5-2020

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Recommended Citation

Sanwick, Alexis, "Heteroatom-Doped Chemical Vapor Deposition Carbon Ultramicroelectrodes" (2020). *Undergraduate Honors Theses.* Paper 592. https://dc.etsu.edu/honors/592

Heteroatom-Doped Chemical Vapor Deposition Carbon Ultramicroelectrodes

A thesis/dissertation
presented to
the faculty of the Department of Chemistry
East Tennessee State University

In partial fulfillment
of the requirements for the degree
Bachelor of Science in Chemistry

by
Alexis Sanwick
April 2020

Dr. Gregory W. Bishop, Chair
Dr. Dane W. Scott

Keywords: Ultramicroelectrodes, nitrogen-doping, phosphorus-doping, gold nanoparticles, oxygen reduction reaction

ABSTRACT

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by

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Metal nanoparticles have been a primary focus in areas of catalysis and electrocatalysis applications as a result of their large surface area-to-volume ratios. While there is an increased interest in understanding the properties and behaviors of metal nanoparticles, they can become expensive over time. Recent research has incorporated the idea of using heteroatom-doped materials as a cheaper catalytic alternative to metal nanoparticles. In this study nitrogen-doping and phosphorous-doping techniques were applied to chemical vapor-deposited carbon ultramicroelectrodes in order to study the electrocatalytic properties toward the oxygen reduction reaction and the enhanced affinity for the deposition of gold nanoparticles onto the electrodes.

DEDICATION

This work is dedicated to my family for always supporting me throughout my undergraduate career.

ACKNOWLEDGMENTS

I would like to thank Dr. Gregory W. Bishop for allowing me to be a part of his research group and always being supportive and patient about my work. I would also like to thank Dr. Dane W. Scott for agreeing to be my committee member and helping me with my undergraduate studies. I am extremely grateful to both of you for helping me expand my knowledge and lab skills as a chemist. Additionally, I would like to thank previous graduate students Enoch Amoah and Chidiebere Ogbu for help with the success of this research and to Daniel Mawudoku for always helping me understand difficult concepts in the lab.

Additionally, I would like to thank the honors college for providing me with the Honors-in-Discipline scholarship and the American Chemical Society Petroleum Research Fund (Award # 58123 – UN15) for providing funds for this work.

I would like to acknowledge Somin Park from the Graham research group at the University of Kentucky for the XPS data and Enoch Amoah for preparing the XPS samples.

TABLE OF CONTENTS

Page

Chapter

LIST OF FIGURES

LIST OF ABBREVIATIONS

NPs	Nanoparticles
AuNP	Gold Nanoparticles
CV	Cyclic Voltammogram
CVD	Chemical Vapor Deposition
NP	Nanoparticles
UME	Ultramicroelectrode
CVD-C-UME	Chemical Vapor Deposition-Carbon Ultramicroelectrode
N-Doped	Nitrogen-Doped
P-Doped	Phosphorus-Doped
XPS	X-Ray Photoelectron Spectroscopy
PBS	Phosphate Buffered Saline
ORR	Oxygen Reduction Reaction

CHAPTER 1

INTRODUCTION

Ultramicroelectrodes

Ultramicroelectrodes (UME) are electrodes that are less than 25 µm in at least one dimension.[1] They have become increasingly popular since the 1950s because they are small, have a high sensitivity, fast steady state response, and small ohmic losses.[2] These properties make UMEs particularly useful in the detection of neurotransmitters,[3] for detection in biological systems,[4] such as detecting hydrogen peroxide,[5] and for studying fuel cell reactions like the oxygen reduction reaction (ORR).[6]

Although UMEs can be purchased from commercial sources, stable UMEs can be fabricated quickly and at a low cost.[7] One method for fabricating UMEs begins using a pipette puller and quartz tubing. The pipette puller sends a series of laser pulses to heat the quartz tubing, which is positioned between two arms that pull the heated tubing into two separate pieces. Using chemical vapor deposition (CVD) methods,[8] carbon can be deposited into the tip of each pulled capillary tube to form electrodes. Carbon CVD works by heating the tip of the pulled capillary under argon as a hydrocarbon fuel, such as a mixture of propane and butane gas is forced through the opposite end to the tip. Pyrolysis occurring on the tip of the electrode allows for the deposition of solid carbon into the quartz tubing. The electrode is completed by placing a metal wire in contact with the carbon through the open end of the capillary tube to create an electrical connection for electrochemical experiments.

CVD carbon UMEs (CVD-C-UMEs) often require modification in order to improve their sensitivity and selectivity for practical applications. Electrocatalytic materials such as precious metals or heteroatom-doped carbons are some common examples of electrode modifiers.[9,10,11]

Electrocatalysts

Electrocatalysts work to increase the rate of oxidation or reduction in an electrochemical cell by accelerating the transfer of electrons.[7] Electrocatalysts lower the potential where the electron transfer takes place while enhancing the current. With a lower energy barrier, reactions can proceed under more energy efficient conditions. The efficiency of electrocatalysts can vary based on physical properties like particle size, shape, surface composition, and distribution.

Previous research has shown metal nanoparticles (NPs) to be effective electrocatalysts for many reactions. NPs are particles that are between 1 and 100 nm in at least one of the three dimensions.[12] The small size of NPs lead to a high surface area-to-volume ratio, which is important due to the high proportion of surface atoms as this translates to relatively more reactive sites than a typical particle.[13] The amount of reactive sites that are present in NPs versus bulk materials have a significant impact on the properties of the compound whether it concerns the reactivity, color, malleability, conductivity, etc.

Metal NPs composed of platinum, gold, and palladium are some of the most important in heterogeneous catalytic reactions. It has been generally reported, with a few exceptions, that smaller NPs exhibit a higher catalytic activity than smaller NPs. For example, research by Liu et al.[17] showed that platinum NPs that were 2 nm in diameter exhibited a larger electrocatalytic current and positively shifted the reduction potential by 100 mV in comparison to 10 nm platinum NPs for the oxygen reduction reaction.[9] While it may seem advantageous that metal NPs can exhibit electrocatalytic activity toward certain reactions, it is tedious to synthesize NPs that are small enough to be electrocatalytic while preventing aggregation in the process. Aside from problems arising during synthesis, the use of metal NPs can be extremely costly. This is where the need for an alternative that is less costly but results in similarly electrocatalytic processes becomes important.

Heteroatom-doping is a promising technique that could serve as an electrocatalytic alternative to metal NPs. Heteroatom-doping is a process where atoms like nitrogen, boron, phosphorus, or sulfur are introduced on the carbon surface. Heteroatoms introduce variation in the size, shape, and electronegativity to the carbon structure. This is important because this change in the charge distribution alters the performance and can enhance the catalytic activity of the carbon reactant. There is hope that heteroatom-doped carbon UMEs can be used to study reactions such as the oxygen reduction reaction and the hydrogen peroxide reduction reaction. It is believed that heteroatom-doping results in a charge transfer, which plays a part in weakening the O-O bond and facilitates electron transfer.[14]

Oxygen Reduction Reaction

The oxygen reduction reaction (ORR) is a reaction crucial to fuel cell research that involves a four-electron transfer pathway occurring at the cathode. The reduction half-reaction can be represented as $O_2 + 4H^+ + 4e^- \rightleftharpoons H_2O$. The kinetics of this reaction are very slow in the O-O bond breakage, which is why a catalyst is required. Fuel cell research previously focused on using platinum NPs as catalysts, but research by groups such as Dai et al.[15] and Liu et al.[16] have supported the use of nitrogen or phosphorus-doping on different types of carbon supports to enhance electrocatalytic activity in the ORR.

Dai et al. showed that nitrogen doped (N-doped) carbon nanotubes demonstrated enhanced electrocatalytic activity in the ORR by introducing graphitic pyridinic groups through annealing of ammonia. They reported that the pyridinic groups created a net positive charge and unpaired electron density on the adjacent carbon atoms. It is believed that the increased electrondonating property weakens the O-O bond through a N-O bond to facilitate O_2 reduction.[15] Other groups have reported similar findings of N-doping through low temperature annealing with urea[17] or ammonium hydroxide[18] to promote O-O bond breakage.

Nitrogen-Doping

Recent research by Liu et al.[17] demonstrated that doping carbon materials like carbon black with heteroatoms can also enable deposition of ultrasmall (< nm) metal NPs. Nitrogen-doping (N-doping) was completed through low temperature annealing of urea and carbon black to produce ammonia and isocyanic acid (Figure 1). Isocyanic acid forms ureido groups with hydroxyl and carboxylic groups on the activated carbon surface, and ammonia integrates nitrogen-containing species into the carbon supports.

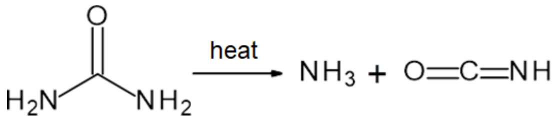


Figure 1: Thermal decomposition reaction of urea to produce ammonia and isocyanic acid.

Previous research in our group has implemented similar N-doping methods on CVD-C-UMEs and carbon fiber UMEs in order to study the electrocatalytic properties of NPs. Work completed by Enoch Amoah[19] adapted an ammonium hydroxide N-doping method to immobilize AuNPs onto the surface of CVD-C-UMEs. In comparison to unmodified electrodes, the N-doped electrodes demonstrated enhanced affinity for deposition of AuNPs on the carbon surface. The success of AuNP deposition on the modified versus unmodified electrodes supported the presence of nitrogen-containing groups on the carbon surface. In addition to enhanced affinity for the deposition of AuNPs, the electrodes modified through this method proved to be electrocatalytic towards the methanol oxidation reaction.

Additionally, research completed by Daniel Mawudoku[20] and George Affadu-Danful[21] applied an N-doping procedure previously demonstrated by Liu et al.[17] in order to immobilize AuNPs onto carbon fiber UMEs. The presence of nitrogen containing groups on the electrode surface was demonstrated through x-ray photoelectron spectroscopy (XPS), where pyridinic and amide/amine nitrogen groups were determined to be present.[21] Similarly to the work completed by Amoah,[19] the AuNPs present on the N-doped carbon fiber electrodes were determined to be catalytic towards the methanol oxidation reaction.

Thus far, our group has demonstrated that both the N-doped CVD-C-UMEs and N-doped carbon fiber UMEs demonstrate an enhanced affinity for deposition of AuNPs, and the deposited AuNPs exhibit superior catalytic activity towards methanol oxidation than unmodified electrodes. However, previous results indicate that the AuNPs that have been deposited onto the electrodes have been much larger than those reported to have been deposited on carbon black by similar methods.[17] For example, the AuNPs that have been deposited onto N-doped CVD-C-UMEs at a pH of 4.6 ranged from 9 to 69 nm in radius and from 60 to 206 nm in radius at a pH of 2.5.[19] In comparison, Liu et al.[17] reported ligand-free Au nanoclusters less than 2 nm in size when the pH was between 4 and 10 and particles ranging between 6 and 10 nm at a pH outside that range. We believe that the larger AuNPs are a result of using small sized electrodes, which have fewer nucleation sites and provide less competition for particle growth than carbon powders. In an attempt to control particle loading size and uniformity, Liu et al.[22] reported a phosphorus-doping (P-doping) procedure where they were able to grow electrocatalytic precious metal nanocrystals ranging from 1 to 3 nm. They stated that the valence states of phosphorus are key in tuning the affinity between the metal precursors and carbon supports. Our research group wants to explore P-doping as a technique to deposit smaller electrocatalytic AuNPs onto CVD-C-UMEs.

Research Goals

In this study, N-doping and P-doping were explored as methods to deposit small AuNPs on CVD-C-UMEs. Previous reports of heteroatom-doped carbon materials demonstrate enhanced affinity for precious metal NPs. Simple, low-cost carbon UMEs were fabricated using a previously reported CVD technique[23] and modified using methods adapted for low temperature annealing with ammonium hydroxide[18] or sodium hypophosphite.[22] Electrochemical measurements were obtained using cyclic voltammetry. Additionally, the electrocatalytic activity of N-doped CVD-C-UMEs was studied to examine the potential for the use of N-doped CVD-C-UMEs as electrocatalysts for the ORR in fuel cells.

CHAPTER 2

EXPERIMENTAL

Materials

All chemicals used for these experiments were used without further purification. 30% ammonium hydroxide, potassium chloride, and ferrocene methanol were obtained from Sigma-Aldrich. Tetrachloroaurate (III) trihydrate was obtained through Alfa Aesar. Perchloric acid was obtained from Fluka Analytical. Sodium borohydride and PBS tablets were obtained from Fischer Scientific. Sodium hypophosphite was obtained from Akros Organics. Nitrogen gas was obtained from Airgas. Quartz glass capillaries were obtained from Sutter Instrument Company. The propane/butane (30:70) mixture was obtained from Coleman. All aqueous solutions were prepared using ultrapure water (18.2 MΩ·cm).

Fabrication of CVD Carbon Ultramicroelectrodes

Quartz capillary tubes (0.5 mm I.D.) were pulled into two separate pipettes using a Sutter Instruments P2000 laser-based micropipette puller. A propane/butane mixture (30:70) was heated onto the tip of the pipette using a torch to deposit a layer of solid carbon through a previously reported chemical-vapor deposition method.[23] This was completed in the presence of argon gas to create an inert atmosphere and minimize the production of CO_2. A stainless-steel wire was inserted through the end of the capillary tube to make contact with the deposited carbon and create an electrical connection. The wire was sealed to the end of the capillary tube using epoxy resin to minimize wire movement.

Nitrogen-Doping of CVD Carbon Ultramicroelectrodes

Nitrogen-doping was achieved through slight modification of a previously reported method[18] where the tip of the CVD-C-UME was immersed in an aqueous solution of ammonium hydroxide (2% w/w) and heated on a hotplate at 80 °C for one hour. The electrode was washed with ultrapure water and allowed to dry.

Phosphorus-Doping of CVD Carbon Ultramicroelectrodes

Phosphorus-doping of the CVD carbon was completed using sodium hypophosphite through a modified procedure previously reported by Liu et al.[22] The tip of the CVD-C-UME was immersed in sodium hypophosphite solution and heated to 80 °C for 10 minutes. The electrode was rinsed with ultrapure water and allowed to dry.

Immobilization of AuNPs

All glassware was cleaned with aqua regia prior to the start of the experiment. Modified or unmodified electrodes were immersed into a 0.1 mM solution of $HAuCl_4$ (10 mL) on a magnetic stirrer. A freshly prepared solution of 0.1 M $NaBH_4$ (90 µL) was quickly injected into the $HAuCl_4$ solution. The electrode was submerged in the solution for one hour, washed with ultrapure water, and allowed to dry.

Voltammetric Characterization of CVD-Carbon Ultramicroelectrodes

All electrochemical measurements were obtained with a CHI760E electrochemical workstation using cyclic voltammetry (CV). Results were obtained using a two-electrode electrochemical cell where the CVD-C-UME served as the working electrode, and an Ag/AgCl electrode served as both the reference and counter electrode. Characterization of electrodes was completed using a 0.5 mM ferrocene methanol in 0.1 M KCl solution. CVs were run from 0 V to 0.4 V to 0 V with a scan rate of 0.025 V/s and examined for determination of size and stability. Stable CVD-C-UMEs CVs produce sigmoidal responses (Figure 2). Size estimation of electrodes comes from the previously determined equation[24] based on the limiting current:

$$i_d = 4nFDCr$$

where i_d is the limiting current, n is the number of electrons transferred, F is Faraday's constant, D is the diffusion constant, C is the concentration of the ferrocene methanol, and r is the radius of the electrode. The approximate sizes of the electrodes used in this study ranged from 710 nm to 13 µm in diameter.

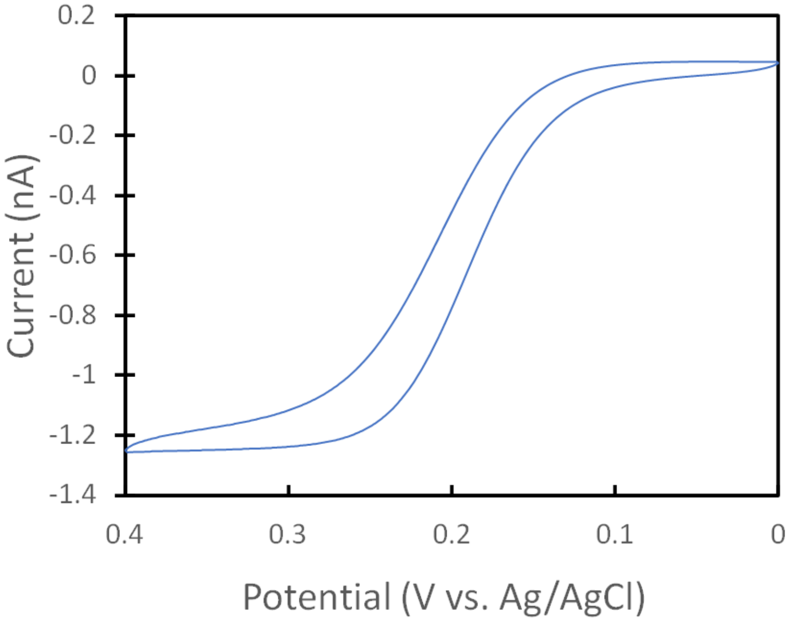


Figure 2: CV of a CVD-C-UME exhibiting a sigmoidal behavior in 0.5 mM ferrocene methanol and 0.1 M KCl.

Voltammetric Response of the Oxygen Reduction Reaction

Electrochemical measurements used to study the oxygen reduction reaction were obtained in phosphate buffered saline (pH 7.4) in the presence and absence of oxygen. Oxygen was removed from the system by bubbling nitrogen gas through the electrochemical cell for 15 minutes. The working electrode potential was scanned from -0.6 V to 0.8 V and back using a scan rate of 50 mV/s.

AuNP Characterization

Electrochemical measurements used for AuNP characterization took place using 0.1 M perchloric acid. The working electrode potential was scanned from -0.2 V to 1.4 V and back using scan rate of 100 mV/s in 0.5 mM ferrocene methanol.

X-Ray Photoelectron Spectroscopy

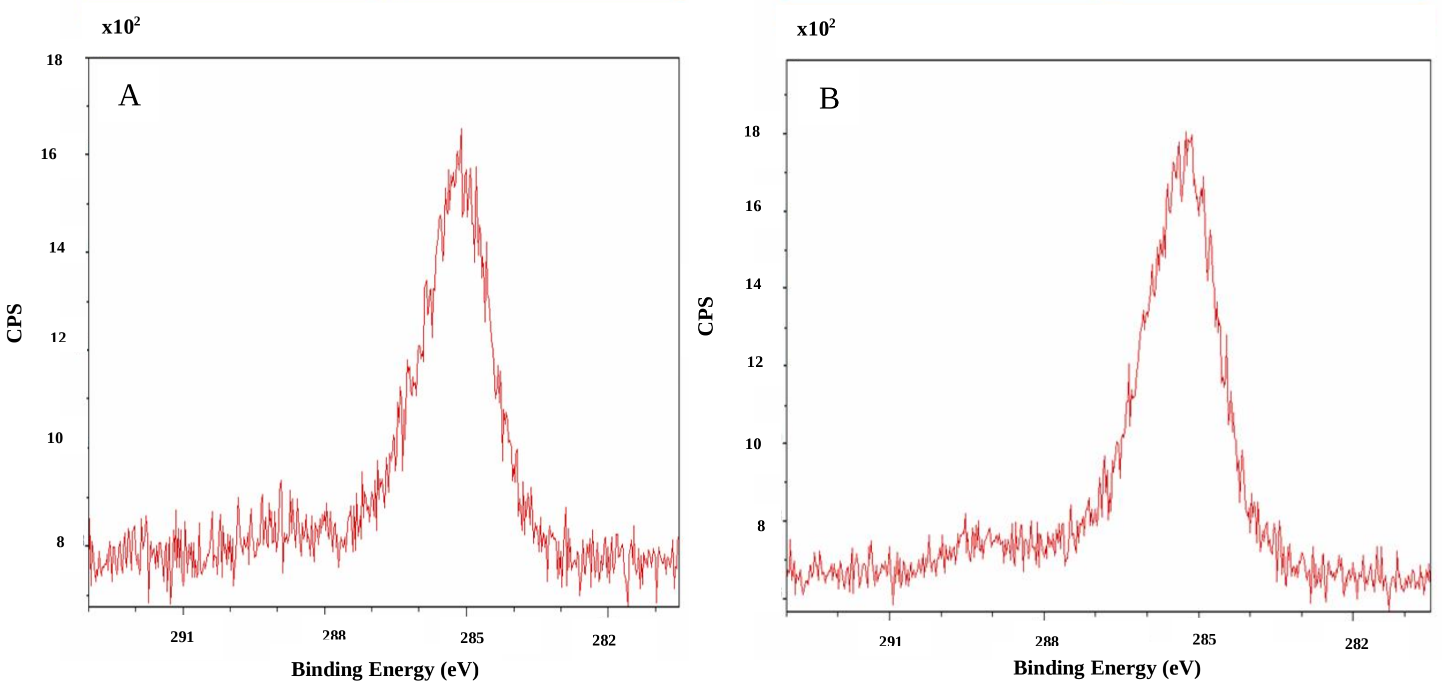
X-ray photoelectron spectroscopy analysis was carried out by Somin Park from the Graham research group at the University of Kentucky using a PHI 5600 instrument with a multichannel plate detector, 11-inch diameter hemisphere, and dual anode (Mg and Al) X-ray source. The system operates in the Bremsstrahlung isochromat mode. N-doped CVD carbon in tapered quartz capillaries were secured to indium tin oxide substrates using a silver paste. Chemical states of elements were assigned based on the PHI and NIST XPS Databases.

CHAPTER 3

RESULTS AND DISCUSSION

Characterization of N-Doped CVD-C-UMEs

XPS (Figure 3) of unmodified and N-doped CVD carbon in tapered quartz capillaries showed similar peaks in the C1s (Figure 1A,B) and O1s (Figure 1E,F) regions of the spectrum. Both the unmodified and N-doped CVD carbon exhibited intense C1s peaks at 284 eV and weak O1s peaks at 532 eV. A slight peak at 401 eV was visible only in the N-doped CVD carbon sample (Figure 1C,D). Research from Liu et al.[17] reported a similar C1s peak for graphitic carbon at approximately 284 eV corresponding to graphite sp2 hybridized carbon and a nitrided-graphite N1s peak around 400 eV where N atoms had replaced graphitic carbons XPS data further supports the success of N-doping CVD carbon through aqueous ammonium hydroxide. The peak that the N-doped CVD carbon exhibited at 401 eV serves as evidence of the success of introducing surface nitrogen groups into the carbon structure through the ammonium hydroxide procedure.



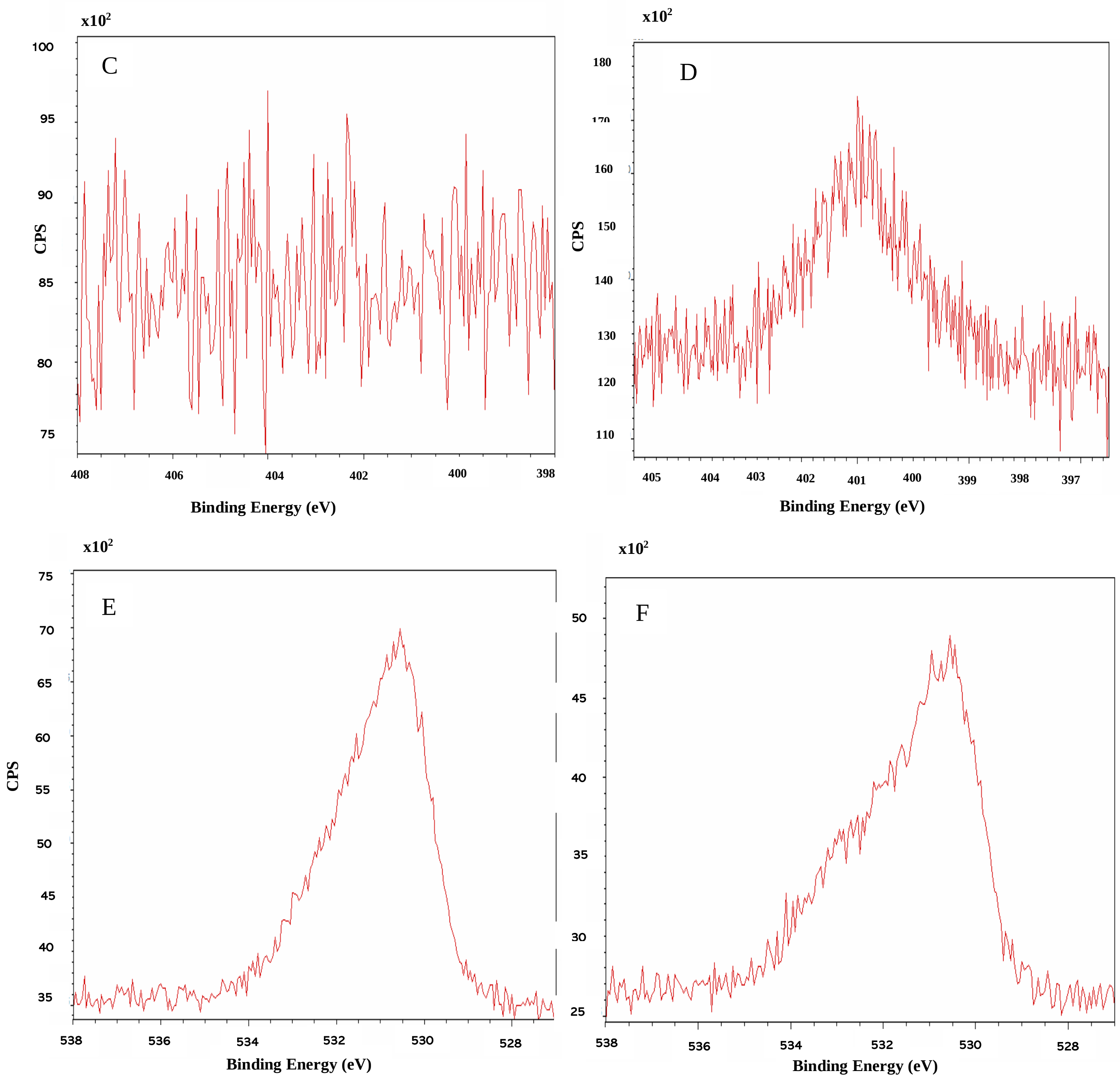


Figure 3: XPS peaks for unmodified CVD-C-UMEs (A,C,E) and N-doped CVD-C-UMEs (B,D,F) corresponding to C1s (A,B), N1s (C,D), and O1s (E,F) are shown.

Electrocatalytic Activity of N-Doped CVD-C-UMEs

While Amoah previously demonstrated that N-CVD-C-UMEs exhibited electrocatalytic behavior towards hydrogen peroxide reduction, N-doping of CVD carbon also appears to improve electrode performance towards the oxygen reduction reaction. A significant increase in the current associated with the oxygen reduction reaction was observed on N-CVD-C-UMEs compared to unmodified CVD-C-UMEs (Figure 4). The reduction current for ORR at -0.6 V was about 5 times larger with the N-CVD-C-UME than with the unmodified UME. N-doping also positively shifted the onset potential for oxygen reduction by 94 mV from -0.358 V for unmodified CVD-C-UME to -0.252 V for N-CVD-C-UME. This result is similar to the shift that was previously reported for the hydrogen peroxide reduction from -0.199 V to -0.095 V after modification. Both of these reductions demonstrated an approximate 100 mV positive shift in the onset potential.

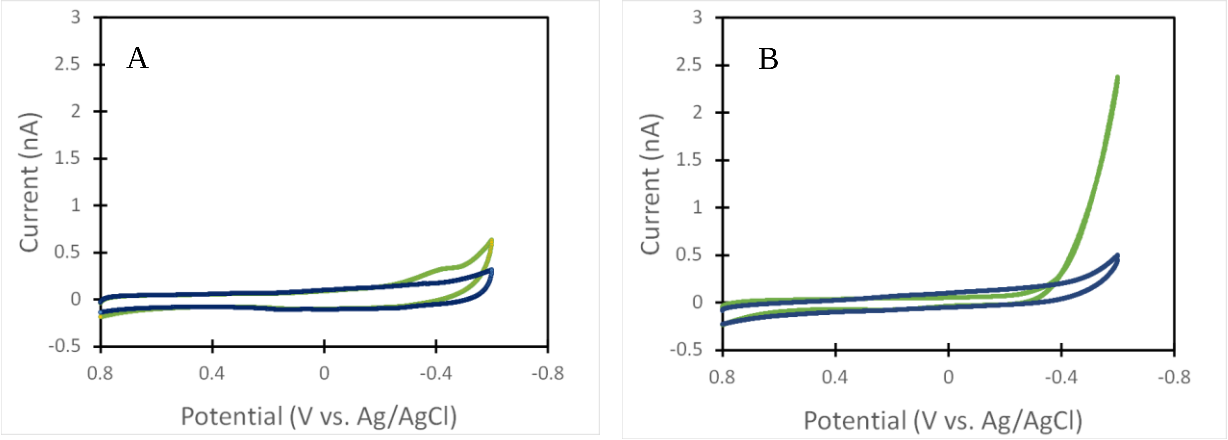


Figure 4: CVs of unmodified (A) and N-doped (B) UMEs in the presence (blue) and absence (green) of oxygen before attempted AuNP deposition.

Immobilization of AuNPs on Phosphorus-Doped CVD-C-UMEs

Through XPS and characterization of electrocatalytic properties, we have obtained direct and indirect evidence that thermal treatment of ammonium hydroxide introduces surface nitrogen species onto CVD-C-UMEs. While our group also previously demonstrated that AuNPs are preferentially deposited onto N-doped CVD-C-UMEs compared to unmodified CVD-C-UMEs, experiments have mostly resulted in larger, less catalytically active aggregates of AuNPs than those deposited onto carbon black in other published reports. As a result, we investigated P-doping using NaH_2PO_2 as a phosphorus source as a possible alternative to N-doping in hopes that it would enable deposition of small, electrocatalytically active AuNPs onto CVD-C-UME surfaces through $NaBH_4$ reduction of $HAuCl_4$.

In order in investigate the ability to immobilize AuNPs onto P-doped CVD-C-UMEs, CVs of unmodified and P-doped electrodes were taken in a perchloric acid solution and a potassium perchlorate/potassium bromide solution. These methods described by Sharma et al.[25] correspond to gold oxide formation and subsequent reduction (Figure 5), and oxidative dissolution of AuNPs in the presence of bromide to form $AuBr_4^-$ (Figure 6) respectively. Equations 1 and 2 show the reactions for gold oxide reduction and for the oxidative dissolution of AuNPs to $AuBr_4^-$.

$$Au_2O_3 + 6H^+ + 6e^- \rightarrow 2Au + 3H_2O \qquad (1)$$

$$Au + 4Br^- \rightarrow AuBr_4^- + 3e^- \qquad (2)$$

The unmodified electrode does not show any sign of gold oxide formation or subsequent reduction in 0.1 M $HClO_4$, as expected. The P-doped electrode showed a small but obvious gold oxide reduction peak around 0.9 V with an area of 49.51 pC. This is clear evidence of gold on the electrode surface.

Consistent with the CV results in 0.1 M $HClO_4$, the CV for the unmodified electrode in $KClO_4$ and KBr showed no apparent peak that can be attributed to oxidative dissolution of gold. On the other hand, the P-doped electrode shows a large oxidation peak at 0.918 V in the first scan taken in $KClO_4$/KBr, which is consistent with oxidation of Au to form soluble $AuBr_4^-$. The oxidative dissolution peak did not appear in subsequent repeat scans, indicating complete oxidative dissolution of Au from the electrode surface.

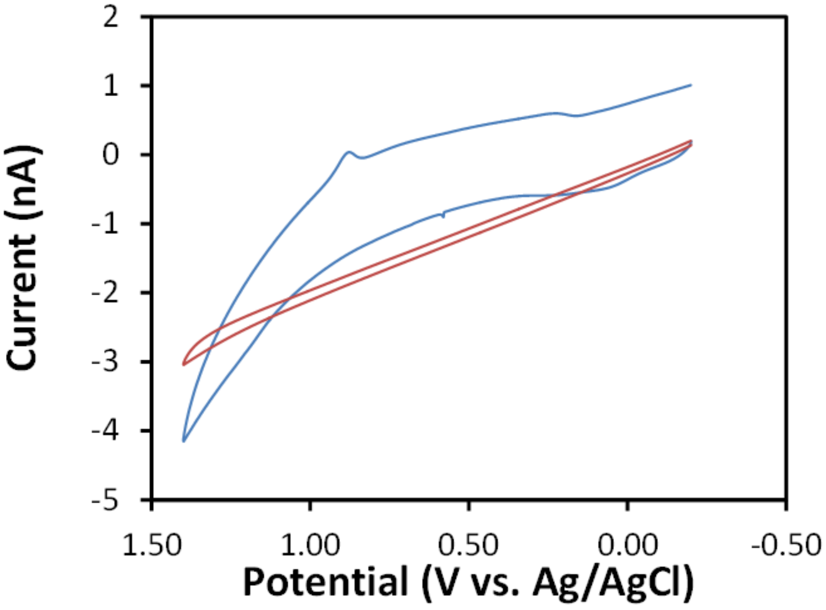


Figure 5: CVs of unmodified (red) and P-doped (blue) CVD-C-UMEs after attempted AuNP deposition in 0.1 M $HClO_4$.

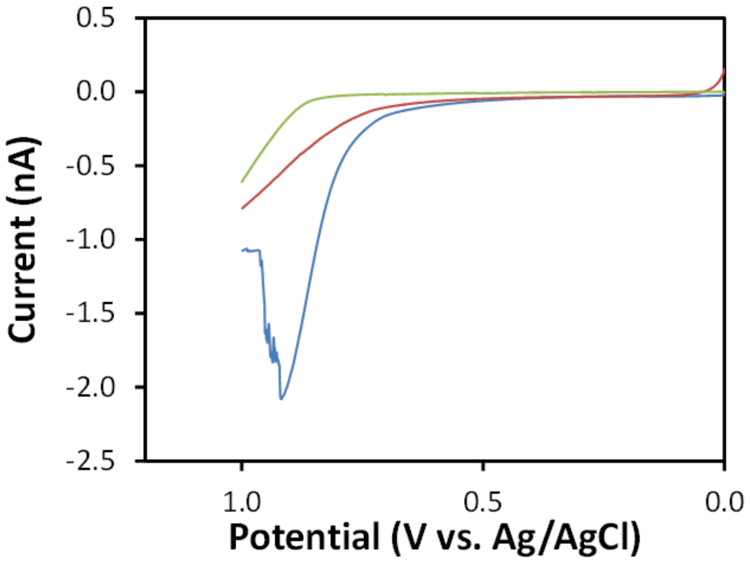


Figure 6: CVs of unmodified (green), first P-doped scan (blue), and second P-dope scan (red) of CVD-C-UMEs in 0.1 M $KClO_4$ and 0.01 M KBr after attempted AuNP deposition.

CHAPTER 4

CONCLUSIONS

Conclusions

In these studies, N-doping and P-doping of CVD carbon, which had previously only been verified through indirect evidence, was shown to introduce surface nitrogen through XPS. Furthermore, N-doped CVD carbon UMEs were also shown to be capable of acting electrocatalytically towards oxygen reduction. Since previous work in our group suggested only large aggregates of AuNPs could be immobilized on N-doped CVD UMEs, P-doping was also evaluated here a possible method for depositing gold nanoparticles onto CVD-C-UMEs.

CVD-C-UMEs were fabricated using a laser-based pipet puller and a propane: butane gas mixture as a carbon source. Electrodes were characterized using cyclic voltammetry and ranged from 710 nm to 13 µm in diameter. The electrodes exhibited sigmoidal electrochemical response for ferrocene methanol oxidation, which is consistent with UME behavior.

N-doping was carried out through low temperature annealing CVD carbon with ammonium hydroxide. N-doped CVD-C-UMEs exhibited a 5 times larger reduction current than unmodified electrodes for the ORR. The success of N-doping was confirmed through both indirect and direct methods using oxygen reduction and XPS respectively. XPS survey exhibited a peak at 401 eV only present for N-doped CVC-C-UMEs confirming the presence of surface nitrogen.

Future Work

Following the P-doping method reported by Liu et al.,[22] we would like to examine the electrocatalytic behavior of P-doped CVD carbon UMEs towards oxygen reduction. The only evidence we have for the success of P-doping is the presence of immobilized AuNPs on the electrode. XPS data has not yet supported the presence of phosphorus on the electrode surface as a result of low sensitivity in response to phosphorus.

Through N-doping with ammonium hydroxide and P-doping with sodium hypophosphite, we have reported very large particles or aggregates of small particles in solution. We would like to further explore the correlation between pH and the size of AuNPs.

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