S. M., Pyrolyzed Photoresist Carbon Electrodes for Microchip Electrophoresis with Dual-Electrode Amperometric Detection. *Electroanal.* **2005**, *17* (13), 1153-1159.
7. Kuhnline, C. D.; Gangel, M. G.; Hulvey, M. K.; Martin, R. S., Detecting thiols in a microchip device using micromolded carbon ink electrodes modified with cobalt phthalocyanine. *Analyst* **2006**, *131* (2), 202-207.
8. Villalba, M. M.; Davis, J., New directions for carbon-based detectors: exploiting the versatility of carbon substrates in electroanalysis. *J. Solid State Electr.* **2008**, *12* (10), 1245-1254.
9. Hamed, M. M.; Unal, B.; Kerr, E.; Glavan, A. C.; Fernandez-Abedul, M. T.; Whitesides, G. M., Coated and uncoated cellophane as materials for microplates and open-channel microfluidics devices. *Lab on a Chip* **2016**, *16* (20), 3885-3897.
10. Pereira, S. V.; Bertolino, F. A.; Fernandez-Baldo, M. A.; Messina, G. A.; Salinas, E.; Sanz, M. I.; Raba, J., A microfluidic device based on a screen-printed carbon electrode with electrodeposited gold nanoparticles for the detection of IgG anti-Trypanosoma cruzi antibodies. *Analyst* **2011**, *136* (22), 4745-4751.
11. Kovarik, M. L.; Torrence, N. J.; Spence, D. M.; Martin, R. S., Fabrication of carbon microelectrodes with a micromolding technique and their use in microchip-based flow analyses. *Analyst* **2004**, *129* (5), 400-405.
12. Moore, C. M.; Minter, S. D.; Martin, R. S., Microchip-based ethanol/oxygen biofuel cell. *Lab on a Chip* **2005**, *5* (2), 218-225.

13. Erkal, J. L.; Selimovic, A.; Gross, B. C.; Lockwood, S. Y.; Walton, E. L.; McNamara, S.; Martin, R. S.; Spence, D. M., 3D Printed Microfluidic Devices with Integrated Versatile and Reusable Electrodes. *Lab on a chip* **2014**, *14* (12), 2023-2032.
14. Wang, J.; Pumera, M.; Chatrathi, M. P.; Escarpa, A.; Konrad, R.; Griebel, A.; Dörner, W.; Löwe, H., Towards disposable lab-on-a-chip: Poly(methylmethacrylate) microchip electrophoresis device with electrochemical detection. *Electrophoresis* **2002**, *23* (4), 596-601.
15. Sameenoi, Y.; Mensack, M. M.; Boonsong, K.; Ewing, R.; Dungchai, W.; Chailapakul, O.; Cropek, D. M.; Henry, C. S., Poly(dimethylsiloxane) cross-linked carbon paste electrodes for microfluidic electrochemical sensing. *Analyst* **2011**, *136* (15), 3177-3184.
16. Selimovic, A.; Johnson, A. S.; Kiss, I. Z.; Martin, R. S., Use of epoxy-embedded electrodes to integrate electrochemical detection with microchip-based analysis systems. *Electrophoresis* **2011**, *32* (8), 822-831.
17. Johnson, A. S.; Selimovic, A.; Martin, R. S., Integration of microchip electrophoresis with electrochemical detection using an epoxy-based molding method to embed multiple electrode materials. *Electrophoresis* **2011**, *32* (22), 3121-3128.
18. Xu, X.; Weber, S. G., Carbon fiber/epoxy composite ring-disk electrode: Fabrication, characterization and application to electrochemical detection in capillary high performance liquid chromatography. *J. Electroanal. Chem.* **2009**, *630* (1), 75-80.
19. Bordes, C.; Fréville, V.; Ruffin, E.; Marote, P.; Gauvrit, J. Y.; Briançon, S.; Lantéri, P., Determination of poly(ϵ -caprolactone) solubility parameters: Application to solvent substitution in a microencapsulation process. *International Journal of Pharmaceutics* **2010**, *383* (1), 236-243.
20. ElMekawy, A.; Hegab, H. M.; Dominguez-Benetton, X.; Pant, D., Internal resistance of microfluidic microbial fuel cell: Challenges and potential opportunities. *Bioresource Technology* **2013**, *142*, 672-682.
21. Davim, J. P.; Barricas, N.; Conceição, M.; Oliveira, C., Some experimental studies on CO₂ laser cutting quality of polymeric materials. *Journal of Materials Processing Technology* **2008**, *198* (1), 99-104.
22. Choudhury, I. A.; Shirley, S., Laser cutting of polymeric materials: An experimental investigation. *Optics & Laser Technology* **2010**, *42* (3), 503-508.
23. Yuan, D.; Das, S., Experimental and theoretical analysis of direct-write laser micromachining of polymethyl methacrylate by CO₂ laser ablation. *Journal of Applied Physics* **2007**, *101* (2), 024901.

24. Shashi, P.; Subrata, K., Profile and depth prediction in single-pass and two-pass CO₂ laser microchanneling processes. *Journal of Micromechanics and Microengineering* **2015**, *25* (3), 035010.
25. Temiz, Y.; Lovchik, R. D.; Kaigala, G. V.; Delamarche, E., Lab-on-a-chip devices: How to close and plug the lab? *Microelectronic Engineering* **2015**, *132*, 156-175.
26. Zhu, X.; Liu, G.; Guo, Y.; Tian, Y., Study of PMMA thermal bonding. *Microsyst Technol* **2007**, *13* (3-4), 403-407.
27. Liu, J.; Qiao, H.; Liu, C.; Xu, Z.; Li, Y.; Wang, L., Plasma assisted thermal bonding for PMMA microfluidic chips with integrated metal microelectrodes. *Sensor. Actuat. B-Chem.* **2009**, *141* (2), 646-651.
28. Duan, H.; Zhang, L.; Chen, G., Plasticizer-assisted bonding of poly(methyl methacrylate) microfluidic chips at low temperature. *Journal of Chromatography A* **2010**, *1217* (1), 160-166.
29. Toossi, A.; Moghadas, H.; Daneshmand, M.; Sameoto, D., Bonding PMMA microfluidics using commercial microwave ovens. *Journal of Micromechanics and Microengineering* **2015**, *25* (8), 085008.
30. Luo, Y.; Zhang, Z.; Wang, X.; Zheng, Y., Ultrasonic bonding for thermoplastic microfluidic devices without energy director. *Microelectronic Engineering* **2010**, *87* (11), 2429-2436.
31. Arshya, B.; Alireza, N.; Hossein, K., A new simple and fast thermally-solvent assisted method to bond PMMA–PMMA in micro-fluidics devices. *Journal of Micromechanics and Microengineering* **2016**, *26* (6), 065017.
32. Gan, Z.; Zhang, L.; Chen, G., Solvent bonding of poly(methyl methacrylate) microfluidic chip using phase-changing agar hydrogel as a sacrificial layer. *Electrophoresis* **2011**, *32* (23), 3319-3323.
33. Ogilvie, I. R. G.; Sieben, V. J.; Floquet, C. F. A.; Zmijan, R.; Mowlem, M. C.; Morgan, H., Reduction of surface roughness for optical quality microfluidic devices in PMMA and COC. *Journal of Micromechanics and Microengineering* **2010**, *20* (6), 065016.
34. Tsao, C.-W.; DeVoe, D., Bonding of thermoplastic polymer microfluidics. *Microfluid Nanofluid* **2009**, *6* (1), 1-16.
35. Wasay, A.; Sameoto, D., Gecko gaskets for self-sealing and high-strength reversible bonding of microfluidics. *Lab on a Chip* **2015**, *15* (13), 2749-2753.
36. Lutz, R.; Oliver, S.; Bernd, F.; Roland, Z.; Peter, K., Adhesive bonding of microfluidic chips: influence of process parameters. *Journal of Micromechanics and Microengineering* **2010**, *20* (8), 087003.

37. Yu, H.; Chong, Z. Z.; Tor, S. B.; Liu, E.; Loh, N. H., Low temperature and deformation-free bonding of PMMA microfluidic devices with stable hydrophilicity via oxygen plasma treatment and PVA coating. *RSC Advances* **2015**, 5 (11), 8377-8388.
38. Myra, T. K.; Jintana, N.; Yuanyuan, W.; Ryan, T. F.; Vincent, T. R., Cost-efficient fabrication techniques for microchips and interconnects enabled by polycaprolactone. *Journal of Micromechanics and Microengineering* **2012**, 22 (11), 115030.
39. Ikawa, M.; Yamada, T.; Matsui, H.; Minemawari, H.; Tsutsumi, J. y.; Horii, Y.; Chikamatsu, M.; Azumi, R.; Kumai, R.; Hasegawa, T., Simple push coating of polymer thin-film transistors. *Nature Communications* **2012**, 3, 1176.
40. Kant, R.; Gupta, A.; Bhattacharya, S.; Joshi, S. N.; Dixit, U. S., Studies on CO₂ Laser Micromachining on PMMA to Fabricate Micro Channel for Microfluidic Applications. *Lasers Based Manufacturing: 5th International and 26th All India Manufacturing Technology* **2015**, 221-238.
41. Muhammad, I.; Rosly, A. R.; Mukhtar, A.; Majid, N. A.; Arslan, U.; Abdul, S., Fabrication of microchannels on PMMA using a low power CO₂ laser. *Laser Physics* **2016**, 26 (9), 096101.
42. Nimai, C. N.; Lam, Y. C.; Yue, C. Y.; Ayan, T. S., CO₂ -laser micromachining of PMMA: the effect of polymer molecular weight. *Journal of Micromechanics and Microengineering* **2008**, 18 (9), 095020.
43. Mashaghi, S.; Abbaspourrad, A.; Weitz, D. A.; van Oijen, A. M., Droplet microfluidics: A tool for biology, chemistry and nanotechnology. *TrAC Trends in Analytical Chemistry* **2016**, 82, 118-125.
44. Tice, J. D.; Song, H.; Lyon, A. D.; Ismagilov, R. F., Formation of Droplets and Mixing in Multiphase Microfluidics at Low Values of the Reynolds and the Capillary Numbers. *Langmuir* **2003**, 19 (22), 9127-9133.
45. Liu, S.; Gu, Y.; Le Roux, R. B.; Matthews, S. M.; Bratton, D.; Yunus, K.; Fisher, A. C.; Huck, W. T. S., The electrochemical detection of droplets in microfluidic devices. *Lab on a Chip* **2008**, 8 (11), 1937-1942.
46. Liu, H.; Crooks, R. M., Highly reproducible chronoamperometric analysis in microdroplets. *Lab on a Chip* **2013**, 13 (7), 1364-1370.
47. Wu, C.; Shah, A.; Ye, H.; Chen, X.; Ye, J.; Jiang, H.; Chen, B.; Wang, X.; Yan, H., Droplet electrochemical study of the pH dependent redox behavior of novel ferrocenyl-carborane derivatives and its application in specific cancer cell recognition. *Anal. Chim. Acta* **2015**, 857, 39-45.
48. Rattanarat, P.; Suea-Ngam, A.; Ruecha, N.; Siangproh, W.; Henry, C. S.; Srisa-Art, M.; Chailapakul, O., Graphene-polyaniline modified electrochemical droplet-based microfluidic

sensor for high-throughput determination of 4-aminophenol. *Anal. Chim. Acta* **2016**, 925, 51-60.

49. Gu, S.; Lu, Y.; Ding, Y.; Li, L.; Song, H.; Wang, J.; Wu, Q., A droplet-based microfluidic electrochemical sensor using platinum-black microelectrode and its application in high sensitive glucose sensing. *Biosens. Bioelectron.* **2014**, 55, 106-112.

50. Lin, X.; Hu, X.; Bai, Z.; He, Q.; Chen, H.; Yan, Y.; Ding, Z., A microfluidic chip capable of switching W/O droplets to vertical laminar flow for electrochemical detection of droplet contents. *Anal. Chim. Acta* **2014**, 828, 70-79.

51. Hu, X.; Lin, X.; He, Q.; Chen, H., Electrochemical detection of droplet contents in polystyrene microfluidic chip with integrated micro film electrodes. *J. Electroanal. Chem.* **2014**, 726, 7-14.

52. Abadie, T.; Sella, C.; Thouin, L., Electrochemical detection of droplet content in microfluidic devices: Evidence of internal recirculating convection within droplets. *Electrochem. Commun.* **2017**, 80, 55-59.

53. Teh, S.-Y.; Lin, R.; Hung, L.-H.; Lee, A. P., Droplet microfluidics. *Lab on a Chip* **2008**, 8 (2), 198-220.

54. Vesel, A.; Mozetic, M., Surface modification and ageing of PMMA polymer by oxygen plasma treatment. *Vacuum* **2012**, 86 (6), 634-637.

55. Henry, A. C.; Tutt, T. J.; Galloway, M.; Davidson, Y. Y.; McWhorter, C. S.; Soper, S. A.; McCarley, R. L., Surface Modification of Poly(methyl methacrylate) Used in the Fabrication of Microanalytical Devices. *Anal. Chem.* **2000**, 72 (21), 5331-5337.

56. Li, D.; Li, X.; Chen, C.; Zheng, Z.; Chang, H., Monodisperse water-in-oil-in-water emulsions generation for synthesising alginate hydrogel microspheres via locally hydrophobic modification to PMMA microchannels. *Sensor. Actuat. B-Chem.* **2018**, 255, 1048-1056.

57. Ortiz, R.; Chen, J. L.; Stuckey, D. C.; Steele, T. W. J., Poly(methyl methacrylate) Surface Modification for Surfactant-Free Real-Time Toxicity Assay on Droplet Microfluidic Platform. *ACS Appl. Mater. Inter.* **2017**, 9 (15), 13801-13811.

58. Xi, H.-D.; Zheng, H.; Guo, W.; Ganan-Calvo, A. M.; Ai, Y.; Tsao, C.-W.; Zhou, J.; Li, W.; Huang, Y.; Nguyen, N.-T.; Tan, S. H., Active droplet sorting in microfluidics: a review. *Lab on a Chip* **2017**, 17 (5), 751-771.

59. Anciaux, S. K.; Geiger, M.; Bowser, M. T., 3D Printed Micro Free-Flow Electrophoresis Device. *Anal. Chem.* **2016**, 88 (15), 7675-7682.

60. Xiaotong, F.; Nicholas, M.; Markela, I.; Francesca, C.; R., G. Z., Microfluidic free-flow zone electrophoresis and isotachopheresis using carbon black nano-composite PDMS sidewall membranes. *Electrophoresis* **2017**, *38* (2), 327-334.
61. Lakey, P. S. J.; Berkemeier, T.; Tong, H.; Arangio, A. M.; Lucas, K.; Pöschl, U.; Shiraiwa, M., Chemical exposure-response relationship between air pollutants and reactive oxygen species in the human respiratory tract. *Scientific Reports* **2016**, *6*, 32916.
62. Pöschl, U.; Shiraiwa, M., Multiphase Chemistry at the Atmosphere–Biosphere Interface Influencing Climate and Public Health in the Anthropocene. *Chem. Rev.* **2015**, *115* (10), 4440-4475.
63. Rich, D. Q.; Özkaynak, H.; Crooks, J.; Baxter, L.; Burke, J.; Ohman-Strickland, P.; Thevenet-Morrison, K.; Kipen, H. M.; Zhang, J.; Kostis, J. B.; Lunden, M.; Hodas, N.; Turpin, B. J., The Triggering of Myocardial Infarction by Fine Particles Is Enhanced When Particles Are Enriched in Secondary Species. *Environmental Science & Technology* **2013**, *47* (16), 9414-9423.
64. Lippmann, M.; Frampton, M.; Schwartz, J.; Dockery, D.; Schlesinger, R.; Koutrakis, P.; Froines, J.; Nel, A.; Finkelstein, J.; Godleski, J.; Kaufman, J.; Koenig, J.; Larson, T.; Luchtel, D.; Liu, L.-J. S.; Oberdörster, G.; Peters, A.; Sarnat, J.; Sioutas, C.; Suh, H.; Sullivan, J.; Utell, M.; Wichmann, E.; Zelikoff, J., The US Environmental Protection Agency particulate matter health effects research centers program: A midcourse report of status, progress, and plans. *Environ Health Persp* **2003**, *111*.
65. Peters, A.; Dockery, D. W.; Muller, J. E.; Mittleman, M. A., Increased particulate air pollution and the triggering of myocardial infarction. *Circulation* **2001**, *103*.
66. Pope, C. A.; Dockery, D. W., Health Effects of Fine Particulate Air Pollution: Lines that Connect. *Journal of the Air & Waste Management Association* **2006**, *56* (6), 709-742.
67. Lelieveld, J.; Evans, J. S.; Fnais, M.; Giannadaki, D.; Pozzer, A., The contribution of outdoor air pollution sources to premature mortality on a global scale. *Nature* **2015**, *525* (7569), 367-371.
68. Verma, V.; Fang, T.; Xu, L.; Peltier, R. E.; Russell, A. G.; Ng, N. L.; Weber, R. J., Organic Aerosols Associated with the Generation of Reactive Oxygen Species (ROS) by Water-Soluble PM_{2.5}. *Environmental Science & Technology* **2015**, *49* (7), 4646-4656.
69. Antinolo, M.; Willis, M. D.; Zhou, S.; Abbatt, J. P. D., Connecting the oxidation of soot to its redox cycling abilities. *Nat Commun* **2015**, *6*.
70. Charrier, J. G.; Anastasio, C., On dithiothreitol (DTT) as a measure of oxidative potential for ambient particles: evidence for the importance of soluble transition metals. *Atmospheric chemistry and physics (Print)* **2012**, *12* (5), 11317-11350.

71. Charrier, J. G.; Richards-Henderson, N. K.; Bein, K. J.; McFall, A. S.; Wexler, A. S.; Anastasio, C., Oxidant production from source-oriented particulate matter – Part 1: Oxidative potential using the dithiothreitol (DTT) assay. *Atmos. Chem. Phys.* **2015**, *15* (5), 2327-2340.
72. Charrier, J. G.; Anastasio, C., Rates of Hydroxyl Radical Production from Transition Metals and Quinones in a Surrogate Lung Fluid. *Environmental Science & Technology* **2015**, *49* (15), 9317-9325.
73. Charrier, J. G.; McFall, A. S.; Richards-Henderson, N. K.; Anastasio, C., Hydrogen Peroxide Formation in a Surrogate Lung Fluid by Transition Metals and Quinones Present in Particulate Matter. *Environmental Science & Technology* **2014**, *48* (12), 7010-7017.
74. Squadrito, G. L.; Cueto, R.; Dellinger, B.; Pryor, W. A., Quinoid redox cycling as a mechanism for sustained free radical generation by inhaled airborne particulate matter. *Free Radic Biol Med* **2001**, *31*.
75. Liu, F.; Huang, Y.; Zhang, F.; Chen, Q.; Wu, B.; Rui, W.; Zheng, J. C.; Ding, W., Macrophages treated with particulate matter PM_{2.5} induce selective neurotoxicity through glutaminase-mediated glutamate generation. *Journal of Neurochemistry* **2015**, *134* (2), 315-326.
76. Xing, Y.-F.; Xu, Y.-H.; Shi, M.-H.; Lian, Y.-X., The impact of PM_{2.5} on the human respiratory system. *Journal of Thoracic Disease* **2016**, *8* (1), E69-E74.
77. Vliet, A. v. d.; O'Neill, C. A.; Cross, C. E.; Koostra, J. M.; Volz, W. G.; Halliwell, B.; Louie, S., Determination of low-molecular-mass antioxidant concentrations in human respiratory tract lining fluids. *American Journal of Physiology-Lung Cellular and Molecular Physiology* **1999**, *276* (2), L289-L296.
78. Shi, J.; Chen, F. e.; Cai, Y.; Fan, S.; Cai, J.; Chen, R.; Kan, H.; Lu, Y.; Zhao, Z., Validation of a light-scattering PM_{2.5} sensor monitor based on the long-term gravimetric measurements in field tests. *PLoS ONE* **2017**, *12* (11), e0185700.
79. Zhang, Y.-L.; Cao, F., Fine particulate matter (PM_{2.5}) in China at a city level. *Scientific Reports* **2015**, *5*, 14884.
80. Pérez, V. I.; Buffenstein, R.; Masamsetti, V.; Leonard, S.; Salmon, A. B.; Mele, J.; Andziak, B.; Yang, T.; Edrey, Y.; Friguet, B.; Ward, W.; Richardson, A.; Chaudhuri, A., Protein stability and resistance to oxidative stress are determinants of longevity in the longest-living rodent, the naked mole-rat. *Proceedings of the National Academy of Sciences* **2009**, *106* (9), 3059-3064.
81. Gurgueira, S. A.; Lawrence, J.; Coull, B.; Murthy, G. G. K.; González-Flecha, B., Rapid increases in the steady-state concentration of reactive oxygen species in the lungs and heart after particulate air pollution inhalation. *Environmental Health Perspectives* **2002**, *110* (8), 749-755.

82. Bates, J. T.; Weber, R. J.; Abrams, J.; Verma, V.; Fang, T.; Klein, M.; Strickland, M. J.; Sarnat, S. E.; Chang, H. H.; Mulholland, J. A.; Tolbert, P. E.; Russell, A. G., Reactive Oxygen Species Generation Linked to Sources of Atmospheric Particulate Matter and Cardiorespiratory Effects. *Environmental Science & Technology* **2015**, 49 (22), 13605-13612.
83. Cho, A. K.; Sioutas, C.; Miguel, A. H.; Kumagai, Y.; Schmitz, D. A.; Singh, M.; Eiguren-Fernandez, A.; Froines, J. R., Redox activity of airborne particulate matter at different sites in the Los Angeles Basin. *Environmental Research* **2005**, 99 (1), 40-47.
84. Cho, A. K.; Di Stefano, E.; You, Y.; Rodriguez, C. E.; Schmitz, D. A.; Kumagai, Y.; Miguel, A. H.; Eiguren-Fernandez, A.; Kobayashi, T.; Avol, E.; Froines, J. R., Determination of Four Quinones in Diesel Exhaust Particles, SRM 1649a, and Atmospheric PM_{2.5} Special Issue of Aerosol Science and Technology on Findings from the Fine Particulate Matter Supersites Program. *Aerosol Science and Technology* **2004**, 38, 68-81.
85. Joseph Y. Abrams, R. J. W., 2 Mitchel Klein, 3 Stefanie E. Samat, 3 Howard H. Chang, 4 Matthew J. Strickland, 5 Vishal Verma, 6 Ting Fang, 2 Josephine T. Bates, 7 James A. Mulholland, 7 Armistead G. Russell, 7 and Paige E. Tolbert 3, Associations between Ambient Fine Particulate Oxidative Potential and Cardiorespiratory Emergency Department Visits. *Environ Health Perspect* **2017**.
86. Xiong, Q.; Yu, H.; Wang, R.; Wei, J.; Verma, V., Rethinking Dithiothreitol-Based Particulate Matter Oxidative Potential: Measuring Dithiothreitol Consumption versus Reactive Oxygen Species Generation. *Environmental Science & Technology* **2017**, 51 (11), 6507-6514.
87. Quinn, C.; Miller-Lionberg, D. D.; Klunder, K.; Kwon, J.; Noth, E. M.; Mehaffy, J.; Leith, D.; Magzamen, S.; Hammond, S. K.; Henry, C. S.; Volckens, J., Personal Exposure to PM_{2.5} Black Carbon and Particles with Oxidative Potential using an Automated Microenvironmental Aerosol Sampler (AMAS). *Submitted* **2018**.
88. Chow, J. C.; Watson, J. G.; Green, M. C.; Frank, N. H., Filter light attenuation as a surrogate for elemental carbon. *Journal of the Air & Waste Management Association* **2010**, 60 (11), 1365-1375.
89. Künzli, N.; Mudway, I. S.; Götschi, T.; Shi, T.; Kelly, F. J.; Cook, S.; Burney, P.; Forsberg, B.; Gauderman, J. W.; Hazenkamp, M. E., Comparison of oxidative properties, light absorbance, and total and elemental mass concentration of ambient PM_{2.5} collected at 20 European sites. *Environmental health perspectives* **2006**, 114 (5), 684.
90. Sameenoi, Y.; Panymeesamer, P.; Supalakorn, N.; Koehler, K.; Chailapakul, O.; Henry, C. S.; Volckens, J., Microfluidic paper-based analytical device for aerosol oxidative activity. *Environmental science & technology* **2012**, 47 (2), 932-940.

91. Charrier, J. G.; McFall, A. S.; Vu, K. K.; Baroi, J.; Olea, C.; Hasson, A.; Anastasio, C., A bias in the “mass-normalized” DTT response–An effect of non-linear concentration-response curves for copper and manganese. *Atmospheric Environment* **2016**, *144*, 325-334.
92. Fang, T.; Verma, V.; Guo, H.; King, L.; Edgerton, E.; Weber, R., A semi-automated system for quantifying the oxidative potential of ambient particles in aqueous extracts using the dithiothreitol (DTT) assay: results from the Southeastern Center for Air Pollution and Epidemiology (SCAPE). *Atmospheric Measurement Techniques* **2015**, *8* (1), 471-482.
93. Griveau, S.; Gulppi, M.; Pavez, J.; Zagal, J. H.; Bedioui, F., Cobalt Phthalocyanine-Based Molecular Materials for the Electrocatalysis and Electroanalysis of 2-Mercaptoethanol, 2-Mercaptoethanesulfonic Acid, Reduced Glutathione and L-Cysteine. *Electroanal.* **2003**, *15* (9), 779-785.
94. Li, H.; Guarr, T. F., Electrochemistry at modified electrodes: Electronically conductive metallophthalocyanine coatings. *Synthetic Met.* **1990**, *38* (2), 243-251.
95. Chapovetsky, A.; Welborn, M.; Luna, J. M.; Haiges, R.; Miller, T. F.; Marinescu, S. C., Pendant Hydrogen-Bond Donors in Cobalt Catalysts Independently Enhance CO₂ Reduction. *ACS Central Science* **2018**, *4* (3), 397-404.
96. Sameenoi, Y.; Koehler, K.; Shapiro, J.; Boonsong, K.; Sun, Y.; Collett, J.; Volckens, J.; Henry, C. S., Microfluidic Electrochemical Sensor for On-Line Monitoring of Aerosol Oxidative Activity. *J. Am. Chem. Soc.* **2012**, *134* (25), 10562-10568.
97. Klunder, K. J.; Nilsson, Z.; Sambur, J. B.; Henry, C. S., Patternable Solvent-Processed Thermoplastic Graphite Electrodes. *J. Am. Chem. Soc.* **2017**, *139* (36), 12623-12631.
98. Charrier, J. G.; McFall, A. S.; Vu, K. K. T.; Baroi, J.; Olea, C.; Hasson, A.; Anastasio, C., A bias in the “mass-normalized” DTT response – An effect of non-linear concentration-response curves for copper and manganese. *Atmospheric Environment* **2016**, *144*, 325-334.

CHAPTER 4: SUBSTITUTED PHTHALOCYANINES- SYNTHESIS, CHARACTERIZATION AND ELECTROCHEMISTRY

4.1 Introduction

Overview

Phthalocyanines (Pc) are a high value molecule used widely in both fundamental research and commercial applications.¹ Commercially, Pcs are found in compact discs, paints, dyes for textiles, and even tattoos.² Cobalt-Pc is used industrially for removing the odor from sulfur compounds found in petroleum.³ Overall, in excess of 60,000 tons of Pcs are synthesized annually.⁴ From a research stand point, Pc have been studied for LCDs,⁵ gas sensors,⁶ non-linear optics,⁷ drug delivery,⁸ photodynamic cancer therapy,⁹ water splitting,¹⁰ a catalyst for methanol oxidation,¹¹ CO₂ and oxygen reduction,¹²⁻¹³ sensitizers and hole transport layers in solar cells,¹⁴⁻¹⁵ electrochromics,¹⁶ and fundamental studies on imaging of single atoms.¹⁷ Pcs are also widely used in sensing, with applications in field-effect transistor (FET) sensors, solid-state ionic and capacitance sensors, mass-sensitive sensors, surface acoustic-wave (SAW) measurements, chemiresistive gas vapor sensors, and electrochemical sensors.¹⁸

Electrochemical sensors are a focus of this thesis and a motivation for the work presented in this chapter. Pcs have a long and successful history within the field of electrochemical sensing. A small list of example sensors, which is in no way all-encompassing, includes the sensing of hydrogen peroxide,¹⁹ dithiotheritol,²⁰ cystiene,²¹ glutathione,²² epinephrine and norepinephrine,²³ 2-mercaptoethanol and 2-

mercaptoethanesulfonic acid,²⁴ acetic acid,²⁵ thiocyanate and selenocyanate,²⁶ rutin,²⁷ 4-chlorophenol,²⁸ guanine,²⁹ acetaminophen,³⁰ diethylstilbestrol,³¹ ascorbic acid,³² dissolved oxygen,³³ 4-aminophenol,³⁴ dopamine,³⁵ NADH,³⁶ bisphenol-A,³⁵ phosphate,³⁷ glyphosate,³⁸ nitrite,³⁹ caffeine,⁴⁰ l-dopa,⁴⁰ hydrazine,⁴¹ carbaryl,⁴² carbofuran and diuron,⁴³ dipyrone,⁴⁴ and heavy metals including Ag⁺ and Hg²⁺.⁴⁵⁻⁴⁷

It is the enormous potential of Pc materials that have motivated the work presented within this chapter. The chapter details the synthesis and electrochemistry of new Pc derivatives specifically designed for electrochemical polymerization and potential electrochemical catalysis applications. Electropolymerization allows for uniform electrode coatings, as well as control over the coating thickness. A brief overview of the electrocatalysis of phthalocyanines is discussed in this chapter, the background underlies the molecules chosen for synthesis and also motivates future work with the newly synthesized Pc derivatives. Pc enabled sensors are discussed in Chapter 3, and some of the knowledge and themes from this chapter can be applied there as well. Chapter 5 will introduce catalytic electrochemically grown polymer films made from tetraaminophthalocyanine which further underscore the utility and applicability of polymeric Pc electrode coatings which are presented in this chapter.

General synthesis of phthalocyanines (Pc) and substituted Pcs

The first phthalocyanines were unknowingly synthesized in chemical factories from 1907 to 1927. The initial reports of a highly stable and brightly colored compound are now understood to be phthalocyanine complexes. The colored products were the side reaction from the use of 1,2 di-substituted benzene derivatives, such as phthalonitrile, combined

with a metal.⁴⁸ Around 1934, Linstead and coworkers were the first to elucidate the structure and report the synthesis of phthalocyanines.⁴⁹ The initial work by Linstead gave chemists the understanding and tools to realize the synthesis of thousands of different Pc derivatives.

The exact mechanism behind the synthesis of phthalocyanines is not fully known. However, the process involves the cyclization of 4 monomer units around a metal center, often referred to as cyclotetramerization. Cyclotetramerization to form Pcs occurs when four di-substituted molecules form oligomers that template around a metal center. One of the more popular di-substituted precursors being phthalonitrile.⁵⁰ A proposed mechanism for phthalocyanine formation is presented in Figure 4.1.⁵¹ The process is catalyzed in the presence of a base, the strong hindered base 1,8-Diazabicycloundecene (DBU) is commonly used with the di-nitrile synthetic route.

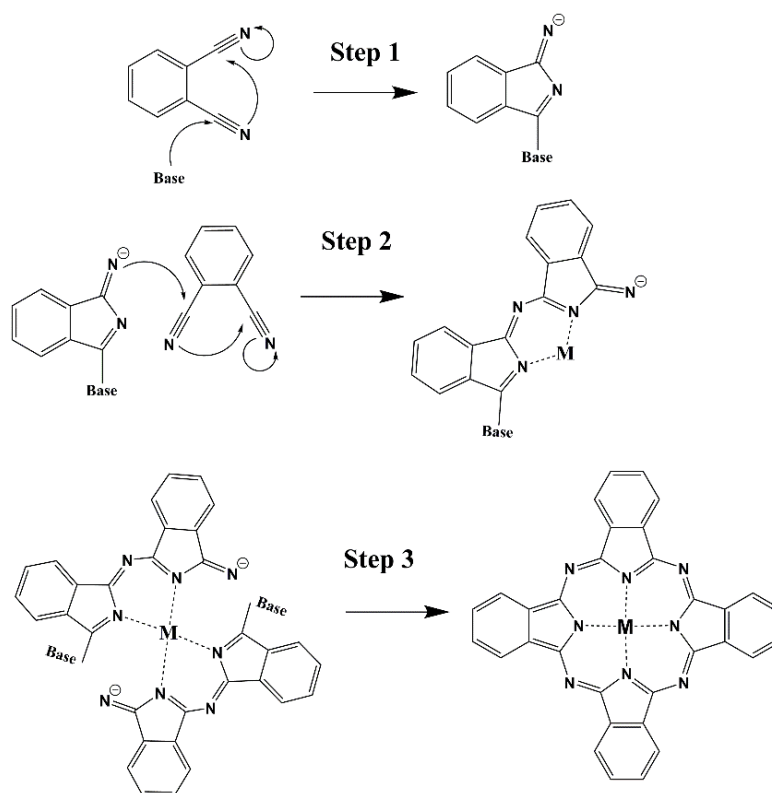


Figure 4.1 Phthalonitrile synthetic route and proposed reaction mechanism for phthalocyanine cyclotetramerization.

In step one of the reaction, a base is proposed to attack the carbon on the cyano-group, which initiates a ring closure. Similar molecules to the product in step one have been isolated as an intermediate, observed as a nickel chelate in the synthesis of NiPc.⁵² The second and third steps most likely happen quickly and involve templating the newly formed diiminoisoindoline-based oligomers around the metal, followed by repeated or concerted nucleophilic attack. The formation of the diiminoisoindoline derivatives often make the reaction mixture a deep red color, which soon changes to deep blue/black upon phthalocyanine formation. Importantly, step 3 involves the oxidation of the base, to

provide 2 e⁻ to the Pc final ring structure. In the case where an alcohol is used as the base, the alcohol is oxidized to form an aldehyde.⁵²

Overview on the functionalization of Pcs

Derivatives of phthalocyanines can be easily synthesized. Since Pc synthesis is a focus of this chapter, it is worthwhile discussing briefly some popular synthetic strategies for creating derivatives. Reasons to make derivatives of the Pc structure are to change the optical or electronic properties, tune solubility, create or prevent aggregation, enhance catalysis, improve chemical resistance or stability, or enable incorporation into polymeric materials.^{50, 53-54} Derivatization can be done before or after cyclization, however, often it is performed first as it is easier to characterize the small molecule Pc precursor. Every position on the ring is available for derivatization, a few simple derivatives are shown in Figure 4.2.

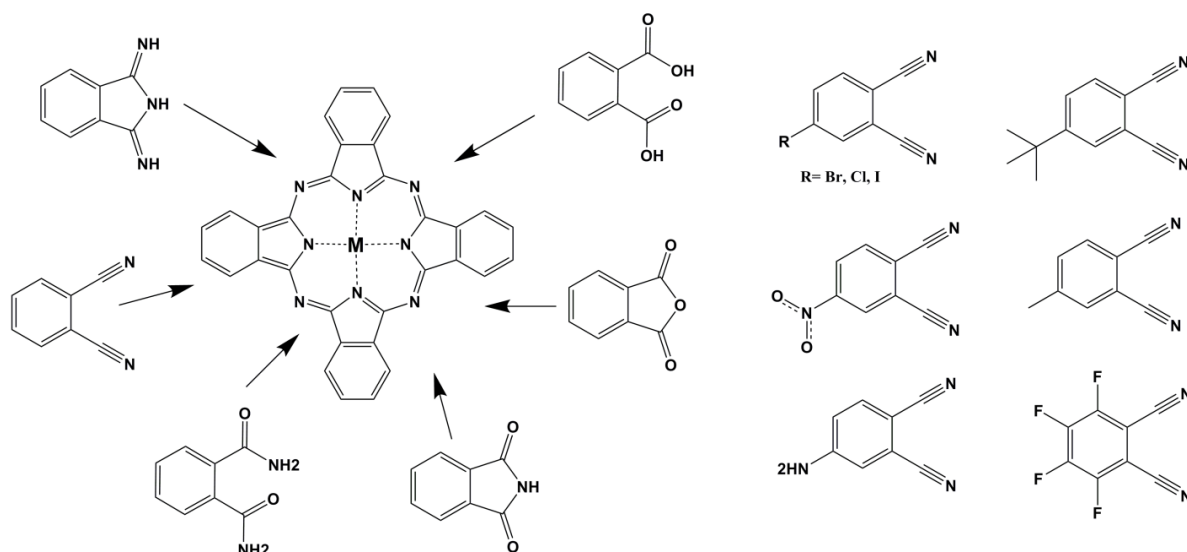


Figure 4.2 (left) Phthalocyanine starting materials commonly used to form the core Pc cyclotetramerization product. (right) commercially available phthalonitrile derivatives commonly used for creating Pc derivatives.

Shown in Figure 4.2 (left) are starting materials commonly used in Pc synthesis, starting materials that contain the amide, anhydride and carboxylic acid moieties require a nitrogen source, most often urea. The nitrogen source converts the oxygen containing functional groups to diiminoisoindoline, the process happens *in-situ*, enabling cyclotetramerization and formation of the Pc ring. Anhydrides are inexpensive, as is urea, and this particular synthetic route is one of the lowest costs ways to produce Pcs. The anhydride route is a dirty process for phthalocyanine synthesis. If possible, the phthalonitrile route is preferred.⁵⁵

When making a Pc derivative, it is often useful to work with starting materials that are commercially available. Figure 2.2 (right) shows some common commercially available phthalonitrile derivatives. Useful molecules for functionalizing phthalocyanines are halides, especially chloro, bromo, or iodo groups.⁵⁶ Halides can undergo Suzuki coupling or Buchwald Hartwig reactions,⁵⁷ as well as others.⁵⁸⁻⁵⁹ Phthalonitrile is an extremely useful reagent as it can undergo a nitro-displacement in the presence of a base and a sufficient nucleophile.⁶⁰ Both nitro displacement and Suzuki couplings are used in this chapter.

Overview & background on the catalytic nature of phthalocyanines

Phthalocyanines are commonly used in catalysis, they are exceptionally chemically stable and can be highly catalytically active. The molecules that are synthesized and tested electrochemically in this chapter are meant for generic electrochemical catalysis applications and it is worth discussing the underlying factors effecting the catalysis of Pcs briefly in this section.

Phthalocyanines can be made without a metal center; however, Pcs containing a metal center are most often used for catalysis. The metal center provides a coordination site to facilitate catalysis. Common metals found in Pcs are Mn, Fe, Cu, Ti, Zn, Co, Ni, Ru, Si, most of which are first row transition metals. First row transitional metals like Fe, Ni, Co, and Cu are normally found in the 2+ state, the Pc ligand carries a 2- charge, which makes a neutral molecule.

Figure 4.3 shows the orbital filling for Fe, Ni, Co, and Cu phthalocyanines and is adapted from an article on the magnetism of phthalocyanines.⁵³ Fe and Co are typically used in catalysis for applications in thiol oxidation, oxygen reduction, or CO₂ reduction.⁶¹ FePc and CoPc are described in simple terms as having more d-orbital character, where these unfilled D orbitals are available to coordinate or bind to a reactant and facilitate charge transfer (catalysis).¹² It has been shown with scanning tunneling microscopy that CoPc has a prominent D_z² protrusion. In contrast there is a hole where the metal center is located in CuPc. ⁶² NiPc and CuPc often make for a poor catalyst, attributed to their mostly full d-orbitals.

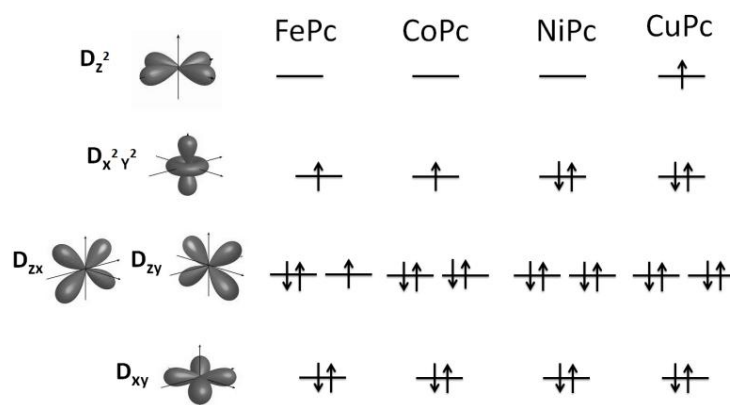


Figure 4.3 (left) Orbital filling for various un-substituted phthalocyanines.

The diagram (Figure 4.3) is a generic representation of un-substituted phthalocyanines d-orbital energy levels. The relative energies of the metal-Pc macrocycle frontier orbitals can shift based on the type of metal center, electron donating or withdrawing groups on the Pc ring, adsorption onto a substrate, as well as interactions with strong or weak field ligands in the axial position on the metal.⁶³⁻⁶⁵

Oxygen reduction reaction (ORR) catalysis is a good example of the influence of the electronic structure of the metal center. CoPc has been reported to bind with O₂ in a head on configuration, in contrast FePc binds side-on with oxygen. The frontier orbitals are thought to influence the type of binding. The difference in the binding orientation of CoPc is reported to facilitate the 2 e⁻ reduction of oxygen, while FePc is a 4 e⁻ process.⁶⁶⁻⁶⁷ An excellent and thorough review by Zagal, Nyokong, and Bediouia, summarizes reactant and catalyst orbital interactions for a variety of reactions.⁶⁸ For brevity, these interactions will not be gone into detail here and a more generic approach to thinking about phthalocyanine catalysis will be considered.

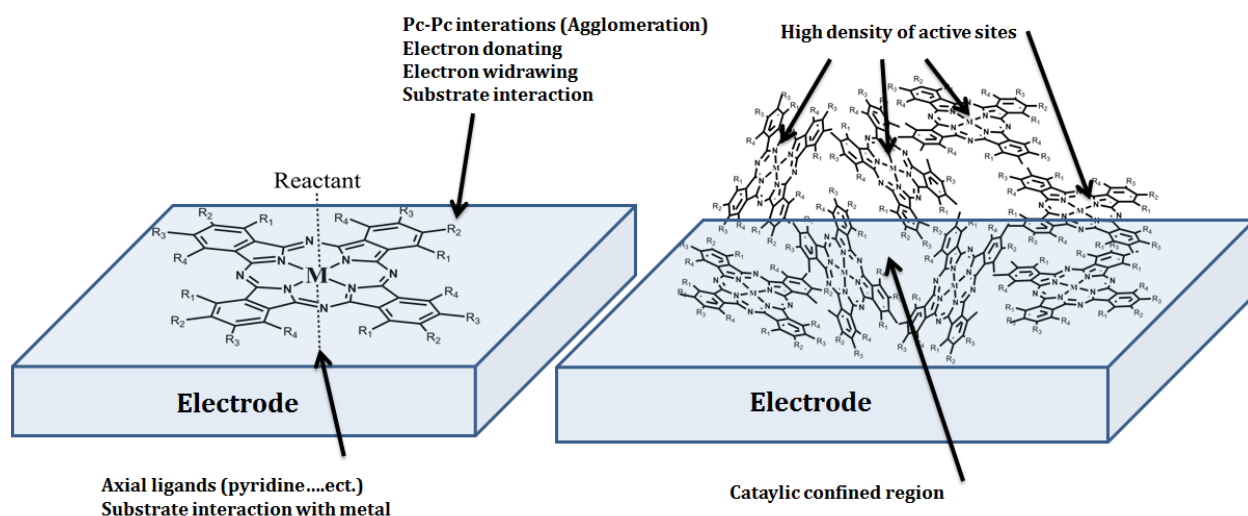


Figure 4.4 Cartoon of the various factors affecting catalysis of M-Pcs.

Figure 4.4 depicts various influences affecting the catalysis of M-Pcs. Depending on the application these factors can be addressed when synthesizing or proposing new phthalocyanines for catalytic applications. Ligation of the metal center or adsorption to a substrates can have dramatic effects on the electronic structure of the metal center in Pcs.⁶³ In a seminal work, FePc axially coordinated to pyridine showed a large increase in the catalysis of ORR.⁶⁹ Through the use of Extended X-Ray Absorption Fine Structure (EXAFs), a shift in the spectra of pyridine-FePc was correlated to a more positive Fe center, and a change in symmetry of the metal atom upon ligation with pyridine. These properties were thought to contribute to the enhanced catalysis towards ORR with the pyridine ligated FePc.

Electron withdrawing and donating substituents on the Pc ring have been extensively studied for a variety of catalytic applications. An excellent example was demonstrated with

a family of fluorinated Pc derivatives for use in thiol oxidation. It was shown that electron withdrawing groups on the ring decreased turn over frequency for thiol oxidation, however the complexes were much more stable and a large increase in turn over number was achieved.⁷⁰⁻⁷¹

The environment around the metal center can also influence catalysis. Unique environments can be created through an electropolymerized polymer which is depicted on the right side of Figure 4.4. The web of polymeric material may induce steric effects which could greatly effect catalysis.⁷² Polymeric materials can also mimic enzymes which have intricate substrate, active site and binding site interactions needed to catalyze difficult reactions.⁷³ The conditions used in electropolymerization can create a high surface area and additional coverage of active catalytic sites.⁷⁴ Related to this, the proposed new Pc derivatives in this thesis chapter should create an entangled web of polymeric phthalocyanines, including nanoconfinements,⁷⁵ which may uniquely influence electrocatalysis.⁷⁶⁻⁷⁷

Finally, volcano plots are often used to determine the optimum Pc catalyst for a given reaction. Volcano plots can help a chemist develop a new catalyst based on previous knowledge of certain Pc derivatives for a specific catalytic application. The plots are based off the Sabatier principle in heterogeneous catalysis. The Sabatier principle describes the interaction of the reacting molecule with the active catalyst site. For optimum catalysis the interaction should not be too weak nor too strong.⁷⁸

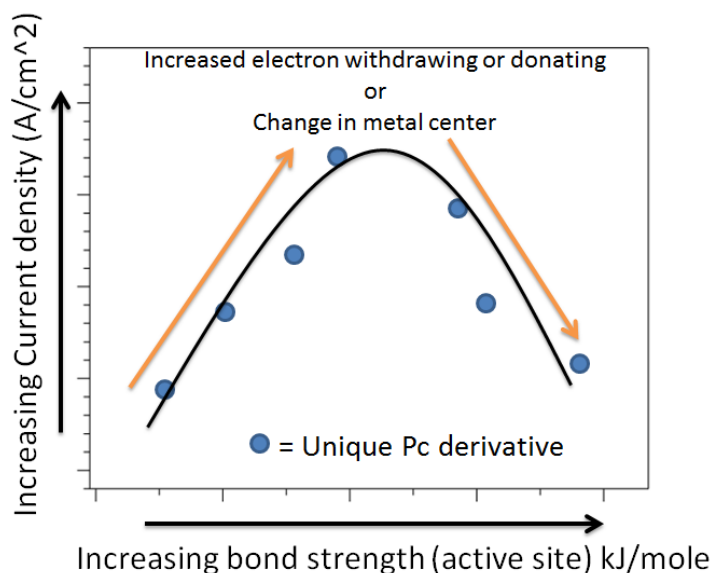


Figure 4.5 Volcano plot of hypothetical phthalocyanine derivatives for a generic catalytic process.

Figure 4.5 is a graphical representation of this concept, which was adapted from a review on Pc catalysis.⁶¹ In the first half of the plot, the current density increases (increased catalysis) with an increase in the reactant-to-active site bond strength. As the bond strength increases the interaction between the reactant and substrate is too strong and negatively affects catalysis.

Strategy for the synthesis of new electropolymerizable Pc derivatives

The strategy chosen was to modify the phthalocyanine ring with polymerizable moieties of thiophene, methoxy-thiophene, and diphenylamine. Conducting polymers such as poly-thiophene, poly-pyrrole, poly-aniline, have been known for quite some time and are well studied.⁷⁹ These molecules undergo a radical polymerization mechanism which

creates aromatic chains. This process is depicted at the top Figure 4.6 for thiophene. The general mechanism is the same for triphenylamine polymerization.⁸⁰

The conductivity of these polymers depends on an ion doping mechanism. It is a redox mechanism which incorporates or ejects ions based on the potential applied to the polymer film.⁷⁴ Thiophene and its derivatives have some of the highest conductivities for organic materials,⁸¹ which was a motivation for their initial use in this work.

Thiophene derivatives of Pcs have been reported, but are not well known. Only a handful of reports exists on their synthesis and electrochemical behavior. T. Nyokong is prominent in field of the Pc electrochemistry and has two papers on thiophene appended Pcs. However, polymerization of these molecules was not attempted.⁸²⁻⁸³ There is also one other report of a zinc thiophene appended Pc, but again, polymerization was not attempted.⁸⁴ Considering the lack of knowledge on simple thiophene Pc derivatives, the molecules shown at the bottom of Figure 4.6 were chosen as a starting point. Nickel was chosen because this metal center is the easiest to electrochemically polymerize in the case of tetraaminophthalocyanine.⁸⁵

It should also be noted that a few reports on thiophene derivatives attached to Pcs do exist. Swagger's group published a single paper on a Pc based biological mimic functionalized with ethylenedioxythiophene.⁸⁶ There is a single report of a unique 2,5-di-2-thiophen-2-yl-pyrrol-1-yl Pc derivative which was successfully electropolymerized. Yildiz and co-workers created Pc polymers using a (2-thienyl)dioxy moiety.⁸⁷ In practice these derivatives are much more complicated to make and require higher cost starting materials.

The proposed Pc derivatives shown in Figure 4.6 (bottom) are based on low cost readily available starting materials.

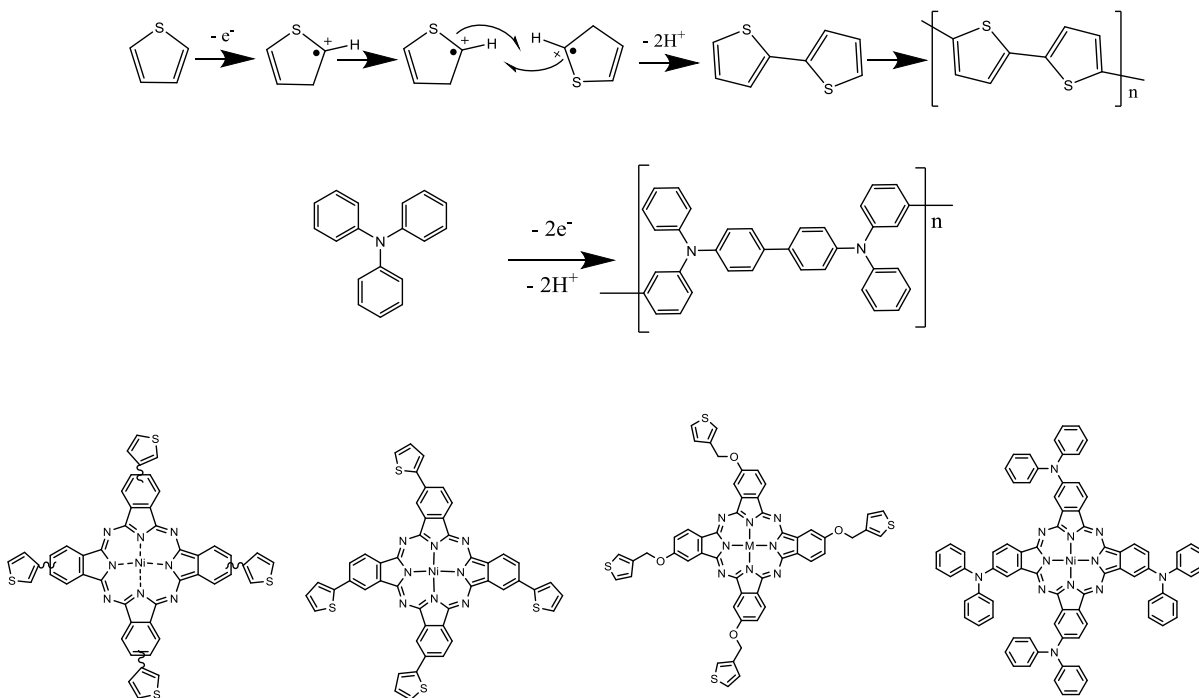


Figure 4.6 (top) Mechanism for polymerization of thiophene, (middle) diphenylamine polymer structure. (bottom) Target thiophene derivatives synthesized in this work. The molecule on the left shows possible ring positions and the molecules to the right depict one of 4 possible isomers.

The last Pc derivative proposed for synthesis is based off of triphenylamine. Triphenylamine is a relatively newer polymer material.⁸⁸⁻⁸⁹ Often triphenylamines are investigated as derivatives. As an example, thiophene is a popular molecule to attach to triphenylamine which can tune the polymerization and redox properties.⁹⁰⁻⁹¹ Various derivatives have also been examined as hole transport layers in photovoltaics.⁹²⁻⁹⁴

The literature on diphenylamine derivatized Pcs is even more sparse than thiophene Pcs derivatives. There is a single report of a similar molecule to that of the target diphenylamine Pc shown in Figure 4.6, however, it was a 3-membered ring sub-phthalocyanine, and electrochemistry was not attempted. The second report is of triphenylamine attached to the Pc ring, electropolymerization of this molecule readily occurred, and it was shown to be electrochromic.⁹⁵ In contrast, the approach in Figure 4.6 has the triphenylamine moiety incorporated into the Pc ring.

4.2 Results and Discussion

Initially 4-bromo-phthalic anhydride was used in the Suzuki reaction seen in Figure 4.7. The reaction was successful in making the desired coupling with thiophene. The phthalocyanine synthesis was then attempted using urea and the anhydride but the synthesis was unsuccessful. Recalling the discussion around Figure 4.2, the anhydride route to Pc synthesis is somewhat crude and is probably not the best choice for synthesizing new derivatives of phthalocyanines. It was decided to convert 4-bromo-phthalic anhydride to 4-bromo-phthalonitrile. The reaction conditions for the conversion are relatively mild and utilize economical chemical feedstocks.⁵⁶ In practice, it was found that high yields and pure products could be made easily with the reactions in Figure 4.7. Note that when making derivatives of phthalocyanines the ability to convert phthalic anhydride (or phthalic acid) is quite powerful in cases where the cyano group may be vulnerable or deactivating.

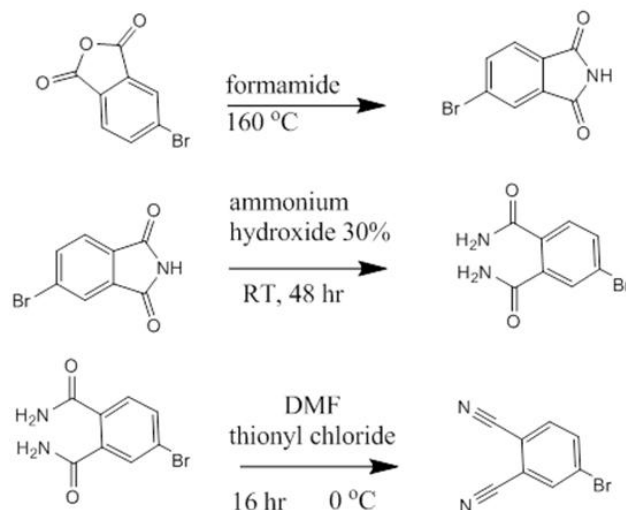


Figure 4.7 Conversion of 4-bromo-phthalic anhydride into 4-bromo-phthalonitrile.

The Suzuki–Miyaura reaction, or Suzuki coupling, was used to couple thiophene to phthalonitrile. The palladium(0) catalyst is quite sensitive to moisture and air and precautions were taken to remove them from the reaction flask. The coupling was performed with a Shlenk line, heating glassware under nitrogen to remove moisture, and a desiccant was used to scrub water from the nitrogen tank. Despite the efforts, the yields were low and the reaction proceeded slowly. The results are surprising since electron withdrawing groups on the halogen containing reactant typically increase oxidative addition, which typically is the rate limiting step in Suzuki couplings.⁹⁶ Nonetheless, 4-(2-thienyl)-phthalonitrile and 4-(3-thienyl)-phthalonitrile were synthesized and the identity was confirmed by proton ¹H-NMR and mass spectrometry.

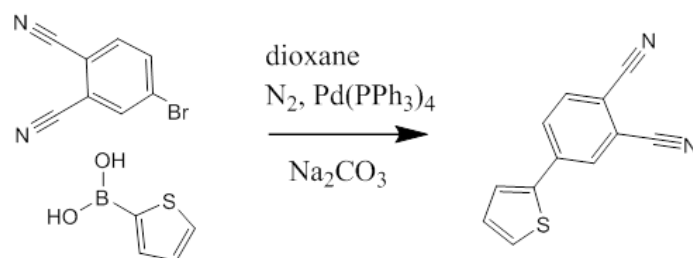


Figure 4.8 Suzuki coupling of 4-bromo-phthalonitrile with 2-thienylboronic acid.

Via Figure 4.9, the nickel derivative of the thiophene appended Pc synthesis was attempted. 1-octanol with DBU was used in the reaction, which is a common environment for the synthesis of Pcs. An oil bath to heat the flask (double boiler) is a useful tool to prevent the phthalocyanines from thermal decomposition. Precipitated Pc on the flask wall can become heated and lead to decomposition. The reaction created a blue black solid, and the resulting material was purified with copious rinsing with acetone as well as stirring in acid and base, common purification methods for Pcs.⁵⁰ Synthesis of the 3-position on thiophene was conducted using 3-thienylboronic acid and the reaction proceeded nearly identical to the 2-position. Synthesis of the phthalocyanine proceeded similar or the 2-position also.

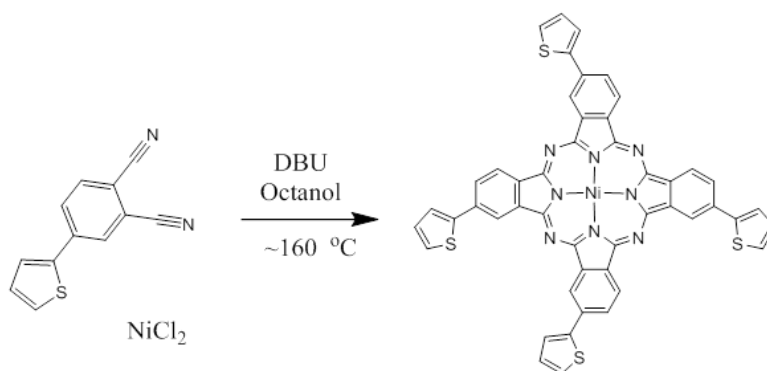


Figure 4.9 Reaction of 4-(2-thienyl)-phthalonitrile with nickel chloride to make nickel-4-(2-thienyl)-phthalocyanine.

Characterization of thiophene appended Pcs

Proton NMR was unsuccessful as a method to characterize and validate the synthesis of the thiophene derivatives. Deuterated sulfuric acid, DMSO, and DMF were attempted as NMR solvents with no real discernable peaks. Aggregation of these molecules is most likely the cause of the lack of a signal by NMR.⁹⁷ The UV-Vis spectra is seen in Figure 4.10, where the typical Q (~685 nm) and Soret (~305 nm) bands are shown. The spectra do not provide many details on purity, however they are quite convincing that the target phthalocyanine was successfully made. The spectra is very similar to the zinc thiophene Pc derivative mentioned earlier.⁸⁴

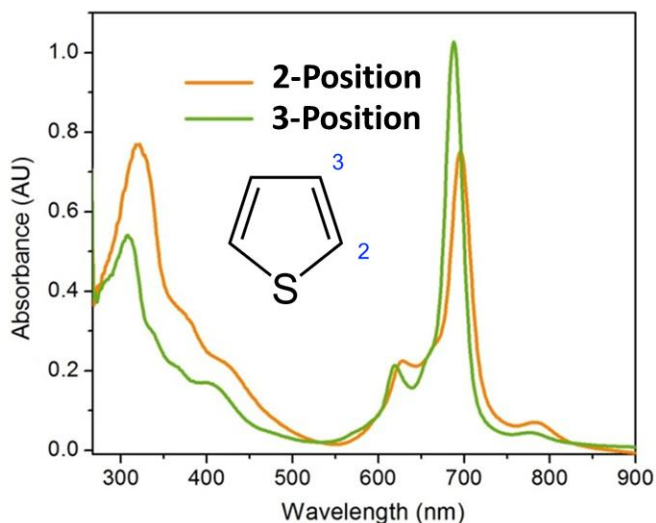


Figure 4.10 UV-Vis spectra of nickel 4-(3-thienyl)-phthalocyanine and 4-(2-thienyl)-phthalocyanine in DMSO.

Electrochemistry of thiophene Pc derivatives

The electrochemistry of nickel 4-(2-thienyl)-phthalocyanine is shown in Figure 4.11. The electrochemistry is somewhat odd in the negative region. There are redox processes occurring at -0.5 and -1.13 V vs. SCE, which are in the range of the typical 2 e⁻ ring reduction of the Pc ring,⁹⁸ however they are ill defined and irreversible. Pc ring reductions are not always, but are often reversible and well defined. The negative region does however look very similar to a previous report of a thiophene appended zinc phthalocyanine derivative.⁹³ Why the ring reductions are not reversible is unclear at this time.

Upon cycling of the monomer there is apparent increased current over the blank signal. The increase in current starts to occur at 0.6 V on the first cycle and then slowly increases in oxidation potential to about 1 V vs. SCE. The oxidation voltage is similar to that described for 3-phenylthiophene (Figure 4.13), which is a similar functional group. The current is also decreasing with increased cycle number, this could be from an insulating film being deposited on the surface of the electrode.

When the electrode was cycled repeatedly on an FTO substrate a very light blue film was observed, however, this film is not electrochemically active, and appears to be insulating. Because the 2-position on the thiophene ring is blocked it may come as no surprise that the polymerization was not successful. However, given that there are 4 thiophene groups that can react per phthalocyanine and the whole structure is aromatic, polymerization should definitely be possible. Possible reasons for the failed polymerization are discussed later in this section.

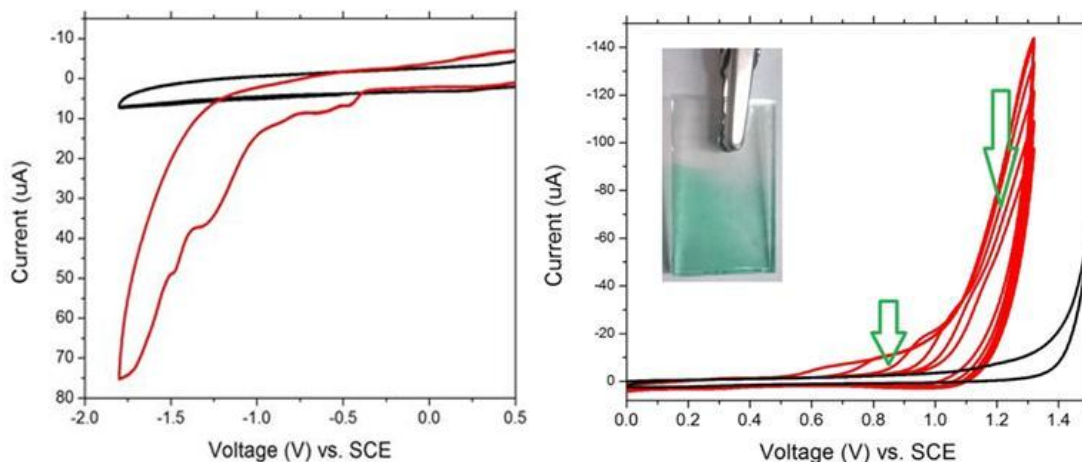


Figure 4.11 Electrochemistry 4-(2-thienyl)-phthalonitrile. (inset) is a 4-(2-thienyl)-phthalonitrile film deposited onto FTO. Black trace is a glassy carbon electrode in blank electrolyte solution. Green arrows indicate decreasing current with repeated cycling.

The electrochemistry of nickel 4-(3-thienyl)-phthalocyanine is shown in Figure 4.12 and it has the typical process that would be expected for this molecule. There are two very well defined ring reductions occurring at -0.75V and -1.1 V vs. SCE. This is quite interesting since the previous derivative had irreversible ring reductions. A somewhat reversible partially hidden peak is visible at around 0.6 V vs. SCE, possibly from the $\text{Ni}^{2+}/\text{Ni}^{3+}$ oxidation.⁸⁵ When scanning the potential to 1 volt an additional redox process most likely occurs from the oxidation of the thiophene moiety. Several attempts were made to polymerize this molecule and all were unsuccessful. When scanning the voltage up to 1.5 V and between 0.7 V vs. SCE there is no conductive film formation. Both solvents of DMSO and DMF were used with the same results. 4-(3-thienyl)-phthalocyanine is only soluble in DMF and DMSO.

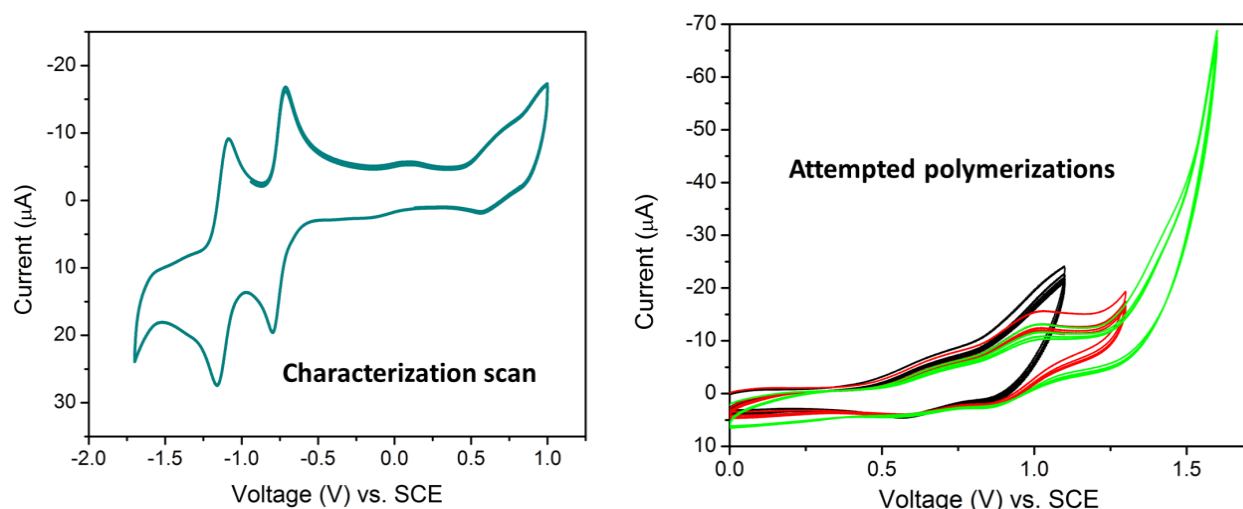


Figure 4.12 Electrochemistry of the 4-(3-thienyl)-phthalocyanine in DMSO.

Possible reasons for failed electropolymerization

The literature of thiophene derivatives is quite extensive, and there are a few derivatives that are analogous to the Pc-thiophene derivatives. Examples of similar thiophene derivatives are shown in Figure 4.13. Molecule 1 which is likely most similar to the Pc derivatives is reportedly non-polymerizable.⁹⁹ Molecules 2-3 in Figure 4.13 are polymerizable however. The oxidation potentials of bithiophene and ethylenedioxythiophene are much lower than thiophene, this may be the reason for the lack of polymerization of molecule 1. The authors attributed the lack of polymer film growth from the radical not being stable and reacting with the solvent.⁹⁹

The unstable radical hypothesis is in somewhat of a disagreement though when considering that 3-phenylthiophene is readily polymerizable from acetonitrile, it was also reported to be more stable than thiophene.¹⁰⁰ However, Pc derivatives synthesized herein

are required to be in DMF and DMSO which have solvent windows around 1.1 V vs. SCE. This solvent window is right near the polymerization range of the Pc thiophene derivatives, it is possible that decomposition products of the solvent are interfering with polymerization, practically there is little that can be done about this.

As discussed previously when thiophene derivatives such as bithiophene or ethylenedioxythiophene are attached to Pc this enables polymerization.⁸⁶ One can draw a conclusion that there needs to be a thiophene moiety with a lower oxidation potential attached to the Pc ring to facilitate polymerization, around the region of 1.2 V vs. SCE. It is conceivable that the radical is migrating onto the Pc ring, where it is no longer available for coupling.

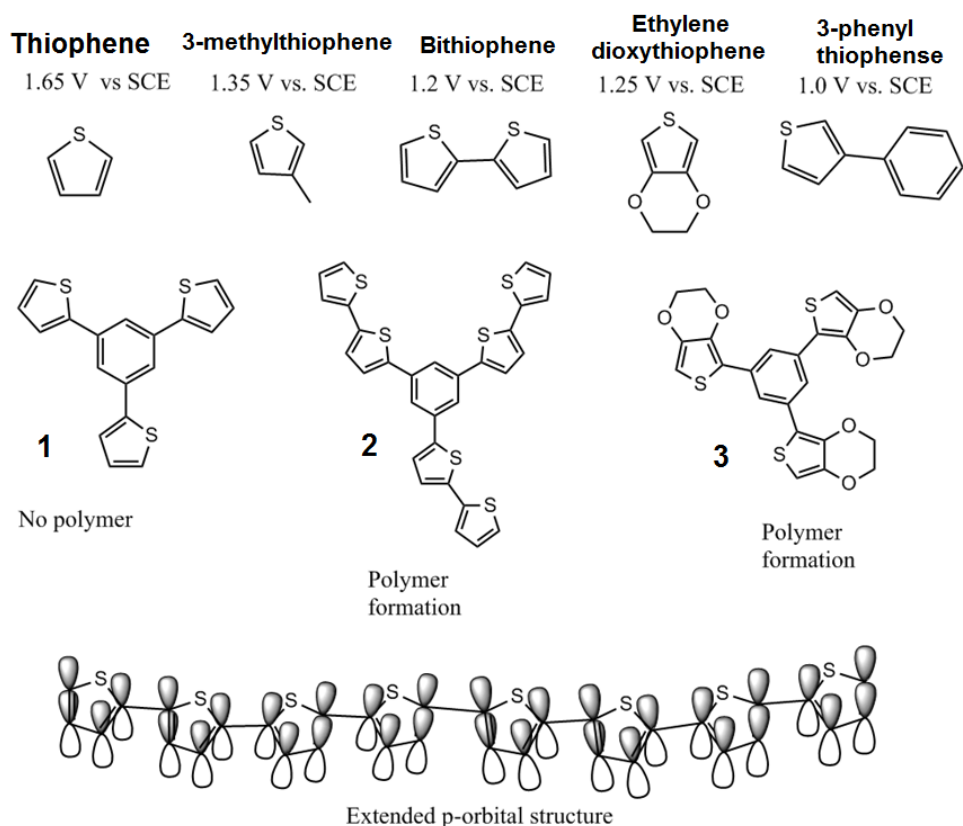


Figure 4.13 Values for redox potentials of thiophene derivatives, (middle) Benzene thiophene derivatives for comparison to Pc thiophene derivatives. Oxidation potentials are taken from previous literature.¹⁰⁰⁻¹⁰²

Poor π -orbital overlap may be an issue as to why there isn't a steady film growth on the electrode. If the polymers are forming oligomers with twisted units, the Pc-thiophene π -overlap will be poor. Poor orbital overlap of the Pc unit and thiophene could cause the polymers to be non-conductive and limit the formation of an electrochemically conductive polymer. The orbital overlap is shown in Figure 4.13, where a twist would break up the π delocalization. It is these orbital interactions that are the cause for the high conductivity of the planar structure of graphene.¹⁰³ To exploit this concept a recent paper used aldol condensation to make a conductive polymer that is completely flat and rigid having double

bond linking units, greatly increasing charge carrier mobility.¹⁰⁴ If it is a conformation issue with the non-polymerization of Pc-thiophene there isn't a straight forward methodology or set up conditions to test this hypothesis. Overall, the lack of film formation or difficulty is discouraging for the wide spread and facile use of these films. For real world use the electropolymerization must be tolerant of small impurities and readily occur under a range of conditions.

Synthesis of nickel 4-(3-methoxythienyl) phthalocyanine

4-(3-methoxythienyl) phthalocyanine was chosen as a synthetic target next. The molecule should be readily synthesized, the starting materials are also low cost and reaction conditions are quite mild. The logic behind trying investigating this molecule is that the ether group may increase solubility by hindering aggregation. This may enable the use of acetonitrile or DCM as a solvent for electrochemistry, which both have larger solvent windows than DMSO and DMF.

With this derivative the thiophene moiety is also isolated from the Pc core, the radical would then be isolated on thiophene, and therefore allow for polymerization. Additionally this derivative is similar to methyl-thiophene which has a lower potential for polymerization than bare thiophene. This molecule is then a good candidate to test some of the proposed hypothesis discussed previously for causes of failed polymerization.

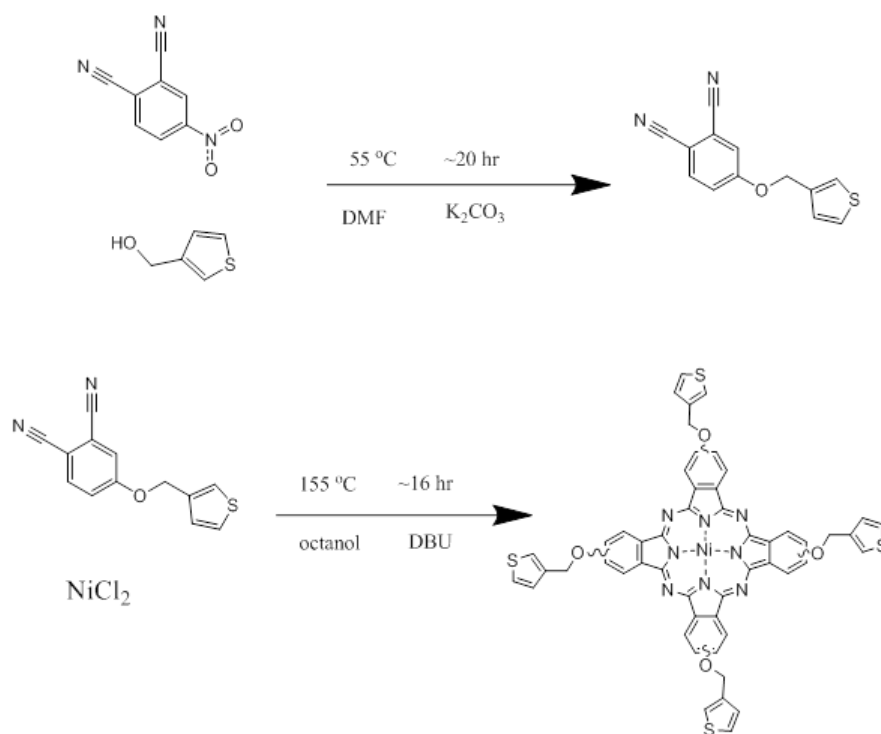


Figure 4.14 Synthesis of 4-(3-methoxythienyl) phthalonitrile and 4-(2-methoxythienyl) phthalocyanine.

The synthesis was attempted according to Figure 4.14, this route has also been reported previously by Nyokong. In that report 3-thiopheneethanol was used for the synthesis of Co, Mn, and Zn Pc-thiophene-derivatives.⁸² Interestingly, in that work the precursor 4-(2-ethoxythienyl)-phthalonitrile was reported as a green compound. Here the synthesis of 4-(3-methoxythienyl)-phthalonitrile was observed as off white in color. However, after being exposed in air a light green color begins to show in the dried material. The previous synthesis reported of a green solid is most likely in error and the green color is some form of impurity.⁸²

The synthesis of nickel 4-(3-methoxythienyl) phthalocyanine was straight forward and the conditions used were similar to the synthesis of the last thiophene Pc derivatives. A dark purple/blue solid was isolated with a 52 % yield. Again, this compound was only soluble in DMF and DMSO, which was somewhat unexpected given the difference in functional groups. Characterization by proton NMR was unsuccessful. The UV-Vis spectra of the compounds show that the peaks at 675 nm and shoulder at 612 nm for the Q-bands and a very broad intense absorption starting at 415 nm extending to 300 nm for the Soret band. The spectra is quite similar to the previous thiophene derivatives and also in close agreement to the other report of the Mn, Co, and Zn ethoxythienyl-Pcs.⁸²

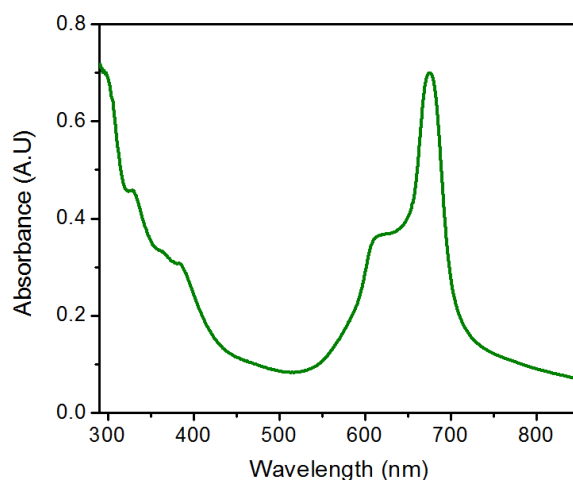


Figure 4.15 UV-Vis and color of nickel 4-(3-methoxythienyl) phthalocyanine complex in DMSO.

The electrochemistry of the new derivative was noticeably different than the previously tested derivatives. Figure 4.16 shows an initial oxidation initially starting at ~ 0.8 V vs. SCE. There are two ring reduction peaks which are occurring in the expected range of -0.9 and -1.3 V vs. SCE. When the compound was tested for oxidative polymer film

formation it was found that under the right conditions a film could be made. The polymerization apparently begins at 0.9 V, and the current grows in with repeated cycling of the electrode. What is quite interesting is that the film de-absorbs from the electrode surface upon cycling to negative potentials, this is indicated by the sharp pointed reductive peak, followed by a loss of electrochemical signal from the polymer.

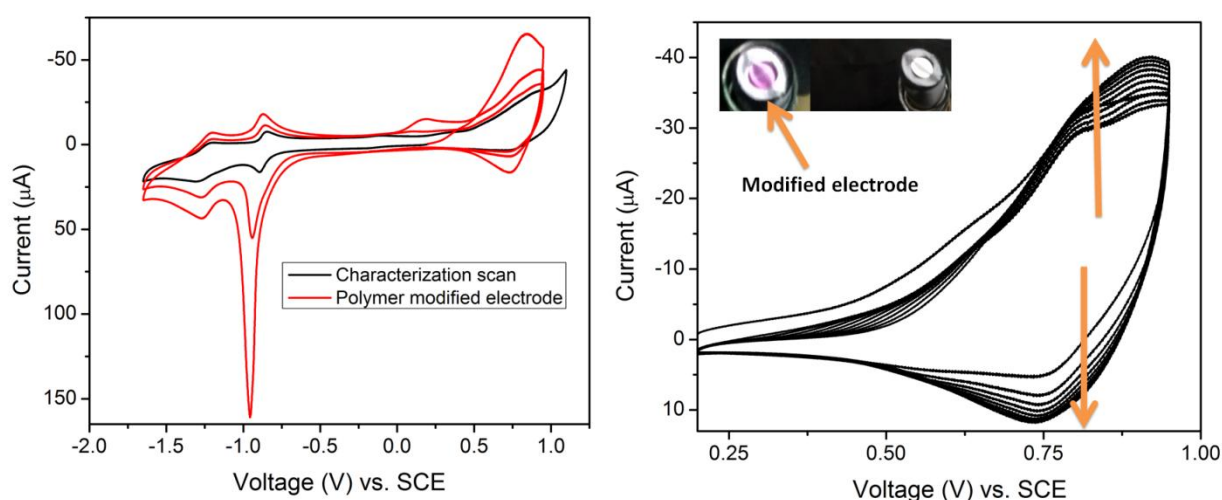


Figure 4.16 Electrochemistry of 4-(3-methoxythienyl) phthalocyanine in DMSO.

Some take away messages relating to the voltammetry are that there is a relatively small working window for this newly reported polymer. The potential window occurs at 0.5 V through 0.9 V vs. SCE, this small window is not ideal for chemical sensors. Additionally upon cycling the polymer in solution by cyclic voltammetry there was a decrease in current response, typical of some sort of degradation of the conductivity mechanism. While it is quite significant that this is the first report of the polymerization of this phthalocyanine derivative, it appears to have little value in electrochemical catalysis.

An excellent advantage of working with Pcs are that derivatives are easy to make, and a different polymerizable moiety is tested next, which moves away from the use of thiophene.

Synthesis of 4-(diphenylamino)-phthalonitrile

Triphenylamine was chosen as a new type of electro-active polymerizable derivative of Pcs. Working off the hypothesis previously formed, triphenylamine was chosen as it has a low initial oxidation potential of ~ 0.7 V vs. SCE and polymerization is typical at a maximum potential of 1.2 V vs. SCE.⁹³ This should provide the appropriate redox match and enable electropolymerizable Pc derivatives.

To make the di-nitrile triphenylamine precursor the reaction in Figure 4.17 was used, which is based off a previous reported synthesis of this molecule. In that work 4-(diphenylamino)-phthalonitrile was synthesized via nitro-displacement with a reported 86 % yield after 12 hours of reaction time.¹⁰⁵ When attempted under nearly identical conditions (DMF was in place of DMAC) there was no discernable formation of products. When the reaction was left to stir for over 3 days upon a second attempt, the formation of 4-(diphenylamino)-phthalonitrile was observed. At the present it is unclear why this reaction proceeded much slower than the previous example. The report of this molecules synthesis via this method is the only known example, and given the issue of reproducibility in chemical research,¹⁰⁶ the vastly conflicting results are not all that surprising.

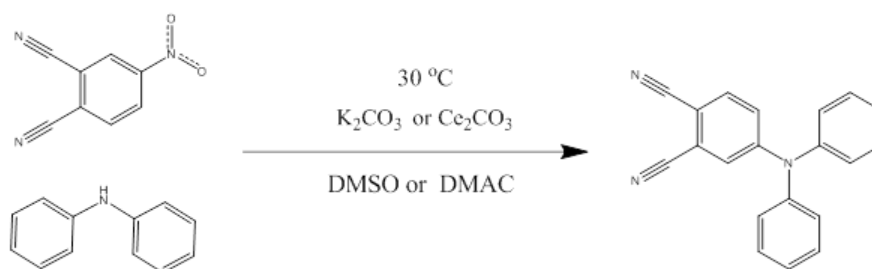


Figure 4.17 4-(diphenylamino)-phthalonitrile synthesis via nitro-displacement.

Objectively, a possible reason for the slow reaction rate may be from steric hindrance from the bulky aryl groups, in which nothing can be done with. The literature on nitro-displacement mechanisms is not all encompassing. However, DMSO is often used as a solvent in these reactions, along with elevated temperatures in excess of 100 Celsius.¹⁰⁷⁻¹⁰⁸ Cesium carbonate is also reported to enhance nitro-displacement reactions.¹⁰⁹ With this in mind follow up smaller scale reactions were attempted in DMSO, at room temperature and with elevated heat, the efforts did not seem to increase the formation of the products significantly. The elevated temperature did however appear to cause the starting material to degrade, which simplified purification to some extent.

Cesium was also placed in the reaction in excess with no major significant changes in the reaction time or increase in yields. The yields of 4-(diphenylamino) phthalonitrile when scaled up were however quite sufficient to attempt synthesis of copper and nickel 4-(diphenylamino)-phthalocyanine. Overall, the reaction described in Figure 4.17 will yield 4-(diphenylamino)-phthalonitrile but is far from optimized, a higher yielding synthesis of this molecule should be investigated if a more prolonged and intensive study of diphenylamine functionalized phthalocyanines is pursued.

Synthesis and characterization of 4-(diphenylamino)-phthalocyanines

The synthesis of nickel and copper 4-(diphenylamino)-phthalocyanine proceeded smoothly under normal phthalocyanine synthesis conditions. The reaction color upon addition of the base (DBU) turned a deep red color, followed by a black dark blue tone after 20 minutes, as expected. The obtained solid was dark blue, insoluble in acetone and methanol, however it was quite soluble in chloroform and dichloromethane. The compounds take on a very odd light pink color when dissolved, a major contrast to most Pc derivatives which appear either intensely dark green or blue in color.

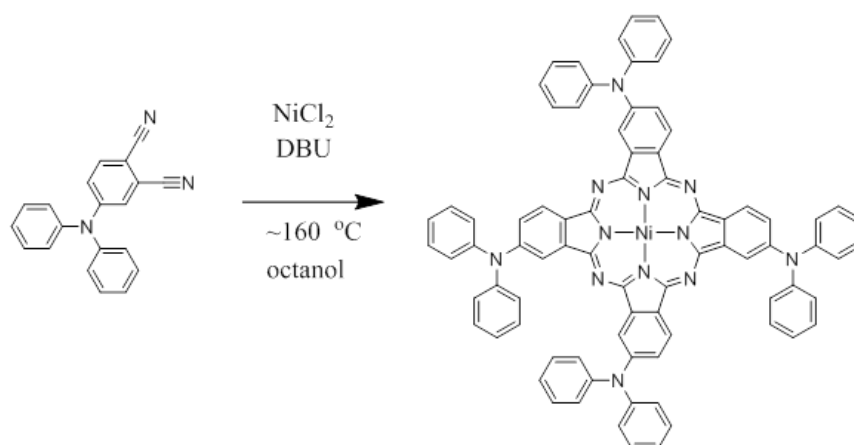


Figure 4.18 Synthesis of nickel 4-(diphenylamino)-phthalocyanine.

The UV-Vis spectra in Figure 4.19 show the normal Q and Soret bands associated with Pcs. The peak located at ~ 500 nm is tentatively associated with the diphenylamine moiety integrated into the Pc ring structure.¹⁰⁵ The shift of the Q-band to 725 nm was somewhat expected and is associated with an extension of aromaticity of the Pc ring. This is a 50 nm shift from the previous methoxy thiophene Pc derivative, which shouldn't have

increased aromaticity. The spectra is also in very good agreement with the sub-phthalocyanine diphenylamine derivatives. In that work they saw a 51 nm shift difference from the un-derivatized core unit to the diphenylamine derivative.¹⁰⁵

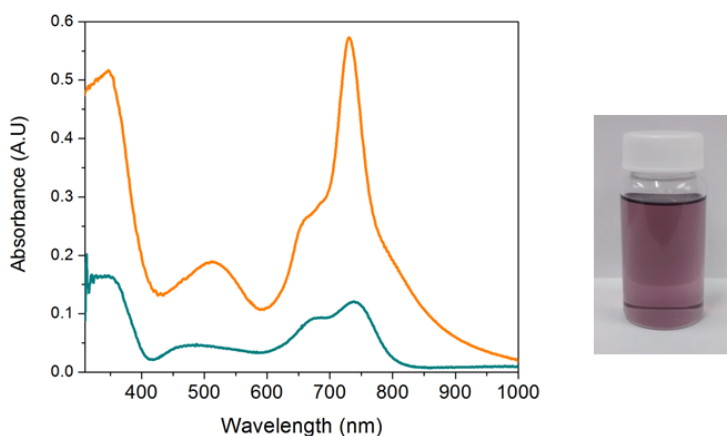


Figure 4.19 UV-Vis spectra of nickel 4-(diphenylamino)-phthalocyanine in dichloromethane (DCM), and the spectra of an electrochemically polymerized film on ITO. (right) nickel 4-(diphenylamino)-phthalocyanine dissolved in DCM.

Electrochemistry of copper 4-(diphenylamino)-Pc

The electrochemistry of the diphenylamine derivatives was noticeably different than with the thiophene appended Pcs. In the negative region two well defined ring reductions are observed, these occur at -0.85 and -0.13 V vs. SCE. In the positive region there are redox peaks at 0.6 V, 0.9 V, 1.1 V and an irreversible wave starting around 1.3 V vs. SCE. The peaks at 0.6 V, 0.9 V are consistent with literature on triphenylamines.⁸⁰

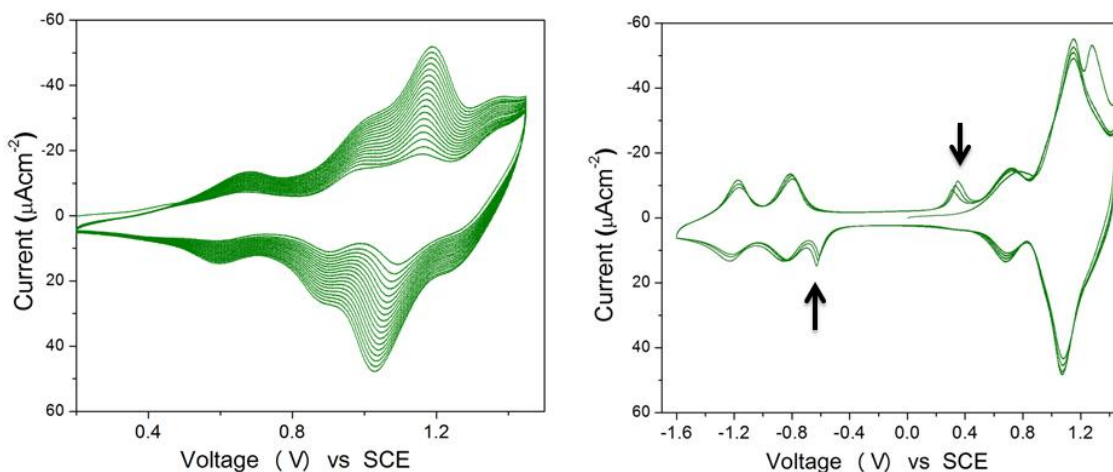


Figure 4.20 (left) Electrochemical polymerization of copper 4-(diphenylamine)-Pc in DCM. (right) copper 4-(diphenylamine)-Pc modified electrode in a blank electrolyte DCM solution.

Upon repeated cycling a polymer film begins to grow on the electrode. The conductivity window in the positive region appears to be from -0.5 V to 1.4 V vs. SCE. The modified electrode was moved into a blank electrolyte solution to confirm the existence of the formed polymer and the electro-active film had nearly identical responses to that formed in solution. Further testing showed that the polymer film only forms above ~ 1.25 V vs. SCE and is related to the semi-irreversible process shown in Figure 4.20.

The black arrows shown in the left image of Figure 4.20 are most likely charge trapping peaks. Charge trapping occurs when an insulating layer surrounds charged areas in the polymer, when a sufficient over-potential is applied the insulating layer becomes conductive and the charge is released. Charge trapping is well known for conjugated conducting polymers.¹¹⁰ Interestingly, the trapped charge peaks look nearly identical to a bis-carbazole-Diimide conductive polymeric film.¹¹¹ The nickel derivative was also

synthesized and had nearly identical behavior as seen with the copper compound. This is similar to tetraaminophthalocyanine electrochemically grown polymers where the electrochemistry of the copper and nickel derivatives are almost identical.⁸⁵

4.3 Conclusions and Future Work

In general, the success in polymerization of 4-(diphenylamine)-Pc derivatives is extraordinarily promising, and represents a new class of Pc conductive polymers, of which there are few examples of within the literature. Importantly, these polymers are stable to repeated cycling, are redox conductors at both negative and positive potentials, making them excellent candidates for electrochemical catalysis.

The work with the thiophene appended phthalocyanines sheds light onto the type of molecule that should be attached to the Pc ring to facilitate electrochemical polymerization. While still a working hypothesis, it appears that lowering the oxidation potential of the Pc substituent is a potential strategy to obtain polymeric electrode coatings. Based on this work and previous literature examples the attached polymerization moiety should have an oxidation potential around 1 to 1.2 V vs. SCE.

The work presented in this chapter is also the first reported examples of the nickel 4-(2-methoxythienyl)-phthalocyanine, nickel 4-(3-thienyl)-phthalocyanine, and nickel 4-(2-thienyl)-phthalocyanine complexes. Therefore, the synthesis and general characterization is of value to the field of phthalocyanines as a whole. Also of interest is the electropolymerization of nickel 4-(2-methoxythienyl) phthalocyanine. While ultimately this

molecule was determined to be of limited use, the polymerization is novel and has yet to be reported in the literature.

Future work

The future work discussion focuses mainly on the triphenylamine phthalocyanines. These derivatives were the most stable and besides this thesis work there are no current reports on these molecules. These two points make the continuation of examining triphenylamine phthalocyanines a high priority. As mentioned in the introduction phthalocyanines are well studied for electrochemical catalysis, this is an area that could easily be explored with this new type of polymer. While currently only the nickel and copper diphenylamine Pc derivatives have been synthesized, the cobalt and iron derivatives would be much more interesting for applications in oxygen and CO₂ reduction, or thiol oxidation. The discussion in the introduction highlights the importance of these metals for catalytic applications. Conceivably, the new diphenylamine Pc derivatives should provide a high surface area network of highly active metal centers, highly desirable for catalytic applications.

Phthalocyanines are known as a N₄ macrocycles because of the 4-coordinating nitrogen pyrrole units. Underscoring the importance of the work herein, N₄ carbon graphitic materials are being aggressively explored for electrochemical catalysis.¹¹²⁻¹¹⁴ These materials are made by creating nitrogen rich graphitic materials which are capable of coordinating iron or cobalt analogous to phthalocyanines. Specifically they are known as Co-N_x-C or Fe-N_x-C as the general structure and composition of these materials is not completely known. By synthesizing the iron and cobalt diphenylamine Pc derivatives they

could be compared to the massive efforts reported for Co-N_x-C or Fe-N_x-C materials, and a logical place to begin is with the study of oxygen reduction reaction.

Besides changing the metal center, synthetically the 3-position should also be explored in terms of polymer film formation and catalysis of the diphenylamine phthalocyanines. The synthetic scheme is shown in Figure 4.21. The increased sterics may pose a serious problem with the synthesis of the 3-substitued molecules, however, similar sterically hindered molecules have been formed within the literature.¹¹⁵ The interesting property of this derivative is that the phenylamine rings cannot lay flat, the rings then must be upright or near upright. The effect is shown on the right side of Figure 4.21.

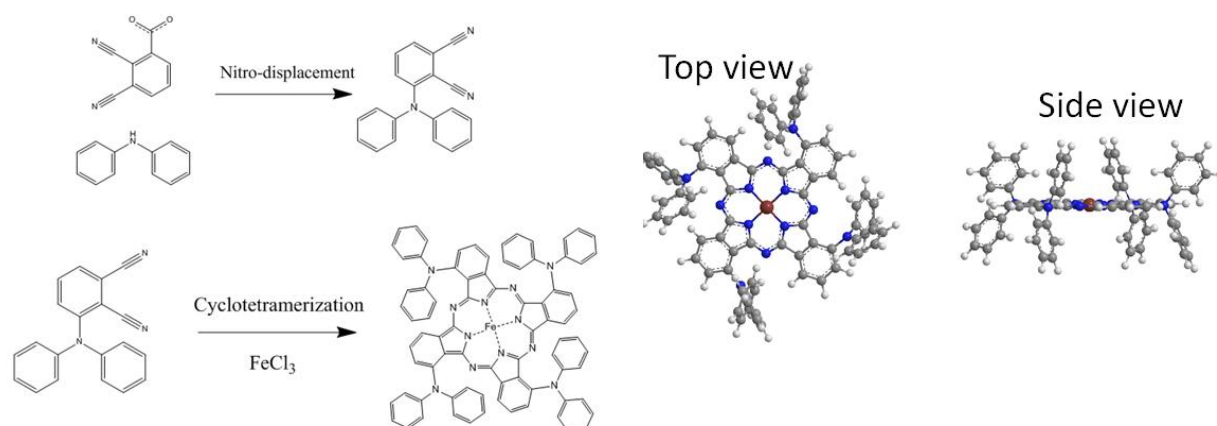


Figure 4.21 Synthesis of iron 3-(diphenylamino)-phthalocyanine. (Right) 3-dimensional representation of iron 3-(diphenylamino)-phthalocyanine, showing the steric effects of the 3-position.

The new orientation of the diphenylamine rings may introduce some unique effects catalytically, whereby creating a pocket around the metal center. The lack of the ability of

the rings to lay flat will drastically alter the ability of the Pc to aggregate, most likely completely changing the solubility and processability.

The 3-position also enables options for new derivatives of this type of molecule. Since the phenyl rings are so close to the Pc ring it can enable close proximity functional groups to the metal center. In Figure 4.22 the 3-position derivative is shown with a pyridine derivative attached to the phenylamine ring. This derivative could be synthesized in a relatively facile route. The proposed reactions use well known chemistries and commercially available starting materials. Having pyridine moieties attached to the phenylamine ring would allow for tuning the redox nature of the Fe metal center on-site, which, at the present appears to be completely novel.¹¹⁶ The ring attached pyridine should be much more stable than attempting axial coordination with single molecules. While this newly proposed molecule may not be polymerizable, it could be tested as a catalyst in composted electrodes or drop-casted onto an electrode surface.

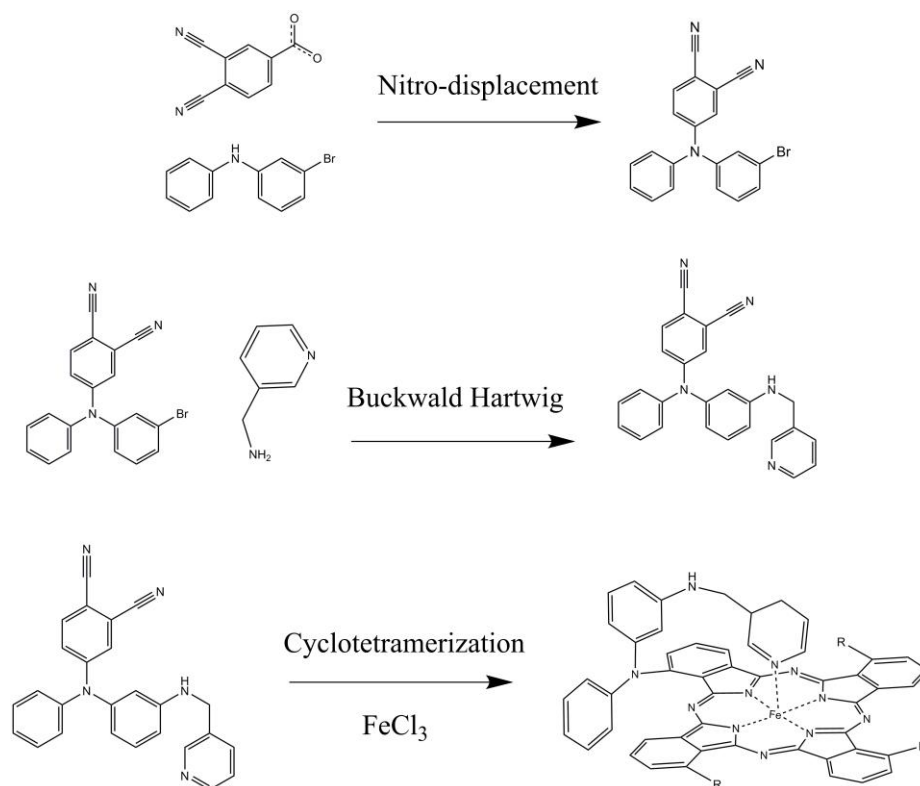


Figure 4.22 Proposed new synthetic targets for next generation diphenylamine Pc conducting Pc catalyst.

Finally, given the overall novelty of these diphenylamine Pcs, the applications are not limited to just electrochemical catalysis. The molecules could be used as gas sensors or electrochemical sensors. The introduction highlights the very broad range of sensing capabilities of Pcs. Pcs are also proposed for electrochromic materials which is an application that can be readily explored. Lastly, both Pcs and triphenylamines are extensively studied as hole transport layers in photovoltaics and organic light emitting diodes, applying the new diphenylamine Pc derivatives to these applications is another possible avenue for further research.

4.4 Materials and Methods

Electrochemistry

Electrochemistry was performed with a CHI 700E potentiostat. All electrochemical experiments used a platinum counter electrode, SCE reference, with either FTO or a glassy carbon electrode with diameter of 0.0706 cm² working electrode. All scan rates were 100 mV s⁻¹. The electrolyte used was tetrabutylammonium tetrafluoroborate at a concentration of 0.1 M. Phthalocyanine concentrations were ~2 mM. All solvents were degassed with N₂ for at least 5 minutes prior to use, with a typical solution volume of around 2 mL.

Chemicals

2-thienylboronic acid (Oakwood), 3-thienylboronic acid (Oakwood), dimethylformamide (Sigma), Tetrakis(triphenylphosphine)palladium (Fisher), 3-methoxy thiophene, 2-thiophenemethanol (Sigma), dimethylsulphoxide (Sigma), dichloromethane (Fisher), DBU (Alfa), octanol (Fisher), diphenylamine (Sigma), ethyl acetate (Sigma), Hexane (Fisher), 4-nitrophthalonitrile (TCI) 4-bromo-phthalonitrile (Oakwood), thionyl chloride (Fisher), ammonium hydroxide (Sigma), sodium hydroxide (Fisher). In the Appendix for this chapter example reactions are provided with details on synthesis and purification of the Pc precursors and the resulting derivatives.

REFERENCES

1. Dini, D.; Hanack, M., Phthalocyanines as materials for advanced technologies: some examples. *J. Porphyr. Phthalocya.* **2004**, *08* (07), 915-933.
2. Gregory, P., Industrial applications of phthalocyanines. *J. Porphyr. Phthalocya.* **2000**, *04* (04), 432-437.
3. Basu, B.; Satapathy, S.; Bhatnagar, A. K., Merox and Related Metal Phthalocyanine Catalyzed Oxidation Processes. *Catalysis Reviews* **1993**, *35* (4), 571-609.
4. Muckley, E. S.; Miller, N.; Jacobs, C. B.; Gredig, T.; Ivanov, I. N., Morphology-defined interaction of copper phthalocyanine. *Journal of Photonics for Energy* **2016**, (6), 045501
5. Lee, W.; Yuk, S. B.; Choi, J.; Jung, D. H.; Choi, S.-H.; Park, J.; Kim, J. P., Synthesis and characterization of solubility enhanced metal-free phthalocyanines for liquid crystal display black matrix of low dielectric constant. *Dyes and Pigments* **2012**, *92* (3), 942-948.
6. Bohrer, F. I.; Sharoni, A.; Colesniuc, C.; Park, J.; Schuller, I. K.; Kummel, A. C.; Trogler, W. C., Gas Sensing Mechanism in Chemiresistive Cobalt and Metal-Free Phthalocyanine Thin Films. *J. Am. Chem. Soc.* **2007**, *129* (17), 5640-5646.
7. Shirk, J. S.; Pong, R. G. S.; Flom, S. R.; Heckmann, H.; Hanack, M., Effect of Axial Substitution on the Optical Limiting Properties of Indium Phthalocyanines. *The Journal of Physical Chemistry A* **2000**, *104* (7), 1438-1449.
8. de Paula, L. B.; Primo, F. L.; Pinto, M. R.; Morais, P. C.; Tedesco, A. C., Evaluation of a chloroaluminium phthalocyanine-loaded magnetic nanoemulsion as a drug delivery device to treat glioblastoma using hyperthermia and photodynamic therapy. *RSC Advances* **2017**, *7* (15), 9115-9122.
9. Mfouo-Tynga, I.; Abrahamse, H., Cell Death Pathways and Phthalocyanine as an Efficient Agent for Photodynamic Cancer Therapy. *International Journal of Molecular Sciences* **2015**, *16* (5), 10228.
10. Geis, C.; Schneider, S. P.; Schlettwein, D., Polymeric phthalocyanine sheets as electrocatalytic electrodes for water-oxidation. *J. Porphyr. Phthalocya.* **2016**, *20* (11), 1166-1172.
11. Lu, Y.; Reddy, R. G., Electrocatalytic properties of carbon supported cobalt phthalocyanine-platinum for methanol electro-oxidation. *International Journal of Hydrogen Energy* **2008**, *33* (14), 3930-3937.
12. Zagal, J. H., Metallophthalocyanines as catalysts in electrochemical reactions. *Coordin. Chem. Rev.* **1992**, *119*, 89-136.

13. Zhang, X.; Wu, Z.; Zhang, X.; Li, L.; Li, Y.; Xu, H.; Li, X.; Yu, X.; Zhang, Z.; Liang, Y.; Wang, H., Highly selective and active CO₂ reduction electrocatalysts based on cobalt phthalocyanine/carbon nanotube hybrid structures. *Nature Communications* **2017**, *8*, 14675.
14. Walter, M. G.; Rudine, A. B.; Wamser, C. C., Porphyrins and phthalocyanines in solar photovoltaic cells. *J. Porphyr. Phthalocya.* **2010**, *14* (09), 759-792.
15. Lin, L.; Peng, B.; Shi, W.; Guo, Y.; Li, R., Synthesis of zinc phthalocyanine with large steric hindrance and its photovoltaic performance for dye-sensitized solar cells. *Dalton Transactions* **2015**, *44* (12), 5867-5874.
16. Li, H.; Guarr, T. F., Reversible electrochromism in polymeric metal phthalocyanine thin films. *J. Electroanal. Chem. Interfac. Electrochem.* **1991**, *297* (1), 169-183.
17. Lippel, P. H.; Wilson, R. J.; Miller, M. D.; Wöll, C.; Chiang, S., High-Resolution Imaging of Copper-Phthalocyanine by Scanning-Tunneling Microscopy. *Phys. Rev. Lett.* **1989**, *62* (2), 171-174.
18. R., Z.; F., J.; W., G.; Z., Ö. Z.; Ö, B., Phthalocyanines as Sensitive Materials for Chemical Sensors. *Applied Organometallic Chemistry* **1996**, *10* (8), 557-577.
19. Cui, L.; Chen, L.; Xu, M.; Su, H.; Ai, S., Nonenzymatic amperometric organic peroxide sensor based on nano-cobalt phthalocyanine loaded functionalized graphene film. *Anal. Chim. Acta* **2012**, *712*, 64-71.
20. Koehler, K. A.; Shapiro, J.; Sameenoi, Y.; Henry, C.; Volckens, J., Laboratory Evaluation of a Microfluidic Electrochemical Sensor for Aerosol Oxidative Load. *Aerosol Science and Technology* **2014**, *48* (5), 489-497.
21. Hosseini, H.; Mahyari, M.; Bagheri, A.; Shaabani, A., A novel bioelectrochemical sensing platform based on covalently attachment of cobalt phthalocyanine to graphene oxide. *Biosens. Bioelectron.* **2014**, *52*, 136-142.
22. Kevin C. Honeychurch, J. P. H., The Chronoamperometric and Voltammetric Behaviour of Glutathione at Screen-Printed Carbon Micro-Band Electrodes Modified with Cobalt Phthalocyanine. **2012**, *2*, 46-52.
23. Mphuthi, N. G.; Adekunle, A. S.; Ebenso, E. E., Electrocatalytic oxidation of Epinephrine and Norepinephrine at metal oxide doped phthalocyanine/MWCNT composite sensor. *Scientific Reports* **2016**, *6*, 26938.
24. Griveau, S.; Gulppi, M.; Pavez, J.; Zagal, J. H.; Bedioui, F., Cobalt Phthalocyanine-Based Molecular Materials for the Electrocatalysis and Electroanalysis of 2-Mercaptoethanol, 2-Mercaptoethanesulfonic Acid, Reduced Glutathione and L-Cysteine. *Electroanal.* **2003**, *15* (9), 779-785.

25. Ndiaye, A.; Delile, S.; Brunet, J.; Varenne, C.; Pauly, A., Electrochemical Sensors Based on Screen-Printed Electrodes: The Use of Phthalocyanine Derivatives for Application in VFA Detection. *Biosensors* **2016**, 6 (3), 46.
26. Cookeas, E. G.; Efstathiou, C. E., Flow injection amperometric determination of thiocyanate and selenocyanate at a cobalt phthalocyanine modified carbon paste electrode. *Analyst* **1994**, 119 (7), 1607-1612.
27. Xing, R.; Yang, H.; Li, S.; Yang, J.; Zhao, X.; Wang, Q.; Liu, S.; Liu, X., A sensitive and reliable rutin electrochemical sensor based on palladium phthalocyanine-MWCNTs-Nafion nanocomposite. *J. Solid State Electr.* **2017**, 21 (5), 1219-1228.
28. Peeters, K.; De Wael, K.; Bogaert, D.; Adriaens, A., The electrochemical detection of 4-chlorophenol at gold electrodes modified with different phthalocyanines. *Sensor. Actuat. B-Chem.* **2008**, 128 (2), 494-499.
29. Balan, I.; David, I. G.; David, V.; Stoica, A.-I.; Mihailciuc, C.; Stamatina, I.; Ciucu, A. A., Electrocatalytic voltammetric determination of guanine at a cobalt phthalocyanine modified carbon nanotubes paste electrode. *J. Electroanal. Chem.* **2011**, 654 (1), 8-12.
30. de Holanda, L. F.; Ribeiro, F. W. P.; Sousa, C. P.; da Silva Casciano, P. N.; de Lima-Neto, P.; Correia, A. N., Multi-walled carbon nanotubes-cobalt phthalocyanine modified electrode for electroanalytical determination of acetaminophen. *J. Electroanal. Chem.* **2016**, 772, 9-16.
31. Aragão, J. S.; Ribeiro, F. W. P.; Portela, R. R.; Santos, V. N.; Sousa, C. P.; Becker, H.; Correia, A. N.; de Lima-Neto, P., Electrochemical determination diethylstilbestrol by a multi-walled carbon nanotube/cobalt phthalocyanine film electrode. *Sensor. Actuat. B-Chem.* **2017**, 239, 933-942.
32. Eken Korkut, S.; Akyuz, D.; Ozdogan, K.; Yerli, Y.; Koca, A.; Sener, M. K., TEMPO-functionalized zinc phthalocyanine: synthesis, magnetic properties, and its utility for electrochemical sensing of ascorbic acid. *Dalton Transactions* **2016**, (7), 3086-3092.
33. Rahim, A.; Santos, L. S. S.; Barros, S. B. A.; Kubota, L. T.; Gushikem, Y., Dissolved O₂ sensor based on cobalt(II) phthalocyanine immobilized in situ on electrically conducting carbon ceramic mesoporous SiO₂/C material. *Sensor. Actuat. B-Chem.* **2013**, 177, 231-238.
34. Rahim, A.; Muhammad, N.; Nishan, U.; Khan, U. S.; Rehman, F.; Kubota, L. T.; Gushikem, Y., Copper phthalocyanine modified SiO₂/C electrode as a biomimetic electrocatalyst for 4-aminophenol in the development of an amperometric sensor. *RSC Advances* **2015**, 5 (106), 87043-87050.
35. Xu, H.; Xiao, J.; Liu, B.; Griveau, S.; Bedioui, F., Enhanced electrochemical sensing of thiols based on cobalt phthalocyanine immobilized on nitrogen-doped graphene. *Biosens. Bioelectron.* **2015**, 66, 438-444.

36. Xu, F.; Li, H.; Cross, S. J.; Guarr, T. F., Electrocatalytic oxidation of NADH at poly(metallophthalocyanine)-modified electrodes. *J. Electroanal. Chem.* **1994**, *368* (1), 221-225.
37. Zina, F.; Nooredeen, N. M.; Azzouzi, S.; Ali, M. B.; Abbas, M. N.; Errachid, A., Novel Sensitive Impedimetric Microsensor for Phosphate Detection Based on a Novel Copper Phthalocyanine Derivative. *Anal. Lett.* **2018**, *51* (3), 371-386.
38. Moraes, F.; Mascaro, L.; Machado, S.; Brett, C., Direct Electrochemical Determination of Glyphosate at Copper Phthalocyanine/Multiwalled Carbon Nanotube Film Electrodes. *Electroanal.* **2010**, *22* (14), 1586-1591.
39. Wen, Z.-H.; Kang, T.-F., Determination of nitrite using sensors based on nickel phthalocyanine polymer modified electrodes. *Talanta* **2004**, *62* (2), 351-355.
40. Jeevagan, A. J.; John, S. A., Electrochemical determination of caffeine in the presence of paracetamol using a self-assembled monolayer of non-peripheral amine substituted copper(II) phthalocyanine. *Electrochim. Acta* **2012**, *77*, 137-142.
41. Jeevagan, A. J.; John, S. A., Synthesis of non-peripheral amine substituted nickel(ii) phthalocyanine capped gold nanoparticles and their immobilization on electrode for the electrocatalytic oxidation of hydrazine. *RSC Advances* **2013**, *3* (7), 2256-2264.
42. Moraes, F. C.; Mascaro, L. H.; Machado, S. A. S.; Brett, C. M. A., Direct electrochemical determination of carbaryl using a multi-walled carbon nanotube/cobalt phthalocyanine modified electrode. *Talanta* **2009**, *79* (5), 1406-1411.
43. Wong, A.; Sotomayor, M. D. P. T., Determination of carbofuran and diuron in FIA system using electrochemical sensor modified with organometallic complexes and graphene oxide. *J. Electroanal. Chem.* **2014**, *731*, 163-171.
44. Boni, A. C.; Wong, A.; Dutra, R. A. F.; Sotomayor, M. D. P. T., Cobalt phthalocyanine as a biomimetic catalyst in the amperometric quantification of dipyrone using FIA. *Talanta* **2011**, *85* (4), 2067-2073.
45. Çeken, B.; Kandaz, M.; Koca, A., Electrochemical metal-ion sensor based on a cobalt phthalocyanine complex captured in Nafion® on a glassy carbon electrode. *Journal of Coordination Chemistry* **2012**, *65* (19), 3383-3394.
46. Liu, X.; Qi, C.; Bing, T.; Cheng, X.; Shangguan, D., Highly Selective Phthalocyanine-Thymine Conjugate Sensor for Hg²⁺ Based on Target Induced Aggregation. *Anal. Chem.* **2009**, *81* (9), 3699-3704.
47. Mızrak, B.; Ağar, M.; Altındal, A.; Abdurrahmanoğlu, Ş., Synthesis, characterization and metal ion sensing properties of novel pyridone derivatives phthalocyanines. *J. Porphyr. Phthalocya.* **2016**, *20* (12), 1457-1462.

48. Dahlen, M. A., The Phthalocyanines A New Class of Synthetic Pigments and Dyes. *Industrial & Engineering Chemistry* **1939**, 31 (7), 839-847.
49. Linstead, R. P., 212. Phthalocyanines. Part I. A new type of synthetic colouring matters. *Journal of the Chemical Society (Resumed)* **1934**, (0), 1016-1017.
50. Sakamoto, K.; Ohno-Okumura, E., Syntheses and Functional Properties of Phthalocyanines. *Materials* **2009**, 2 (3), 1127-1179.
51. Oliver, S. W.; Smith, T. D., Oligomeric cyclization of dinitriles in the synthesis of phthalocyanines and related compounds: the role of the alkoxide anion. *Journal of the Chemical Society, Perkin Transactions 2* **1987**, (11), 1579-1582.
52. Hurley, T. J.; Robinson, M. A.; Trotz, S. I., Complexes derived from 1,3-diiminoisoindoline-containing ligands. II. Stepwise formation of nickel phthalocyanine. *Inorg. Chem.* **1967**, 6 (2), 389-392.
53. Bartolomé, J.; Monton, C.; Schuller, I. K.; Bartolomé, J.; Luis, F.; Fernández, J. F., Magnetism of Metal Phthalocyanines. *Molecular Magnets: Physics and Applications* **2014**, 221-245.
54. Ichikawa, M.; Kimura, T.; Fukuoka, A., Ship-in-Bottle Synthesis of Sterically Crowded Fe-Phthalocyanines in NaY Zeolite Hosts and Their Catalytic Behavior in Regioselective Oxidation of Alkanes. *Studies in Surface Science and Catalysis* **1991**, Volume 60, 335-342.
55. Kharisov, B. I.; Ortiz Mendez, U.; Almaraz Garza, J. L.; Almaguer Rodriguez, J. R., Synthesis of non-substituted phthalocyanines by standard and non-standard techniques. Influence of solvent nature in phthalocyanine preparation at low temperature by UV-treatment of the reaction system. *New Journal of Chemistry* **2005**, 29 (5), 686-692.
56. Wöhrle, D.; Eskes, M.; Shigehara, K.; Yamada, A., A Simple Synthesis of 4,5-Disubstituted 1,2-Dicyanobenzenes and 2,3,9,10,16,17,23,24-Octasubstituted Phthalocyanines. *Synthesis* **1993**, 1993 (02), 194-196.
57. Marion, N.; Navarro, O.; Mei, J.; Stevens, E. D.; Scott, N. M.; Nolan, S. P., Modified (NHC)Pd(allyl)Cl (NHC = N-Heterocyclic Carbene) Complexes for Room-Temperature Suzuki–Miyaura and Buchwald–Hartwig Reactions. *J. Am. Chem. Soc.* **2006**, 128 (12), 4101-4111.
58. Casitas, A.; Canta, M.; Solà, M.; Costas, M.; Ribas, X., Nucleophilic Aryl Fluorination and Aryl Halide Exchange Mediated by a CuI/CuIII Catalytic Cycle. *J. Am. Chem. Soc.* **2011**, 133 (48), 19386-19392.
59. Bunnett, J. F., The remarkable reactivity of aryl halides with nucleophiles. *Journal of Chemical Education* **1974**, 51 (5), 312.

60. Kornblum, N.; Cheng, L.; Kerber, R. C.; Kestner, M. M.; Newton, B. N.; Pinnick, H. W.; Smith, R. G.; Wade, P. A., Displacement of the nitro group of substituted nitrobenzenes-a synthetically useful process. *The Journal of Organic Chemistry* **1976**, *41* (9), 1560-1564.
61. Zagal, J. H.; Griveau, S.; Silva, J. F.; Nyokong, T.; Bedioui, F., Metallophthalocyanine-based molecular materials as catalysts for electrochemical reactions. *Coordin. Chem. Rev.* **2010**, *254* (23), 2755-2791.
62. Lu, X.; Hipps, K. W.; Wang, X. D.; Mazur, U., Scanning Tunneling Microscopy of Metal Phthalocyanines: d7 and d9 Cases. *J. Am. Chem. Soc.* **1996**, *118* (30), 7197-7202.
63. Liao, M.-S.; Kar, T.; Gorun, S. M.; Scheiner, S., Effects of Peripheral Substituents and Axial Ligands on the Electronic Structure and Properties of Iron Phthalocyanine. *Inorg. Chem.* **2004**, *43* (22), 7151-7161.
64. Johnson, P. S.; García-Lastra, J. M.; Kennedy, C. K.; Jersett, N. J.; Boukahil, I.; Himpsel, F. J.; Cook, P. L., Crystal fields of porphyrins and phthalocyanines from polarization-dependent 2p-to-3d multiplets. *The Journal of Chemical Physics* **2014**, *140* (11), 114706.
65. Zagal, J. H.; Gulppi, M. A.; Cárdenas-Jirón, G., Metal-centered redox chemistry of substituted cobalt phthalocyanines adsorbed on graphite and correlations with MO calculations and Hammett parameters. Electrochemical reduction of a disulfide. *Polyhedron* **2000**, *19* (22-23), 2255-2260.
66. Miedema, P. S.; van Schooneveld, M. M.; Bogerd, R.; Rocha, T. C. R.; Hävecker, M.; Knop-Gericke, A.; de Groot, F. M. F., Oxygen Binding to Cobalt and Iron Phthalocyanines As Determined from in Situ X-ray Absorption Spectroscopy. *J. Phys. Chem. C* **2011**, *115* (51), 25422-25428.
67. Sun, S.; Jiang, N.; Xia, D., Density Functional Theory Study of the Oxygen Reduction Reaction on Metalloporphyrins and Metallophthalocyanines. *J. Phys. Chem. C* **2011**, *115* (19), 9511-9517.
68. Zagal, J. H.; Griveau, S.; Silva, J. F.; Nyokong, T.; Bedioui, F., Metallophthalocyanine-based molecular materials as catalysts for electrochemical reactions. *Coordin. Chem. Rev.* **2010**, *254* (23-24), 2755-2791.
69. Cao, R.; Thapa, R.; Kim, H.; Xu, X.; Gyu Kim, M.; Li, Q.; Park, N.; Liu, M.; Cho, J., Promotion of oxygen reduction by a bio-inspired tethered iron phthalocyanine carbon nanotube-based catalyst. *Nat Commun* **2013**, *4*.
70. Loas, A.; Gerdes, R.; Zhang, Y.; Gorun, S. M., Broadening the reactivity spectrum of a phthalocyanine catalyst while suppressing its nucleophilic, electrophilic and radical degradation pathways. *Dalton Transactions* **2011**, *40* (19), 5162-5165.

71. Reid, N.; Barat, R., Impact of Fluorinated Cobalt(II) Phthalocyanine Catalysts on Aerobic Thiol Oxidation Kinetics. *Chemical Engineering Communications* **2015**, *203* (6), 714-723.
72. Tolman, C. A., Steric effects of phosphorus ligands in organometallic chemistry and homogeneous catalysis. *Chem. Rev.* **1977**, *77* (3), 313-348.
73. Wulff, G., Enzyme-like Catalysis by Molecularly Imprinted Polymers. *Chem. Rev.* **2002**, *102* (1), 1-28.
74. Heinze, J.; Frontana-Urbe, B. A.; Ludwigs, S., Electrochemistry of Conducting Polymers—Persistent Models and New Concepts. *Chem. Rev.* **2010**, *110* (8), 4724-4771.
75. Nielsen, T. K.; Bösenberg, U.; Goslawit, R.; Dornheim, M.; Cerenius, Y.; Besenbacher, F.; Jensen, T. R., A Reversible Nanoconfined Chemical Reaction. *ACS Nano* **2010**, *4* (7), 3903-3908.
76. Dong, B.; Pei, Y.; Zhao, F.; Goh, T. W.; Qi, Z.; Xiao, C.; Chen, K.; Huang, W.; Fang, N., In situ quantitative single-molecule study of dynamic catalytic processes in nanoconfinement. *Nature Catalysis* **2018**, *1* (2), 135-140.
77. Pablo, B., Effects of Nanoconfinement on Catalysis. Edited by Rinaldo Poli. *Angew. Chem. Int. Edit.* **2017**, *56* (27), 7713-7714.
78. Medford, A. J.; Vojvodic, A.; Hummelshøj, J. S.; Voss, J.; Abild-Pedersen, F.; Studt, F.; Bligaard, T.; Nilsson, A.; Nørskov, J. K., From the Sabatier principle to a predictive theory of transition-metal heterogeneous catalysis. *Journal of Catalysis* **2015**, *328*, 36-42.
79. Stilwell, D. E.; Park, S. M., Electrochemistry of Conductive Polymers: II . Electrochemical Studies on Growth Properties of Polyaniline. *J. Electrochem. Soc* **1988**, *135* (9), 2254-2262.
80. Campiña, J. M., Potentiostatic Electropolymerization of Triphenylamine: A Low-Cost Cathode for Solid-State Photovoltaics. *J. Electrochem. Soc* **2015**, *162* (3), H142-H150.
81. Hyun, K. Y.; Christoph, S.; L., M. M.; Christian, M.; Lars, M. M.; Karl, L., Highly Conductive PEDOT:PSS Electrode with Optimized Solvent and Thermal Post-Treatment for ITO-Free Organic Solar Cells. *Adv. Funct. Mater.* **2011**, *21* (6), 1076-1081.
82. Obirai, J.; Nyokong, T., Synthesis, electrochemical and electrocatalytic behaviour of thiophene-appended cobalt, manganese and zinc phthalocyanine complexes. *Electrochim. Acta* **2005**, *50* (27), 5427-5434.
83. Sehlotho, N.; Nyokong, T., Electrocatalytic oxidation of thiocyanate, l-cysteine and 2-mercaptoethanol by self-assembled monolayer of cobalt tetraethoxy thiophene phthalocyanine. *Electrochim. Acta* **2006**, *51* (21), 4463-4470.

84. Cogal, S.; Ocakoglu, K.; Oksuz, A. U., The synthesis, photophysical and electrochemical studies of symmetrical phthalocyanines linked thiophene substituents. *Inorganica Chimica Acta* **2014**, *423*, Part A, 139-144.
85. Li, H.; Guarr, T. F., Electrochemistry at modified electrodes: Electronically conductive metallophthalocyanine coatings. *Synthetic Met.* **1990**, *38* (2), 243-251.
86. Kingsborough, R. P.; Swager, T. M., A Highly Conductive Macrocyclic-Linked Metallophthalocyanine Polymer. *Angew. Chem. Int. Edit.* **2000**, *39* (16), 2897-2900.
87. Yıldız, H. K.; Korkut, S. E.; Koca, A.; Kasım Şener, M., 3,4-Ethylenedioxythiophene substituted phthalocyanines. *Synthetic Met.* **2011**, *161* (17-18), 1946-1952.
88. Iwan, A.; Sek, D., Polymers with triphenylamine units: Photonic and electroactive materials. *Prog. Polym. Sci.* **2011**, *36* (10), 1277-1325.
89. Jia-Hao, W.; Guey-Sheng, L., High-Performance Electrofluorochromic Devices Based on Electrochromism and Photoluminescence-Active Novel Poly(4-Cyanotriphenylamine). *Adv. Funct. Mater.* **2014**, *24* (41), 6422-6429.
90. Lin, J.; Ni, X., Synthesis, structures, and electrochromic behaviors of poly(triarylamine)s based on 3-substituted thiophene derivatives. *RSC Advances* **2015**, *5* (19), 14879-14886.
91. Kearns, J. T.; Roberts, M. E., Enhanced performance of triarylamine redox electrodes through directed electrochemical polymerization. *J. Mater. Chem.* **2012**, *22* (6), 2392-2394.
92. Zhao, H.; Tanjutco, C.; Thayumanavan, S., Design and synthesis of stable triarylamine for hole-transport applications. *Tetrahedron Letters* **2001**, *42* (27), 4421-4424.
93. Chou, M.-Y.; Leung, M.-k.; Su, Y. O.; Chiang, C. L.; Lin, C.-C.; Liu, J.-H.; Kuo, C.-K.; Mou, C.-Y., Electropolymerization of Starburst Triarylamine and Their Application to Electrochromism and Electroluminescence. *Chemistry of Materials* **2004**, *16* (4), 654-661.
94. Tang, J.; Hua, J.; Wu, W.; Li, J.; Jin, Z.; Long, Y.; Tian, H., New starburst sensitizer with carbazole antennas for efficient and stable dye-sensitized solar cells. *Energ. Environ. Sci.* **2010**, *3* (11), 1736-1745.
95. Kimura, M.; Yasuta, K.; Adachi, N.; Tatewaki, Y.; Fukawa, T.; Shirai, H., Electrochromic Polymeric Films Derived from (Diphenylamino)phenyl-substituted Metallophthalocyanines. *Chemistry Letters* **2009**, *38* (1), 82-83.
96. Miyaura, N.; Suzuki, A., Palladium-Catalyzed Cross-Coupling Reactions of Organoboron Compounds. *Chem. Rev.* **1995**, *95* (7), 2457-2483.

97. Chen, Z.; Niu, L.; Cheng, Y.; Zhou, X.; Zhong, C.; Zhang, F., Octathienyl/phenyl-substituted zinc phthalocyanines J-aggregated through conformational planarization. *Dalton Transactions* **2011**, 40 (2), 393-401.
98. Yu, B.; Lever, A. B. P.; Swaddle, T. W., Electrochemistry of Metal Phthalocyanines in Organic Solvents at Variable Pressure. *Inorg. Chem.* **2004**, 43 (14), 4496-4504.
99. Yeh, S. J.; Tsai, C. Y.; Huang, C.-Y.; Liou, G.-S.; Cheng, S.-H., Electrochemical characterization of small organic hole-transport molecules based on the triphenylamine unit. *Electrochem. Commun.* **2003**, 5 (5), 373-377.
100. Onoda, M.; Nakayama, H.; Morita, S.; Yoshino, K., Electrochemical doping properties and electronic states of poly(3-phenylthiophene). *Journal of Applied Physics* **1993**, 73 (6), 2859-2865.
101. Tourillon, G.; Garnier, F., Structural effect on the electrochemical properties of polythiophene and derivatives. *J. Electroanal. Chem. Interfac. Electrochem.* **1984**, 161 (1), 51-58.
102. Pei, Q.; Zuccarello, G.; Ahlskog, M.; Inganäs, O., Electrochromic and highly stable poly(3,4-ethylenedioxythiophene) switches between opaque blue-black and transparent sky blue. *Polymer* **1994**, 35 (7), 1347-1351.
103. Van Tuan, D., Electronic and Transport Properties of Graphene. *Charge and Spin Transport in Disordered Graphene-Based Materials* **2016**, 5-34.
104. Onwubiko, A.; Yue, W.; Jellett, C.; Xiao, M.; Chen, H.-Y.; Ravva, M. K.; Hanifi, D. A.; Knall, A.-C.; Purushothaman, B.; Nikolka, M.; Flores, J.-C.; Salleo, A.; Bredas, J.-L.; Sirringhaus, H.; Hayoz, P.; McCulloch, I., Fused electron deficient semiconducting polymers for air stable electron transport. *Nature Communications* **2018**, 9 (1), 416.
105. González-Rodríguez, D.; Torres, T., Peripheral Functionalization of Subphthalocyanines. *European Journal of Organic Chemistry* **2009**, 2009 (12), 1871-1879.
106. G., B. R.; L., D. R., Reproducibility in Chemical Research. *Angew. Chem. Int. Edit.* **2016**, 55 (41), 12548-12549.
107. Gorvin, J. H., The synthesis of diarylamines by nitro-group displacement. Activation of anilines containing electron-withdrawing groups by potassium carbonate. *J. Chem. Soc. Chem. Comm.* **1985**, (4), 238-239.
108. Gorvin, J. H.; Whalley, D. P., Aromatic nitro-group displacement reactions. Part 1. A novel route to substituted 10-phenylacridones. *Journal of the Chemical Society, Perkin Transactions 1* **1979**, (0), 1364-1370.

109. Kondoh, A.; Yorimitsu, H.; Oshima, K., Nucleophilic aromatic substitution reaction of nitroarenes with alkyl- or arylthio groups in dimethyl sulfoxide by means of cesium carbonate. *Tetrahedron* **2006**, 62 (10), 2357-2360.
110. Kaake, L. G.; Barbara, P. F.; Zhu, X. Y., Intrinsic Charge Trapping in Organic and Polymeric Semiconductors: A Physical Chemistry Perspective. *The Journal of Physical Chemistry Letters* **2010**, 1 (3), 628-635.
111. Kortekaas, L.; Lancia, F.; Steen, J. D.; Browne, W. R., Reversible Charge Trapping in Bis-Carbazole-Diimide Redox Polymers with Complete Luminescence Quenching Enabling Nondestructive Read-Out by Resonance Raman Spectroscopy. *J. Phys. Chem. C* **2017**, 121 (27), 14688-14702.
112. Orellana, W., Catalytic Properties of Transition Metal-N₄ Moieties in Graphene for the Oxygen Reduction Reaction: Evidence of Spin-Dependent Mechanisms. *J. Phys. Chem. C* **2013**, 117 (19), 9812-9818.
113. Deng, D.; Chen, X.; Yu, L.; Wu, X.; Liu, Q.; Liu, Y.; Yang, H.; Tian, H.; Hu, Y.; Du, P.; Si, R.; Wang, J.; Cui, X.; Li, H.; Xiao, J.; Xu, T.; Deng, J.; Yang, F.; Duchesne, P. N.; Zhang, P.; Zhou, J.; Sun, L.; Li, J.; Pan, X.; Bao, X., A single iron site confined in a graphene matrix for the catalytic oxidation of benzene at room temperature. *Science Advances* **2015**, 1 (11).
114. Bezerra, C. W. B.; Zhang, L.; Lee, K.; Liu, H.; Marques, A. L. B.; Marques, E. P.; Wang, H.; Zhang, J., A review of Fe-N/C and Co-N/C catalysts for the oxygen reduction reaction. *Electrochim. Acta* **2008**, 53 (15), 4937-4951.
115. Walter, F.; Vratilav, K., Aromatic Nucleophilic Substitution. Part 1. Regiospecific Substitution of the Nitro Groups in 3,5-Dinitrophthalic-Acid Derivatives. *Helvetica Chimica Acta* **1985**, 68 (4), 846-853.
116. Dumoulin, F.; Durmuş, M.; Ahsen, V.; Nyokong, T., Synthetic pathways to water-soluble phthalocyanines and close analogs. *Coordin. Chem. Rev.* **2010**, 254 (23), 2792-2847.

5.1 Introduction

Overview

Dye sensitized solar cells (DSSC) are a class of thin film solar cells. DSSCs uniquely rely on photoelectrochemistry to generate electricity through the adsorption of light. This means that DSSCs are not fully solid materials and have liquid junctions. In the beginning, the concept of DSSCs originated from work highlighting dye sensitization of a semiconductor to generate photocurrent.¹⁻³ The concept culminated with the seminal paper from Grätzel and O'Reagan, where a fully functional DSSC was demonstrated.¹ At the time of writing this thesis chapter (2018), the original paper has over 25,000 citations.

The seminal paper incorporated an anode and cathode combined with iodine as the redox shuttle or mediator. The cathode material was platinum and the anode consisted of mesoporous TiO₂ layers sensitized with a ruthenium dye.¹ The initial report achieved an impressive 7.12% efficiency, with a 10% photocurrent degradation over 2 months of illumination,¹ setting a very high bar for the newly discovered photovoltaic devices.

Since the original paper nearly every aspect of the DSSC has been studied with great detail. For brevity the particulars of all the processes occurring in a DSSC will not be gone into with great detail. For background, an energy diagram of the general processes occurring in a DSSC are shown in Figure 5.1. The orange arrows in the diagram represent the ideal path an electron travels to perform work in a DSSC. The first part of the process, labeled 1, is excitation of the sensitizer or dye. Dyes are chosen and engineered to have

long excited lifetimes and fast injection into the conduction band of the TiO_2 layer.⁴ The injection process is label 2 in the diagram. At the cathode an electron reduces the mediator (process 3). Reduced mediator molecules can then diffuse to the anode to reduce the oxidized dye and complete the circuit (process 4). The black arrow in the diagram represent the maximum voltage obtainable in the solar cell which is the difference between the conduction band of TiO_2 and the E° of the mediator. This amounts to roughly ~ 1 V in a cobalt bipyridine mediated DSSC. In practice 1 V is typically not obtainable since there are efficiency losses within the cell.

The purple arrows in Figure 5.1 show some of the efficiency loss mechanisms. The dotted purple line represent relaxation of the excited dye, however this process is not favorable with current sensitizers. The purple arrow showing electrons moving from the conduction band of the TiO_2 to the dye or the mediator are most common (recombination). Dyes can be engineered to limit the recombination, there are additives which adsorb to the TiO_2 to block the surface also limiting recombination.⁵ Choosing mediators that have slower electron transfer rates for reduction is an additional strategy to impede recombination.⁶

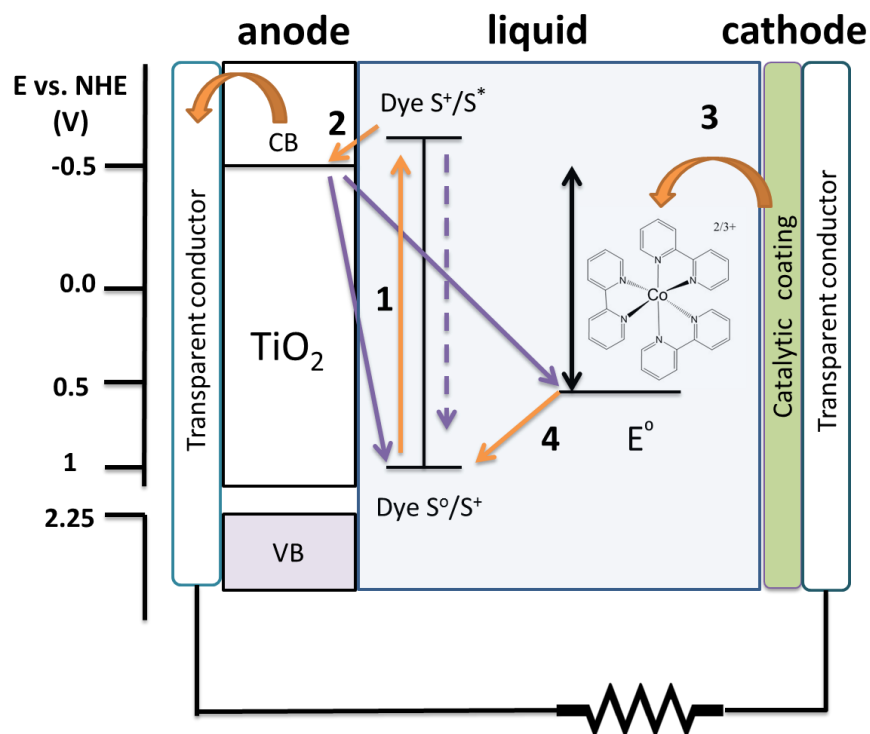


Figure 5.1 Energy diagram for cobalt bipyridine mediated DSSC. The orange and purple arrows represent electron transfer processes. CB designates the conduction band and VB is the valence band.

To improve DSSCs performance typically researchers have focused on the anode side of the solar cell. In the first demonstration of DSSCs ruthenium dyes were used and they are still a popular dye.⁷ To lower costs, organic dyes have been developed and now have efficiencies that meet or exceed ruthenium based dyes.⁸⁻⁹ Relevant to the work in this chapter and Chapter 4, phthalocyanines (Pc) have been extensively studied as sensitizers in DSSCs.¹⁰⁻¹² One of the highest efficiency DSSC to date was made with a porphyrin (similar structure to Pc) sensitizer.¹³ Pcs and porphyrins are desirable because they have a high molar absorptivity and as shown in Chapter 4 they can be easily derivatized.

For the mediator solution, iodine has been historically used, but now new redox shuttles of polypyridyl, copper coordination complexes, tempo, or ferrocene are quite popular.^{6, 14-16} The newer mediators have the ability to reach a higher theoretical photovoltage and are less corrosive than iodine. These new mediators have also been coupled with gel electrolytes to make quasi solid state DSSCs, limiting evaporation issues seen with the earlier acetonitrile based DSSCs.¹⁷ The TiO₂ layer is a topic of immense study, many different strategies have been proposed to try and minimize slow diffusion through the mesoporous TiO₂ network and maximize the sensitizer loading.¹⁸⁻²⁰ At the present there is an expanding plethora of materials and chemical strategies in which to fabricate a DSSC.

Quite promising for the commercial outlook of DSSCs, the issue of expensive dyes, volatile solvents, and corrosive mediators have been addressed. Current DSSCs can now readily achieve modest efficiencies (~5-10%) with low cost, readily available materials and can be fabricated with standard commercial techniques. While DSSCs may not be installed in mass on roof tops or in large arrays, they have the most potential for use in building integrated photovoltaics. Because of the colored semi-transparent properties of DSSC they are ideal for applications such as windows or building facades. They also could have uses in disposable electronics, since they can be made at a low cost with non-toxic materials. The rest of the Chapter 5 describes the development of a transparent catalytic coating for DSSC cathodes. The goal of these coatings is to enable use of DSSCs for transparent solar cell applications.

Cathode development for DSSCs

As discussed in the previous section, much attention has been placed on optimizing and understanding the anode and mediator components.^{21,13} It has only been recently (past ~5 years) that significant effort has been made on cathode optimization, with a near exponential increase in newly proposed cathode materials for both iodine and polypyridyl (and others)-based DSSCs.²²⁻²⁵ Historically, platinum has been used as a catalyst to facilitate electron transfer at the cathode.²⁶⁻²⁹ While the electron transfer kinetics with a platinum cathode are often sufficient for research purposes, the underlying cost is impractical for large scale production. Additionally, advances relating to increasing the efficiency of DSSCs have revealed that sluggish electron transfer and limited transparency at a platinum cathode can hinder the overall performance of a DSSC.³⁰⁻³⁴ Noble metal cathodes, including gold, can also present stability problems due most likely to surface fouling.³⁵ Therefore, the lack lustre performance and high cost of noble metal cathodes has led to research into alternative materials.

Graphene,^{30-32, 36} carbon nanotubes,³⁷⁻³⁹ carbon nanofibers,⁴⁰ carbon black,⁴¹ poly-aniline,⁴²⁻⁴³ polydioxothiophene (PEDOT),⁴⁴⁻⁴⁸ and others,⁴⁹⁻⁵¹ have been proposed as DSSC cathode materials. time consuming to make and have elaborate fabrication methods, which could lead to elevated cost.^{38, 40, 43} While many materials have been proposed, there still remains a need for stable, cheap, highly transparent cathode materials.

A transparent cathode allows for bifacial solar cells,⁵²⁻⁵³ a potential major advantage of DSSCs, in that nearly all angles of irradiance can generate photocurrent. Sequentially stacked DSSCs, which can enhance efficiency and tune voltage, are also possible with a clear cathode.⁵⁴ Transparent cathodes can also reduce the cost of DSSCs; a back illuminated DSSC can utilize less expensive anode substrates like Ti foil and stainless steel.⁵⁵ Additionally, by using substrates other than FTO, it leaves the option of growing TiO₂ films directly on the substrate with advanced control over morphology.⁵⁶⁻⁵⁷ Transparent cathodes are also desirable to make colored photovoltaics for windows and consumer products.⁵⁸⁻⁶⁰ Kavan detailed the need for a transparent highly catalytic cathode, with a focus on the transmittance at 550 nm (near the solar power maximum).²³ The proposed optimal values are a charge transfer resistance of 1.3 $\Omega \text{ cm}^2$, and a 100 % transmittance at 550 nm (T550).²³ Therefore, an inexpensive, stable material meeting these conditions would be the “holy grail” for a DSSC cathode.

Herein, we explore electrochemically polymerized nickel tetraaminophthalocyanine (NiTAPc) films as novel DSSC cathode materials. Phthalocyanines (Pcs) have a rich history in electrocatalysis due to their chemical stability, high activity, and low cost.⁶¹⁻⁶² Pcs are used commercially in many applications such as data storage (CDs), paints, printing inks and tattoos.⁶³⁻⁶⁵ More specifically, the use of metal tetraaminophthalocyanine-modified electrodes are widely varied, where they have been shown to be useful in sensors, are electrochromic, and have possible energy storage applications.⁶⁶⁻⁷⁰ Previous studies on polymeric tetraaminophthalocyanine films demonstrated them to be catalytic for

a variety of electrochemical reactions.^{67-68, 71-73} More importantly, it has been reported that M-TAPc films have favourable electrochemistry towards ruthenium and cobalt tris(bipyridine) complexes.⁷⁴ However, in that work the conditions were not the same as those of a DSSC, nor were the electrochemical techniques used fully comparable to those found in current DSSC cathode research.⁷⁴ The present study highlights conditions in a typical DSSC, as well as optimizing the NiTAPc films for a high transparency. Serendipitously, it was found that very thin layers of NiTAPc with a high transparency were the most catalytic, achieving a T550 of over 95% and R_{ct} below $1.3 \Omega \text{ cm}^{-2}$. The findings imply that tetraaminophthalocyanines are an immediate candidate for use as back and front illuminated (bifacial) DSSCs, as well as opening the door for the use of a wide range of phthalocyanines as cathode materials in DSSCs.

5.2 Results and discussion

Electropolymerization of NiTAPc

Initially, the polymerization of NiTAPc was examined on FTO (Figure 5.2A), demonstrating the typical redox process previously reported for this polymer.⁶⁹ At $\sim 0.25 \text{ V}$ vs. SCE the $\text{Ni}^{3+/2+}$ couple is proposed, with oxidation of the amine functionalized ring occurring at $\sim 0.7 \text{ V}$ vs. SCE. Other redox process of the polymer are two ring reductions at -1.00 V and -1.45 V vs. SCE (not shown).⁶⁹ Upon cycling the electrode past $\sim 0.7 \text{ V}$ vs. SCE the formation of a conductive polymer occurs, with increasing current as a function of cycle number.⁶⁹

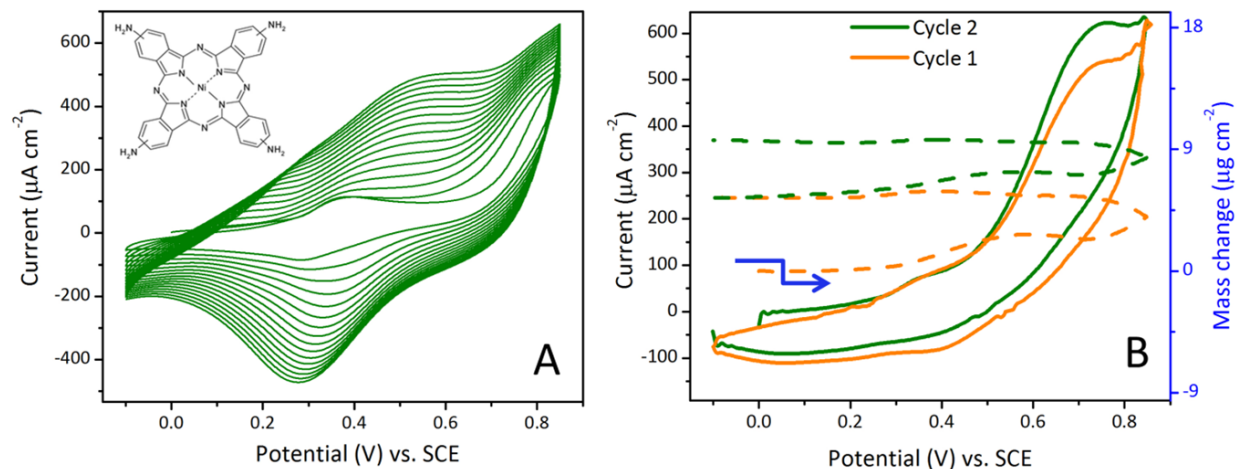


Figure 5.2 (A) Electropolymerization of 2 mM NiTAPc in DMSO on a FTO electrode with 16 CV cycles. Inset shows the structure of NiTAPc monomer. (B) Polymerization of a 2-cycle film on a gold electrode with the use of an EQCM, dotted lines represent the right Y2 axis (blue).

Figure 5.2B shows the deposition of the polymer as a function of current, with the use of EQCM to determine the mass change during polymerization.⁷⁵ Equation 5.1 in the materials and method section was used to relate frequency change to the mass change. On the initial anodic sweep (cycle 1), the first mass increase is speculated to be from ions or NiTAPc monomer adsorbed onto the electrode. The mass increase appears to start at the the $\text{Ni}^{3+}/2+$ redox process at ~ 0.3 V vs. SCE, plateauing around ~ 0.65 V vs. SCE. Adsorption is likely at potentials less than 0.65 V vs. SCE since polymerization does not occur below this voltage.⁶⁹ The second mass increase event occurs above 0.65 V, most likely from polymerization. The mass increase is continued on the cathodic sweep until ~ 0.6 V where it plateaus. To our knowledge EQCM has not been used previously to examine the polymerization of NiTAPc, however, the mass change events corroborate the earlier redox assignments for metal-TAPc electropolymerization.⁶⁹

Mass loading is related not only to electrode performance, but cost can be considered from the measured mass gained from EQCM experiments. Solvent, electrolyte, and porosity can all inflate the mass change seen in EQCM experiments of film growth,⁷⁶⁻⁷⁷ however, they will be not accounted for here. If an assumption that only NiTAPc is being deposited on the electrode, $\sim 6 \mu\text{g cm}^{-2}$ of material was deposited after the first cycle and $\sim 4 \mu\text{g cm}^{-2}$ with the second cycle, for a total of $10 \mu\text{g cm}^{-2}$. Using $10 \mu\text{g cm}^{-2}$, the cost of a 2-cycle film was estimated to be $\$0.65 \text{ m}^{-2}$. The material cost is based on synthetic cost of NiTAPc using retail sources and assumes a 50% yield. Additional details on cost analysis can be found in Table 5.1. While the cost analysis is not all encompassing, as an estimate, it demonstrates that NiTAPc can be a potentially cost effective and a scalable option as a polymeric coating for DSSC cathodes, as well as other catalytic electrochemical applications.

Charge transfer resistance to CoBipy

The data shown in Figure 5.3 is the Nyquist plot from a NiTAPc 2-cycle film in a thin layer cell. The Nyquist plot was constructed from electrochemical impedance spectroscopy (EIS) and the experimental details can be found in the methods section. The thin layer cells contain Co(bipy) and have the expected spectra for a simple charge transfer process where the cobalt metal center is switching from the 2+ to the 3+ oxidation state. Impedance is quite useful to evaluate electrochemical kinetics because the processes of diffusion and charge transfer are often decoupled. Importantly, cell resistance is also decoupled from charge transfer resistance.

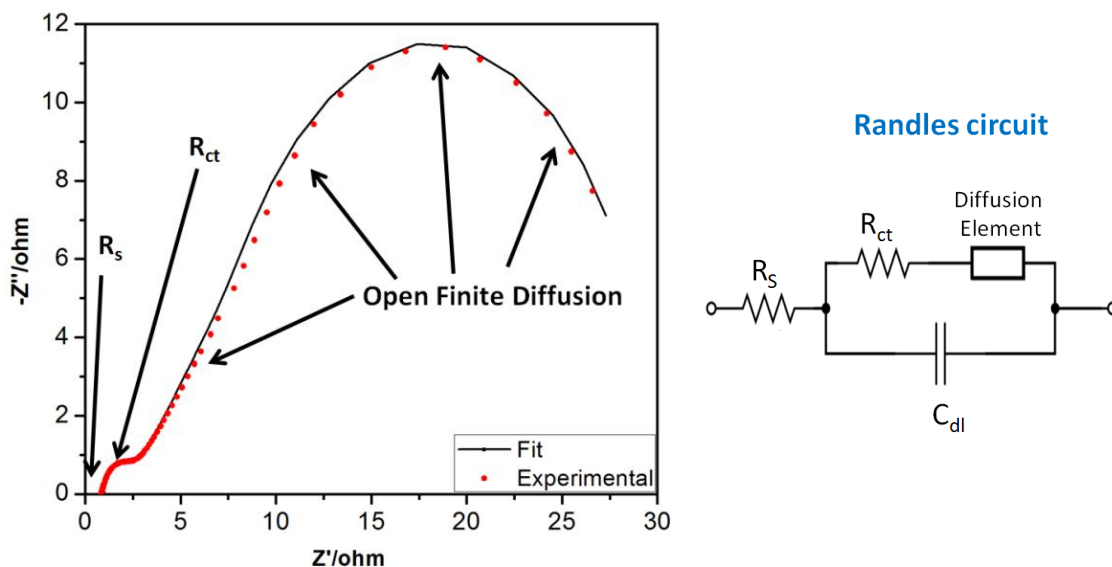


Figure 5.3. Typical 2-electrode symmetric cell (containing Co(bipy)) impedance spectra (Nyquist) for a 2-cycle NiTAPc film on a glassy carbon electrode. The circuit elements present in the circuit diagram are pointed out relative to their respective location on the Nyquist plot. Experimental fit is also shown as a black line.

EIS spectra can be modelled with circuit elements which define the individual processes. Most if not all commercial potentiostats provide software for modelling EIS spectra. The combination of the circuit elements of a resistor, capacitor and resistor in series, and an open boundary finite-length Warburg element are shown on the right of Figure 5.3 (Randles circuit). This circuit describes a charge transfer process in a thin layer two electrode electrochemical cell, where both layers are electrochemically active.³⁰ In general, the data from the symmetric cells fit well to the proposed model as seen in Figure 5.3 as the black trace.

Upon successfully polymerizing NiTAPc and demonstrating the ability to adjust the mass and/or film thickness, the electrode coatings were investigated for

their catalytic properties towards the popular Co(Bipy) DSSC mediator through the use of EIS.²⁹ It was found that the charge transfer resistance increased with the number of deposition cycles, as shown in Figure 5.4. The thin 2-cycle NiTAPc films gave R_{ct} values in the range of $0.5 \Omega \text{ cm}^2$, with $2.3 \Omega \text{ cm}^2$ for a 6-cycle film, and $23 \Omega \text{ cm}^2$ for 16-cycle films. The 16-cycle film Nyquist plot cannot be fit with a simple Randles circuit. The spectra is better fit with two kinetically controlled processes, where a second charge transfer process is denoted here as $R_{ct} \text{ (polymer)}$. The additional charge transfer process is not uncommon in DSSC cathode research and it has been attributed to ionic mobility within the pores of PEDOT.⁴⁵ A similar second transfer process was also seen with a porous graphene coated FTO electrode.³² An alternative explanation for the second charge transfer process may be from the rate of electron transport through the polymer matrix, which would scale with film thickness,⁶⁸ this has been seen with other polymeric catalytic coatings as well.⁷⁸ The calculated R_{ct} for the 16-cycle film is then the sum of $R_{ct} \text{ (polymer)} + R_{ct} \text{ Co(Bipy)}$, and values of $9 \Omega \text{ cm}^2$ and $14 \Omega \text{ cm}^2$ were found, respectively.

Propylene carbonate was chosen as the solvent to minimize evaporation during testing, but the data in Figure 5.4 demonstrates that an R_{ct} using acetonitrile of $0.7 \Omega \text{ cm}^2$ (2-cycle film) can be achieved. Acetonitrile is a popular solvent for testing DSSC's,⁷⁹ therefore the NiTAPc films should perform well in the solvent. The similar R_{ct} of PC and ACN is unusual as increased viscosity is typically related to slower kinetics with Co(bipy).⁸⁰ Perhaps the high Co(Bipy) and additive concentrations used here are causing deviations from previous observations for Co(bipy) in ACN and PC, where nearly an order of magnitude slower kinetics was

seen in PC.⁸⁰ In any event, both higher viscosity PC (2.5 cP), and lower viscosity ACN (0.33 cP),⁷⁹ do not have vastly different charge transfer resistance to Co(bpy) in this system. Both solvents have an R_{ct} below the desired $1.3 \Omega \text{ cm}^2$. Finally, the reproducibility of R_{ct} was briefly examined with the 2-cycle cells in PC, and a value of $0.67 \pm 0.26 \Omega \text{ cm}^2$ was found for 10 symmetric cells (20 electrodes total) over the period of one year. Overall, the lack of any highly specific set of optimized conditions to achieve R_{ct} values below $1.3 \Omega \text{ cm}^2$ is promising (Figure 5.6) for practical use of these coatings.

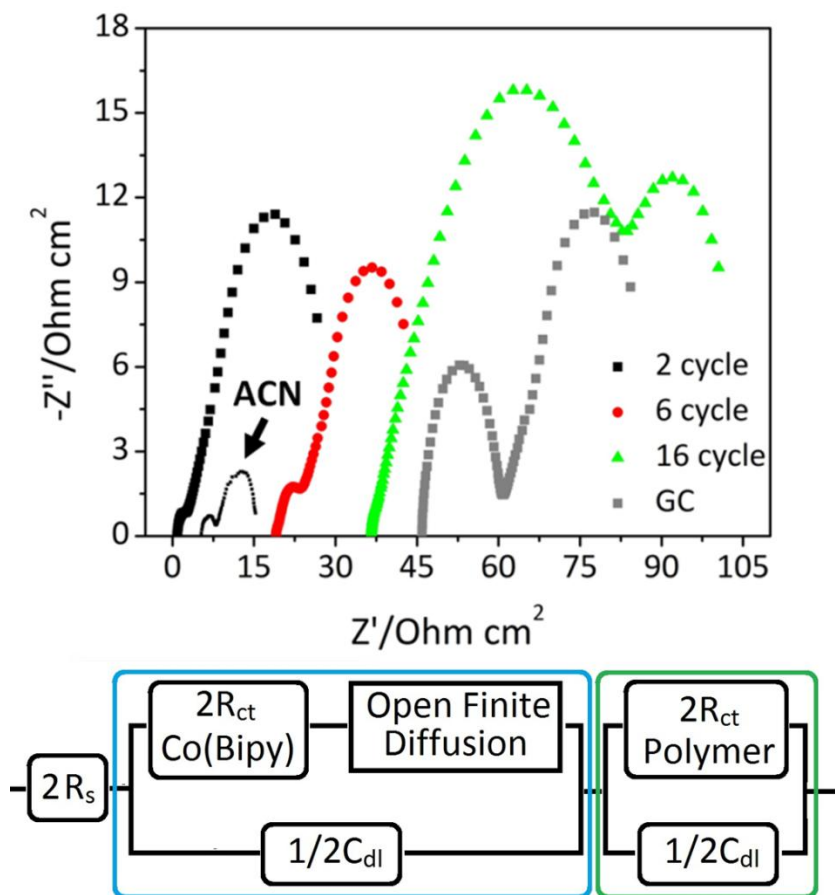


Figure 5.4 Impedance spectra of Co(Bipy) in PC at glassy carbon (GC) modified with NiTAPc. The 2-cycle film was also tested with Co(Bipy) in acetonitrile (ACN). (Bottom) The 2-cycle and 6-cycle NiTAPc modified electrodes are fit to a standard Randles circuit (blue outline). 16-cycle film was fit with the modified circuit which combines the green and blue outlines in the circuit diagram. Spectra are manually shifted on X-axis for clarity.

Polarization curves and Tafel plots of the symmetric cells used in Figure 5.4 can be found in Figure 5.5. In a Tafel plot a steeper slope that approaches plateau sooner is indicative of fast kinetics,⁴¹ this is seen with the 2-cycle and 6-cycle films. The 16-cycle and GC Tafel plots approached plateau with a slightly less steep slope, which agrees with the larger charge transfer resistance seen in Figure 5.5. The fast

kinetics of NiTAPc observed by EIS are then qualitatively corroborated with the Tafel plots.

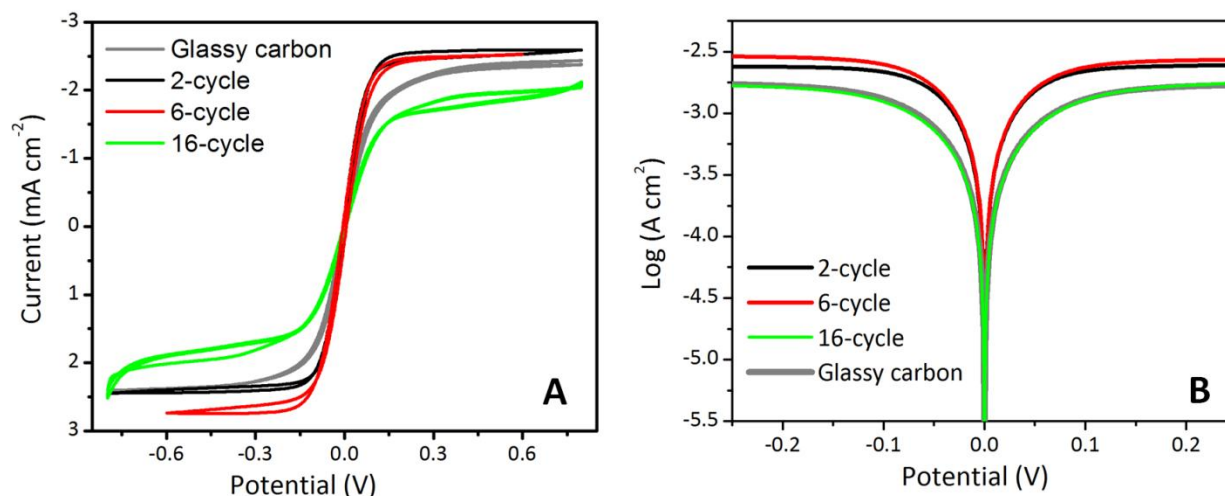


Figure 5.5 (A) Cyclic voltammetry of bare glassy carbon as well as electrodes coated with NiTAPc formed through increasing cycle numbers. (B) Tafel plots derived from Figure 5.5A. The data was collected with a scan rate of 10 mV s⁻¹ in propylene carbonate based mediator.

Increased mass transfer resistance which can lower steady state current is seen with some DSSC counter electrode (CE) coating.⁴² Therefore, measuring diffusion coefficients is important for CE characterization. Diffusion coefficients of Co(Bipy) were calculated with PC as the solvent. Values of $9.8 \times 10^{-7} \pm 1.2 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ were calculated from the diffusion region in the Nyquist plots for all cells shown in Fig. 5.4 (details methods). Diffusion coefficients were calculated a second way by using the limiting currents from the polarization curves in Figure 5.5 and values of $6.2 \times 10^{-7} \pm 0.7 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ were found (see methods). The polarization curves may be more accurate since they more resemble a working DSSC. As shown in Figure 5.5

the 16-cycle film has a reduced limiting current, possibly from mass transfer resistances induced by the thicker film, further demonstrating the enhanced performance of thinner NiTAPc films. Both methods for measuring diffusion coefficients gave values that are similar to previous reports of Co(Bipy) in PC.⁸⁰

Optical transmittance and charge transfer resistance to Co(Bipy)

The polymer films were examined with UV-Vis spectroscopy to determine the relationship between transmittance and cycle number. Figure 5.6 shows that the transmittance decreases with increasing cycle number, as expected. The transmittance of the NiTAPc films mimics the monomer spectra and has typical Q and Soret band absorptions at 716 nm and 304 nm along with shoulders at 639 nm and 418 nm, respectively. The monomer UV-Vis spectra can be found in the methods section Figure 5.15 and agrees quite well with a previous report for NiTAPc.⁸¹ Additionally, the broadening of the peaks seen in Figure 5.6 are typical of polymeric and layer-by-layer Pcs.⁸²⁻⁸³ Interestingly, the thin films show an interference pattern from ~750 nm to 1000 nm that is indicative of a highly uniform coating.⁸⁴

Visually, the absorptions of poly-NiTAPc create a deep green color on the FTO substrate for thicker films (bottom Figure 5.6). The 2-cycle NiTAPc film seems to have a less pronounced green appearance, probably from the thinner film having a more uniform transmittance from 300 nm to 900 nm. While the films are not fully transparent in the entire visible region, they are highly transparent at 550 nm near the solar spectrum power maxima (Y2 axis Figure 5.6).⁸⁵

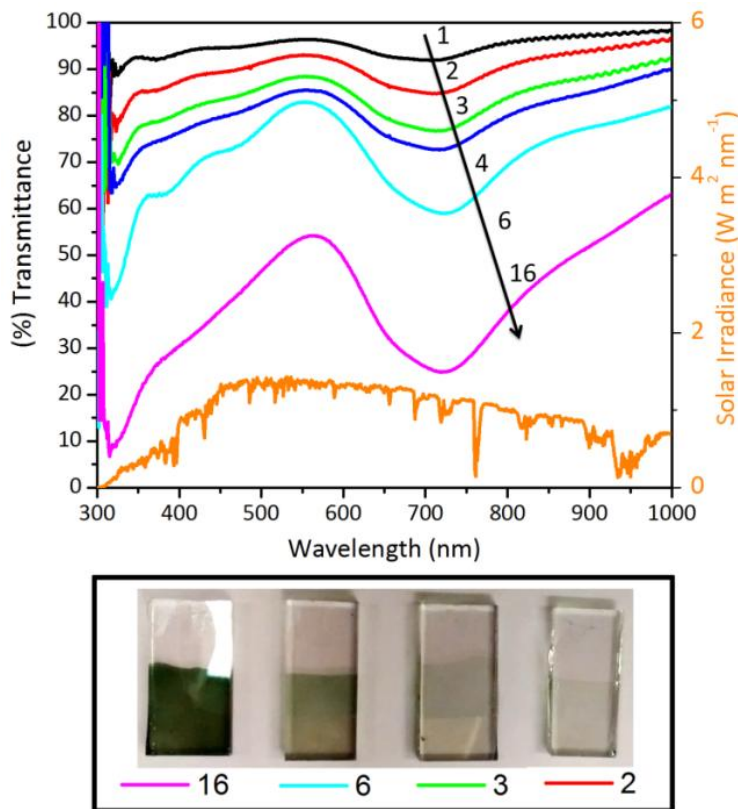


Figure 5.6 Transmittance spectra of FTO coated with poly-NiTAPc with various cyclic voltammetry cycle numbers. The transmittance of FTO was subtracted. (Bottom) images of coated electrodes as a function of cycle number.

In Figure 5.7, the 1-cycle electrode made from 0.5 mM NiTAPc had a transmittance of 97.5% and R_{ct} of $1 \Omega \text{ cm}^2$, which is very close to “the holy grail” values mentioned in the introduction. An apparent linear relationship is seen for the 2 mM condition, and the linear fit was $Y = -2.7(\pm 0.1)X + 97.5(\pm 0.8)$ with an R^2 of 0.993. Since thin films appear to be the most catalytic and have the highest transmittance, a lower monomer concentration was also tested to see if polymerization could be slowed down. The equation for the 0.5 mM condition was $Y = -1.2(\pm 0.4)X + 98.7(\pm 1)$, implying that (within error) the rate of film formation can

be adjusted. Lower NiTAPc monomer concentrations may help with further optimization, whereby fine tuning the transmittance and R_{ct} .

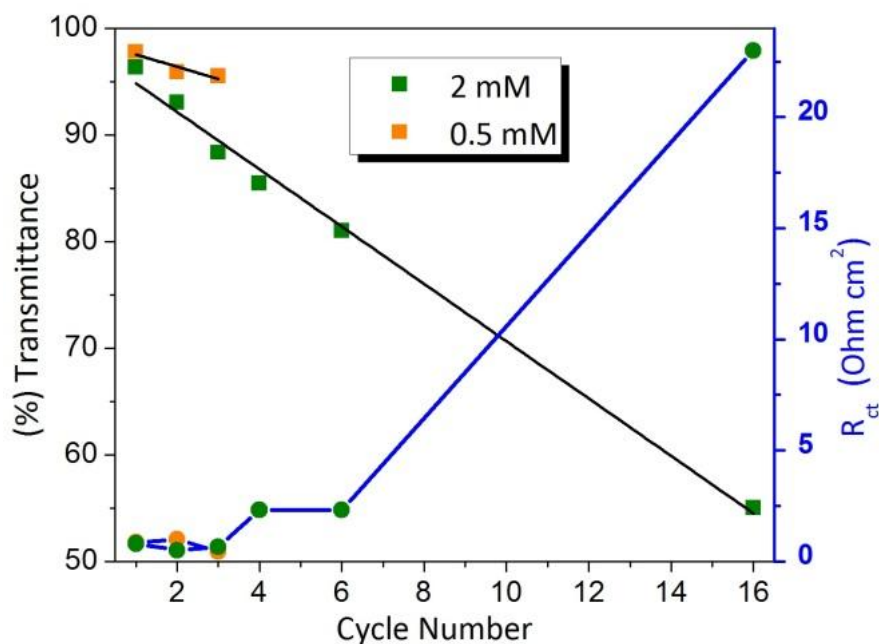


Figure 5.7 Transmittance of NiTAPc films at 550 nm as a function of CV cycle. Charge transfer resistance is located on the Y2 axis. Circles are R_{ct} with blue connecting lines, squares are the transmittance with black lines as the linear fits.

Effect of 4-tert-Butylpyridine on R_{ct} to Co(bipy)

4-tert-Butylpyridine (TBP) is a common additive to DSSCs,⁸⁶ but it has been shown to have deleterious effects on the charge transfer kinetics at the cathode.³⁵ While the kinetic effects of TBP are known at the anode (recombination),⁸⁶ it is rarely studied at the cathode. TBP effects are shown in Figure 5.8 where the R_{ct} at glassy carbon increases from $9 \Omega \text{ cm}^2$ to $\sim 20 \Omega \text{ cm}^2$ upon the addition of 0.2 M TBP. The increase may arise from adsorption of TBP to the carbon surface. McCreery has shown that a glassy carbon electrode contaminated with adventitious carbon can be

cleaned with pyridine to improve kinetics, implying that pyridine strongly interacts with carbon surfaces.⁸⁷ In our work, the pyridine is never removed from the system, which may explain the different result. If adsorbed to the surface, TBP has an aliphatic moiety which would likely further hinder electron transfer. The opposite trend was seen for a glassy carbon electrode modified with a 2-cycle NiTAPc film. The NiTAPc-modified electrode had a nearly 60% decrease with R_{ct} with the addition of TBP. Apparently the TBP is not fouling the electrode in the same manner on NiTAPc films as it is with GC. Changing solvent dynamics with TBP may explain a lower R_{ct} . Murray,⁸⁰ as well as others,⁸⁸⁻⁸⁹ have discussed various solvent effects for reaction rates of polypyridyl complexes, which can be related to ion-pairing, double layer effects, and viscosity. However, a detailed analysis of why TBP is lowering the R_{ct} will not be done here.

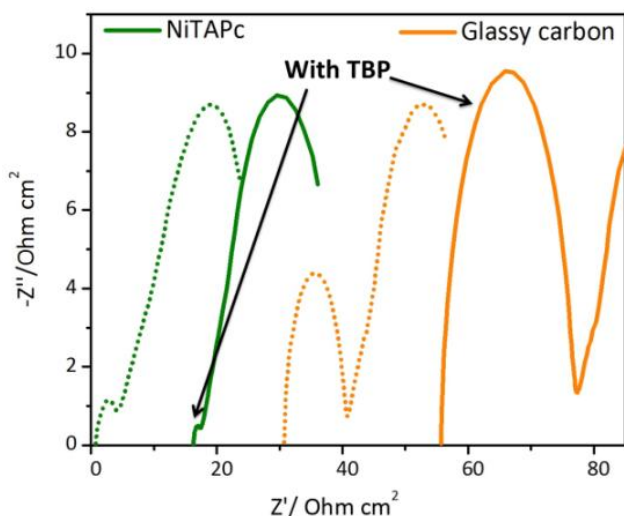


Figure 5.8 Nyquist plots highlighting the effect of TBP on the charge transfer kinetics of 2-cycle NiTAPc modified and unmodified glassy carbon electrodes. Dotted lines are without TBP. Spectra are manually shifted on X-axis for clarity.

Stability of NiTAPc in CoBipy mediator solutions

The stability of catalytic coatings are of concern in DSSC applications given that the films are required to maintain catalysis over years of continued use.⁹⁰ Briefly, NiTAPc 2-cycle films were investigated for stability (Figure 5.9). The 2-cycle NiTAPc films maintained excellent stability under cycling. After 2000 cycles, the R_{ct} value had a negligible increase from 0.4 to 0.6 $\Omega \text{ cm}^2$. However, in another set of experiments, after 24 hrs in mediator solution (ambient conditions), the R_{ct} value increased from 0.5 $\Omega \text{ cm}^2$ to 1.7 $\Omega \text{ cm}^2$, and on the fourth day climbed to 2.5 $\Omega \text{ cm}^2$.

The stability over four days suggests that the NiTAPc films have some kinetically slow physical or chemical change within the polymer, which is increasing the R_{ct} value over time. It was thought that ambient oxygen was causing a change in

the chemical structure of the NiTAPc films, however, stability experiments performed in oxygen free (≤ 1 ppm) drybox conditions gave similar results. The doping mechanism of metal-TAPc can change with the donor number of the solvent,⁸² suggesting the slow change in R_{ct} could be related to the ion/solvent doping mechanism in PC. Related, remarkable stability of 1 million cycles has been reported for poly-aniline (a similar polymerizable moiety to NiTAPc) in ionic liquids,⁹¹ attributed to a more reversible intercalation/doping mechanism. It is conceivable that a different solvent or electrolyte system may stabilize the NiTAPc polymer, whereby stabilizing the R_{ct} in a working DSSC. Solvent and electrolyte effects would make for a logical follow-up study to this initial work.

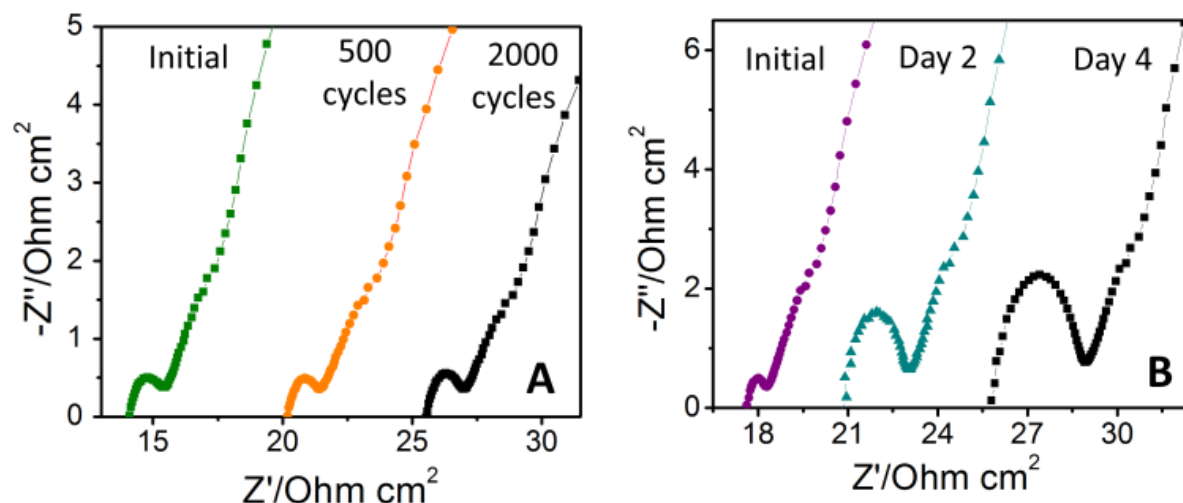


Figure 5.9 (A) Impedance spectra of the 2-cycle films after repeated CV cycling at 400 mV s^{-1} from -0.5 to 0.5 V in DSSC mediator solution in a symmetric cell. (B) Spectra taken after days of aging in mediator solution. Spectra are manually shifted on X-axis for clarity.

XPS analysis of NiTAPc coated electrodes

To further examine the effects of cycling and aging on the NiTAPc films XPS measurements were performed. The “fresh” designation are for NiTAPc (2-cycle) films created about 1-2 hrs before XPS measurements. The “cycled & aged” films were left in mediator solution for 2 days, as well as cycled 1500 times. Figure 5.10 has a representative survey spectrum for a NiTAPc 2-cycle film. The presence of tin in the spectra suggests that the NiTAPc film is only a few nanometers thick.

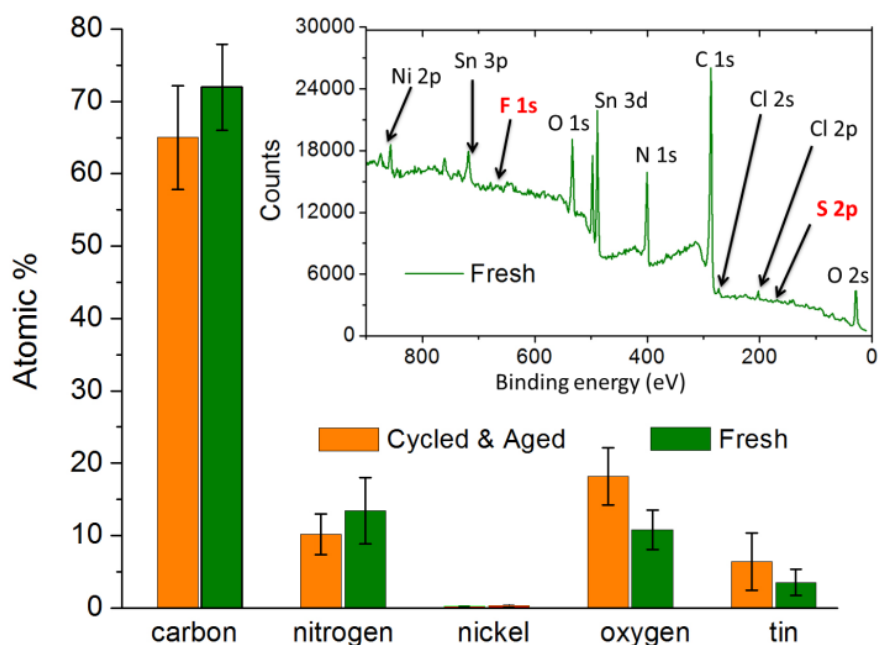


Figure 5.10 Atomic percentage from XPS for NiTAPc (2-cycle) on FTO, and after aging for 2 days and cycled 1500 times. Nickel had a percentage of $0.32 \pm 0.17\%$ for fresh film and $0.24 \pm 0.10\%$ for the aged film. Error bars are from six individual electrodes for both conditions. Inset is a typical survey scan of a fresh 2-cycle NiTAPc film.

Interestingly, the spectrum lacks a fluorine signal that could arise from the substrate or the PF₆ electrolyte. Sulphur from DMSO was also not present. The only potential electrolyte present was chloride, possibly from the reference electrode or from lithium perchlorate. Not all the samples had measurable Cl, and the samples that did were ≤ 2 atomic %. A carbon to nitrogen ratio of 2.6 would be expected in pure NiTAPc, however, a ratio of ~ 5.2 was found in typical spectra. The difference is most likely from adventitious carbon. The bar graph in Figure 5.10 shows that, within error, the Sn, N, C, and Ni elemental atomic % (from peak area) is not changing significantly for the two conditions. However, the O 1s atomic % does appear to be slightly increased for the aged films. This is examined further in the high-resolution spectra in Figure 5.11.

The high resolution XPS collected for carbon, oxygen, tin and nitrogen are shown in Figure 5.11. The shape of the C 1s and O 1s peaks change significantly with cycling, shifting to higher binding energies. One hypothesis for the peak shift could be that propylene carbonate has been incorporated into the polymer. PC incorporation would most likely raise the carbon %, however, this is not observed (Figure 5.10). Alternatively, if NiTAPc was replaced by other carbon rich species, that would explain the different binding environments seen in Figure 5.11. Related, in Figure 5.10 it appears that on average the N and C content is lower for aged films, as well as increased Sn signal, somewhat supporting the loss of NiTAPc with aging hypothesis. Loss of material and polymer rearrangement is not unprecedented with N4 macro-cycles, where poly-(tetraaminophenyl) porphyrin was reported to have a

loss of oligomer/polymer material during aging & cycling.⁹² If NiTAPc is lost, it may then be replaced by species from the mediator solution, or adventitious carbon.

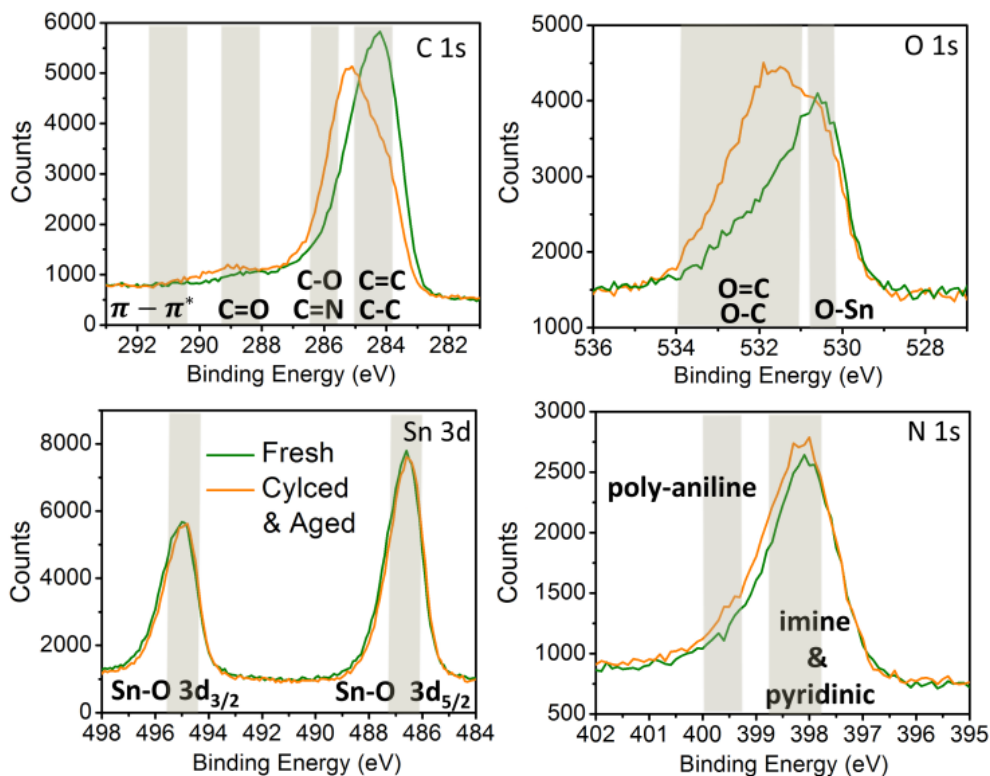


Figure 5.11 Typical high resolution C, O, Sn, and N XPS of 2-cycle NiTAPc films on FTO before and after being cycled and aged. Grey bars represent general binding energies for specific chemical environments.

Lost NiTAPc, if occurring, may expose surface hydroxyls on the FTO a possible reason for the higher binding energies seen in the O 1s peak in Figure 5.11.⁹³ Oxidative attack on the Pc ring structure could be a possible explanation for the C 1s and O 1s peaks, but this seems unlikely since phthalocyanines are notoriously stable under ambient, as well as harsh, conditions.⁶⁵ Overall, there is no simple answer at the present for changes to the C 1s and O 1s peaks, nonetheless these chemical

changes could be related to the instability of the poly-NiTAPc films. Finally, the nitrogen peak is changing very little, indicating the N binding environments are not drastically changing, this is promising because poly-NiTAPc are formed through amine linkages.

5.3 Conclusion and Future Work

Overview

Thin layer nickel tetraamino phthalocyanine polymer coated cathodes were tested for electrochemical catalysis in cobalt mediated DSSCs. The thin films were found to be highly catalytic and highly transparent, having a T_{550} of $\sim 95\%$. The coatings were determined to be sufficiently stable during testing in a fundamental research setting; however, under the conditions tested, long term stability was not achieved. The findings warrant further examination of phthalocyanines for transparent cathodes in DSSCs. Continued research need not be limited to tetraaminophthalocyanine polymers, and a wide variety of central metals and ring substituted single molecule and polymeric phthalocyanines are worth investigating. Phthalocyanines are currently made on the ton scale for the dye industry, meaning they are cheap to produce, and are generally considered safe for consumer use. This fact is highly motivating for future examination of this already prolific class of molecules for DSSC applications.

Future work

The future work relating to Pc coated electrodes would most likely benefit from developing strategies to stabilize the Pc on the surface of the electrode. Stabilizing coatings of Pc would not only benefit work with DSSCs but also generic application in electrochemical catalysis which utilize Pc (see Chapter 4). Related, the copper (diphenylamino) films made in Chapter 4 were tested for their catalytic activity with Co(bipy), but they were found to be inactive, possibly from not being sufficiently conductive at the potentials needed to facilitate electron transfer to Co(bipy).

Another method to apply phthalocyanines to an electrode surface could be from covalent bonds. Carboxylic acids can react with FTO to form a covalent linkage. The Elliott lab has shown that an osmium (bipy) complex grafted to FTO can serve as a relatively stable and transparent DSSC cathode.⁴⁹ Tetracarboxyphthalocyanines are a well-known compound which could be used within this covalent electrode modification scheme also.

Vapor deposition of phthalocyanines is quite common. Sublimation is also a method used to purify phthalocyanines.⁹⁴ Vapor deposited Pcs should be able to be applied in the thin layers needed for an optically transparent electrode. One issue may however arise from the layer being slightly soluble in the solvent used in the DSSC. To try and avoid desorption from the electrode, the Pc vapor deposited films could be pyrolyzed. Pyrolysis of Pc films forms a graphitic nitrogen rich conductive network. Pyrolyzed Pc has been used previously in supercapacitor and fuel cell application with success.⁹⁵⁻⁹⁶

Finally, the work with conductive polymers and ionic liquids is quite interesting in terms of enhanced stability.⁹¹ When in the presence of ionic liquids some conducting

polymers can be stable for up to a million charge discharge cycles. Investigating the stability of the NiTAPc films in ionic liquids is a logical next step to achieve temporal stability of Pc based cathodes. Ionic liquids have been proposed for use in DSSCs, which makes working with them as a stabilizer relevant.⁹⁷⁻⁹⁹ Overall ionic liquids, to the best of knowledge, have not been explored with polymerizable Pc. This work with ionic liquids would have broad impacts for applications such as charge storage, electrochromics, or possibly synthetic electrochemistry.

5.4 Materials and Methods

Electrochemistry in symmetric cells and UV-Vis measurements

The electrochemistry was performed on a CHI-750 potentiostat. Polymerization was done in a 3-electrode cell with 2.5 cm² Pt counter and saturated calomel (SCE) reference electrodes. Electropolymerization was done starting at -0.1 and swept to 0.85 V, followed by a return scan, all at 100 mV s⁻¹. The polymerization solution was 2 mM NiTAPc (except Fig. 4) in dimethylsulfoxide (Alfa) with 0.1 M tetrabutylammonium hexafluorophosphate (Sigma).⁶⁹ The mediator was composed of 0.3 M [Co²⁺(Bipy)₃](PF₆)₂, 0.055 M [Co³⁺(Bipy)₃](PF₆)₃, 0.2 M LiClO₄ (Sigma), 0.2 M 4-tertbutylpyridine (TBP) (Sigma) in propylene carbonate (PC) (sigma) or acetonitrile (ACN) (Sigma). The two electrode cells used FTO (Sigma) or glassy carbon (Tokai) and a 25 μm Kapton spacer with working area 1 cm². AC impedance measurements were conducted from 0.1 to 10000 Hz, at 0 V with perturbation amplitude of 10 mV.

Nickel tetraaminophthalocyanine was synthesized using the phthalonitrile route, details can be found in further down in this section. NiTAPc characterization by H^1 -NMR, IR, and UV-Vis are in Figure 5.13-5.14. For UV-Vis measurements, a thin layer cell was used, with a 25 μm Kapton spacer and neat PC between two NiTAPc coated electrodes, bare FTO in the same configuration was used for background subtraction.

XPS measurements

X-ray photoelectron spectroscopy (XPS) was performed with a 5800 MultiTechnique XPS system, with Al $K\alpha$ x-ray source. The high resolution spectra were fit with CasaXPS, using a Shirley background. The spectra of NiTAPc have been shifted by 1.2 eV as a correction to align the Sn 3d and O 1s peaks with known values for FTO. For FTO, Sn peaks occur at 495 eV for $3d_{3/2}$ and 486.5 eV for $3d_{5/2}$, and the O 1s in SnO_2 is at 530.5 eV.¹⁰⁰ General assignments for the O 1s,¹⁰¹ N 1s,¹⁰²⁻¹⁰³ and C 1s¹⁰¹ are taken from previous literature precedent.

Mass determination with EQCM

A Gamry EQCM 10M was used to monitor mass changes, using a gold coated 10 MHz quartz crystal with a working area of 0.209 cm^2 . The added mass onto the electrode was related to the change in frequency using a reduced form of the Sauerbrey equation.¹⁰⁴ Δf is the change in frequency, C_f is the calibration constant ($226\text{ Hz cm}^2\text{ }\mu\text{g}^{-1}$) for a 10 MHz quartz crystal. NiTAPc film formation typically caused a change in frequency no greater than 0.3 %, this is well under a 2 % change in frequency, which is the general acceptable limit to use Equation 5.1

$$\Delta f = C_f (\Delta \text{mass } (\mu\text{g cm}^{-2})) \quad \text{Equation 5.1}$$

Calculation of diffusion coefficients of Co(Bipy)

Using Nyquist plots obtained from symmetric cell impedance, diffusion coefficients were calculated with the CH instruments software with an open finite diffusion circuit element. Fitting is shown in the Figure 5.3. The circuit element is described by Hauch for diffusion within a symmetric cell,³⁴ $i\omega$ are variables determined from fitting the spectra, W is the Warburg parameter, D is diffusion coefficient, δ is the diffusion layer thickness (l), for a symmetric cell $\delta=0.5 \cdot l$.

$$K_N = \frac{D}{\delta^2} \quad Z_{Open\ Finite} = \frac{W}{\sqrt{i\omega}} \tanh\left(\sqrt{\frac{i\omega}{K_N}}\right) \quad \text{Equation 5.2}$$

By measuring the limiting current in symmetric cell slow scan cyclic voltammetry experiments, the diffusion coefficients for Co(Bipy) was calculated using Equation 5.5,³⁴ where δ is the diffusion layer thickness, n is the number of electrons, F is Faraday's constant. c is the concentration of the limiting species $[\text{Co}^{3+}(\text{Bipy})_3]$.

$$D = \frac{J_{limiting}(\frac{\delta}{2})}{nFc}$$

Equation 5.5

Synthesis of nickel tetranitrophthalocyanine (NiTNPc)

To a 25 mL round bottom flask fitted with a condenser, 10 mL (129 mmol) of DMF was added and heated to 110 °C, while being degassed (N₂) with stirring. 1.307 g (5.5 mmol) of NiCl₂*6H₂O was then added, followed by 4.15 g (24 mmol) of 4-nitrophthalonitrile. The whole mixture was then brought up to 140 °C, the reaction was blue in color. Then 0.8 mL (5.25 mmol) of 1,8 diazabicyclo(5,4)undecene (DBU) was added and the reaction turned a maroon color. The reaction temperature is above the boiling point of DBU, however, the reaction is under mild reflux. Roughly 20 min later the reaction mixture appears to be heterogeneous black/dark blue in color. 40 min after reaching 140°C, another 0.3 mL (1.97 mmol) of DBU was added, the reaction seemed to fume slightly. An oil bath is recommended for heat control, as to not char any precipitated reaction products from heat gradients.

The reaction was stopped 5 hours after the last addition of DBU and was poured into 50 mL of water, and was left to sit overnight. The suspension was filtered and washed with 200 mL of water. The material formed a thick cake, which appears to be slightly soluble in acetone. The solid was then stirred in a 0.5 M HCl solution then filtered and washed with copious water. The cake was then stirred in 0.5 M NaOH, then vacuum filtered. The filtrate was light brown in color. Again, the solid was stirred in 0.5 M HCl filter and then treated again with 0.5 M NaOH, filtered, and finally washed with copious water. At this

point, the consistency of the solid was quite fine, and was similar to wet clay. Some of the solid was pulling through the filter paper, given the small particle size, a fine pore size frit is recommended. Chunky solids can trap impurities and the phthalocyanine should be ground up if they are present. The wet solid was then brought to a pH of ~ 7 , then dried in a vacuum oven overnight at $\sim 70^\circ\text{C}$. Total mass of the recovered solid was 2.39 grams (3.18 mmol), 57.8 % yield.

Synthesis of nickel tetraaminophthalocyanine (NiTAPc)

1.72 g (2.29 mmol) NiTNPc was added to ~ 50 mL of water, then 10.1 g (42 mmol) of sodium sulfide was added. The RBF (100 mL) fitted with a condenser was then placed in an oil bath. The reaction was held at $\sim 70^\circ\text{C}$ with stirring for ~ 8 hrs. The mixture was then vacuum filtered, and washed with copious amounts of water, then washed with 100 mL of acetone. The solid was stirred in 0.5 M HCl, vacuum filtered, then washed with water. This procedure was repeated with a 0.5 M NaOH solution. The solid was then neutralized (pH ~ 7) and washed with copious water, followed by ~ 50 mL of methanol in aliquots. The cake was then placed in vacuum oven and dried at 80°C for 18 hrs. The recovered mass was 1.1 g (1.64 mmol), 71.6% yield.

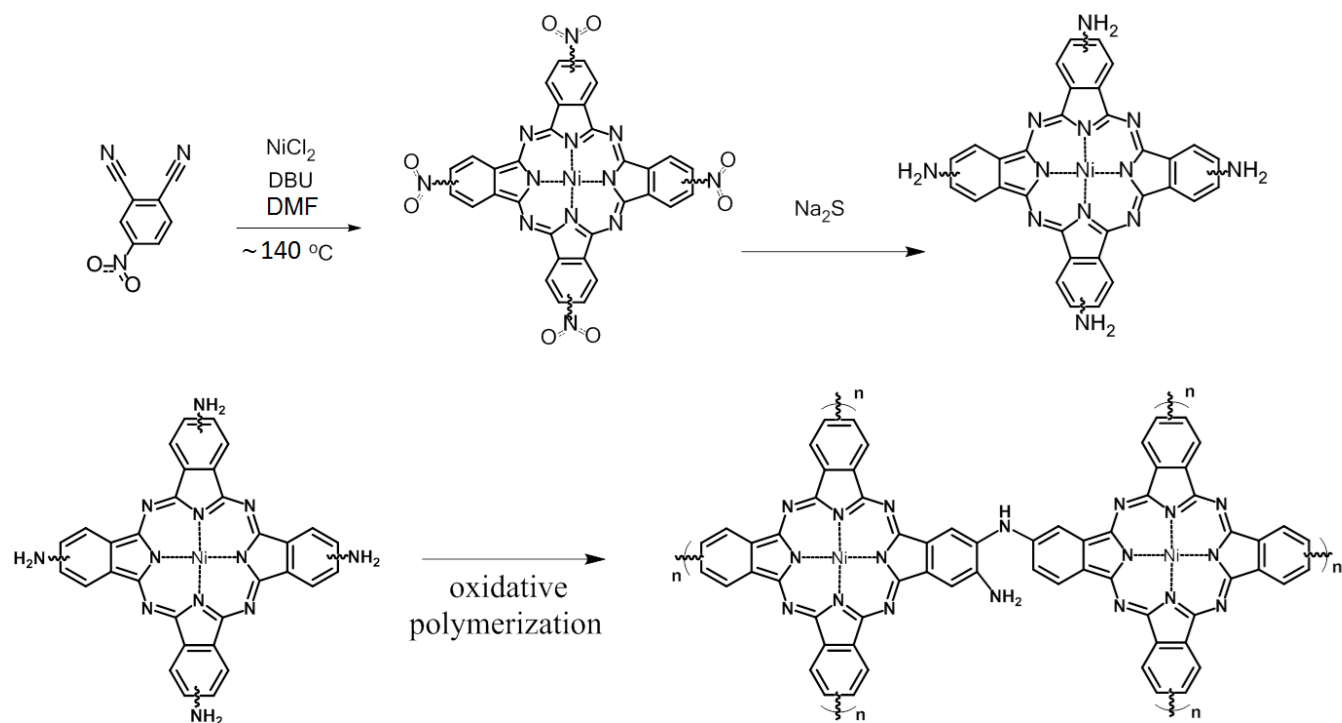


Figure 5.12 Reaction scheme for the synthesis and a proposed structure for the oxidative polymerization of nickel tetraaminophthalocyanine. Four isomers of the monomer are possible.

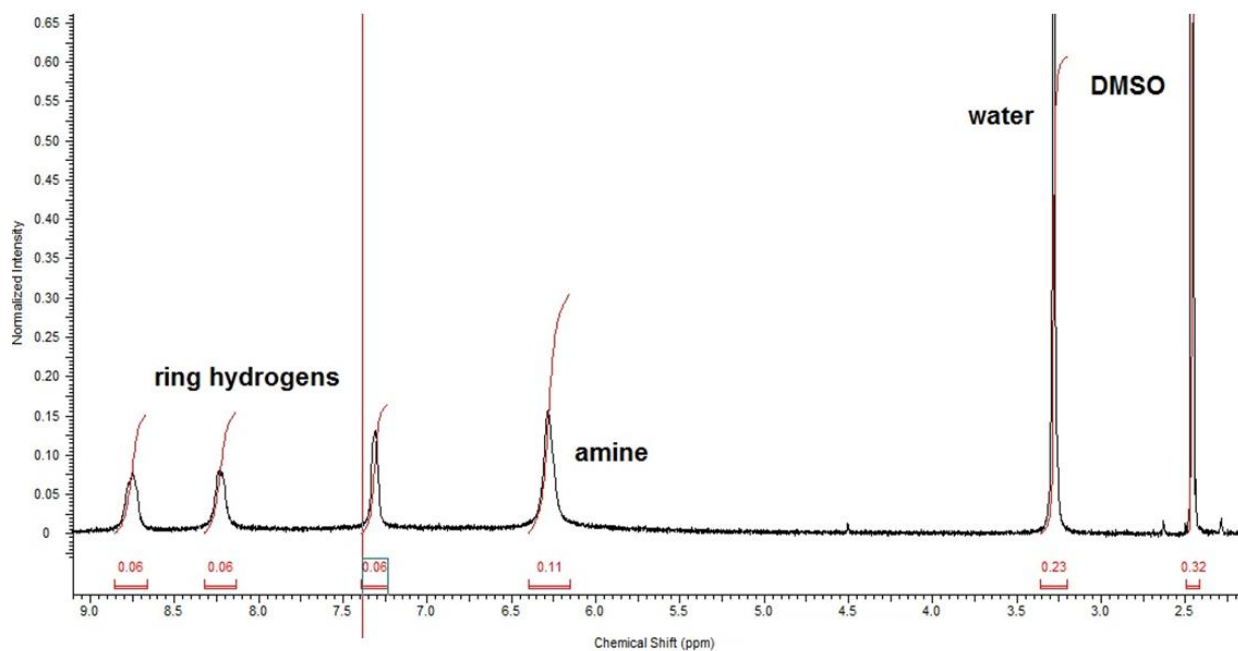


Figure 5.13 ^1H -NMR spectra of NiTAPc monomer in DMSO-d_6 .

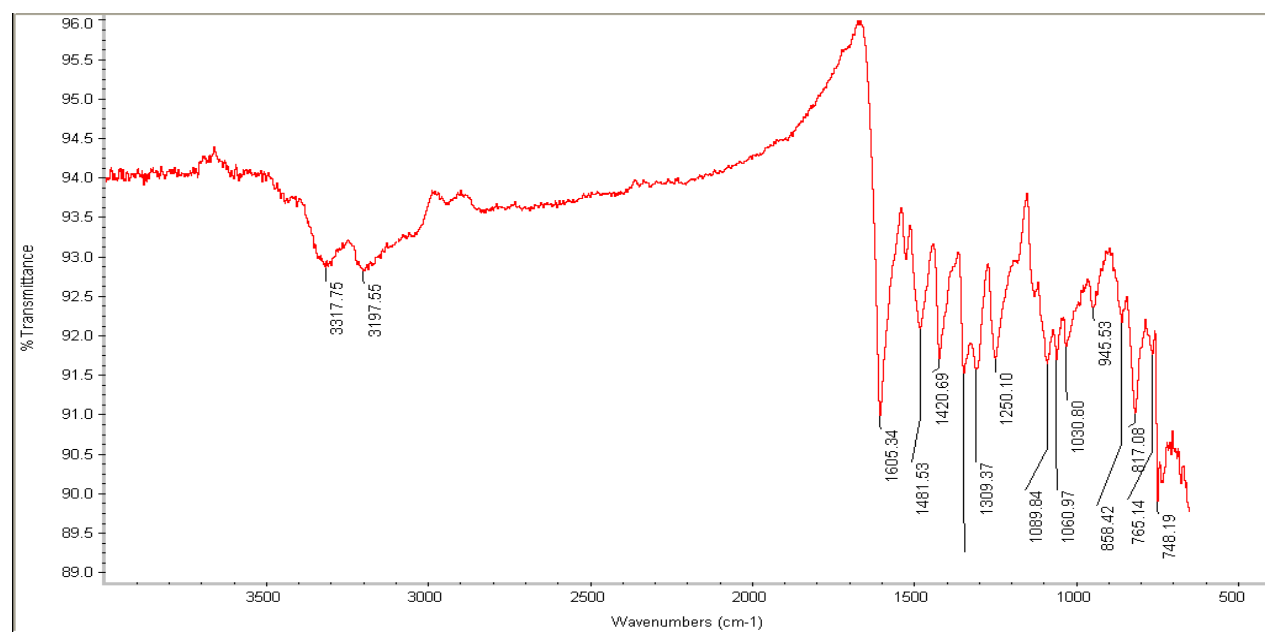


Figure 5.14 FTIR spectra of monomeric NiTAPc powder.

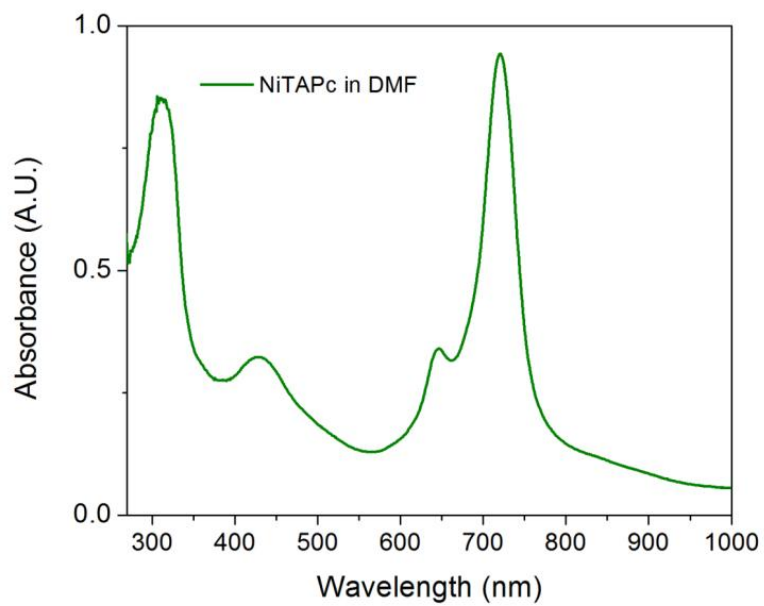


Figure 5.15 UV-Vis spectra of NiTAPc monomer in dimethylformamide (DMF).

Table 5.1 Estimated costs for synthesis and coating electrodes with poly-NiTAPc. Film mass is taken from 2-cycle EQCM experiments in the main text. 0.5 M solutions of NaOH and HCl used for NiTAPc purification were left out as they contributed a negligible amount to the cost.

Source Step-1	Purity (%)	Purchase amount (g)	Cost (dollar)	Dollar/ g	g/mol	Mole equiv.	Dollar/g of chemical
4-nitrophthalonitrile (TCI America) accessed 11-11-2017	>98	100	192	1.92	173.13	4	1.76
DBU (Sigma) accessed 11-11-2017	>98	2500	855	0.342	152.2	0.1	0.00689
NiCl*6H2O (Acros Organics) accessed 11-11-2017	>98	1000	202	0.202	237.7	1	0.0636
DMF (Sigma) accessed 11-11-2017	>99.5	42480	1405	0.0331	73.09	23.5	0.0752
NiTNPc					755.2		1.87
Step-2							
sodium sulphide (9H2O) (Acros Organics) 11-11-2017	>98	500	92	0.184	240.18	20	1.39
NiTAPc 100% yield cost					635.2		3.26
NiTAPc 50 % yield cost					635.2		6.52
Estimated cost of electrode coated with 2-cycle NiTAPc film							
	\$ Dollar /μg		Film mass μg/m²		Cost per \$/m²		
	0.00000652		100000		0.652		

REFERENCES

1. O'Regan, B.; Gratzel, M., A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO₂ films. *Nature* **1991**, 353 (6346), 737-740.
2. Nazeeruddin, M. K.; Liska, P.; Moser, J.; Vlachopoulos, N.; Grätzel, M., Conversion of Light into Electricity with Trinuclear Ruthenium Complexes Adsorbed on Textured TiO₂ Films. *Helvetica Chimica Acta* **1990**, 73 (6), 1788-1803.
3. O'Regan, B.; Moser, J.; Anderson, M.; Graetzel, M., Vectorial electron injection into transparent semiconductor membranes and electric field effects on the dynamics of light-induced charge separation. *The Journal of Physical Chemistry* **1990**, 94 (24), 8720-8726.
4. Nok, T. H.; Chenyi, Y.; Thomas, M.; Jun-Ho, Y.; M., Z. S.; K., N. M.; Michael, G., Cyclopentadithiophene Bridged Donor-Acceptor Dyes Achieve High Power Conversion Efficiencies in Dye-Sensitized Solar Cells Based on the tris-Cobalt Bipyridine Redox Couple. *ChemSusChem* **2011**, 4 (5), 591-594.
5. Gregg, B. A.; Pichot, F.; Ferrere, S.; Fields, C. L., Interfacial Recombination Processes in Dye-Sensitized Solar Cells and Methods To Passivate the Interfaces. *J. Phys. Chem. B* **2001**, 105 (7), 1422-1429.
6. Saygili, Y.; Söderberg, M.; Pellet, N.; Giordano, F.; Cao, Y.; Muñoz-García, A. B.; Zakeeruddin, S. M.; Vlachopoulos, N.; Pavone, M.; Boschloo, G.; Kavan, L.; Moser, J.-E.; Grätzel, M.; Hagfeldt, A.; Freitag, M., Copper Bipyridyl Redox Mediators for Dye-Sensitized Solar Cells with High Photovoltage. *J. Am. Chem. Soc.* **2016**, 138 (45), 15087-15096.
7. Colombo, A.; Dragonetti, C.; Magni, M.; Meroni, D.; Ugo, R.; Marotta, G.; Grazia Lobello, M.; Salvatori, P.; De Angelis, F., New thiocyanate-free ruthenium(ii) sensitizers with different pyrid-2-yl tetrazolate ligands for dye-sensitized solar cells. *Dalton Transactions* **2015**, 44 (26), 11788-11796.
8. Lee, C.-P.; Li, C.-T.; Ho, K.-C., Use of organic materials in dye-sensitized solar cells. *Materials Today* **2017**, 20 (5), 267-283.
9. Kuang, D.; Klein, C.; Ito, S.; Moser, J. E.; Humphry-Baker, R.; Evans, N.; Duriaux, F.; Grätzel, C.; Zakeeruddin, S. M.; Grätzel, M., High-Efficiency and Stable Mesoscopic Dye-Sensitized Solar Cells Based on a High Molar Extinction Coefficient Ruthenium Sensitizer and Nonvolatile Electrolyte. *Adv. Mat.* **2007**, 19 (8), 1133-1137.
10. Lin, L.; Peng, B.; Shi, W.; Guo, Y.; Li, R., Synthesis of zinc phthalocyanine with large steric hindrance and its photovoltaic performance for dye-sensitized solar cells. *Dalton Transactions* **2015**, 44 (12), 5867-5874.

11. Cogal, S.; Erten-Ela, S.; Ocakoglu, K.; Oksuz, A. U., Asymmetric phthalocyanine derivatives containing 4-carboxyphenyl substituents for dye-sensitized solar cells. *Dyes and Pigments* **2015**, *113*, 474-480.
12. Martin-Gomis, L.; Fernandez-Lazaro, F.; Sastre-Santos, A., Advances in phthalocyanine-sensitized solar cells (PcSSCs). *J. Mater. Chem. A* **2014**, *2* (38), 15672-15682.
13. Mathew, S.; Yella, A.; Gao, P.; Humphry-Baker, R.; Curchod, B. F. E.; Ashari-Astani, N.; Tavernelli, I.; Rothlisberger, U.; Nazeeruddin, M. K.; Grätzel, M., Dye-sensitized solar cells with 13% efficiency achieved through the molecular engineering of porphyrin sensitizers. *Nat. Chem.* **2014**, *6*, 242.
14. Marina, F.; Wenxing, Y.; A., F. L.; Luca, D. A.; Martin, K. K.; Anders, H.; Gerrit, B., Supramolecular Hemicage Cobalt Mediators for Dye-Sensitized Solar Cells. *ChemPhysChem* **2016**, *17* (23), 3845-3852.
15. Yang, W.; Vlachopoulos, N.; Hao, Y.; Hagfeldt, A.; Boschloo, G., Efficient dye regeneration at low driving force achieved in triphenylamine dye LEG4 and TEMPO redox mediator based dye-sensitized solar cells. *Phys. Chem. Chem. Phys.* **2015**, *17* (24), 15868-15875.
16. El-Zohry, A. M.; Cong, J.; Karlsson, M.; Kloo, L.; Zietz, B., Ferrocene as a rapid charge regenerator in dye-sensitized solar cells. *Dyes and Pigments* **2016**, *132*, 360-368.
17. Bella, F.; Lamberti, A.; Sacco, A.; Bianco, S.; Chiodoni, A.; Bongiovanni, R., Novel electrode and electrolyte membranes: Towards flexible dye-sensitized solar cell combining vertically aligned TiO₂ nanotube array and light-cured polymer network. *Journal of Membrane Science* **2014**, *470*, 125-131.
18. Papageorgiou, N.; Barbé, C.; Grätzel, M., Morphology and Adsorbate Dependence of Ionic Transport in Dye Sensitized Mesoporous TiO₂ Films. *J. Phys. Chem. B* **1998**, *102* (21), 4156-4164.
19. Wang, Q.; Ito, S.; Grätzel, M.; Fabregat-Santiago, F.; Mora-Seró, I.; Bisquert, J.; Bessho, T.; Imai, H., Characteristics of High Efficiency Dye-Sensitized Solar Cells†. *J. Phys. Chem. B* **2006**, *110* (50), 25210-25221.
20. Lee, B.-K.; Kim, J.-J., Enhanced efficiency of dye-sensitized solar cells by UV-O₃ treatment of TiO₂ layer. *Current Applied Physics* **2009**, *9* (2), 404-408.
21. Grätzel, M., Dye-sensitized solar cells. *J. Photoch. Photobio. C* **2003**, *4* (2), 145-153.
22. Hao, F.; Dong, P.; Luo, Q.; Li, J.; Lou, J.; Lin, H., Recent advances in alternative cathode materials for iodine-free dye-sensitized solar cells. *Energ. Environ. Sci.* **2013**, *6* (7), 2003-2019.

23. Kavan, L.; Yum, J.-H.; Graetzel, M., Graphene-based cathodes for liquid-junction dye sensitized solar cells: Electrocatalytic and mass transport effects. *Electrochim. Acta* **2014**, *128* (0), 349-359.
24. Theerthagiri, J.; Senthil, A. R.; Madhavan, J.; Maiyalagan, T., Recent Progress in Non-Platinum Counter Electrode Materials for Dye-Sensitized Solar Cells. *ChemElectroChem* **2015**, *2* (7), 928-945.
25. Yun, S.; Liu, Y.; Zhang, T.; Ahmad, S., Recent advances in alternative counter electrode materials for Co-mediated dye-sensitized solar cells. *Nanoscale* **2015**, *7* (28), 11877-11893.
26. Kashif, M. K.; Nippe, M.; Duffy, N. W.; Forsyth, C. M.; Chang, C. J.; Long, J. R.; Spiccia, L.; Bach, U., Stable Dye-Sensitized Solar Cell Electrolytes Based on Cobalt(II)/(III) Complexes of a Hexadentate Pyridyl Ligand. *Angew. Chem. Int. Edit.* **2013**, *52* (21), 5527-5531.
27. Boschloo, G.; Hagfeldt, A., Characteristics of the Iodide/Triiodide Redox Mediator in Dye-Sensitized Solar Cells. *Acc. Chem. Res.* **2009**, *42* (11), 1819-1826.
28. Yanagida, S.; Yu, Y.; Manseki, K., Iodine/Iodide-Free Dye-Sensitized Solar Cells. *Acc. Chem. Res.* **2009**, *42* (11), 1827-1838.
29. Sapp, S. A.; Elliott, C. M.; Contado, C.; Caramori, S.; Bignozzi, C. A., Substituted Polypyridine Complexes of Cobalt(II/III) as Efficient Electron-Transfer Mediators in Dye-Sensitized Solar Cells. *J. Am. Chem. Soc.* **2002**, *124* (37), 11215-11222.
30. Kavan, L.; Yum, J. H.; Grätzel, M., Optically Transparent Cathode for Dye-Sensitized Solar Cells Based on Graphene Nanoplatelets. *ACS Nano* **2011**, *5* (1), 165-172.
31. Kavan, L.; Yum, J.-H.; Grätzel, M., Graphene Nanoplatelets Outperforming Platinum as the Electrocatalyst in Co-Bipyridine-Mediated Dye-Sensitized Solar Cells. *Nano Lett.* **2011**, *11* (12), 5501-5506.
32. Kavan, L.; Yum, J.-H.; Nazeeruddin, M. K.; Grätzel, M., Graphene Nanoplatelet Cathode for Co(III)/(II) Mediated Dye-Sensitized Solar Cells. *ACS Nano* **2011**, *5* (11), 9171-9178.
33. Yun, S.; Hagfeldt, A.; Ma, T., Pt-Free Counter Electrode for Dye-Sensitized Solar Cells with High Efficiency. *Adv. Mat.* **2014**, *26* (36), 6210-6237.
34. Hauch, A.; Georg, A., Diffusion in the electrolyte and charge-transfer reaction at the platinum electrode in dye-sensitized solar cells. *Electrochim. Acta* **2001**, *46* (22), 3457-3466.
35. Ashbrook, L. N.; Elliott, C. M., Sulfide Modification of Dye-Sensitized Solar Cell Gold Cathodes for Use with Cobalt Polypyridyl Mediators. *J. Phys. Chem. C* **2014**, *118* (30), 16643-16650.

36. Kim, H. M.; Jeon, I.-Y.; Choi, I. T.; Kang, S. H.; Shin, S.-H.; Jeong, H. Y.; Ju, M. J.; Baek, J.-B.; Kim, H. K., Edge-selectively antimony-doped graphene nanoplatelets as an outstanding counter electrode with an unusual electrochemical stability for dye-sensitized solar cells employing cobalt electrolytes. *J. Mater. Chem. A* **2016**, *4* (23), 9029-9037.
37. Dong, P.; Zhu, Y.; Zhang, J.; Hao, F.; Wu, J.; Lei, S.; Lin, H.; Hauge, R. H.; Tour, J. M.; Lou, J., Vertically Aligned Carbon Nanotubes/Graphene Hybrid Electrode as a TCO- and Pt-Free Flexible Cathode for Application in Solar Cells. *J. Mater. Chem. A* **2014**, *2* (48), 20902-20907.
38. Hao, F.; Wang, Z.; Luo, Q.; Lou, J.; Li, J.; Wang, J.; Fan, S.; Jiang, K.; Lin, H., Highly catalytic cross-stacked superaligned carbon nanotube sheets for iodine-free dye-sensitized solar cells. *J. Mater. Chem.* **2012**, *22* (42), 22756-22762.
39. Trancik, J. E.; Barton, S. C.; Hone, J., Transparent and Catalytic Carbon Nanotube Films. *Nano Lett.* **2008**, *8* (4), 982-987.
40. Sebastián, D.; Baglio, V.; Girolamo, M.; Moliner, R.; Lázaro, M. J.; Aricò, A. S., Carbon nanofiber-based counter electrodes for low cost dye-sensitized solar cells. *J. Power Sources* **2014**, *250* (0), 242-249.
41. Liu, I. P.; Hou, Y.-C.; Li, C.-W.; Lee, Y.-L., Highly electrocatalytic counter electrodes based on carbon black for cobalt(iii)/(ii)-mediated dye-sensitized solar cells. *J. Mater. Chem. A* **2017**, *5* (1), 240-249.
42. Wang, H.; Feng, Q.; Gong, F.; Li, Y.; Zhou, G.; Wang, Z.-S., In situ growth of oriented polyaniline nanowires array for efficient cathode of Co(iii)/Co(ii) mediated dye-sensitized solar cell. *J. Mater. Chem. A* **2013**, *1* (1), 97-104.
43. Wu, J.; Li, Y.; Tang, Q.; Yue, G.; Lin, J.; Huang, M.; Meng, L., Bifacial dye-sensitized solar cells: A strategy to enhance overall efficiency based on transparent polyaniline electrode. *Sci. Rep.* **2014**, *4*, 4028.
44. Idigoras, J.; Guillen, E.; Ramos, F. J.; Anta, J. A.; Nazeeruddin, M. K.; Ahmad, S., Highly efficient flexible cathodes for dye sensitized solar cells to complement Pt@TCO coatings. *J. Mater. Chem. A* **2014**, *2* (9), 3175-3181.
45. Park, B.-w.; Pazoki, M.; Aitola, K.; Jeong, S.; Johansson, E. M. J.; Hagfeldt, A.; Boschloo, G., Understanding Interfacial Charge Transfer between Metallic PEDOT Counter Electrodes and a Cobalt Redox Shuttle in Dye-Sensitized Solar Cells. *ACS Appl. Mater. Inter.* **2014**, *6* (3), 2074-2079.
46. Tsao, H. N.; Burschka, J.; Yi, C.; Kessler, F.; Nazeeruddin, M. K.; Gratzel, M., Influence of the interfacial charge-transfer resistance at the counter electrode in dye-sensitized solar cells employing cobalt redox shuttles. *Energ. Environ. Sci.* **2011**, *4* (12), 4921-4924.

47. Wei, W.; Wang, H.; Hu, Y. H., A review on PEDOT-based counter electrodes for dye-sensitized solar cells. *Int. J. Energ. Res.* **2014**, *38* (9), 1099-1111.
48. Lin, Y.-F.; Li, C.-T.; Ho, K.-C., A template-free synthesis of the hierarchical hydroxymethyl PEDOT tube-coral array and its application in dye-sensitized solar cells. *J. Mater. Chem. A* **2016**, *4* (2), 384-394.
49. Scott, M. J.; Nelson, J. J.; Caramori, S.; Bignozzi, C. A.; Elliott, C. M., cis-Dichloro-bis(4,4'-dicarboxy-2,2-bipyridine)osmium(II)-Modified Optically Transparent Electrodes: Application as Cathodes in Stacked Dye-Sensitized Solar Cells. *Inorg. Chem.* **2007**, *46* (24), 10071-10078.
50. Yue, G.; Wu, J.; Xiao, Y.; Huang, M.; Lin, J.; Lin, J.-Y., High performance platinum-free counter electrode of molybdenum sulfide-carbon used in dye-sensitized solar cells. *J. Mater. Chem. A* **2013**, *1* (4), 1495-1501.
51. Liu, F.; Hu, S.; Ding, X.; Zhu, J.; Wen, J.; Pan, X.; Chen, S.; Nazeeruddin, M. K.; Dai, S., Ligand-free nano-grain Cu₂SnS₃ as a potential cathode alternative for both cobalt and iodine redox electrolyte dye-sensitized solar cells. *J. Mater. Chem. A* **2016**, *4* (38), 14865-14876.
52. Khan, A.; Huang, Y.-T.; Miyasaka, T.; Ikegami, M.; Feng, S.-P.; Li, W.-D., Solution-Processed Transparent Nickel-Mesh Counter Electrode with in-Situ Electrodeposited Platinum Nanoparticles for Full-Plastic Bifacial Dye-Sensitized Solar Cells. *ACS Appl. Mater. Inter.* **2017**, *9* (9), 8083-8091.
53. Miranda-Munoz, J. M.; Carretero-Palacios, S.; Jimenez-Solano, A.; Li, Y.; Lozano, G.; Miguez, H., Efficient bifacial dye-sensitized solar cells through disorder by design. *J. Mater. Chem. A* **2016**, *4* (5), 1953-1961.
54. Cheema, H.; Rodrigues, R. R.; Delcamp, J. H., Sequential series multijunction dye-sensitized solar cells (SSM-DSCs): 4.7 volts from a single illuminated area. *Energ. Environ. Sci.* **2017**, *10* (8), 1764-1769.
55. Balasingam, S. K.; Kang, M. G.; Jun, Y., Metal substrate based electrodes for flexible dye-sensitized solar cells: fabrication methods, progress and challenges. *Chem. Commun.* **2013**, *49* (98), 11457-11475.
56. Park, J. H.; Jun, Y.; Yun, H.-G.; Lee, S.-Y.; Kang, M. G., Fabrication of an Efficient Dye-Sensitized Solar Cell with Stainless Steel Substrate. *J. Electrochem. Soc.* **2008**, *155* (7), F145-F149.
57. Roy, P.; Berger, S.; Schmuki, P., TiO₂ Nanotubes: Synthesis and Applications. *Angew. Chem. Int. Edit.* **2011**, *50* (13), 2904-2939.

58. Emmott, C. J. M.; Rohr, J. A.; Campoy-Quiles, M.; Kirchartz, T.; Urbina, A.; Ekins-Daukes, N. J.; Nelson, J., Organic photovoltaic greenhouses: a unique application for semi-transparent PV? *Energ. Environ. Sci.* **2015**, *8* (4), 1317-1328.
59. Saifullah, M.; Gwak, J.; Yun, J. H., Comprehensive review on material requirements, present status, and future prospects for building-integrated semitransparent photovoltaics (BISTPV). *J. Mater. Chem. A* **2016**, *4* (22), 8512-8540.
60. Tai, Q.; Yan, F., Emerging Semitransparent Solar Cells: Materials and Device Design. *Adv. Mat.* **2017**, *29* (34), 1700192.
61. Zagal, J. H., Metallophthalocyanines as catalysts in electrochemical reactions. *Coordin. Chem. Rev.* **1992**, *119*, 89-136.
62. Zagal, J. H.; Griveau, S.; Silva, J. F.; Nyokong, T.; Bedioui, F., Metallophthalocyanine-based molecular materials as catalysts for electrochemical reactions. *Coordin. Chem. Rev.* **2010**, *254* (23), 2755-2791.
63. Schreiver, I.; Hutzler, C.; Laux, P.; Berlien, H.-P.; Luch, A., Formation of highly toxic hydrogen cyanide upon ruby laser irradiation of the tattoo pigment phthalocyanine blue. *Sci. Rep.* **2015**, *5*, 12915.
64. Dini, D.; Hanack, M., Phthalocyanines as materials for advanced technologies: some examples. *J. Porphyr. Phthalocya.* **2004**, *08* (07), 915-933.
65. Gregory, P., Industrial applications of phthalocyanines. *J. Porphyr. Phthalocya.* **2000**, *04* (04), 432-437.
66. Li, H.; Guarr, T. F., Reversible electrochromism in polymeric metal phthalocyanine thin films. *J. Electroanal. Chem. Interfac. Electrochem.* **1991**, *297* (1), 169-183.
67. Li, H.; Guarr, T. F., Electrochemistry at modified electrodes: Electronically conductive metallophthalocyanine coatings. *Synthetic Met.* **1990**, *38* (2), 243-251.
68. Li, H.; Guarr, T. F., Electrocatalytic oxidation of oxalic acid at electrodes coated with polymeric metallophthalocyanines. *J. Electroanal. Chem. Interfac. Electrochem.* **1991**, *317* (1-2), 189-202.
69. Li, H.; Guarr, T. F., Formation of electronically conductive thin films of metal phthalocyanines via electropolymerization. *J. Chem. Soc. Chem. Comm.* **1989**, *0* (13), 832-834.
70. Sivanesan, A.; John, S. A., Determination of l-dopa using electropolymerized 3,3',3'',3'''-tetraaminophthalocyanatonickel(II) film on glassy carbon electrode. *Biosens. Bioelectron.* **2007**, *23* (5), 708-713.

71. Wen, Z.-H.; Kang, T.-F., Determination of nitrite using sensors based on nickel phthalocyanine polymer modified electrodes. *Talanta* **2004**, 62 (2), 351-355.
72. Sun, Z.; Tachikawa, H., Enzyme-based bilayer conducting polymer electrodes consisting of polymetallophthalocyanines and polypyrrole-glucose oxidase thin films. *Anal. Chem.* **1992**, 64 (10), 1112-1117.
73. Peng, Q.-Y.; Guarr, T. F., Electro-oxidation of hydrazine at electrodes modified with polymeric cobalt phthalocyanine. *Electrochim. Acta* **1994**, 39 (17), 2629-2632.
74. Xi, H. M.; Schultz, F. A., Heterogeneous electron transfer at electrodes coated with electronically conducting nickel-tetraaminophthalocyanine polymer films. *J. Electroanal. Chem.* **1993**, 361 (1-2), 49-56.
75. Hillman, A. R., The EQCM: electrogravimetry with a light touch. *J. Solid State Electr.* **2011**, 15 (7), 1647-1660.
76. Martin, S. J.; Granstaff, V. E.; Frye, G. C., Characterization of a quartz crystal microbalance with simultaneous mass and liquid loading. *Anal. Chem.* **1991**, 63 (20), 2272-2281.
77. Schumacher, R.; Borges, G.; Kanazawa, K. K., The quartz microbalance: A sensitive tool to probe surface reconstructions on gold electrodes in liquid. *Surf. Sci.* **1985**, 163 (1), L621-L626.
78. Ulyanova, Y. V.; Blackwell, A. E.; Minter, S. D., Poly(methylene green) employed as molecularly imprinted polymer matrix for electrochemical sensing. *Analyst* **2006**, 131 (2), 257-261.
79. Wu, J.; Lan, Z.; Lin, J.; Huang, M.; Huang, Y.; Fan, L.; Luo, G., Electrolytes in Dye-Sensitized Solar Cells. *Chem. Rev.* **2015**, 115 (5), 2136-2173.
80. Pyati, R.; Murray, R. W., Solvent Dynamics Effects on Heterogeneous Electron Transfer Rate Constants of Cobalt Tris(bipyridine). *J. Am. Chem. Soc.* **1996**, 118 (7), 1743-1749.
81. Mugadza, T.; Nyokong, T., Synthesis, characterization and the electrocatalytic behaviour of nickel (II) tetraamino-phthalocyanine chemically linked to single walled carbon nanotubes. *Electrochim. Acta* **2010**, 55 (20), 6049-6057.
82. Alpatova, N. M.; Ovsyannikova, E. V.; Tomilova, L. G.; Korenchenko, O. V.; Kondrashov, Y. V., Anodic Doping of Electropolymerized Copper 2,9,16,23-Tetraaminophthalocyanine. *Russ. J. Electrochem.* **2001**, 37 (10), 1012-1016.
83. Açıkbaş, Y.; Evyapan, M.; Ceyhan, T.; Çapan, R.; Bekaroğlu, Ö., Characterisation of Langmuir-Blodgett films of new multinuclear copper and zinc phthalocyanines and their

sensing properties to volatile organic vapours. *Sensor. Actuat. B-Chem.* **2007**, *123* (2), 1017-1024.

84. Swanepoel, R., Determination of the thickness and optical constants of amorphous silicon. *J. Phys. E. Sc. Instrum.* **1983**, *16* (12), 1214.

85. *ASTM G173-03 Reference Spectra Derived from SMARTS v. 2.9.2.*

86. Koh, T. M.; Nonomura, K.; Mathews, N.; Hagfeldt, A.; Grätzel, M.; Mhaisalkar, S. G.; Grimsdale, A. C., Influence of 4-tert-Butylpyridine in DSCs with CoII/III Redox Mediator. *J. Phys. Chem. C* **2013**, *117* (30), 15515-15522.

87. DuVall, S. H.; McCreery, R. L., Control of Catechol and Hydroquinone Electron-Transfer Kinetics on Native and Modified Glassy Carbon Electrodes. *Anal. Chem.* **1999**, *71*, 4594-4602.

88. Winkler, K.; McKnight, N.; Fawcett, W. R., Electron Transfer Kinetics of Tris(1,10-phenanthroline)ruthenium(II) Electrooxidation in Aprotic Solvents. *J. Phys. Chem. B* **2000**, *104* (15), 3575-3580.

89. Fu, Y.; Cole, A. S.; Swaddle, T. W., Solvent Dynamics and Pressure Effects in the Kinetics of the Tris(bipyridine)cobalt(III/II) Electrode Reaction in Various Solvents. *J. Am. Chem. Soc.* **1999**, *121* (44), 10410-10415.

90. Yun, S.; Lund, P. D.; Hinsch, A., Stability assessment of alternative platinum free counter electrodes for dye-sensitized solar cells. *Energ. Environ. Sci.* **2015**, *8* (12), 3495-3514.

91. Lu, W.; Fadeev, A. G.; Qi, B.; Smela, E.; Mattes, B. R.; Ding, J.; Spinks, G. M.; Mazurkiewicz, J.; Zhou, D.; Wallace, G. G.; MacFarlane, D. R.; Forsyth, S. A.; Forsyth, M., Use of Ionic Liquids for π -Conjugated Polymer Electrochemical Devices. *Science* **2002**, *297* (5583), 983-987.

92. C Goya, M.; Lucero, M.; Orive, A.; Marín, A.; Gimeno, Y.; Creus, A.; J Aguirre, M.; C Arévalo, M.; Armijo, J., Surface Effect on Fe (III)Poly-(Tetraaminophenyl) Porphyrin Modified Electrodes After Electrocatalytic Reactions. An Electrochemical and Atomic Force Microscopy Study. *Int. J. Electrochem. Sci.* **2011**, *6* (6), 4984 - 4998.

93. Samadi Khoshkhoo, M.; Maiti, S.; Schreiber, F.; Chassé, T.; Scheele, M., Surface Functionalization with Copper Tetraaminophthalocyanine Enables Efficient Charge Transport in Indium Tin Oxide Nanocrystal Thin Films. *ACS Appl. Mater. Inter.* **2017**, *9* (16), 14197-14206.

94. Wagner, H. J.; Loutfy, R. O.; Hsiao, C.-K., Purification and characterization of phthalocyanines. *Journal of Materials Science* **1982**, *17* (10), 2781-2791.

95. Zhao, F.; Harnisch, F.; Schröder, U.; Scholz, F.; Bogdanoff, P.; Herrmann, I., Application of pyrolysed iron(II) phthalocyanine and CoTMPP based oxygen reduction catalysts as cathode materials in microbial fuel cells. *Electrochem. Commun.* **2005**, 7 (12), 1405-1410.
96. Xu, Z.; Li, Z.; Holt, C. M. B.; Tan, X.; Wang, H.; Amirkhiz, B. S.; Stephenson, T.; Mitlin, D., Electrochemical Supercapacitor Electrodes from Sponge-like Graphene Nanoarchitectures with Ultrahigh Power Density. *The Journal of Physical Chemistry Letters* **2012**, 3 (20), 2928-2933.
97. Fabregat-Santiago, F.; Bisquert, J.; Palomares, E.; Otero, L.; Kuang, D.; Zakeeruddin, S. M.; Grätzel, M., Correlation between Photovoltaic Performance and Impedance Spectroscopy of Dye-Sensitized Solar Cells Based on Ionic Liquids. *J. Phys. Chem. C* **2007**, 111 (17), 6550-6560.
98. Li, F.; Jennings, J. R.; Wang, X.; Fan, L.; Koh, Z. Y.; Yu, H.; Yan, L.; Wang, Q., Influence of Ionic Liquid on Recombination and Regeneration Kinetics in Dye-Sensitized Solar Cells. *J. Phys. Chem. C* **2014**, 118 (30), 17153-17159.
99. Wang, P.; Zakeeruddin, S. M.; Comte, P.; Exnar, I.; Grätzel, M., Gelation of Ionic Liquid-Based Electrolytes with Silica Nanoparticles for Quasi-Solid-State Dye-Sensitized Solar Cells. *J. Am. Chem. Soc.* **2003**, 125 (5), 1166-1167.
100. Martínez, A. I.; Huerta, L.; León, J. M. O. R. d.; Acosta, D.; Malik, O.; Aguilar, M., Physicochemical characteristics of fluorine doped tin oxide films. *J. Phys. D. Appl. Phys.* **2006**, 39 (23), 5091.
101. Hantsche, H., High resolution XPS of organic polymers, the scienta ESCA300 database. By G. Beamson and D. Briggs, Wiley, Chichester 1992, 295 pp., hardcover, £ 65.00, ISBN 0-471-93592-1. *Adv. Mat.* **1993**, 5 (10), 778-778.
102. Rignanesi, G. M.; Pasquarello, A.; Charlier, J. C.; Gonze, X.; Car, R., Nitrogen Incorporation at {SiO} Interfaces: Relation between N Core-Level Shifts and Microscopic Structure. *Phys. Rev. Lett.* **1997**, 79 (25), 5174-5177.
103. Mohtasebi, A.; Chowdhury, T.; Hsu, L. H. H.; Biesinger, M. C.; Kruse, P., Interfacial Charge Transfer between Phenyl-Capped Aniline Tetramer Films and Iron Oxide Surfaces. *J. Phys. Chem. C* **2016**, 120 (51), 29248-29263.
104. Sauerbrey, G., Verwendung von Schwingquarzen zur Wägung dünner Schichten und zur Mikrowägung. *Zeitschrift für Physik* **1959**, 155 (2), 206-222.

APPENDIX I

CHAPTER 2: DEVELOPMENT AND CHARACTERIZATION OF THERMOPLASTIC CARBON COMPOSITE ELECTRODES

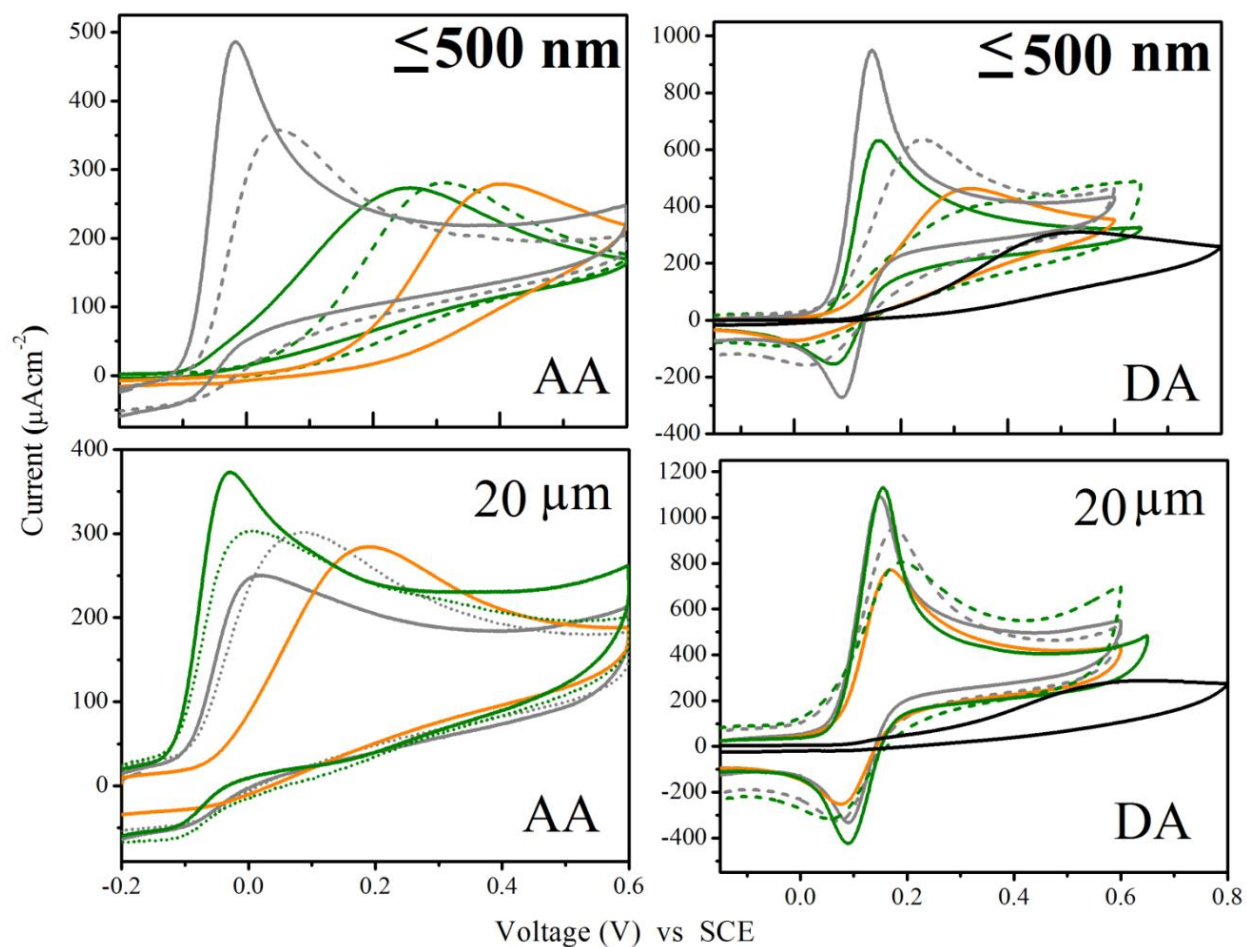


Figure S2.1. Cyclic voltammograms of a 1:0.55 ≤ 500 nm, and 1:3 $20\ \mu\text{m}$ TPE with 1mM ascorbic acid (AA), 1mM dopamine (DA), at 100mV/s, in 0.1 M phosphate buffer at pH 7.4. Orange = polished, green = sanded, grey = plasma treated, black = untreated. Dashed lines are a cyclic voltammograms after the electrode has been cycled in the respective solution for 25 cycles.

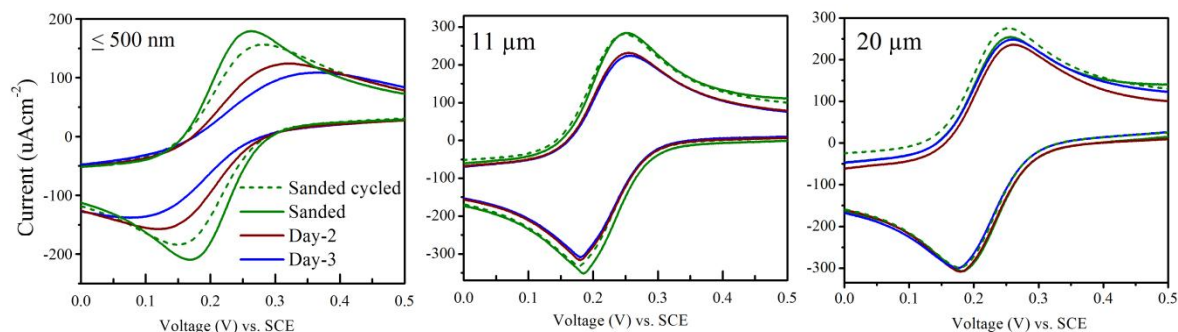


Figure S2.2. Stability data for a 1:0.55 ≤ 500 nm TPE, 1:2 $11 \mu\text{m}$ TPE, and 1:3 $20 \mu\text{m}$ TPE over the course of 3 days in 0.5 M KCl with 1 mM ferricyanide at 100 mV s^{-1} . The dotted lines are after repeated cycling (25 cycles) in ferricyanide on the first day of testing. The electrodes were left, dry, in ambient atmosphere between trials, Fresh solution was used for each day of testing and minor changes in concentration from day to day may be expected.

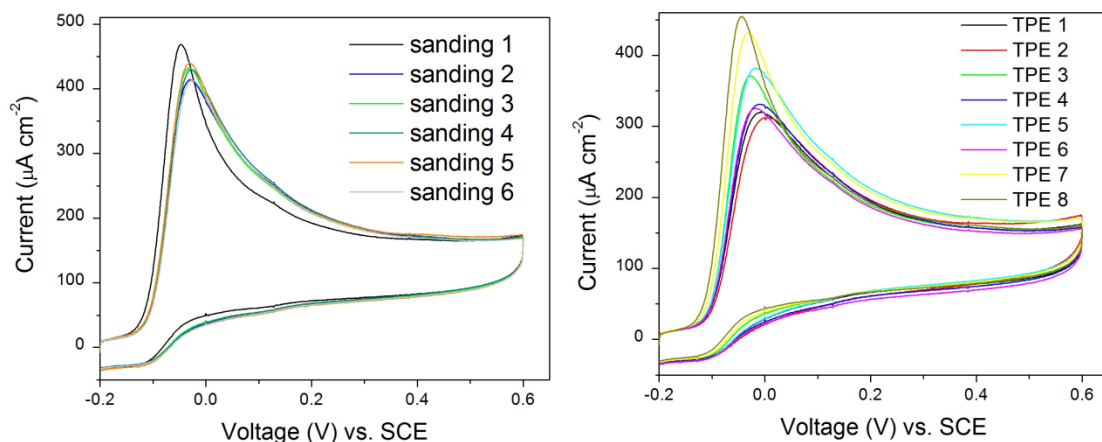


Figure S2.3. (left) Cyclic voltammetry of $11 \mu\text{m}$ TPE in a ratio of 1:2 PMMA:carbon with 1 mM AA in phosphate buffer at pH 7.4. (right) Cyclic voltammetry for 8 individual $11 \mu\text{m}$ TPE in a ratio of 1:2 PMMA:carbon with 1 mM AA in phosphate buffer at pH 7.4. Scan rates for all trials were 100 mV s^{-1} .

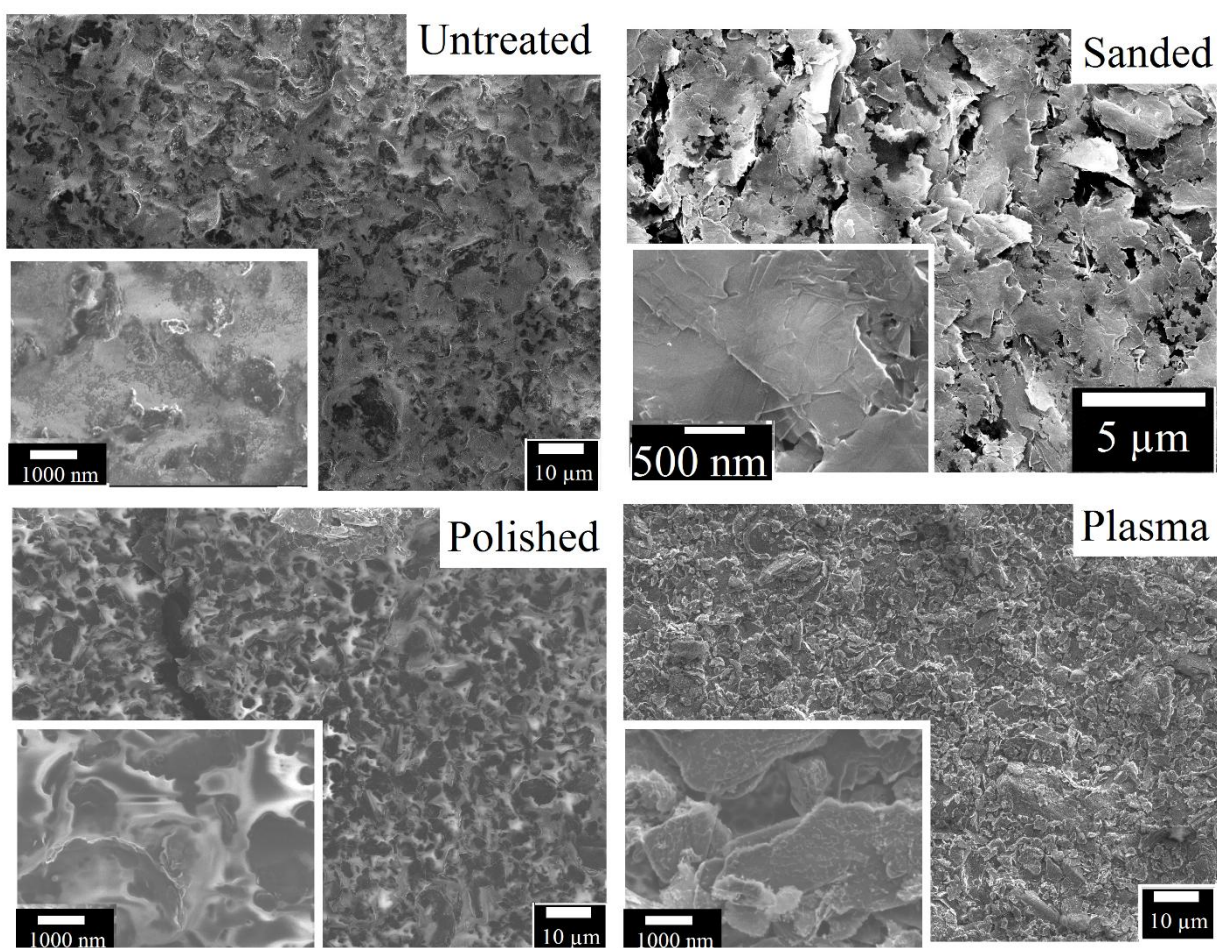


Figure S2.4. SEM images of a 1:3 20 μm TPE with various surface treatments.

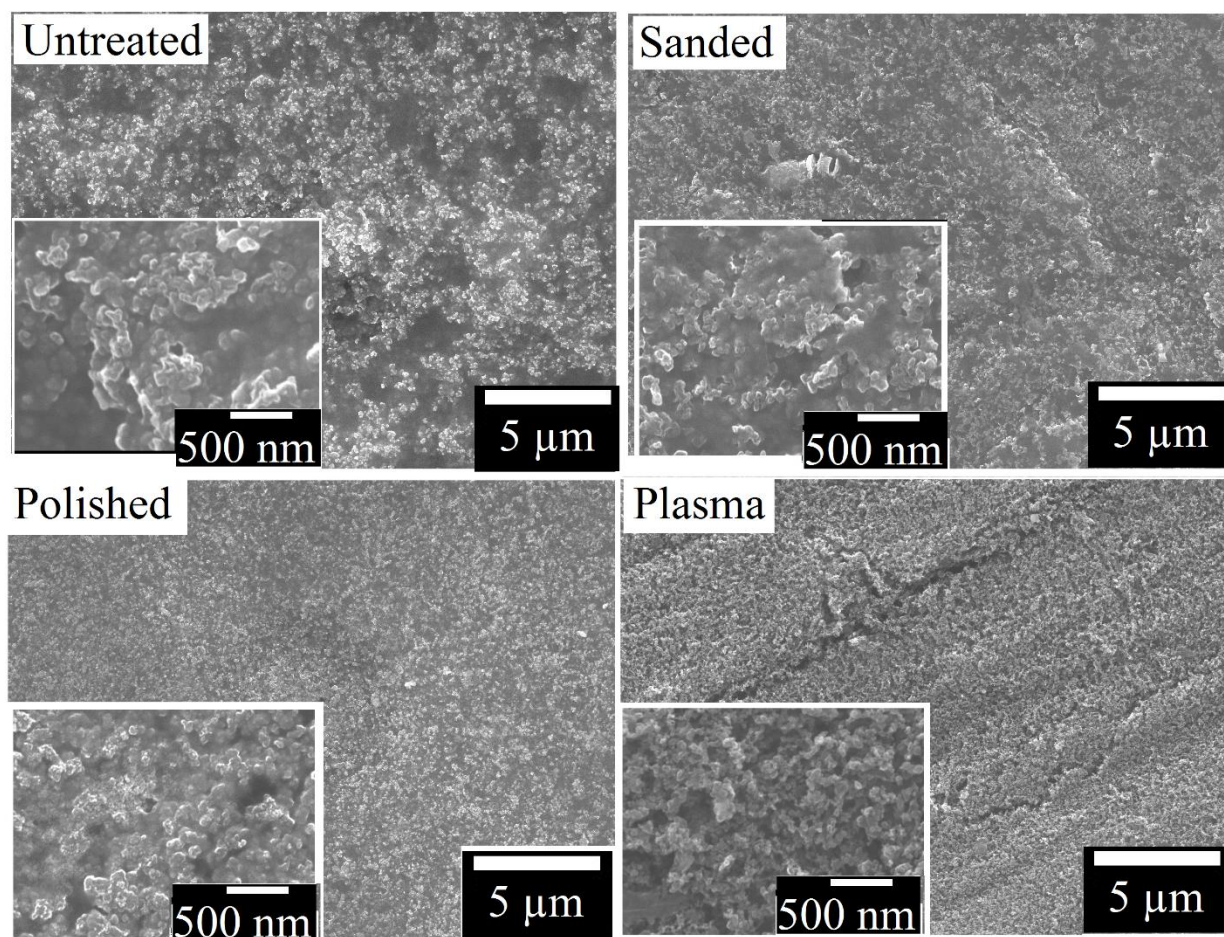


Figure S2.5. SEM images of a 1:0.55 $\leq$ 500 nm TPE with various surface treatments.

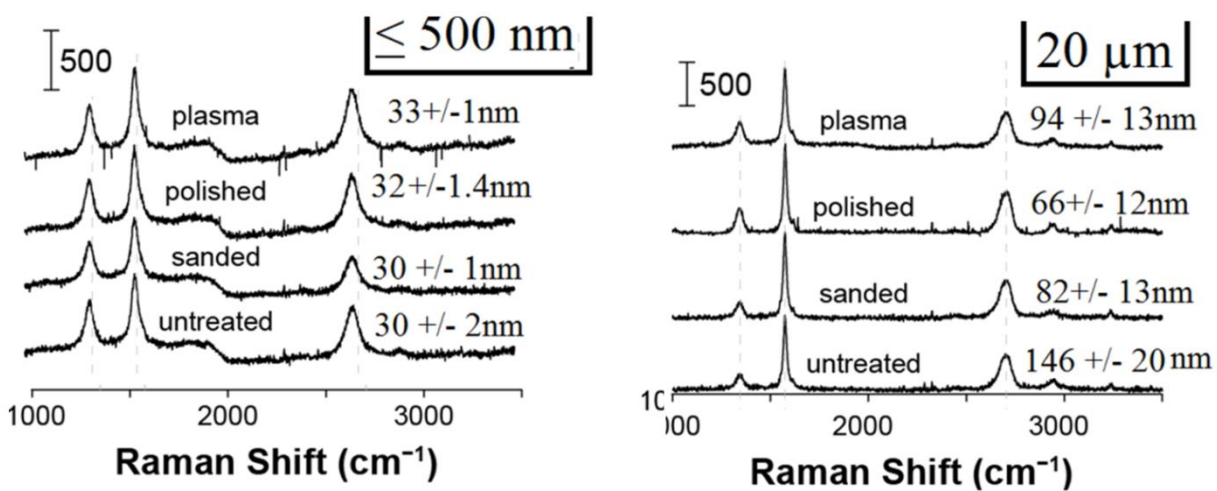


Figure S2.6. Averaged Raman spectra of a 1:3 20 μ m and 1:0.55 ≤ 500 nm TPE with various surface treatments. The crystallite domains are above the respective spectra.

Table S2.1 Average and standard deviation of PMMA:Carbon of 1:2 11 μm , 1:3 20 μm and 1:0.55 ≤ 500 nm TPE with various surface treatments.

20 μm	2D' peak location	error	2D' Height	error	2D' Width	error	D+G peak location	error	D+G Height	error	D+G Width	error
<i>untreated</i>	3239.5	2.6	54.0	6.5	23.2	2.8	2941.5	3.4	42.7	4.0	42.7	7.7
<i>sanded</i>	3238.9	2.0	73.4	9.6	14.3	2.1	2941.1	2.8	36.7	8.6	44.1	7.8
<i>polished</i>	3239.7	1.6	89.4	9.2	14.8	1.3	2939.8	1.9	66.1	16.6	45.1	4.5
<i>plasma</i>	3239.2	2.0	79.9	6.2	18.1	2.1	2939.3	2.3	48.9	19.3	45.0	3.9
20 μm	2D peak location	error	2D Height	error	2D Width	error	G peak location	error	G Height	error	G Width	error
<i>untreated</i>	2702.8	1.4	386.9	30.4	60.0	1.4	1574.4	1.3	862.8	46.9	18.3	0.6
<i>sanded</i>	2701.7	1.5	532.1	44.7	60.5	1.2	1574.9	0.9	1018.9	55.2	19.7	0.7
<i>polished</i>	2702.2	1.3	519.6	38.6	61.1	1.0	1575.9	0.5	999.8	85.7	19.1	0.7
<i>plasma</i>	2703.2	1.6	470.4	41.6	60.4	1.3	1575.7	1.0	990.2	68.7	18.9	0.5
20 μm	D' peak location	error	D' Height	error	D' Width	error	D peak location	error	D Height	error	D Width	error
<i>untreated</i>	1611.4	2.4	24.0	11.0	22.5	3.8	1342.8	1.8	109.7	11.0	36.7	2.1
<i>sanded</i>	1616.0	2.1	50.9	12.0	8.1	3.7	1343.4	1.0	231.2	39.5	35.1	1.4
<i>polished</i>	1616.9	1.5	78.1	14.4	8.6	2.1	1343.0	0.9	287.4	38.7	34.1	1.0
<i>plasma</i>	1615.4	1.5	54.4	6.8	7.3	2.3	1343.2	1.1	203.3	31.8	37.5	1.4

11 μm	2D' peak location	err or	2D' Height	error	2D' Width	err or	D+G peak location	err or	D+G Height	error	D+G Width	err or
<i>untreated</i>	3238.0	1.7	56.1	8.0	17.7	2.0	2942.6	2.1	81.7	24.6	41.8	4.8
<i>sanded</i>	3238.1	2.0	63.7	8.9	17.3	1.7	2938.9	1.9	47.9	17.0	53.7	8.7
<i>polished</i>	3239.6	2.2	67.9	10.3	15.2	1.3	2941.1	2.7	64.2	14.0	33.9	2.2
<i>plasma</i>	3238.5	1.8	60.1	8.8	13.9	1.7	2939.4	2.0	68.1	23.9	48.3	7.3
11 μm	2D peak location		2D Height		2D Width		G peak location		G Height		G Width	
<i>untreated</i>	2701.3	0.6	402.6	23.8	60.1	1.9	1574.5	0.9	821.0	56.1	19.5	0.5
<i>sanded</i>	2701.3	0.9	444.6	31.2	58.8	1.1	1573.6	1.2	979.8	72.0	19.2	0.5
<i>polished</i>	2701.4	1.3	507.1	39.6	59.9	1.0	1574.9	0.8	997.7	108. 7	18.9	0.5
<i>plasma</i>	2701.8	1.6	414.4	30.1	61.5	1.8	1574.3	1.6	929.2	58.3	20.0	1.0
11 μm	D' peak location	err or	D' Height	error	D' Width	err or	D peak location	err or	D Height	error	D Width	err or
<i>untreated</i>	1614.2	1.6	41.4	10.2	8.3	2.4	1344.0	1.4	157.5	12.7	35.0	1.8
<i>sanded</i>	1614.6	1.9	44.1	4.7	5.5	2.5	1342.3	1.8	169.0	19.2	34.3	1.5
<i>polished</i>	1616.9	2.4	67.5	13.6	7.2	2.8	1342.0	1.8	275.2	37.3	32.4	0.6
<i>plasma</i>	1613.6	2.3	61.3	17.9	11.4	3.9	1342.7	1.5	234.7	70.2	35.1	1.4

400 nm	2D'	error	2D'	error	2D'	error	D+G	error	D+G	error	D+G	error
---------------	-----	-------	-----	-------	-----	-------	-----	-------	-----	-------	-----	-------

	peak location		Height		Width		peak location		Height		Width	
<i>untreated</i>	NA		NA		NA		2918.5	1.7	37.3	4.4	40.8	8.6
<i>sanded</i>	NA		NA		NA		2921.1	4.1	17.5	3.5	44.0	13.5
<i>polished</i>	NA		NA		NA		2921.5	3.3	36.6	6.9	53.4	12.0
<i>plasma</i>	NA		NA		NA		2919.5	2.9	38.1	6.0	44.7	7.8
400 nm	2D peak location		2D Height		2D Width		G peak location		G Height		G Width	
<i>untreated</i>	2670.9	1.3	413.1	21.4	70.7	3.1	1562.0	1.0	551.0	32.3	34.8	0.8
<i>sanded</i>	2670.4	1.5	287.0	8.2	75.1	3.8	1561.4	0.8	468.8	11.2	35.5	0.8
<i>polished</i>	2670.0	0.8	425.6	17.5	68.8	1.9	1560.8	0.8	570.6	20.1	35.3	0.7
<i>plasma</i>	2670.5	1.3	513.2	17.1	71.6	3.5	1561.2	0.7	635.2	27.7	34.5	0.9
400 nm	D' peak location	error	D' Height	error	D' Width	error	D peak location	error	D Height	error	D Width	error
<i>untreated</i>	1598.3	1.1	47.0	8.1	17.6	2.6	1330.1	1.1	345.1	12.6	38.7	0.5
<i>sanded</i>	1598.1	0.5	35.4	8.4	14.4	2.4	1330.1	1.3	295.4	9.5	40.6	1.2
<i>polished</i>	1598.2	0.5	35.8	9.4	14.6	3.0	1329.3	0.8	340.5	8.7	38.0	1.1
<i>plasma</i>	1598.1	0.4	43.0	7.8	20.1	2.6	1330.3	1.2	370.1	16.2	39.6	0.3

APPENDIX II

CHAPTER 4: SUBSTITUTED PHTHALOCYANINES- SYNTHESIS, CHARACTERIZATION AND ELECTROCHEMISTRY

Synthesis of 4-bromo-phthalonitrile

The synthesis started with the commercially available and economical 4-bromophthalic anhydride (24.2g). Following a well-known procedure of converting the anhydride into an isoindole with formamide, care was taken not to let the reaction get above 140 °C. The isoindole was then converted into a di-amide with ammonium hydroxide.⁵⁶ These reactions were found to be robust and straight forward, with yields upwards of 90%, which is in agreement with previous published results.

The synthesis of 4-bromo-phthalonitrile proceeded as follows. To a 150 mL dried round bottom flask submerged in an ice bath and attached to a Shlenk line (~ 0 °C), 36 mL of thionyl chloride (0.5 mol), and 50 mL of DMF were added while under nitrogen atmosphere. The thionyl chloride and DMF were degassed via a stainless steel needle submerged in the liquid, with light stirring for ~ 45 minutes. 18.7 grams (0.77 mol) of solid 4-bromo-1,2 diimido benzene was then added under nitrogen. The reaction was left to stir for 14 hours, over the course of many hours the ice melted and the reaction warmed to room temperature. The reaction mixture was then very slowly poured onto ice, left to stand for 10 minutes, and then vacuum filtered. The remaining solid was washed with copious amounts of DI water. The resulting mass was dried in a vacuum oven at 60 °C for 12 hours. After drying, 14.4 grams of a bright white solid was massed, for a 90 % yield, and an overall yield of ~ 70 %.

Synthesis and characterization of 4-(2-thienyl)-phthalonitrile

The synthesis was performed many times, with a typical reaction having 4-bromophthalonitrile (1 mole eq.), 2-thienylboronic acid (97%) (1.35 mol eq.), sodium carbonate (8 mol eq.), palladium tetrakis triphenylphosphine (0.045 mol eq.), dioxane (17 mL/ 1 gram 4-phthalonitrile). Solvent was added to a dry round bottom flask attached to a Schlenk line. The solvent was vigorously degassed with stirring for 15 minutes. The catalyst (stored under argon at ~ -15 °C) was then added under nitrogen and left to stir for 5 minutes, followed by addition of 4-bromophthalonitrile. The mixture was then heated to 60 °C with an oil bath, and stirred for 15 minutes; the color went from orange to light yellow. The Na_2CO_3 was then added under nitrogen, much of which does not dissolve. The reaction is then monitored by GC-MS, and typically conversions of $\sim 50\%$ are seen within 12 to 24 hours. However, complete disappearance of the starting material took anywhere from 3 to 6 days.

When the reaction had finished it was poured onto a small amount of ice, the organics are then extracted with diethylether in a separatory funnel. The dissolved solid is run through multiple plugs of silica to remove triphenylphosphine and triphenylphosphine oxide impurities. The ether is then removed via rotary evaporation, and the light brown solid is recrystallized from methanol or toluene. The resulting solid is pale white, with typical yields in the range of 60-70%. Purity was confirmed with ^1H -NMR and GC-MS.

Synthesis and characterization of 4-(3-thienyl)-phthalonitrile

The synthesis of 4-(3-thienyl)-phthalonitrile proceeded in the same manner as 4-(2-thienyl)-phthalonitrile, however, 3-thienylboronic acid was used in place of 2-

thienylboronic acid. No real apparent differences in the behavior of the reaction or yield where observed.

Synthesis of nickel 4-(2-thienyl)-phthalocyanine

To a 25 mL round bottom flask fitted with a condenser, 0.0544 g of nickel chloride ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$), 0.192 g 4-thienyl phthalonitrile, 0.034 mL of 1,8-Diazabicycloundec-7-ene, 4 mL of hexanol and 4 mL of octanol were added. The mixture was slowly brought up to 150 °C and left for 14 hours. The suspension was then cooled to ~70 °C and poured onto ice. The ice solid mixture was then vacuum filtered and washed with copious amounts of water. While in the vacuum filter, the solid was washed with 150 mL of acetone, 150 mL of ethyl acetate, and 100 mL of ethyl ether in portions. The resulting solid was then dried in a vacuum oven overnight at ~60 °C. The dried solid was then dissolved in chilled sulfuric acid, and poured onto ice which caused precipitation of the phthalocyanine. The green solid was recovered by vacuum filtration, washed until the filtrate was pH neutral, then dried in a vacuum oven over night at ~60 °C. The recovered lustrous dark bluish black solid had a mass of 0.085 g, for a ~47% yield. The solid is seemingly only soluble in DMF, DMSO and sulfuric acid.

Synthesis of 4-(3-methoxythienyl)-phthalonitrile

To a 25 mL round bottom flask fitted with a condenser, 0.34g of 2-(2-thienyl)methanol was added, 10 mL of DMF, 2.3 g of K_2CO_3 , 0.41g of 4-nitrophthalonitrile. The mixture was brought up to 55 °C in an oil bath, and held there for 24 hours under ambient atmosphere. It is unknown if the reaction required this amount of time. The resulting mixture was poured into 100 mL of DI water and placed in the refrigerator for

~20 minutes, and then vacuum filtered, followed by washing with copious amounts of DI (at least 500 mL in portions). The semi wet solid was then dissolved in a mixture of diethylether and ethyl acetate and run through a plug of silica packed in a fritted funnel. A small amount of bright green impurity is left in a top layer in the silica. The solvent was removed by rotary evaporation and light heating, where an oily yellow liquid was recovered. The oil was covered and placed in a freezer where a light yellow solid precipitated; the solid was then dried in a vacuum oven at room temperature for 24 hours. 0.38g of a pale yellow solid was recovered for a total yield of 67%. The solid was stored in air in a freezer until used for phthalocyanine synthesis.

It is acknowledge that previous reports with this and similar reactions used a nitrogen atmosphere and a reaction time of 7 days, with DMSO as a solvent. The obtained product is reported as a green solid. In our hands, excessive handling during work up and long exposure to ambient condition on the bench top seemed to spontaneously produce a green impurity.

Synthesis of nickel 4-(3-methoxythienyl) phthalocyanine

To a 25mL round bottom flask fitted to a condenser fitted to a Schlenk line, then 0.48g of 4-(3-methoxythienyl)phthalonitrile, 0.123g of NiCl_2 and 0.6 mL of 1,8-Diazabicycloundec-7-ene, and 7 mL of octanol were added under a nitrogen atmosphere. The mixture was heated to 70 °C in an oil bath for 3 hours, then the temperature was ramped up to ~160 °C for 16 hours. The mixture was allowed to cool and poured into DI water, vacuum filtered, and washed with copious amounts of water. The solid was then washed under vacuum filtration with many aliquots of acetone (~ 200 mL total), and finally

with 100 mL of diethyl ether in aliquots. The dark purple solid was dried in the vacuum oven overnight at 40 °C for 24 hours. Final obtained mass was 0.21 grams for a 52% yield.

Synthesis 4-(diphenlamino)-phthalonitrile

In one iteration, to a 2-neck round bottom flask 40 mL of dimethyl formamide was added along with 2.5 g of 4-nitrophthalonitrile, the solution was degassed and stirred for 15 minutes with N₂. 10 g of K₂CO₃ was then added under blanket of nitrogen. K₂CO₃ is not fully soluble in the mixture. 3.9 g of diphenylamine was then added to the reaction flask, the mixture was then allowed to stir with degassing for 10 minutes. After the addition of the amine the solution went from a purple color to a dark red. The reaction was stirred under nitrogen for 7 days total at R.T and monitored with thin layer chromatography. Example TLC plates can be found in the Appendix (Figure X), the plates were run with 1:4 ethyl acetate to hexane. Two columns were run with 1:4 ethyl acetate to hexane solution, the fractions containing small amounts of starting materials were recombined and run through another column to obtain 0.46 g of 4-diphenylamine phthalonitrile (10% yield).

Synthesis of nickel 4-(diphenylamino)-phthalocyanines-

0.028g of nickel Nickel chloride (NiCl₂*6H₂O), 6 mL of octanol, 0.04 mL of DBU, and 0.14 g of 4-(Diphenylamino)phthalonitrile were added to a 2-neck round bottom flask with condensor. The mixture was degassed with N₂ for 10 minutes, the reaction was then slowly heated to 140 Celsius with stirring. The heat was administered with an mineral oil bath. The reaction was left to stir for 6 hours under a blanket of nitrogen. The reaction was stopped by pouring the black/blue mixture onto ice/water mixture and left to stand for 1 hour. The octanol and water then vacuum filtered off, followed by rinsing with copious

amount of DI water. The solid was then rinsed with 8 aliquots (~15 mL each) of methanol. The solid was collected from the filter and stirred in 15 mL of 0.1 M NaOH for 20 minutes with stirring, followed by collection by vacuum filtration. The process was repeated with 0.1 M HCL. The solid was then rinsed in the filter flask with copious amounts of water until netral, followed by washing with 50 mL of acetone and 50 mL methanol in aliquots. The blue black solid material was then dried in a vacuum oven at 50 Celsius overnight. The final obtained mass was 0.06 g, for a 41% yield.

Synthesis of copper 4-(diphenylamino)-phthalocyanine-

The synthesis of the copper derivative was identical to 4-diarylamine nickel 4-(diphenylamino)-phthalocyanine except copper chloride ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) was used. The reaction used 0.17 g of 4-(diphenylamino)-phthalonitrile as the limiting reagent and achieved a 55 % yield.

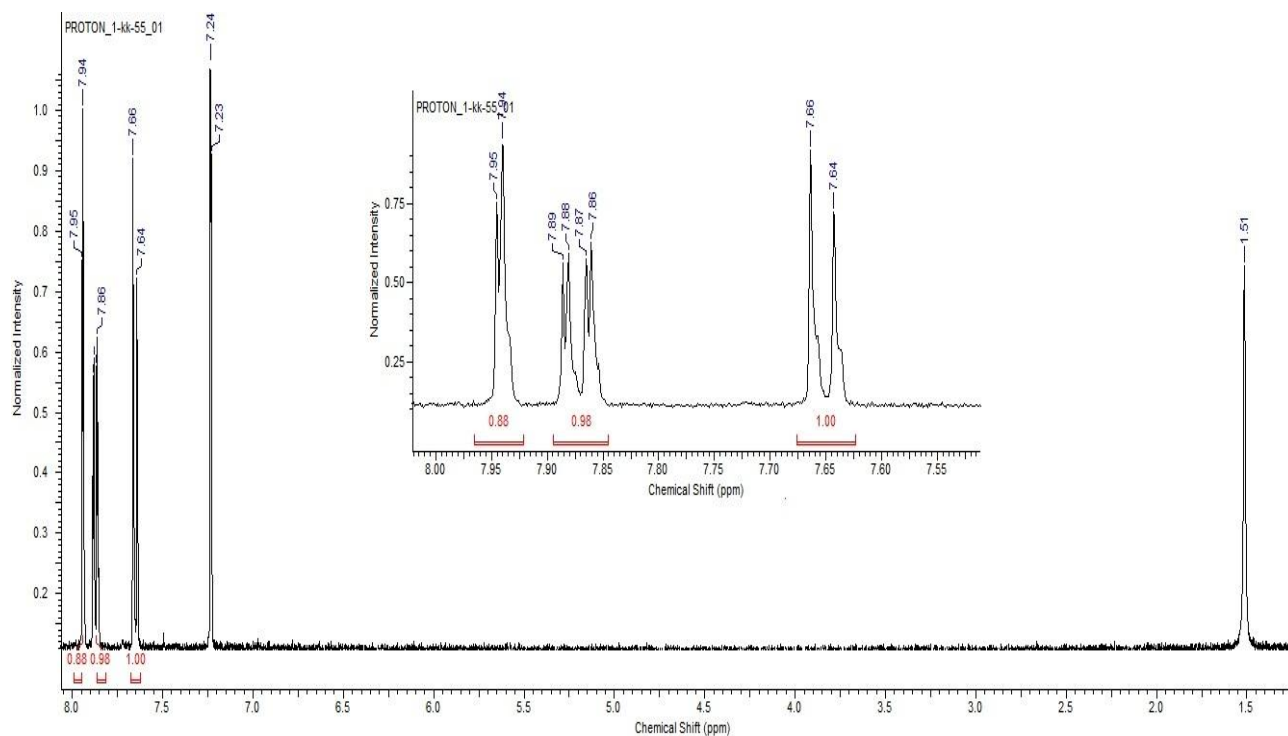


Figure S4.1 ^1H -NMR of 4-bromo-phthalonitrile in CDCl_3 .

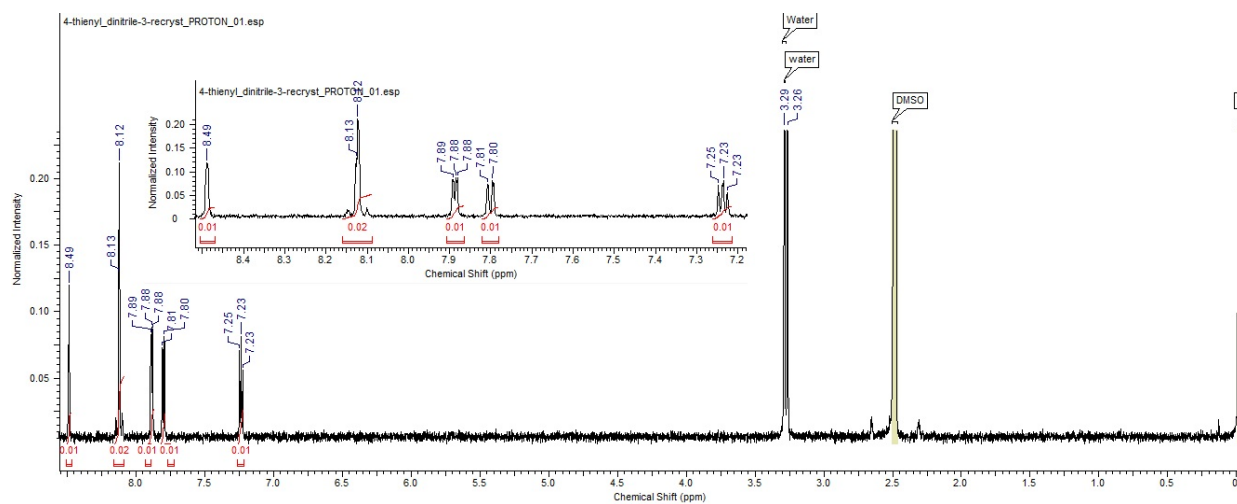


Figure S4.2 ^1H -NMR of 4-(2-thienyl)-phthalonitrile in DMSO.

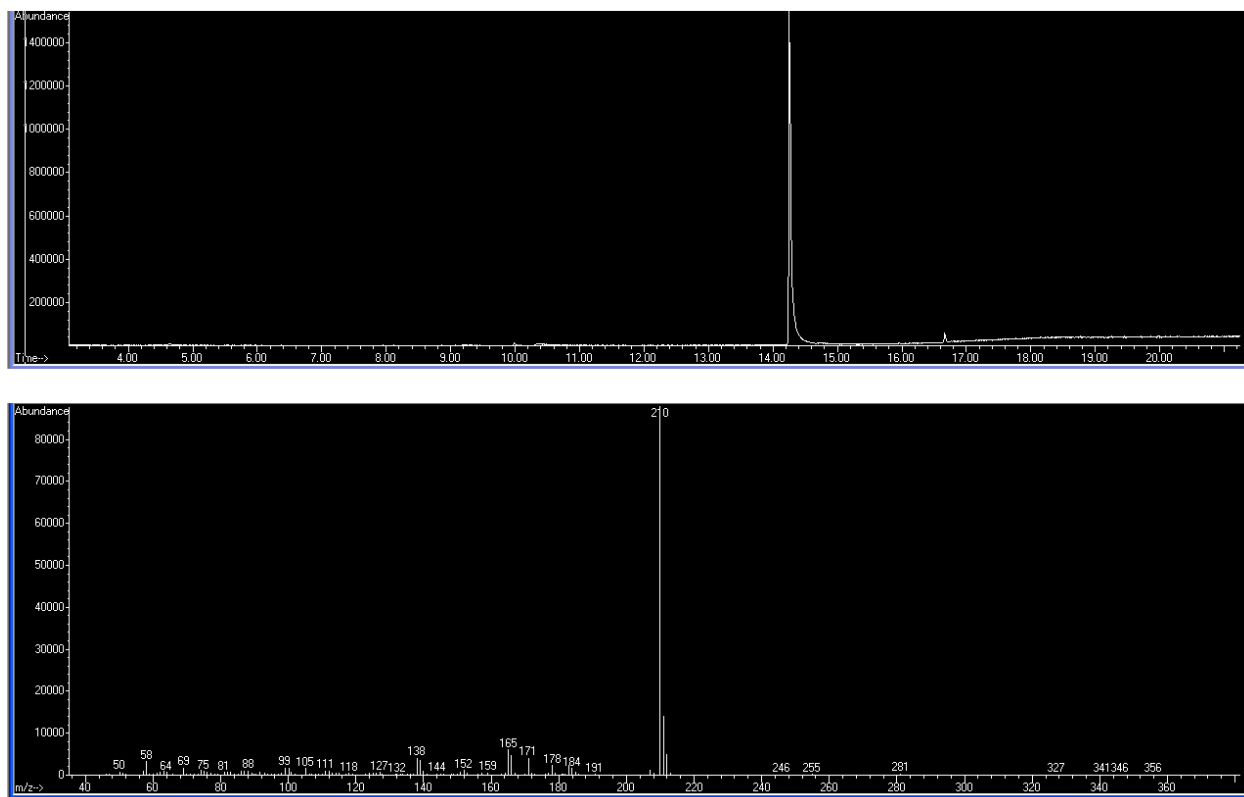


Figure S4.3 GC-MS of 4-(2-thienyl)-phthalonitrile.

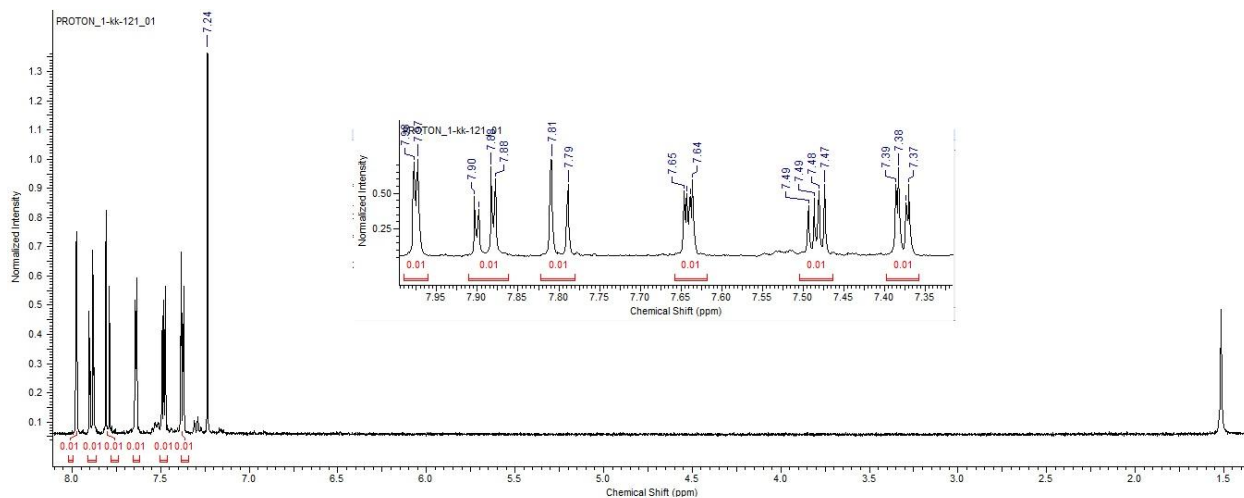


Figure S4.4 ^1H -NMR of 4-(3-thienyl)-phthalonitrile in CDCl_3 .

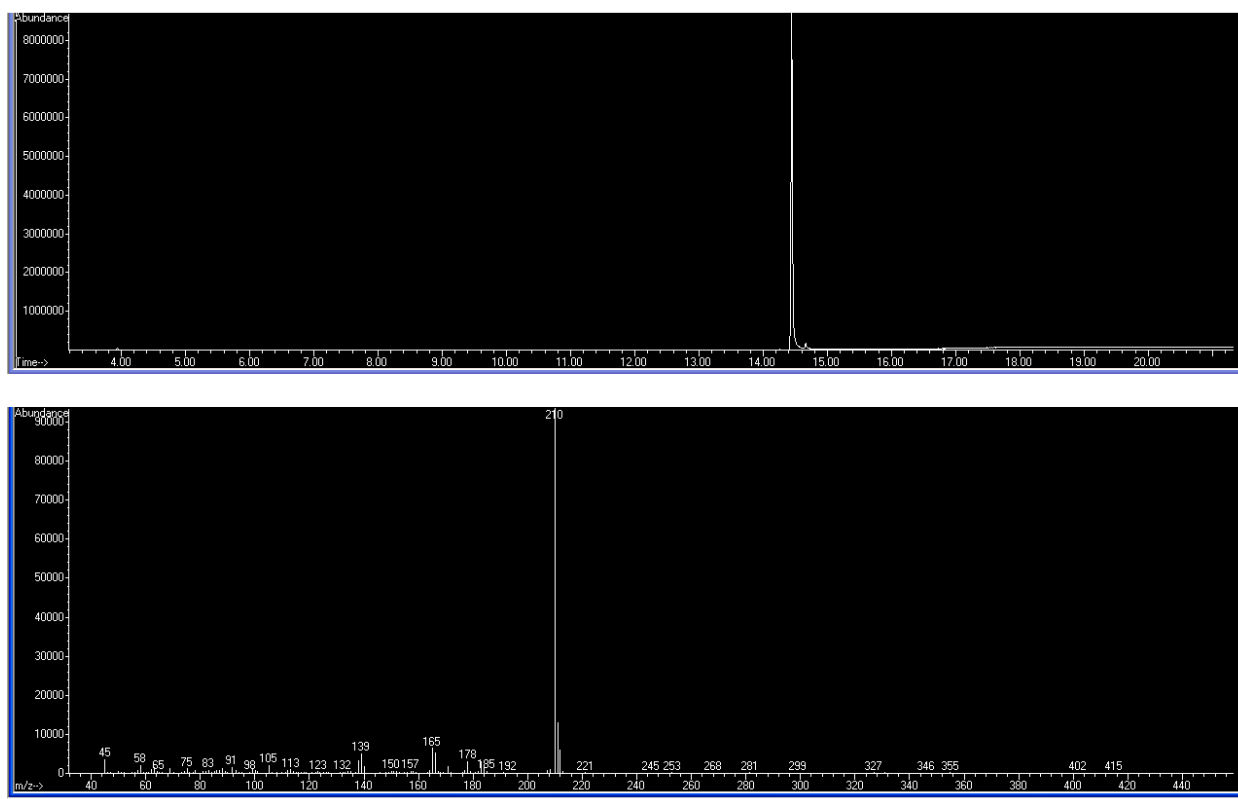


Figure S4.5 GC-MS of 4-(3-thienyl)-phthalonitrile.

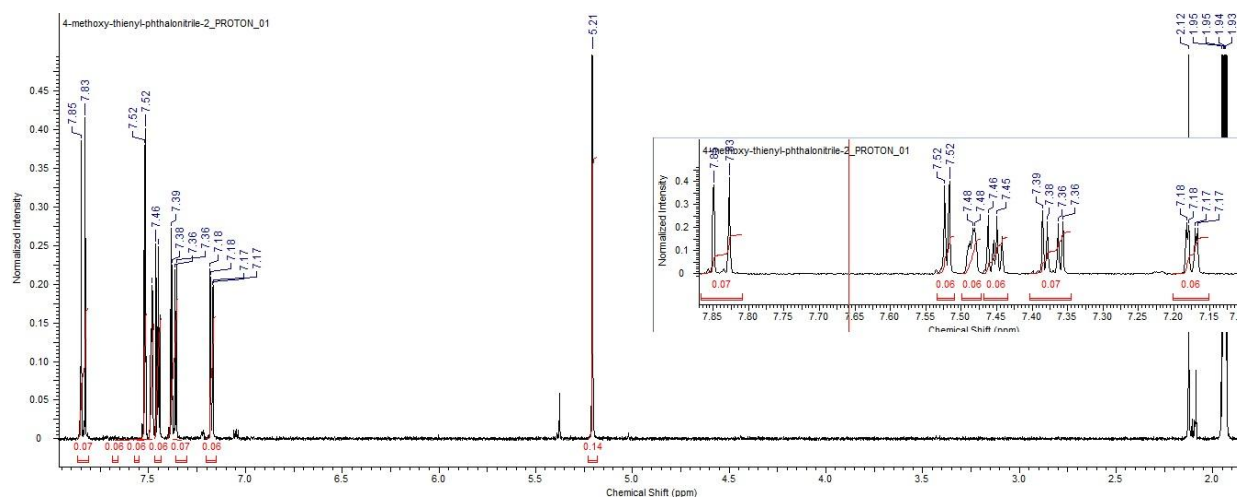


Figure S4.6 ¹H-NMR of 4-(3-methoxythienyl)-phthalonitrile in CD₃CN.

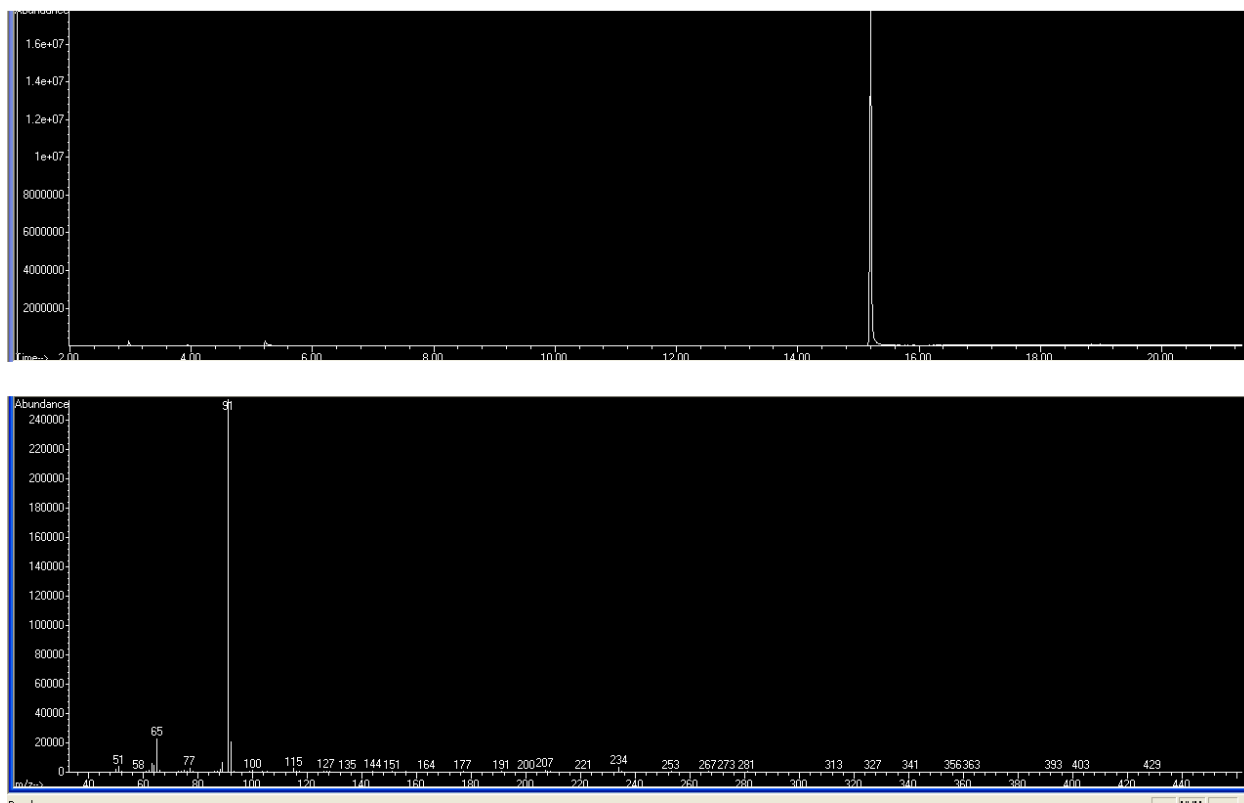


Figure S4.7 GC-MS of 4-(3-methoxythienyl)-phthalonitrile. Compound may have decomposed in the MS leaving only a fragment.

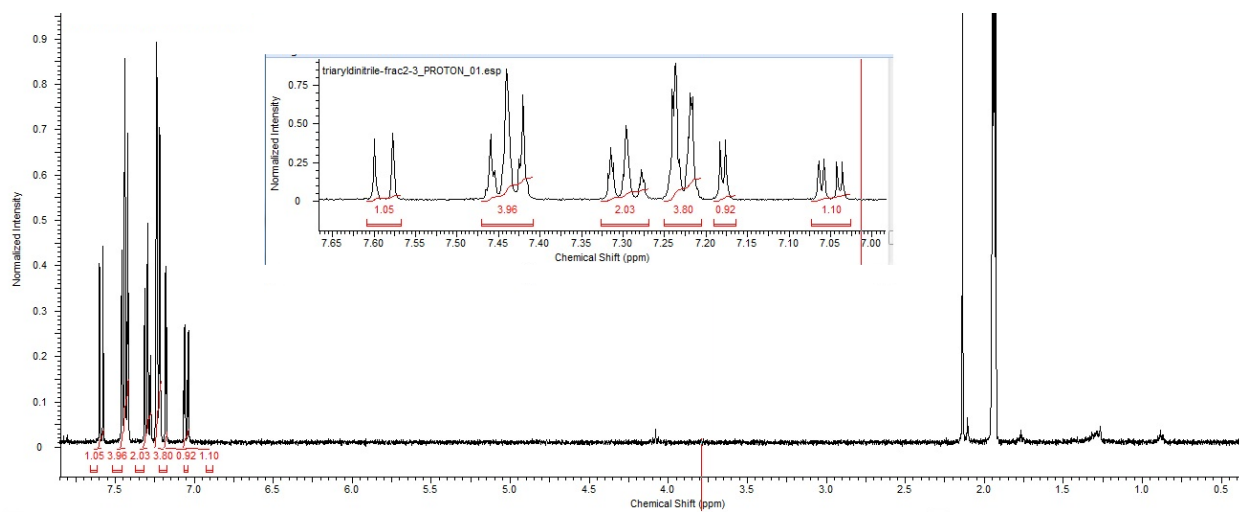


Figure S4.8 ^1H -NMR of 4-(diphenylamino)-phthalonitrile.

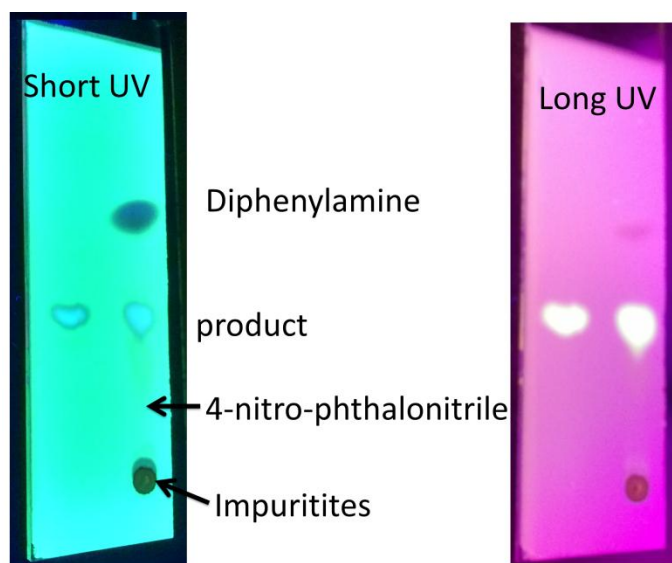


Figure S4.9 TLC plate of the reaction mixture from the synthesis of 4-(diphenylamino)-phthalonitrile. The 4-nitro-phthalonitrile has been consumed. TLC plate was run with 1:4 ethyl acetate:hexanes.