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Preparation and Characterization of Nitrogen Doped Carbon Nanotube Electrode Materials

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Dedication

To BQ
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This dissertation describes the preparation and characterization of nitrogen doped carbon nanotube films by a chemical vapor deposition (CVD) process. Thorough description of the preparation method is given. A variety of techniques are used to demonstrate the relationship between the physicochemical properties and electrochemical properties of nitrogen doped carbon nanotubes, shedding insight to the influence of nitrogen doping on observed electrocatalysis phenomena. Chapter 1 comprises a general overview of the presented material and scope of the work. Chapter 2 details the CVD preparation of nitrogen doped carbon nanotubes. Scanning electron microscopy, thermal gravimetric analysis, and x-ray photoelectron spectroscopy are used to demonstrate the degree of control afforded by the CVD process over the resultant properties of the prepared carbon nanotubes. The direct preparation of carbon nanotube films on a current
collector is shown. Chapter 3 consists of a thorough characterization and comparison of nitrogen doped carbon nanotubes and non-doped carbon nanotubes. Transmission electron microscopy, thermal gravimetric analysis, and Raman spectroscopy demonstrate the increased disorder caused by nitrogen doping into the graphitic lattice structure of carbon nanotubes. X-ray photoelectron spectroscopy highlights the existence of multiple carbon-nitrogen surface functionalities that change in relative abundance as the nitrogen content is varied. Titration analyses indicate that nitrogen doped carbon nanotubes are basic and acquire a cationic surface charge in solutions of neutral pH. Chapter 4 presents a collection of voltammetric responses of several outer-sphere and inner-sphere redox probes. The similarities and differences between the responses at non-doped carbon nanotube electrodes and nitrogen doped carbon nanotube electrodes are noted and discussed in the context of the conclusions of the physical characterizations. A detailed mechanistic analysis of the O$_2$ reduction process at nitrogen doped carbon nanotube electrodes is presented. Chapter 5 details continuing work with carbon nanotube materials for fundamental and applied studies.
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CHAPTER 1

Nanocarbons: Nitrogen Doped Carbon Nanotubes

1.1 INTRODUCTION

Epitomized by Georges Leclanche’s first dry cell battery and Michael Faraday’s charcoal electrodes, graphitic carbons have a longstanding history as electrode materials in energy storage/conversion technologies and electroanalytical studies. Most graphitic carbon electrode materials currently encountered in laboratory and industrial settings are the ‘traditional’ graphitic carbons, i.e. carbon blacks, pyrolytic graphite, carbon fibers, and glassy carbons. Their widespread use is testament to their excellent physical malleability, mechanical durability, low density, high electronic conductivity, and high corrosion resistivity.\textsuperscript{1-3} Despite these shared favorable characteristics, the various traditional graphitic carbon types each have distinct interfacial properties (e.g. surface area, density of exposed edge plane sites, surface functionalities) which are strongly influenced by their respective solid/liquid carbon source (e.g. coconut shells, furfuryl alcohol, polyacrylonitrile). Unfortunately, solid/liquid carbon precursors require extreme preparative conditions that do not allow systematic or subtle variations in their resultant physicochemical properties. Post-synthesis modification of the interfacial characteristics of traditional graphitic carbons is often problematic, with poor reproducibility\textsuperscript{4-6} and short lived stability\textsuperscript{7}. Hence,
while several reviews and texts have been devoted to cataloging the preparations and physical properties of traditional graphitic carbons,\textsuperscript{8-11} there is still great interest and opportunity to develop more intrinsically usable and active graphitic carbon electrode materials.

Alternative graphitic carbons from gas-phase carbon precursors have been actively pursued for the last four decades,\textsuperscript{12} with verdant interest in the last fifteen years stemming from landmark fullerene publications.\textsuperscript{13} Gas-phase precursors are attractive because they require milder graphitization conditions than those necessary for traditional graphitic carbons, e.g. graphitization temperatures for glassy carbon are \textasciitilde 2000°C\textsuperscript{14} but only \textasciitilde 700°C\textsuperscript{15} for carbon nanotubes, allowing judicious changes in temperature, pressure, and carrier gas to influence systematically and deterministically the size, shape, crystalline structure/orientation, and elemental composition of the produced carbon material at the nanometer scale. The variability and controllability of such carbons at this fine level have prompted many to classify them as ‘nanocarbons.’\textsuperscript{12,16,17}

The benefits of nanocarbons as electrode materials with tailored shapes and orientations have been reported by several groups. For example, the Crooks group has demonstrated that discrete ultramicroelectrodes can be prepared from individual carbon nanotubes;\textsuperscript{18,19} Ren et. al. have fabricated ordered arrays of carbon nanofibers as electrochemical sensors that show low background currents;\textsuperscript{20} and Lipka and co-workers have shown higher measured capacitances in supercapacitor electrodes that utilize carbon nanohorns.\textsuperscript{21} However, the advantages of nanocarbons with deterministically controlled electrochemical
properties have not yet been explored, due in large part to poorly supported claims that nanocarbons, specifically carbon nanotubes (CNTs), inherently possess extraordinary electrocatalytic activities (e.g. fast heterogeneous electron transfer) that manifest from 1D electronic quantum confinement.\textsuperscript{22-24} Groups like Compton and co-workers have begun to contest these claims, citing evidence that structural defects in the form of edge plane sites are the source of electrochemical activities rather than 1D quantum confinement phenomena.\textsuperscript{25-28} Hence, in order to successfully produce graphitic carbons with tailored/optimized electrocatalytic activities, a thorough understanding of the relevant physicochemical properties that most strongly influence the electrochemical properties is necessary.

One method for drastically improving catalytic activities of graphitic carbon for both reductive and oxidative processes is the doping of heteroatoms into the graphitic lattice and/or the peripheral surface functionalities.\textsuperscript{29,30} For example, Mrha demonstrated increased O\textsubscript{2} reduction electrocatalytic activity of nitrogen-enriched carbon powders.\textsuperscript{30} However, since the facile production of such activated traditional carbons has been arduous for the reasons mentioned previously, there is presently a limited understanding of how nitrogen incorporation influences electrochemical processes like O\textsubscript{2} reduction. In this regard, chemical vapor deposition (CVD) methods are ideal for controllably producing nitrogen-doped CNTs (N-CNTs)\textsuperscript{31-37} and serve as viable methods for producing graphitic carbons with controlled electrochemical properties. The work contained herein represents the first efforts to utilize the CVD production of N-CNTs with the primary goals of (1) understanding more comprehensively the
influence of nitrogen doping on electron transfer systems like $O_2$ reduction and (2) deterministically producing a graphitic carbon material that is inherently active for a desired electrochemical reaction.

Since the focus of this work are carbon nanotubes, it is important to define at the outset what is meant in this context by the term carbon ‘nanotube.’ The carbon ‘nanotube’ moniker initially referred only to elongated fullerene molecules that demonstrated 1D quantum confinement phenomena but now is used to describe all hollow fibril carbon structures, even those with large diameters (> 30 nm) and disordered wall structure where 1D quantum confinement phenomena are not operative. These larger, less ordered cylindrical carbons are more accurately described as ‘nanofibers’ or ‘filamentous carbons,’ as they have been for nearly half a century prior to the use of ‘nanotube.’ The confusion from improper ‘nanotube’ usage has been noted and addressed, but the lax ‘nanotube’ lexicon permeates the recent literature to such a great extent (ca. 17,000 carbon ‘nanotube’ publications since 1992) that the terms such as ‘nanotube,’ ‘nanofiber,’ ‘filamentous,’... etc. hold little descriptive information. Hence, while rigorous differentiation of cylindrical carbon materials is unfortunately now somewhat counterproductive, it should be emphasized here that the materials studied in this work do not manifest 1D quantum-confinement phenomena. These materials are relatively large, moderately to heavily disordered, hollow carbon fibrils with wall structures composed of several graphene layers. They will be referred herein as simply carbon nanotubes (CNTs).
In this regard, this dissertation discusses in detail the facile preparation of vertically aligned, high density CNT films directly on conductive supports by chemical vapor deposition (CVD) involving metal phthalocyanines and metallocenes. Through the described methodology, CNTs are prepared with defined features such as size, diameter, orientation, structure, and composition. This approach affords the opportunity to identify the electrochemical properties of ‘as-grown’ CNT electrodes. Presented data demonstrate that N-CNTs show enhanced electrocatalytic ability for select inner-sphere redox processes. The influence of structural and compositional properties on manifested electron transfer of N-CNTs is studied.

This dissertation is organized into five chapters, with Chapter 1 serving as a general introduction. The remaining four chapters detail the preparation and characterization of CNTs possessing nitrogen concentrations in the range of 0 - 10 at. %, with an emphasis on identifying the influence nitrogen doping has on the CNT physicochemical and electrochemical properties. The direct growth of CNTs via specifically the floating catalyst CVD methodology is the subject of Chapter 2. A growth model is reviewed and the use of organometallic precursors as carbon/graphitization catalyst sources is discussed. The influence of temperature, carrier gas composition, and growth substrate on the obtained CNT materials is reported, specifically detailing the CNT films prepared on nickel mesh supports. Methods for controlling the nitrogen and residual iron contents are detailed.
Chapter 3 describes in detail the structure and composition of the CNTs. Transmission electron microscopy (TEM), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, and thermal gravimetric analysis (TGA) are used to study the effect of nitrogen doping. SEM images detail the uniform nature of all CNT coatings on the nickel substrates. TEM images and Raman spectra demonstrate increased structural disorder in N-CNTs relative to otherwise similar non-doped CNTs that tracks with nitrogen content. XPS spectra identify the existence of multiple surface nitrogen functionalities decorating the surface of N-CNTs. Results from titrations for the determination of the CNTs’ pH_{pzc} and iodimetric titrations suggest the surface nitrogen functionalities impart an alkaline character on N-CNTs.

The electrochemical responses of non-doped CNTs and N-CNTs towards inner sphere and outer sphere redox couples are the focus of Chapter 4. The key structural features identified and discussed in Chapter 3 are shown to influence the electron transfer at non-doped CNTs and N-CNTs for some redox couples. Potential step and potential sweep methods are used to demonstrate the observed electrochemical responses for Ru(NH₃)₆^{3+/2+} and Fe(CN)₆^{2-/3-} at non-doped CNTs and N-CNTs are not readily distinguishable. For several catechol/orthoquinone couples and O₂/HO₂⁻, the observed voltammetric responses are significantly influenced by nitrogen doping, due to the ionic character of N-CNTs in aqueous solution. In particular, the two successive, two-electron mechanism for O₂ reduction in aqueous solutions is discussed at length, highlighting key differences for N-CNTs.
Chapter 5 discusses further topics of study involving CNTs. The continuing development of the CVD preparation method for N-CNTs is discussed. In particular, N-CNTs made with nickel rather than iron growth catalysts are used to demonstrate the irrelevance of the identity of the residual metal for the observed activities. Two new methods are presented to measure the rate constant for the heterogeneous decomposition of hydrogen peroxide at CNT/solution interfaces. SECM measurements and fluorescence-based detection of hydrogen peroxide represent methods that require much less quantities of materials, have a high throughput, and can be used to measure the potential dependence of this reaction. Finally, the direct application of the CNT electrode architectures in industrial abatement processes and battery technologies are discussed. Comparisons between commercial air cathodes and as-prepared N-CNT electrodes are shown.
1.2 REFERENCES.


43. As of 10/01/05 according to the CAS database
CHAPTER 2

Preparation of Nitrogen Doped Carbon Nanotubes

2.1 INTRODUCTION

Heteroatom doping (e.g. boron, sulfur, phosphorous, and nitrogen) of graphitic carbon lattices effects various physicochemical properties of sp\(^2\) carbon materials.\(^{1,2}\) In particular, the substitutional doping of nitrogen has received focused attention because significant changes in hardness, electrical conductivity, and chemical reactivity have been theoretically predicted and experimentally observed.\(^{3-5}\) Several methods for preparation of nitrogen doped carbon materials have been used including sputter deposition,\(^{6}\) graphitization of nitrogen-containing polymers,\(^{7}\) and exposure of pre-formed carbons at elevated temperatures to reactive gases (HCN and NH\(_3\)).\(^{8}\) While the former two routes typically produce materials useful as inert coatings\(^{6}\) and adsorbents,\(^{9,10}\) respectively, the latter route has been particularly promising for the preparation of activated carbons that demonstrate enhanced chemical reactivity for electron transfer processes,\(^{8,11-13}\) including those important to battery and fuel cell applications.\(^{14,15}\) Although many studies have evaluated structure-composition-property relationships of these N-doped carbons, the influence of nitrogen doping on resultant physicochemical properties has not been directly identified.\(^{8,14}\) For

\(^{*}\) Portions of this chapter are taken from a manuscript accepted by Carbon.
example, carbon surface areas, surface functionalities, and degree of graphitization vary strongly with the different carbon materials used and their pretreatment and processing histories. Further, the nitrogen doping process is a complex function of the activation conditions employed (e.g., reactant gas concentration, reaction time, temperature). As such, many diverse and sometimes conflicting conclusions have been made about N-doped carbons.16

Numerous methodologies are known for preparing nitrogen-doped CNTs (N-CNTs). Exhaustive descriptions of all the variant details of carbon nanotube synthesis can be found in the reviews by Rodriguez,17 Dai,18 and Melechko.19 Generally, all CNT synthetic strategies can be classified into one of two categories, either as flash sublimations of solid phase carbon precursor(s) or as chemical vapor depositions of gaseous carbon precursors over metal graphitization catalysts. Three notable exceptions to these classifications are the methods of CNT synthesis by ball milling carbon powders,20 electrolysis of organic/liquid NH3 solutions,21 and controlled combustion of carbonaceous gases at gas/solid interfaces.22 Since these methods do not demonstrate a high degree of control over the composition of CNTs (i.e. they result in amorphous, ill-defined carbon structures that are tubular but may or may not be largely sp2 hybridized) they will not be further addressed here in any detail.

The two most common methods of subliming solid precursors are plasma arcing23 and laser ablation.24 The former method consists of a sudden application of a large bias between two closely spaced carbon electrodes under an inert atmosphere at low pressures. The sparking between the two electrodes results in
intense heating that sublimes surface carbon atoms from one or both of the electrodes. The gaseous carbon atoms quickly react, cool, and deposit as carbon nanotubes. Similarly, laser ablations feature quick bursts of photons that sharply heat and sublime surface carbon atoms. Highly crystalline CNTs can be made as well as CNTs doped with heteroatoms by flash sublimations. However, there are several drawbacks for these preparation routes. For either sublimation method, the reaction pathway(s) for the formation of carbon nanotubes is unclear and complex, involving radical species. As a result, regulated nitrogen doping at specified levels is not practical. In other words, the textural and compositional features of the CNTs cannot be precisely defined by a priori. In addition, the overall yields of CNTs relative to simultaneously generated amorphous carbon structures can be low (e.g. 35 wt. %). Perhaps the biggest drawbacks are that CNTs cannot be directly grown on any substrate, cannot be prepared as highly oriented films, and cannot be scaled up to produce large amounts of high purity CNTs.

Chemical vapor deposition (CVD) methods are more attractive for controlled CNT synthesis. In general, CVD methods are conducted at lower process temperatures and pressures, can deposit CNTs directly upon substrates (as highly aligned, dense films if desired), can be readily scaled up, and, most importantly, can selectively produce structurally and compositionally defined CNTs in the absence of amorphous graphitic carbon impurities. All of these advantages directly arise from the use of transition metal catalysts. Metals like iron, nickel, and cobalt have been used to produce graphites at relatively low
process temperatures for several decades. For all CVD methods, there is a generally accepted model of CNT formation which is depicted in Figure 2.1. The CNT is formed through a precipitation process, where the metal seed particle on a surface becomes first saturated with gaseous carbon (i), and then supersaturated to such an extent that graphene layers precipitate out (ii) as a hollow, tubular structure. The cylindrical graphene layers can emanate from a stationary metal particle (base growth, iiiA) or can push the particle off the surface (top growth, iiiB) as the tube lengthens. Both base and top growth routes can occur but the former mechanism is believed to be predominant. Figure 2.1 illustrates that if there are gaseous species containing heteroatoms (e.g. CXg), those heteroatoms can dissolve in and precipitate out of the metal catalyst and become trapped/doped in the graphitic lattice. As such, an attractive aspect is that control over the type and amount of gaseous species will regulate the resultant CNT composition.

CVD methods can be parsed into two sub-categories, those involving separately deposited metal films/particles on a support substrate or those utilizing in-situ generated metal growth catalysts. The former sub-type describes the process patented by Hyperion Catalysis and involves the distribution of growth catalyst material on a substrate, activation of the catalyst material, and then exposure to gaseous carbon for CNT growth. An additional advantage of this scheme is that lithographic patterning of the growth catalyst on the support substrate can produce 2D patterned CNT films. The disadvantages of this form of CVD are the inefficient use of catalyst material, the adhesion of the catalyst material on the supporting substrate, and the numerous process steps required for
Figure 2.1 An idealized representation of the metal-catalyzed formation of a CNT. The metal seed particle is initially saturated with gaseous carbon atoms (i) until graphene layers precipitate out of the particle (ii). The tube structure may then form with the seed particle remaining at the top (iiiA) or fixed at the base (iiiB).
CNT growth.\textsuperscript{34} In addition, as the method of the catalyst activation step strongly determines the measured CNT yields,\textsuperscript{34} the conditions for each process step must be strictly regulated.

CVD methods that use a precursor(s) (solid and/or liquid) to generate carbon atoms, dopant atoms, and metal atoms in-situ are more advantageous. In this process, first introduced by Endo et al as a “floating catalyst CVD,”\textsuperscript{35} the gas phase carbon and metal atoms are generated simultaneously from the pyrolysis of organometallic compounds such as ferrocene, nickel phthalocyanine,\textsuperscript{36} iron pentacarbonyl,\textsuperscript{37} and iron chloride.\textsuperscript{38} We choose to denote methods using solid precursors as ‘dry’ floating catalyst CVD processes and those using liquid precursors as ‘wet’ floating catalyst CVD processes. Both forms of floating catalyst CVD consist of the volatization/sublimation of precursor compound(s) in a heated chamber followed by the movement of the gaseous species downstream to a second heated chamber that is sufficiently hot to cause pyrolysis/decomposition of all starting molecular species. The free metal atoms coagulate, deposit as molten metal nanoparticles ($d \sim 1–100$ nm) on available surfaces, and catalyze the growth of CNTs as depicted in Figure 2.1. Like the previous CVD sub-type, the floating catalyst route also allows the fast production of large amounts of CNT and/or the possible fabrication of lithographically prepared complex 2D patterns.\textsuperscript{39} However, the production of CNTs in a single step minimizes the required equipment and the residual catalyst loading can be closely regulated.

In this chapter, data are presented to demonstrate and distinguish the aforementioned advantages of our floating catalyst CVD systems. Scanning and
transmission electron microscopies, XPS, and TGA data are used to show the fidelity of regulation over the produced CNT films. Ultimately, the level of deterministic control detailed in this chapter will allow us to delineate the influences of nitrogen doping on the physicochemical and electrochemical properties of nitrogen doped graphitic carbons described in Chapters 3 and 4.

2.2 EXPERIMENTAL

2.2.1 Floating Catalyst CVD Systems

2.2.1.1 Dry Floating Catalyst CVD

The preparation was similar to that described by Huang et. al.\textsuperscript{39} Briefly, the carbon, nitrogen, and iron catalyst source was iron(II) phthalocyanine, (98%, Aldrich) used as received. Approximately 0.2 g of dry iron(II) phthalocyanine were collected in a ceramic boat and loaded into a quartz tube (35 mm OD, 32 mm ID) resting inside a two zone tube furnace fit with temperature controllers (Thermcraft, Model 2158-6-3Z8). The setup is depicted in Figure 2.2A. 0.63 x 0.63 cm\textsuperscript{2} nickel mesh squares (100 mesh, Alfa Aesar) (1.1 cm\textsuperscript{2} geometric area) spot-welded onto a nickel wire (Alfa Aesar) stem were used as the deposition substrates and placed in the center of the second zone (Z2). After purging for 10 minutes with Ar (99.997%, Praxair), the first and second zones were heated to 500 and 1000 °C, respectively, under a carrier gas consisting of 44 % H\textsubscript{2} (99.95%, Praxair) and 56 % Ar. The flow of the carrier gas was 47 ccm, controlled with flowmeters (Cole-Parmer, A-03216-04 and A-03216-08). When zone 1 reached 500 °C, the iron (II) phthalocyanine was pushed in and allowed to sublime for 5
Figure 2.2 A schematic of the two floating catalyst CVD deposition systems. (A) ‘Dry’ (solid phase) C/N/Fe precursors are sublimed in Zone 1 and then pyrolyzed in Zone 2. (B) ‘Wet’ (liquid) C/N/Fe precursors are injected into and immediately volatized in Furnace 1 and then pyrolyzed in Furnace 2.
minutes, at which time the temperature of zone 1 was increased to 1000 °C for an additional 15 minutes. Subsequently, the heating of zones 1 and 2 was stopped and the system was allowed to cool. When the system had cooled to 850 °C, the H₂ flow was stopped while simultaneously the Ar flow was increased to 45 ccm so as to maintain a constant total gas flow. Upon reaching room temperature, the N-CNT coated substrates were removed and stored in sealed gas tight vials until subsequent use.

2.2.1.2 Wet floating catalyst CVD

The preparation method was similar to that described by Rao et. al.\textsuperscript{40} Ferrocene (99%, Fisher) was used as received as the source for the iron growth catalyst. Xylene (Aldrich) was used as the carbon source for non-doped CNTs. Distilled and dried pyridine (Aldrich) was used as the carbon and nitrogen sources for N-CNTs. To augment the nitrogen doping levels, NH₃ (99.99%, Aldrich) was included in the carrier gas. The setup is depicted in Figure 2.2B. Programmable syringe pumps (New Era Pump Systems NE-1000), electronic gas mass flow controllers (MKS Type 1179A and 1479A), and two single zone tube furnaces (Carbolite, HST 12/35/200/2416CG) were integrated and interfaced through a customized LabVIEW program. Solutions consisting of 20 mg ml⁻¹ of ferrocene in xylene or pyridine were loaded into 1.0 ml gas tight glass syringes (Hamilton 81320). The syringes were interfaced with stainless steel lines that fed into the center of the front half of an air tight quartz tube (26 mm OD, 22 mm ID). Following a 15 minute Ar purge (200 sccm), furnace 2 (F2) was heated to the appropriate pyrolysis temperature (700/800 °C for non-doped and N-doped CNTs,
respectively). Furnace 1 (F1) was then heated to the vaporization temperature of the feed solution (150/130 °C for xylene and pyridine, respectively), and the carrier gas flow of 575 sccm was started. After thermal equilibration, 1 ml of the ferrocene solution was injected at a rate of 0.1 ml s⁻¹. Furnaces 1 and 2 were shut off and allowed to cool to room temperature while the carrier gas flow was switched to 200 sccm Ar. CNTs/N-CNTs were collected from the interior of the quartz tube in furnace 2 and/or the CNT-coated nickel mesh was removed and stored as described above.

2.2.2 Electron Microscopies

Scanning electron microscopic (SEM) examination of the resultant CNT films was carried out on a LEO 1530 operating at 10 kV. Transmission electron microscopic (TEM) analysis of the CNTs was performed with a JEOL 2010F operating at 200 kV. Prior to analysis, the CNTs were dispersed in methanol and then drop cast onto a Cu TEM grid covered with a thin amorphous carbon film.

2.2.3 Thermal Gravimetric Analysis

Thermal gravimetric analysis (TGA) data were collected with a TA Instruments Q500. Sample sizes of 1 to 5 mg of N-CNTs were loaded into platinum pans and heated to 900 °C in flowing air (Praxair, 99.998%) with a 60 ml min⁻¹ flow rate to the sample and a 40 mL min⁻¹ flow rate of N₂ (Praxair, 99.998%) to the balance.
2.2.4 X-ray Photoelectron Spectroscopy

Nitrogen contents were estimated by integrating the signal between 398 and 402 eV in survey scans. Atomic concentrations are relative to the total carbon, nitrogen, and iron signals. More detailed analyses of the N1s spectra are contained in Chapter 3.

2.2.5 Iron Leaching Rate Determination

Four sets of seven suspensions of either non-doped CNTs or N-CNTs (4.0 at. %) at 0.1 mg ml\(^{-1}\) in NANOpure water (Barnstead) with 0.25 % (vol/vol) methanol (Fisher) were prepared in a single neck round bottom flask. Sufficient HNO\(_3\) (Fisher) was added to make two of the suspension sets 1 M in HNO\(_3\) while sufficient KNO\(_3\) (Fisher) was added to make the other two suspension 1 M in KNO\(_3\). The flasks were closed with a septa and allowed to sit. At intervals of 24 hours, a 3 ml extract was taken from a designated flask in each set, filtered to remove CNTs, and injected into a flame atomization atomic absorption spectrometer (GBC 908AA) equipped with a hollow cathode lamp (Fe, Buck Scientific). Concentrations were determined from a calibration plot taken with standard iron solutions in 2 % HNO\(_3\) (Claritus).

2.3 RESULTS AND DISCUSSION

2.3.1 CNT Growth Observations

The parameters listed in the Section 2.2 were determined to be adequate conditions for obtaining reproducible, aligned, and dense CNT films but thorough optimization of the process conditions (e.g. pressure, flow rate) was not attempted. CNT production through both ‘dry’ and ‘wet’ floating catalyst CVD
systems was strongly dependent upon pyrolysis temperature, as variations greater than ± 50 °C severely diminished overall yields. For the ‘wet’ floating catalyst CVD method, pyrolysis temperatures above the cracking temperature of the injected solvent resulted in no CNT formation. The molar efficiencies (i.e. the moles of carbon retained in the CNTs relative the moles of carbons in the precursor material) for the ‘dry’ and ‘wet’ floating catalyst CVDs were approximately 0.1 mol %. Molar efficiencies were strongly dependent upon the identity of the organometallic, with those containing iron centers (e.g. ferrocene, iron phthalocyanine) giving significantly better yields than those with nickel centers. The yields were also limited by the size (length) of the pyrolysis zones (Z2 and F2 in Figure 2.2) and diameter of the quartz process tube.

Several substrate materials were tested for supporting complete, uniform, and reproducible CNT film growth. In general, it was found that porous oxides supported uniform growth and coverages of CNT films better than other materials, as indicated by Ajayan et al. For example, silicon wafers with only a native oxide layer were poor growth substrates. However, similar silicon platforms with a thick oxide layer (> 100 nm) were excellent substrates for CNT growth. Figure 2.3 demonstrates typical CNT films using a variety of substrates. On SiO₂, the film is composed of densely packed CNTs that are adherent to the underlying substrate. The deposited CNTs are uniform in diameter and height and aligned normal to the substrate. The alignment arises from the high density of tubes, which can be controlled by diluting the amount of iron in the growth precursors. The films can be lifted off the substrate by abrasion while maintaining
Figure 2.3  Representative SEM micrographs demonstrating CNT film growths on several substrates. (A) Silicon with 100 nm SiO$_2$. Scale bar: 2 µm (B) Titanium. Scale bar: 2 µm (C) Molybdenum. Scale bar: 10 µm (D) Platinum. Scale bar: 100 µm (10 µm, inset). (E) LaAlO$_3$. Scale bar: 5 µm
their integrity after being peeled off. Metallic substrates typically exhibited sparse patches of CNT growth under the same conditions (i.e. location in Z2/F2, orientation to the direction of the carrier gas stream, and substrate size) that produced rich CNT films on SiO2. The metallic substrates that best supported CNT film coverages similar to those deposited on SiO2 were iron, titanium, platinum, and nickel. Iron and titanium planar substrates both supported reasonable film growth. For titanium, presumably the native oxide layer allowed CNT growth while the high solubility of carbon in iron likely facilitated CNT formation. The latter two metals only exhibited continuous films in mesh or foam networks instead of planar substrates. The open structure of mesh and foam allowed a more uniform flow of gaseous carbon which facilitated the supersaturation of the metal seed particles. Ultimately, nickel mesh was chosen as the substrate of choice for the fabrication of CNT electrodes because of the low material cost, minimal contact resistance with the CNT films (no insulating oxide layer), and poor electrocatalytic nature of nickel for the redox processes discussed in Chapter 4. The latter point is tantamount because it eliminates any possible convolution of the observed electrochemical phenomena ascribed to the CNT films with the underlying substrate. In addition, CNT films produced directly on nickel mesh are very similar in physical composition to fibrous composite electrodes used in fuel cells and for the abatement of pollutants, providing several direct industrial applications.

Examples of CNT film growth on nickel substrates are shown in Figure 2.4. A low magnification micrograph of a deposited film is shown in Figure 2.4A.
Figure 2.4 SEM images of a CNT electrode consisting of a CNT film on top of a nickel mesh substrate. (A) A low-resolution, large area micrograph showing mesh structure. Scale bar: 400 µm (B) A higher resolution micrograph showing local CNT film structure. Scale bar: 70 µm (C) A view of the CNT alignment. Scale bar: 5 µm
where a homogeneous distribution of CNTs is evident with no discernible uncoated spots /bare regions. Figure 2.4B further illustrates the dense packing on and directed growth by the nickel substrate of the CNTs. The CNTs have diameters in the nominal range of 15 – 40 nm with lengths greater than 10 \( \mu \text{m} \). Again, the film consists of CNTs that are uniform in height and diameter, as illustrated in Figure 2.4C. The conformal growth and structural coherency of the CNT films are further illustrated in Figure 2.5. Figure 2.5A shows a CNT film deposited on a nickel mesh support after the removal of the mesh by acid etching (conc. HNO\(_3\), 1 hr). The CNT film maintains the original shape of the nickel mesh substrate even though all supporting material has been removed from underneath the CNT film, evidenced by the open ends indicated by arrows. Figure 2.5B displays a higher magnification image of one of the open ends. The alignment and orientation of the CNTs are not significantly affected by the removal of the underlying support. The CNT film illustrated in Figure 2.5 could be physically manipulated (i.e. lifted, moved, and flipped over) with minimal damage, indicating these architectures are readily processable.

2.3.2 Control of CNT Properties

Initial efforts centered on the ‘dry’ floating catalyst CVD system. However, it was soon realized that the high process temperature (1000 °C) and physical dimensions of the tube furnace could not provide the same fidelity that the ‘wet’ floating catalyst CVD system could. Only nitrogen dopant levels of 1.0 ± 0.5 at. % were obtainable by the ‘dry’ floating catalyst CVD process. Hence, following our preliminary work demonstrating the activity of nitrogen-doped
Figure 2.5. (A) Low magnification SEM image of a free-standing CNT film following the removal of the growth substrate. Scale bar: 300 µm (B) High magnification SEM image demonstrating conformal growth of CNT film. Scale bar: 25 µm (10 µm, inset)
carbon nanotubes, we focused our attention on CNTs prepared by the ‘wet’
floating catalyst CVD.

The choice of solvent for the precursor solution in the ‘wet’ floating
catalyst CVD method had the strongest effect on the elemental composition of the
resultant CNTs. Table 2.1 summarizes the influence of three organic solvents on
the detectable surface nitrogen contents as measured by XPS. Xylenes resulted in
no detectable nitrogen content, but the use of either pyridine or acetonitrile
resulted in significant nitrogen contents. Assuming a 100% incorporation
efficiency of carbon and nitrogen atoms into the CNTs, the expected nitrogen
contents are 16 at % and 50 at % for CNTs produced from pyridine and
acetonitrile, respectively. The experimentally determined nitrogen quantities
were much less for both solvents, suggesting that either significant fractions of the
solvent nitrogen atoms are lost as unincorporated gaseous nitrogen species or that
only a small fraction of nitrogen can be incorporated into CNTs. Quantitative
measurement of the effluent gas compositions via gas chromatography-mass
spectrometry analysis was beyond the intended scope of this work.

To test whether increased nitrogen doping beyond the values of Table 2.1
was possible, NH3 was added to the feed stream of the pyridine-based ‘wet’
floating catalyst CVD. It was found that only additional NH3 was necessary to
controllably augment the nitrogen content without variation of any other
parameters, as shown in Figure 2.6. Importantly, the linear trend in Figure 2.6
illustrates the ability to precisely dope graphitic carbons at a constant
temperature, highlighting a subtle but important distinction between our scheme
<table>
<thead>
<tr>
<th>Solvent</th>
<th>Conc. (mg ml$^{-1}$)</th>
<th>% N (at. %)</th>
</tr>
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<tbody>
<tr>
<td>xylene</td>
<td>20</td>
<td>0.0</td>
</tr>
<tr>
<td>pyridine</td>
<td>20</td>
<td>4.0</td>
</tr>
<tr>
<td>acetonitrile</td>
<td>20</td>
<td>4.0</td>
</tr>
</tbody>
</table>
Figure 2.6 The total nitrogen content in N-CNTs as measured by XPS as a function of the NH₃ fraction in the carrier gas.
and other nitrogen doping methods. Increasing the NH$_3$ fraction in the carrier gas stream yielded a linear increase (0.43 ± 0.03 at. % N per % NH$_3$) in the nitrogen doping of the N-CNTs, with contents up to ~ 10 at. % when the NH$_3$ feed stream fraction was less than 14 %. NH$_3$ feed stream fractions above 15 % showed no additional influence on increasing nitrogen content; rather, slightly depressed doping levels were measured (inset of Figure 2.6), presumably due to significant gasification of carbon at high NH$_3$ concentrations. Similar trends of the influence of NH$_3$ levels on nitrogen doping have been noted by Jang et al., Kim et al., and Lee et al.

At elevated temperatures, decomposition of NH$_3$ in the presence of graphitic carbons results in free radical species, e.g. NH$_2$.$^{11}$ At low levels the produced radicals facilitate nitrogen incorporation in the CNT graphitic structure, but at high levels these radicals attack the graphitic carbon and hasten its gasification to methane and cyanogens species. This is supported by the change in residual iron contents with increased NH$_3$ fractions in the feed stream. Table 2.2 shows that modest increases in the relative amounts of residual iron in the N-CNTs follows increases in the fractional amount of NH$_3$ in the feed stream. Assuming the total number of iron particles generated from the decomposition of ferrocene is roughly independent of feed stream gas composition, the relative proportion of residual iron in the CNTs then likely increased with NH$_3$ fraction from increased carbon gasification. This is consistent with reports from Lee et al.$^{49}$ that describe an inhibitory effect of high NH$_3$ levels on CNT growth rates for a similar CVD methodology. Hence, since fractions of NH$_3$ > 15% were determined to be detrimental to CNT production, the studies reported within this
Table 2.2 Residual Iron Content as Determined from TGA analysis\textsuperscript{a}

<table>
<thead>
<tr>
<th>CNT preparation conditions</th>
<th>Iron Content (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeCp\textsubscript{2}/xylene</td>
<td>7 ± 1</td>
</tr>
<tr>
<td>FePc\textsuperscript{b}</td>
<td>9 ± 3</td>
</tr>
<tr>
<td>FeCp\textsubscript{2}/pyridine</td>
<td>9 ± 1</td>
</tr>
<tr>
<td>FeCp\textsubscript{2}/pyridine (2.5 % NH\textsubscript{3})\textsuperscript{c}</td>
<td>12 ± 1</td>
</tr>
<tr>
<td>FeCp\textsubscript{2}/pyridine (5.0 % NH\textsubscript{3})\textsuperscript{c}</td>
<td>12 ± 2</td>
</tr>
<tr>
<td>FeCp\textsubscript{2}/pyridine (7.5 % NH\textsubscript{3})\textsuperscript{c}</td>
<td>17 ± 3</td>
</tr>
</tbody>
</table>

\textsuperscript{a}After correction for oxygen content in hematite, Fe\textsubscript{2}O\textsubscript{3}

\textsuperscript{b}FeCp\textsubscript{2} = ferrocene, FePc = iron (II) phthalocyanine

\textsuperscript{c}Amount of NH\textsubscript{3} in gas feed stream
work are limited to N-CNTs produced with small fractions of NH$_3$ in the process feed stream.

TEM analysis indicated that iron particles located either within the interior or on the exterior of CNTs were typically encapsulated with several graphene layers (Figure 2.7). To determine the degree of exposure of the iron particles, leaching studies were employed, summarized by Figure 2.8 In neutral pH solutions, aqueous suspensions of CNTs showed no detectable leached iron species after 7 days, implying the leach rate for non-doped CNTs and N-CNTs (4.0 at. %) must be less than 10 femtomole L$^{-1}$ s$^{-1}$. Contrastingly, significant fractions of the encapsulated iron particles leached into strongly acidic solutions after only 24 hours. After 7 days approximately 13.4 ± 0.1 % and 12.0 ± 0.2 % leached out for non-doped CNTs and N-CNTs, respectively, corresponding to a leaching rate on the order of 6 picomole L$^{-1}$ s$^{-1}$. The dramatic rise in leaching rates for both CNT types in acidic solutions is attributed to oxidative attack of the acid on the CNTs, thereby damaging the encapsulating graphene layers on the iron particles and exposing them to solution. Two critical points can be drawn from Figure 2.8. In neutral pH solutions, the leaching rate is negligible and the residual iron is not detected in the solution even after several days exposure. More importantly, in conditions where the carbon structure is damaged, the rate of iron leaching appears nominally the same for non-doped CNTs and N-CNTs, indicating residual iron is equally protected in the two CNT types. These points will become important in the discussion of electrochemical properties in Chapter 4.
Figure 2.7 A representative TEM micrograph illustrating the passivation of residual iron catalysts by multiple graphene layers. Scale bar: 5 nm.
Figure 2.8 Leached iron (wt. %) from dispersions of CNTs measured over seven days. Dispersions of non-doped CNTs and N-CNTs (4.0 at. % N) were prepared in 0.1 M HNO₃ (pH = 1.0) and 0.1 M KNO₃ (pH = 6.5).
In addition to the nitrogen doping levels of the CNTs, the residual iron contents can also be regulated in this CVD method. Initially, more dilute ferrocene solutions were used to lower the iron contents in CNTs. However, dilution of the precursor solution drastically affected the density of the CNT films which also impacted the orientation of the CNTs. An interesting alternative was to inject two solutions, the growth solution with ferrocene at a high concentration and the pure solvent, but keep the total volume of injected solution constant. The growth solution was injected initially to form seed particles at a high density but the rest of the injected volume consisted of only the pure solvent. Figure 2.9 shows that the residual iron content can be reduced by a factor of 4 through this approach. Raman spectroscopy can be used to determine structural order. While the detailed interpretation of Raman spectra for graphitic carbon is discussed at length in Chapter 3, a general lack of changes (peak number, shape, intensity... etc.) in the spectral features implies no substantial structural changes. Figure 2.10 demonstrates there are no observable differences between the first order Raman spectra for N-CNT samples produced with 4 and 9 mass % Fe, i.e. the residual Fe content does not influence the carbon lattice structure. This is in strong contrast to reported methods for lowering residual metal contents post-production by acid washing. As discussed above, such treatments alter the native structural and, consequently, interfacial characteristics of the carbon.

2.4 Conclusions

The versatility of our floating catalyst CVD system was demonstrated. Aspects pertinent to the deposition of CNT films with this system were discussed.
Figure 2.9 The residual iron contents in N-CNTs as measured by TGA as a function of the volume fraction of injected pure pyridine. Total volume injected: 1 ml
**Figure 2.10** First order Raman spectra for N-CNTs with (top, solid line) 4.5 wt. % Fe and (bottom, dashed line) 8.2 wt. % Fe. Both spectra have been normalized to the intensity of the band at 1580 cm\(^{-1}\). The spectra are offset for clarity.
Ample CNT growth was discussed for several materials and shown for silicon wafers with thick oxide layers and nickel mesh substrates. CNT films grown on nickel mesh were shown to be uniform, dense, highly aligned, and conformal to the shape of the mesh. The structural rigidity of the CNT films was demonstrated by removal of the underlying support. The ‘wet’ floating catalyst CVD system was shown to be particularly useful for precisely controlling nitrogen contents (0 to 10 at. %) through the use of NH₃. The effect of NH₃ on the residual iron content was shown to be minimal at low levels of NH₃. The residual iron particles were shown to be mostly passivated by several graphene layers, evidenced by TEM and leaching rate studies. Finally, a novel method for lowering the residual iron content is shown that does not result in significant structural changes in the CNTs.

2.5 REFERENCES


CHAPTER 3

Physical Characterization of Nitrogen Doped Carbon Nanotubes*

3.1 INTRODUCTION

The intimate relationship between the physicochemical properties (i.e. lattice structure, composition, and chemical functionalization) and the electrochemical properties (e.g. capacitance, heterogeneous electron transfer rates) of graphitic carbon electrode materials is well documented. While the properties of many traditional carbons are compiled and cataloged, the physicochemical and electrochemical properties of nanocarbons are, in general, not as extensively described. The paucity of tabulated reference values for nanocarbons is a direct consequence of the plasticity that nanocarbon preparation methods allow, i.e. they can possess numerous different physical properties depending on their method of preparation. Since no physicochemical properties are necessarily inherent to nanocarbons, no electrochemical properties are necessarily native to nanocarbons, particularly carbon nanotubes. Therefore, the nitrogen doped CNT (N-CNT) materials demonstrated in Chapter 2 must first be rigorously defined and characterized physically as a whole if any understanding or insight is to be gained on their performance as electrode materials.

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The structural features of graphitic lattices can be assessed by a set of parameters which are illustrated in Figure 3.1.\textsuperscript{1,2} The height over which the constituent parallel graphene layers stack is denoted as the interplanar microcrystalline size, $L_c$. For CNTs, $L_c$ describes the wall thickness. The average interlayer spacing between graphene layers is defined by $d_{002}$. The distinction between fully coordinated carbon atoms within the interior of the graphene layers (basal plane atoms) and those atoms that are only partially coordinated on the periphery of the graphene layers (edge plane atoms) is shown in Figure 3.1, where the lateral distance between edge plane sites is referred to as the average in-plane crystalline length, $L_a$. The difference in coordinations between basal and edge plane carbon atoms leads to substantial changes in chemical and electrochemical behaviors, where edge plane atoms are typically sites of surface chemical functionalities.

There is no single analytical method for accurately and quantitatively describing all the relevant features of graphitic carbon. Instead, a variety of well established analytical techniques must be employed. Transmission electron microscopy (TEM) has been used to illustrate qualitatively and quantitatively the physical structure of graphitic carbons at the nanometer size regime, i.e. $L_c$ and $d_{002}$. Coupled with electron energy loss spectroscopy, TEM can also provide compositional information with high spatial resolution (~ 1 nm). Thermal gravimetric analysis (TGA) in air can be used to determine relative differences in the edge plane graphite contents of several samples by comparing the temperatures for carbon gasification. Through analysis of relative peak heights in
Figure 3.1 An idealized representation of a section of \( sp^2 \) hybridized carbon composed of three graphene layers.
the first order spectra, Raman spectroscopy can be used to determine quantitatively $L_a$. X-ray photoelectron spectroscopy (XPS) can elucidate the coordinations of nitrogen atoms in the graphitic lattice by studying the spectroscopic signatures in high resolution C1s and N1s spectra. The pH at which carbons in unbuffered aqueous solutions attain no net surface charge ($pH_{pzc}$) can be determined through mass titrations. The reductive character of carbons in aqueous suspensions can be evaluated by iodimetric titrations. Used in conjunction with results from XPS, these wet chemical techniques can be used to determine trends in chemical reactivities and specific surface functionalities.

Our efforts to elucidate and understand the effects of nitrogen doping on electrochemical phenomena have focused on the preparation of graphitic carbons doped with nitrogen \textit{as-prepared}. The controlled preparation of CNTs by CVD described in Chapter 2 offers a novel route to delineate the effects of nitrogen doping in graphitic carbons because nitrogen-rich carbons can be readily and deterministically tailored. In this way, N-CNTs can be prepared with a range of inherent nitrogen contents but nominally invariant aspects like surface area, morphology, and porosity. Several other groups have also reported the preparation of N-CNTs with varied nitrogen contents\textsuperscript{3-7} but none have attempted extensive characterization of the physicochemical properties of N-CNTs and their correlation with electrochemical and chemical reactivity. In this chapter, the focus is to comprehensively evaluate the physical properties of N-CNTs with varied levels of nitrogen in order to rationalize and understand the electrochemical data presented in Chapter 4. In particular, data from TEM, TGA,
Raman spectroscopy, XPS, pH_{pzc} mass titrations, and iodimetric titrations are presented in this chapter to show that lattice structure, surface functionalization, and chemical reactivity track directly with nitrogen content.

3.2 EXPERIMENTAL.

3.2.1 Compositional and Structural Characterization

3.2.1.1 Transmission Electron Microscopy

Transmission electron microscopic (TEM) analysis of the CNTs was performed with a JEOL 2010F operating at 200 kV. Prior to analysis, the CNTs were dispersed in methanol and then drop cast onto a Cu TEM grid covered with a thin amorphous carbon film. Parallel electron energy loss spectra (PEELS) were acquired with a Gatan 2D digital-parallel electron energy loss spectrometer. The beam waist of the probe beam was kept below 1 nm. Image analysis was performed with DigitalMicrograph 3.6.1 (Gatan) software.

3.2.1.2 X-Ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy was conducted with a PHI 5700 ESCA system possessing a scan step size of 0.1 eV and an Al K-alpha monochromatic line (1486.6 eV), calibrated with the signals for Au\textit{4f}_{7/2}, Ag\textit{3d}_{5/2}, and Cu\textit{2p}_{3/2}. The C1s spectra were collected with a single scan. N1s spectra were scan averaged five times. Fe2p spectra were scan averaged at least ten times. Atomic percentages were determined from elemental survey scans and are reported relative to the total signals for carbon, nitrogen, and iron. Spectra were analyzed
using a freeware software package, FITT 1.2 (Photoelectron Spectroscopy Lab, Seoul National University) with Shirley background corrections.

3.2.1.3 Thermogravimetric Analysis

Thermal gravimetric analysis (TGA) data were collected with a TA Instruments Q500. Sample sizes of 1 to 5 mg of N-CNTs were loaded into platinum pans and heated to 900 °C in flowing air (Praxair, 99.998%) with a 60 mL min⁻¹ flow rate to the sample and a 40 mL min⁻¹ flow rate of N₂ (Praxair, 99.998%) to the balance.

3.2.1.4 Raman Analysis

Spectra were obtained with a Renishaw In Via system equipped with 4 laser wavelengths. The laser power, objective magnification, and beam waist used for each respective laser line are listed in Table 3.1. The power density was below 20 mW cm⁻² for all acquired spectra and no polarizer was used for collection. Spectra were acquired in a single scan with an acquisition time of 500 seconds. Raw spectra taken with 514 nm incident radiation were fit with GRAMS/Al 7.02 ® software by the Levenberg-Marquadt method⁸ using 5 bands located at 1624, 1583, 1487, 1351, and 1220 cm⁻¹, denoted as $D'$, $G$, $D''$, $D$, and $I$, respectively, according to the convention of Cuesta et al.⁹ A linear baseline correction was used for all spectra to compensate for the photoluminescence background. All spectral fits had correlation factor ($R^2$) values greater than 0.998.
Table 3.1 Conditions used for Raman Spectra Collection

<table>
<thead>
<tr>
<th>Laser - $\lambda$ (nm)</th>
<th>P (10% of max)</th>
<th>Beam Waist, $w_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HeCd - 325</td>
<td>0.3 mW</td>
<td>$\sim 1$ $\mu$ (50x)</td>
</tr>
<tr>
<td>HeCd - 442</td>
<td>1.4 mW</td>
<td>$\sim 1$ $\mu$ (50x)</td>
</tr>
<tr>
<td>Ar - 514.5</td>
<td>3.0 mW</td>
<td>$\sim 1$ $\mu$ (50x)</td>
</tr>
<tr>
<td>Diode - 785</td>
<td>30.0 mW</td>
<td>$\sim 3$ $\mu$ (40x)</td>
</tr>
</tbody>
</table>
3.2.2. Chemical Characterization

3.2.2.1 Determination of $pH_{pzc}$

The pH of point of zero charge ($pH_{pzc}$) for undoped and N-doped CNTs were determined using mass titration analysis.\textsuperscript{10} Briefly, approximately 60 mg of non-doped CNT or N-CNT was dispersed in 3 mL of 0.1 M KNO\textsubscript{3} (Fisher, 99.8 %) made with boiled NANOpure® water (Barnstead, 18 MΩ•cm). The ~2 wt. % suspension was capped, purged with N\textsubscript{2} (Praxair), and agitated for 24 hours. Following, the pH of the slurry (no filtration) was measured and recorded as the $pH_{pzc}$ value. Measurements were done in triplicate.

3.2.2.2 Iodimetric Titrations

Iodimetric analysis was conducted as described by Oliveira et al.\textsuperscript{11} Dried K\textsubscript{2}Cr\textsubscript{2}O\textsubscript{7} (Fisher, 99.98%), Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3} (99.8%, Fisher), and starch indicator (99.6 %, MCB reagents) were dissolved in NANOpure® (18 MΩ•cm, Barnstead) water. I\textsubscript{2} (99.8 %, Fisher) was dissolved with excess NaI to generate I\textsubscript{3}-. The Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3} and I\textsubscript{3} solutions were stored in covered containers to avoid light exposure. 0.1 M Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3} solutions were standardized with 0.05 M K\textsubscript{2}Cr\textsubscript{2}O\textsubscript{7} and NaI (99.7 %, Baker) and then used to standardize the 0.05 M I\textsubscript{3} solution. 10 ml of I\textsubscript{3} solution and 20 mg of either non-doped CNTs or N-CNTs were combined in a clean 25 ml round bottom flask with a stir bar. The flask was then sealed with a septum, mounted onto a stirrer, covered completely with aluminum foil, purged with N\textsubscript{2} (99.999%, Praxair), and vigorously stirred for 24 hours. Following, the CNT suspension was filtered into a clean Erlenmeyer flask through a 60 ml medium
porosity glass frit filter. Approximately 90 ml of NANO-pure® water were used to rinse off I⁻³ solution from the CNTs. The excess I⁻³ filtrate was back titrated with Na₂S₂O₃ until a golden yellow color was observed. 800 µl of starch indicator were added, rendering the solution a deep blue hue. Further Na₂S₂O₃ was added until the solution became clear, denoting the endpoint. Measurements were done in triplicate.

3.3 RESULTS AND DISCUSSION.

3.3.1 Structure

3.3.1.1 Transmission Electron Microscopy

Figure 3.2 displays representative high resolution TEM images of non-doped CNTs and N-CNTs prepared by the floating catalyst CVD method. All of the CNTs represented in Figure 3.2 exhibit similar fibril morphologies with 15 – 40 nm diameters, > 10 μm lengths, and hollow interiors for individual CNTs. A decrease in Lc for the three micrographs in Figure 3.2 is clear. For large graphitic carbons (e.g. pyrolytic graphite), Lc is critical in determining the material’s softness.¹ In this discussion, material hardness is not particularly critical, but the decrease in Lc is consistent with the hypothesis that nitrogen doping interferes with graphene layer stacking. i.e. disrupting the van der Waals interactions between graphene layers.¹²

Subtle structural differences are seen between the two CNT varieties in Figure 3.3, with the sidewall structures of N-CNTs with 4.0 at. % nitrogen appearing more compartmentalized and disordered than non-doped analogues.
Figure 3.2. Representative transmission electron micrographs of (A) non-doped CNTs, (B) N-CNTs [5.1 ± 0.5 at. %], and (C) N-CNTs [9.6 ± 0.5 at. %] prepared by floating catalyst CVD. Scale bars: 10 nm.
Figure 3.3  Representative TEM images of (A) non-doped, and (C) N-CNTs prepared by floating catalyst CVD. High resolution TEM images (B) and (D) are of highlighted regions in (A) and (C), respectively. Scale bars: (A) and (C) 20 nm, and (B) and (D) 5 nm.
Additionally, the sidewalls of the N-doped CNTs contain more dislocations and disruptions in the graphene stacking (turbostratic disorder), in agreement with observations of Sjostrom\textsuperscript{12} who noted that disruptions and irregular curvature in graphene stacking in N-doped carbons is due to the propensity of incorporated nitrogen to form pentagonal defects in the graphene sheets. The introduction of pentagons into the basal planes disrupts the planar hexagonal arrangement of C atoms found in graphite, causes buckling of the graphene layers, and results in interlayer distances that fluctuate between wider and thinner distances than found in pristine graphite. The average difference in interlayer spacings ($d_{002}$) between the two varieties can be estimated from the TEM images.\textsuperscript{13} Fourier transforms\textsuperscript{14} of Figures 3.3B and 3.3D yield $d_{002}$ spacings of $3.448 \pm 0.005$ Å and $3.53 \pm 0.02$ Å for the non-doped and N-doped varieties, respectively, suggesting that N-CNTs are more turbostratic. Localized parallel electron energy loss spectroscopy (PEELS) experiments (Figure 3.4) on the N-CNTs verified the presence of nitrogen at edge plane sites on the periphery of the walls, consistent with that of Tang et al\textsuperscript{15} for similarly prepared materials. The inset of Figure 3.4 displays the $\pi^*$ signal of the incorporated nitrogen. Although the signal near 400 eV is broad enough to suggest multiple nitrogen coordinations, damage to the sample induced by the probe beam prohibited sufficient signal resolution.

3.3.1.2 Thermal Gravimetric Analysis

TGA was conducted to assess thermal stabilities and residual iron catalyst concentrations in both non-doped and N-doped CNT types. Figure 3.5 presents typical TGA curves for non-doped and N-doped CNTs with 4.0 at. % nitrogen.
Figure 3.4 EELS spectrum of the periphery of an individual N-CNT (4.0 at. %). Inset shows the π* region of the N K-shell.
Figure 3.5 Representative TGA mass loss plots for non-doped CNTs (blue) and N-CNTs (red, 4.0 at. % N) conducted in air. The residual mass above 550 °C is Fe$_2$O$_3$ (hematite) for both CNT types.
The maxima in first derivative plots of these curves were used to estimate burn-off temperatures of CNT materials in an oxidative environment. Burn-off temperatures are functions of analysis conditions (e.g. analysis gas composition, flow rate, sample heating rate) and are thus potentially misleading if compared between dissimilar studies. However, comparisons of burn-off temperatures for samples analyzed under identical conditions can distinguish materials that are more easily thermally decomposed. For five measurements of each CNT type, burn-off temperatures for non-doped and these N-CNTs were 540 ± 40 °C (1σ) and 450 ± 10 °C (1σ), respectively. The observed ~90 °C lower thermal decomposition temperature for the N-CNTs supports the TEM and Raman data that these materials are more disordered and possess considerably more edge plane sites. This data is consistent with early reports of Kinoshita et. al. which indicate that thermal decomposition temperatures for natural graphite powders decrease as the density of edge plane sites increase.

3.3.1.3 Raman Spectroscopy

To determine quantitatively the structural order in bulk CNT samples, Raman spectra were taken. Figure 3.6 shows representative first order Raman spectra for CNTs containing 0.0 and 9.7 at. % nitrogen. Two maxima are apparent in both spectra, occurring near 1355 cm⁻¹ and 1585 cm⁻¹. A dramatic broadening of the two peaks for N-CNTs is visible in Figure 3.6B relative to 3.6A, as reported previously and elsewhere. In addition, two other spectral features become more pronounced with nitrogen doping. First, overlap between the two signals at 1355 cm⁻¹ and 1585 cm⁻¹ in Figure 3.6B becomes so great that
Figure 3.6 Comparison of the intensities and widths of peaks used in the fitting of the first order Raman spectra for CNTs doped with (A) 0.0 at. % and (B) 9.7 at. % N.
the direct measurement of distinct FWHM values is not possible. Second, asymmetric tailing of the peak at 1355 cm$^{-1}$ results in a shoulder with measurable intensity extended out to $\sim$1000 cm$^{-1}$ for N-CNTs containing 9.7 at. % nitrogen nearly 300 cm$^{-1}$ farther than the corresponding tailing for non-doped CNTs. Simple line broadening does not account for these phenomena, as both spectra in Figure 3.6 cannot be deconvoluted into just two Lorentzian or Gaussian shapes. Cuesta et al.$^9$, Angoni,$^{21}$ and Darmstadt et al.$^{22}$ similarly noted that several bands were necessary to fit the Raman spectra of polycrystalline graphitic materials. Accordingly, five bands at 1624, 1583, 1487, 1355, and 1220 cm$^{-1}$ referred to as $D'$, $G$, $D''$, $D$, and $I$, respectively, following the convention of Cuesta et al.$^9,23$, were used for fitting. For both Figure 3.6A and 3.6B, the $G$ and $D$ bands are the most intense spectral features. The $G$ band arises from a E$_{2g}$ vibrational mode in the D$^{4}_{6h}$ symmetry group of graphite crystal planes and is seen for all sp$^{2}$ carbon Raman spectra.$^{24}$ There is less consensus for the origin of the $D$ band, but it is generally accepted as a Raman inactive mode (e.g. A$_{1g}$) that becomes active from a reduction in symmetry at or near crystalline edges$^{25}$ and is subsequently used as an indicator of edge plane density. The $D'$ and $D''$ bands differ in relative intensity between Figure 3.6A and 3.6B. For CNTs with 0.0 at. % nitrogen in Figure 3.6A, the two bands are visible, but are minor constituents in the overall shape of the spectrum. In contrast, for N-CNTs (Figure 3.6B), the $D'$ and $D''$ bands are very intense and significantly contribute to the shape of the curve. Although the sources of the $D'$ and $D''$ bands are unclear,$^9$ the $D'$ band has been attributed to irregular d$_{002}$ spacing$^{26}$ while the $D''$ band has also tentatively been
designated as an indicator of defects in graphene layer stacking. Interestingly, both the $D'$ and $D''$ bands occur at Raman shifts near or at peaks in the phonon density of states for graphite that are predicted to be Raman inactive but, like the $D$ band, may become active due to relaxations in local symmetry arising from lattice distortions. The increases in $D'$ and $D''$ band generally suggest a larger turbostratic character in graphene plane stacking, i.e. loss of coherent $d_{002}$, in nitrogen doped carbons as predicted by Sjostrom et al., and is in agreement with a previous TEM observation. The occurrence of the $I$ band is the most striking difference between Figures 3.6A and 3.6B, as the $I$ band is not at all apparent in the spectrum for CNTs, but is strong enough to give the broad shoulder in the N-CNTs Raman spectra. The $I$ band has been observed in moderately to heavily disordered graphitic carbons. Angoni has ascribed the $I$ band to impurities in the graphite lattice, but it was not observed in the first order Raman spectra of boron-doped graphite. As with the $D'$ and $D''$ bands, a relaxation in symmetry from a $sp^2$ lattice distortion may allow a Raman inactive peak in the predicted density of phonon states $\sim 1220 \text{ cm}^{-1}$ to be Raman active. However, since the $I$ band is not visible in Raman spectra for non-doped CNTs, the specific type of lattice distortion causing the relaxation of symmetry may be distinct from the structural distortions responsible for the $D$, $D'$, and $D''$ bands, i.e. not specifically edge plane density or turbostratic character. Hence, while the $I$ band may not be a direct consequence of nitrogen doping, the corresponding symmetry breaks may be directly a result of the incorporation of nitrogen and so the $I$ band in this case reports on its presence. As shown in Figure 3.6B, the correlation of the $I$ band to
nitrogen doping is further supported by the Gaussian nature of the peak shape. Heterogeneous distributions of spectroscopically-active elements produce Gaussian line shapes in the corresponding spectroscopic signatures.\textsuperscript{21} The Gaussian shape of the $I$ band agrees qualitatively with the observance of a heterogeneous distribution of nitrogen atoms, consistent with the multiple nitrogen functionalities indicated by XPS.

The relative positions, intensities, and broadness of the aforementioned bands can vary with different incident radiations, i.e. laser wavelengths ($\lambda$). Figure 3.7 highlights the changes in the first order Raman spectra for $\lambda$ between 325 nm and 785 nm. The spectra for non-doped CNTs in Figure 3.7A show minimal changes in the intensities of the $I$ and $D''$ bands, with only the $I$ band becoming noticeable at long $\lambda$. Similarly, the features of these bands do not change substantially in the corresponding spectra for N-CNTs in Figure 3.7B. Moreover, the shape and position at 1583 cm$^{-1}$ of the $G$ band remains nominally constant for all values of $\lambda$ for both CNT types. Conversely, the $D$ and $D'$ band both increase dramatically in intensity with longer laser wavelengths, with the $D'$ band nearly eclipsing the $G$ band and the $D$ band becoming the dominant spectral signature at $\lambda = 785$ nm in Figure 3.7A. Similar changes are seen in Figure 3.7B, although the overall broader shapes of all the bands mask the emergence of the $D'$ band in N-CNTs. The parallel trends of all the spectra from non-doped CNTs and N-CNTs affirm the strong overall structural similarities between the two CNT types, i.e. both are highly graphitized carbon materials that differ primarily in the abundance of symmetry-breaking structural elements. Figure 3.8 summarizes the
Figure 3.7 First order Raman spectra for non-doped CNTs (left set) and N-CNTs (4.0 at. %, right set) using different excitation wavelengths. The spectra are normalized to the intensity of the peak at 1580 cm\(^{-1}\).
Figure 3.8 A plot of the ratio of the integrated intensities of the D and G bands as a function of laser wavelength for non-doped CNTs (□) and N-CNTs (4.0 at. %, •). Data for glassy carbon (GC, ×) and fractured highly oriented pyrolytic graphite (HOPG, ▲) from reference 25 are shown for comparison.
shifts of the $D$ and $G$ bands for the two CNT types and compares them to reference graphitic carbon materials,\textsuperscript{25} glassy carbon and pyrolytic graphite (basal plane). The agreement of the data for both CNT types and the reference materials affirms the strong sp\textsuperscript{2} hybridization of the CNTs included in this work. More specifically, though, the N-CNTs are not amorphous and should not be confused with other carbon nitride materials.\textsuperscript{28}

Interestingly, changes in the ratio of the $D$ and $G$ band intensities as a function of $\lambda$ in Figure 3.7 can also be used to identify more specific structural information. Applying the assignments of Figure 3.6 to all the spectra of Figure 3.7, the ratios of the integrated intensities of the $D$ and $G$ bands were obtained. Figure 3.9 compares the behaviors of the $D/G$ ratios of the CNT types to reference data\textsuperscript{25} for glassy carbon (highly disordered) and the basal plane of pyrolytic graphite (minimal disorder). For this range of $\lambda$, the changes in the $D/G$ ratios were linear for all discussed materials. The rate of increase in the $D/G$ ratio for non-doped CNTs ($3.1 \pm 0.2 \times 10^{-3} \text{ nm}^{-1}$) was significantly lower than that for N-CNTs or glassy carbon, but similar to the trend for fractured HOPG ($1.2 \times 10^{-3} \text{ nm}^{-1}$). The slopes for N-CNTs and glassy carbon are virtually identical ($6.5 \pm 0.5 \times 10^{-3} \text{ nm}^{-1}$ and $6.4 \pm 0.3 \times 10^{-3} \text{ nm}^{-1}$, respectively). It is evident from Figure 3.9 that the non-doped CNTs of this work are qualitatively similar to ordered graphitic carbon with relatively minor disruptions in the graphene layers (edge plane sites) while N-CNTs are much more similar to graphitic carbon with considerable edge plane content. To more quantitatively identify the structural influence of nitrogen doping in CNTs on the defect character of the graphene
Figure 3.9 A plot of the peak positions of the D and G bands as a function of laser wavelength for non-doped CNTs (□) and N-CNTs (4.0 at. %, ). Data for glassy carbon (GC,×) and fractured highly oriented pyrolytic graphite (HOPG,▲) from reference 25 are shown for comparison.
layers, i.e. the average in-plane crystalline length ($L_a$), first order Raman spectra using 514 nm incident radiation are presented in Figure 3.10. The spectra in Figure 3.10A are all normalized to the intensity of the 1583 cm$^{-1}$ peak, but a decrease in the absolute magnitude of the Raman signal with increasing nitrogen doping is evident, resulting in a decrease in signal-to-noise of the spectra for N-CNTs with higher nitrogen contents for identical acquisition conditions. Again, applying the assignments of Figure 3.6 to all the spectra of Figure 3.10A, the ratios of the integrated intensities of the $D$ and $G$ bands were obtained. A quantitative determination of $L_a$ from the ratio of the integrated intensities of the $D$ and $G$ bands is possible through Eq 1,

$$\frac{I_D}{I_G} = \frac{\beta}{L_a}$$

where $\beta$ is a proportionality factor that is 4.4 nm for $\lambda = 514$ nm. Cuesta et. al. have demonstrated the limitations in the direct application using D and G bands ratios to estimate for $L_a$ since relative errors ca. 100% have been seen with heavily disordered carbons. Nevertheless, the ratio is still a useful diagnostic tool for following the increase in disorder in N-CNTs with increasing nitrogen content as shown in Figure 3.10B. A linear increase in the ratio of integrated intensities with nitrogen doping suggests that the edge plane density increases, i.e. shorter $L_a$, in more heavily doped N-CNTs (Figure 3.10B). For N-CNTs with 4.0 at. % nitrogen content, the edge plane density is about 2.5 times greater than for non-
Figure 3.10 (A) Normalized and base-line corrected first order Raman spectra of non-doped CNTs and N-CNTs with increasing nitrogen doping levels. (B) Ratio of the integrated intensity of the D and G bands (as in Figure 3.6) as a function of nitrogen doping levels.
doped CNTs, with \( L_a = 3.3 \) nm, very close to the value for glassy carbon (\( L_a \sim 2.5 \) nm).\(^{31}\)

3.3.2 Compositional Analysis

3.3.2.1 X-ray Photoelectron Spectroscopy

Figure 3.11 shows 10-scan averaged Fe 2p spectra. The total surface iron content for the non-doped and N-doped CNTs is 1.2 and 1.1 at. %, respectively, which corresponds to \( \sim 4.5 \) wt % of the total amount of iron measured from TGA. Remarkably, the apparent oxidation state(s) of the iron in the two CNT varieties is different, with the N-doped CNTs exhibiting one pair of Fe 2p\(_{1/2}\) and 2p\(_{3/2}\) bands (707 \& 720 eV) and the non-doped CNTs showing two pairs of bands (707 \& 720 eV and 711 \& 725 eV). The two sets of bands for non-doped CNTs are consistent with metallic (Fe\(^0\)) iron/iron carbide and iron oxides (Fe\(^{+2/+3}\)), respectively.\(^{45,46}\) In contrast, the surface iron content of the N-doped CNT materials appear to be solely metallic or iron carbide with the sharpness of the Fe bands strikingly similar to the standard Fe 2p spectrum for metallic iron,\(^{32}\) suggesting that the iron is metallic rather than carbide. XPS peak areas indicate that the relative abundances of the metallic iron and iron oxides for non-doped CNTs is 45 % and 55 %, respectively. The broad nature of the 711 eV and 725 eV bands make it difficult to determine specifically which oxide form (e.g. hematite, ferrihydrite, ...etc.) is predominant in the non-doped CNTs.\(^{33}\) Still, it seems clear that the surface iron of non-doped CNTs is of a mixed valent nature while that of the N-doped CNTs consists of zero-valent (metallic) iron.
**Figure 3.11** Normalized X-ray photoelectron Fe2p spectra (ten scan average) for (A) non-doped CNTs, and (B) N-CNTs with 4.0 at.% nitrogen.
Figure 3.12 shows representative C1s spectra for CNTs doped with increasing amounts of nitrogen. The peak position at 284.4 eV for CNTs with 0.0 at. % nitrogen is very close to the accepted value (284.3 eV) for pure sp² C-C bonding in pristine highly oriented pyrolytic graphite (HOPG), indicating carbon atoms are almost exclusively sp² hybridized in non-doped CNTs. The peak positions for all N-CNTs in Figure 3.12A are shifted to 284.7 eV. Any subtle differences in the peak positions of the various N-CNTs exceeded the resolution of the XPS instrument. This 0.3 eV shift for N-CNTs is consistent with previously reported values for nitrogenated thin carbon films and is in agreement with increased structural disorder, i.e. more disruptions in the sp² carbon framework from the incorporation of nitrogen within the graphene lattice. While a small, broad band centered near 291 eV is present in all CNT spectra, (Figure 3.12A) no discernable side bands commensurate with extensive oxygen-like functionalities (e.g. quinones, carboxyl groups) are visible in the 286 - 289 eV shoulder region. The band located at 291 eV is assigned to the π-π* interband, a common feature in graphitic carbon XPS spectra which does not strongly correlate with structural disorder. However, the signal at 284 eV does broaden and become slightly more asymmetric with increasing nitrogen content. The FWHM values for the peak in Figure 3.12A are plotted against the respective nitrogen doping levels in Figure 3.12B. The FWHM for CNTs with 0.0 at. % nitrogen is very close to the reported 0.6 eV FWHM value for HOPG and is also indicative of sp² carbon, while the FWHM values for N-CNTs increase with additional nitrogen content. There are several possible sources for the observed
Figure 3.12  (A) Normalized X-ray photoelectron C1s spectra (single scan) of non-doped CNTs and N-CNTs with increasing nitrogen doping levels. (B) Full widths at half maximum of the C1s spectra in (A) as a function of nitrogen doping levels.
broadening and asymmetry in the spectra for N-CNTs. Since core-hole screening in conductive materials unavoidably imparts line asymmetry in XPS spectra,\textsuperscript{37-39} the increased asymmetry of the C1s peak of N-CNTs may denote a change in the excitation spectrum of the conduction electrons, i.e. the electronic density of states. Terrones et. al.\textsuperscript{4} have demonstrated an increase in the population of states in the electronic band gap of N-CNTs produces carbons with more metallic/conductive character. However, asymmetry and broadening of the peak in C1s spectra have also been attributed to a sideband at 285.6 eV arising from lattice disorder, i.e. sp\textsuperscript{3} bonding character.\textsuperscript{37} For a series of semi-coke materials with negligible heteroatom content, the intensity and contribution of this "defect" band was shown to scale with increasing structural disorder. Further, there are several contradictory reports of C1s bands associated with C-N functionalities in the 285-286 eV region, complicated by strong band overlap in this range that prevents definitive band assignment(s).\textsuperscript{34,40-42} Although contributions from the aforementioned sources to the peak in the C1s spectra are hard to differentiate, the observed changes in Figure 3.12 are nevertheless indicative of doping-induced changes in the electronic, structural, and bonding character of the N-CNTs.

High resolution N1s XPS spectra were obtained to elucidate more fully the identity of nitrogen coordination in the N-CNTs. Figure 3.13 demonstrates representative N1s spectra for CNTs doped with varied nitrogen levels. For all NH\textsubscript{3}-derived N-CNTs, the N1s spectra in Figure 3.13A exhibit three strong, distinct peaks at 398.6, 400.9, and 404.2 eV. Assignment of the latter peak is unclear, as several authors have reported peaks at 402.9 - 403.2 eV for pyridine-
Figure 3.13 (A) Normalized X-ray photoelectron N1s spectra (5 scan averaged) of non-doped CNTs and N-CNTs for increasing nitrogen doping levels. (B) Relative abundances of the peaks at 401 and 399 eV in the spectra of N-CNTs in (A).
N-oxide functionalities, at 404.9 - 405.6 eV for chemisorbed nitrogen oxide at 403.9 eV for physisorbed N₂, and at 402 - 404.2 eV for \( \pi-\pi^* \) shake-up satellites. Designation of the 404.2 eV bands as pyridine-N-oxide or physisorbed nitrogen oxide necessitates an excessively large shift of ~ 1 eV, which is particularly unlikely given the peak's sharp and well-defined shape in Figure 3.13A. Assignment as either a \( \pi-\pi^* \) shake-up satellite or physisorbed N₂ more accurately fits the experimental peak positions. N1s shake-up satellites have been reported with moderate intensity but typically when identified they are very broad. Formation of N₂ during the pyrolitic formation/doping of the CNTs is plausible and binding of N₂ to the CNT surface may comment on the sorptive nature of the carbon. However, physisorbed N₂ is typically not observed on graphite unless pre-cleaned surfaces are strongly dosed with N₂ at low temperatures. Although specific assignment is not made to the peak at 402.2 eV, it is most likely not due to incorporated nitrogen. Regardless, since this is not a predominant peak we focus our main attention on peaks near 400 eV. A large number of C-N functionalities have been assigned to the region near 400 eV. Typically, for carbon nitride materials, the N1s spectra contains two very broad peaks that overlap considerably, a consequence of either a heterogeneous spatial distribution of the functionalities arising from extensively disordered sp³ carbon framework or to the overlap of several closely spaced bands resulting from numerous C-N functionalities. The sharpness of the peaks in Figure 3.13A imply that the nitrogen atoms of the N-CNTs are homogeneously dispersed and that the distribution of possible C-N functionalities is narrow. The
peak at 398.6 eV was fitted with a single Lorentzian band which correlates well with binding energies reported by Boehm et. al.\textsuperscript{51} and Pels et. al.\textsuperscript{43} for pyridinic functionalities decorating the surface of NH\textsubscript{3}-treated activated carbons. The peak at 400.9 eV was also fitted with two Lorentzian bands at 400.4 eV and 401.4 eV, suggestive of pyrrolic-like and quaternary-like nitrogen coordination, respectively.\textsuperscript{43} The relative intensities of the two bands at 399 and 400 eV in the N1s spectra change with increasing levels of incorporated nitrogen. Figure 3.13B displays the relative abundances of these two peaks as a function of total nitrogen content in the N-CNTs. While both peaks increase in abundance with higher total nitrogen doping, the pyridinic peak (398.6 eV) shows a two-fold greater rise in abundance (0.24 ± 0.01 at. \% per \% NH\textsubscript{3}) than the pyrrolic/quaternary (400.9 eV) peak (0.11 ± 0.01 at. \% per \% NH\textsubscript{3}). This two-fold increase in relative abundance suggests that doping via NH\textsubscript{3} results in a selective bias for nitrogen coordination as pyridinic like functionalities.

### 3.3.3 Chemical Reactivity

#### 3.3.3.1 Titration Studies

Pyridinic surface functionalities on carbons can act as Bronsted-Lowry bases and consequently exist as positively charged moieties when protonated.\textsuperscript{43} The estimation of surface pK\textsubscript{A} values for polar surfaces is commonly referred to as the pH\textsubscript{pzc}.\textsuperscript{54} For traditional graphitic materials, pH\textsubscript{pzc} values are typically near or below 7, dictated by acidic oxygen functionalities imparted from exposure to ambient conditions and/or from oxidative preparation steps. Measurements of the pH\textsubscript{pzc} for non-doped CNTs and N-CNTs (4.0 at. \% N) yielded values of 8.0 ± 0.4
and 9.2 ± 0.4, respectively, consistent with other reports for traditional and nitrogenated carbons.\textsuperscript{54,55} We attribute the alkaline nature of the N-CNTs to the basic nitrogen functionalities identified by XPS. In solutions with pH > pH\textsubscript{pzc}, these functionalities should impart a net cationic character to the N-CNTs.

The reductive character of graphitic carbons, i.e. the nucleophilicity of the material, may also be influenced by nitrogen doping. Strelko et al.\textsuperscript{56} and Boehm et al.\textsuperscript{51} have reported that nitrogenated graphitic carbons exhibit increased electron donating character, demonstrated by the reductive gas phase adsorption of molecular oxygen. We also have observed that oxygen adsorption at N-CNTs is facile and promotes the electrocatalysis of oxygen in aqueous solutions.\textsuperscript{18} We believe that this has a strong influence on catalytic activity observed.\textsuperscript{51} To assess the reductive nature of the N-CNTs, an iodimetric analysis was employed as described in the literature.\textsuperscript{11} Oliveira et al. estimated the relative number of reducing sites of thermally activated carbons (AC) by measuring the consumed equivalents of iodine in a suspension of AC and I\textsuperscript{3−}. Interaction of I\textsuperscript{3−} with reducing surface sites on AC catalyzed the reduction of I\textsuperscript{3−} to I\textsuperscript{−}. Figure 3.14 shows preliminary results of iodimetric analysis on various N-CNTs containing increasing amounts of nitrogen. A direct correlation between nitrogen content and the number of reducing sites is apparent in Figure 3.14A, with triple the number of active sites observed for N-CNTs containing 7.5 at. % nitrogen over non-doped CNTs. The increase in reductive character of more heavily doped N-CNTs moderately follows the rise in the amount of nitrogen coordinated as pyridinic-like functionalities as discussed above and illustrated in Figure 3.14B.
Figure 3.14  Equivalents of $I_3^-$ neutralized during mass titration with CNTs as a function of increasing (A) total nitrogen contents and (B) pyridinic nitrogen contents.
Attempts to correlate enhancements in chemical reactivity with nitrogen doping have been reported previously. For instance, Szymanski et al.\textsuperscript{57} noted an increase in the basicity of NH\textsubscript{3}-treated activated carbons tracks with the increase in the amount of pyridinic-type nitrogen. Boehm et al.\textsuperscript{51} hypothesized that the increased activity for oxidative reactions of activated carbon tracked with the increase in pyridinic nitrogen functionalities, but they were not able to directly correlate its influence. At this juncture is not possible to discern the specific role of nitrogen on the enhancement of activity of nitrogenated carbons. However, the plausibility of pyridinic nitrogen's importance is supported by the availability of the extra lone pair of electrons on the nitrogen atom, which increases electron density on graphitic edge planes. It is reasonable to expect that edge planes, which are commonly known to be reactive sites, will show increased reactivity due to additional electron density garnered from incorporation of nitrogen in pyridinic-like coordination at edge plane sites.

3.4 CONCLUSIONS

The structure, composition, and chemical reactivity of CNTs doped with various amounts of nitrogen were assessed through an array of analytical techniques. TEM images highlighted minimal changes between the gross morphologies of the non-doped and nitrogen doped CNT varieties. TGA data demonstrated nominally equivalent loadings of residual iron particles in the as-prepared materials but significant differences in edge plane content. Corresponding changes in XPS and Raman signatures verified increases in the degree of structural disorder in N-CNTs. In addition, the selective enrichment of
pyridinic functionalities in the studied N-CNTs was shown. Iodimetry and $pH_{pzc}$
mass titrations suggested that N-CNTs possess a net cationic character in aqueous
suspensions at neutral pH and that reducing sites increase with the nitrogen
content, specifically pyridinic functionalities. The work contained in this chapter
represents the base structural and chemical characterization necessary for
delineating the influence of nitrogen doping on electrochemical properties, the
topic of Chapter 4.

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CHAPTER 4

Electrochemical Characterization of Nitrogen Doped Carbon Nanotubes

4.1 INTRODUCTION

While traditional active carbons (e.g. carbon black, Vulcan XC-72) demonstrate requisite characteristics as a good catalyst support,\(^1\) they generally exhibit poor inherent catalytic activity for many technologically relevant reactions, particularly for O\(_2\) reduction in aqueous solutions.\(^2,3\) O\(_2\) reduction in acidic and alkaline solutions at low and moderate temperatures is a topic of tremendous interest in the field of electrocatalysis, chiefly in fuel cells,\(^4\) metal-air batteries,\(^5\) and air breathing cathodes.\(^6\) Historically, several methods have been used to modify carbon supports in effort to improve electrocatalytic performance. Besides optimization of morphological properties (e.g. surface area and porosity), chemical modification of the carbon surface has been explored to stabilize catalyst-support interactions and to increase the reactivity of the carbon in the absence of additional catalyst materials. For instance, carbon containing oxygen or nitrogen heteroatom functional groups can be prepared via chemical pretreatments with reactive species such as HNO\(_3\), NH\(_3\), or HCN.\(^7-10\) These pretreatments however, generally produce carbon-heteroatom functionalities (e.g., hydroxyls, carboxyls, amines) that are unstable under typical catalysis conditions.

Other more viable routes entail the dispersion of typically iron or cobalt containing N₄-macrocycles (e.g., porphyrins and phthalocyanines) on high surface area carbons.¹¹ While these modified carbons demonstrate improved catalytic activity for O₂ reduction, the corrosion resistance is poor when used under operational catalysis conditions.¹² Janke et al¹³ found that more stable, but less active, O₂ reduction catalysts could be formed by subjecting carbon-supported transition metal-centered N₄-macrocycles to extended heat treatments (>800 °C) in inert atmospheres, such as Ar and N₂. Yeager,²¹³ Dodelet,¹⁴ and Savinell¹⁵ later demonstrated that the specific nature of the precursor was unimportant, as long as the pyrolysis mixture contained carbon along with nitrogen and iron, cobalt, or nickel.

Despite decades of research on O₂ reduction catalysts consisting of carbon, nitrogen, and transition metal (predominantly iron or cobalt), their O₂ reduction mechanistic steps are poorly understood. While nitrogen has been generally identified as an essential element for catalytic activity, poor surface and electrochemical characterizations of these materials and of the O₂ reduction process have led to several conflicting views on the specific identity/stoichiometry of the active site. The broad range of methodologies and materials employed to produce active oxygen reduction catalysts makes it difficult to discern controlling parameters for preparing active catalysts. Specifically, the widely variable properties (i.e., porosity, surface area, crystallinity, surface functionalities)¹⁶ of commercially available active carbons complicate systematic correlation of inherent carbon, transition metal, and nitrogen interactions and
obscure the elucidation of their respective roles in the formation of catalytic materials. Furthermore, the difficulty in uniformly and reproducibly dispersing the transition metal and nitrogen precursors with poorly defined activated carbons makes consistent and reproducible activity challenging to obtain.

Rather than dispersing active O₂ reduction catalysts on a preformed carbon support, an attractive alternative scheme is to produce the catalytic sites and carbon support simultaneously. One method for achieving this is through N-CNTs. Chapters 2 and 3 detailed the preparation and physical characterization of N-CNTs with controlled nitrogen contents. This chapter presents extensive electrochemical data for the inherent activity of N-CNT electrodes relative to non-doped CNT electrodes and glassy carbons. Specifically, voltammetric responses for Ru(NH₃)₆³⁺, Fe(CN)₆⁴⁻, dopamine, norepinephrine, dihydroxyphenylacetic acid (DOPAC), and O₂ are examined. Collectively, these well-studied outer-sphere and inner-sphere redox couples highlight the unique interfacial and electrochemical properties of N-CNT electrodes.

4.2 EXPERIMENTAL

4.2.1 Electrochemical Analysis

All electrochemical studies were performed with either a CH Instruments 700A, Autolab PGSTAT 30, or EG&G 263A potentiostat interfaced to a PC. Unless stated otherwise, measurements were taken at room temperature (23 ± 2 °C) and ambient pressure. All solutions were prepared with NANOpure® water. Potassium nitrate (99.9%, EM Science), sodium hydroxide (99.99%, Aldrich), boric acid (99.9%, Spectrum), potassium sulfate (99.9%, Fisher), potassium
acetate (99.92%, Fisher), acetic acid (99.7%, Fisher), potassium phosphate monobasic (99.998%, Fisher), potassium phosphate dibasic (99.99%, Fisher) were used as supporting electrolytes and were used as received. A single compartment, gas-tight, three electrode glass cell was employed for all cyclic voltammetry and chronocoulometry studies. Pt mesh (Aldrich) and Hg/Hg$_2$SO$_4$ (sat’d K$_2$SO$_4$, CH Instruments) were used as the counter and reference electrodes, respectively. All potentials are referenced to Hg/Hg$_2$SO$_4$. The CNT-coated nickel mesh substrates were used as the working electrodes after an initial wetting procedure that consisted of cycling the applied potential from +0.4 to -1.5 V in O$_2$ saturated 1 M KNO$_3$ until there were no apparent bubbles on the electrode surface and the capacitive currents remained constant. Glassy carbon electrodes used for comparative studies were polished with 0.3 and 0.05 µm diameter alumina slurries and sonicated in NANOpure® water (Barnstead, 18 MΩ·cm) for 30 minutes prior to use. Geometric surface areas of the working electrodes were determined by chronocoulometry using hexaammineruthenium (III) chloride (99%, Strem Chemicals) in 1 M KNO$_3$. Solutions in the absence or presence of O$_2$ were prepared by purging with either Ar or O$_2$ (99.5%, Praxair) introduced through a gas inlet of the electrochemical cell. The diffusivity of dissolved O$_2$ was taken to be 1.75 x 10$^{-5}$ cm s$^{-1}$. Prior to all electrochemical measurements, Ar was bubbled through the test solution for 20 minutes to fully purge the solution prior to the start of measurements. For O$_2$ reduction measurements, O$_2$ was bubbled for 20 minutes to fully oxygenate the solution. For experiments involving CO, CO (99.95%, Aldrich) was bubbled for 20 minutes prior to the start
of the experiment. 1,4 bis (2-methylstyryl) benzene (99%, Aldrich), acetone (99.7%, Aldrich), potassium cyanide (98.3%, Aldrich), dopamine (98%, Aldrich), (-)norepinepherine (98%, Aldrich), and dihydroxyphenylacetic acid (98%, Aldrich) were used as received. Convolution of obtained cyclic voltammograms was carried out through the semiintegral data processing function of the CH Instruments 700A software. Observed electron transfer rate constants ($k_{\text{obs}}$) were estimated from peak separations by the method of Nicholson.18

4.2.2 Determination of H$_2$O$_2$ Decomposition Rate Constant

All measurements were taken at room temperature (23 ± 2 °C). For measurements in alkaline conditions, a preweighed 1 to 10 mg sample of CNTs was dispersed in 75 mL of 1 M KOH (99.99%, Aldrich) in a 5 neck cell that included a gold rotating disk electrode (RDE) (PINE AFE2MO50AU), gas inlet/outlet, gold counter electrode, and Hg/Hg$_2$SO$_4$ reference electrode. The solution was purged with N$_2$ for 10 minutes while the gold RDE was rotated at 2000 rpm (PINE AFM SRX). Approximately 0.75 mL of 1 M hydrogen peroxide (standardized 30%, Aldrich) was then injected into the suspension. The gold RDE was swept from -0.7 V to -0.4 V at 0.05 V s$^{-1}$ to oxidize HO$_2^-$ at 60 second intervals for a total of 20 minutes. For measurements in solutions of neutral pH, a manometer filled with O$_2$-saturated 1 M KNO$_3$ was attached to a 50 mL burette filled with O$_2$-saturated 1 M KNO$_3$, similar to that described by Tseung, et al.19

The suspension was saturated with O$_2$ for 10 minutes while vigorously stirred with a magnetic stir bar. 0.5 mL of 5 M H$_2$O$_2$ were then injected into the solution and the cell was immediately attached to the manometer. The burette valve was
opened periodically and the volume necessary to level the manometer was recorded every 30 to 60 seconds for up to 60 minutes. First order heterogeneous decomposition rate constants were determined from plots of $\ln[H_2O_2]$ vs. time.

4.3 RESULTS AND DISCUSSION

4.3.1 Wetting and Capacitance

CNTs grown by the methods described in Chapter 2 were generally hydrophobic as prepared and did not wet when immersed in aqueous solutions. Typically, for carbon fibril materials to be used in electrochemical applications involving aqueous electrolytes, the carbon electrode must be preconditioned, e.g. soaked in concentrated nitric or sulfuric acids or held at +1.4 V vs. Hg/Hg$_2$SO$_4$ for an extended period, in order to be fully wetted. Unfortunately, these treatments lead to breakdown or fracture of graphitic lattices and introduce polar oxygen containing surface functionalities (carboxyl and carboxylic anhydride groups). A mild form of electrochemical conditioning consisting of cycling between +0.7 to –1.5 V vs. Hg/Hg$_2$SO$_4$ at 0.1 V s$^{-1}$ in aqueous 1 M KNO$_3$ for a period of two minutes was initially used to induce uniform wetting of all CNT electrodes. Full wetting was evidenced by a sudden increase in the voltammetric current at the moment the electrode surface fully saturates with electrolyte. However, we also noted at very positive potentials there was evidence of anion insertion into the graphitic structure of N-CNTs. Figure 4.1 shows typical voltammetric responses for wetted N-CNT electrodes immersed in deaerated KNO$_3$ solutions of varied concentrations for potential cycles between +0.7 V and –0.8 V vs Hg/Hg$_2$SO$_4$. In relatively dilute KNO$_3$ concentrations, the
Figure 4.1 Voltammetric responses of a N-CNT (1.0 at. % N) electrode immersed in deaerated solutions containing various concentrations of KNO₃. Scan rate: 0.1 V s⁻¹.
voltammograms for N-CNTs in Figure 4.1 are mostly featureless (i.e. only capacitive currents). In concentrated KNO$_3$ solutions, there is a set of quasireversible peaks near +0.5 V for NO$_3^-$ insertion/de-insertion. The sharpness of the anodic insertion wave and the broadness of the cathodic de-insertion wave in concentrated KNO$_3$ solutions are qualitatively consistent with behavior associated with anion intercalation at graphite electrodes as described by Siegenthaler et al.$^{21}$ This is a manifestation of the more open lattice structure, as NO$_3^-$ anions are known to insert into disordered graphitic lattices more readily than highly ordered graphitic carbons at low overpotentials.$^{22}$ Although not a focus of this work, it should be noted that the disorder induced by nitrogen doping facilitates ion insertion into the CNT wall structure, highlighting that nitrogen doping may be adventitious for application in secondary battery technologies.

Both non-doped CNT and N-CNT electrodes were stable during extended cycling out to +0.7 V vs. Hg/Hg$_2$SO$_4$, showing no changes in the voltammetric responses to suggest the creation of quinone-like oxygen-containing functionalities$^{23}$ or graphene oxides$^{24,25}$. However, to avoid confusion with more severe electrochemical pretreatment activation (ECP) methods$^{26}$ a less positive potential range (+0.4 V to –1.2 V) for the wetting procedure was chosen where no anion insertion was observed to occur.

Figure 4.2 shows typical voltammetric responses for wetted non-doped CNT and N-CNT electrodes cycled between –0.2 V and –0.8 V vs Hg/Hg$_2$SO$_4$ in deaerated 1 M KNO$_3$. The current measured for all CNT-coated nickel mesh electrode were several orders of magnitude higher than that for the uncoated
Figure 4.2 (A) Voltammetric responses of N-CNT electrodes doped with 0.0 at. % (black), 4.0 at. % (green), and 7.5 at. % (orange) immersed in deaerated 1 M KNO₃. A bare nickel mesh electrode (dotted line) is shown for comparison. Scan rate: 0.1 V s⁻¹ (B) Measured capacitances from cyclic voltammograms at -0.5 V vs. Hg/Hg₂SO₄
nickel mesh electrode of the same area, indicating that the observed electrochemical response is dominated by the CNT film and not the underlying nickel support. N-CNT electrodes exhibit much larger background charging (capacitive) currents over non-doped CNTs (Figure 4.2A) which appear to track with the amount of incorporated nitrogen (Figure 4.2B). The gravimetric capacitance for the electrodes shown in Figure 4.2B were estimated from voltammograms at -0.5 V vs. Hg/HgSO₄ in 1 M KNO₃ using
\[ C = \frac{1}{2 \nu} \left( i_c - i_a \right) \]
where, \( \nu \) is the scan rate, \( C \) is the measured capacitance, and \( i_c \) and \( i_a \) are the anodic and cathodic charging currents, respectively. The gravimetric capacitance (normalizing the observed capacitance by the CNT film mass) is observed to increase by over a factor of five for non-doped CNTs and N-CNTs containing 7.5 at. % N. These values are in agreement with the broad range of measured gravimetric capacitance values, reported for CNT electrode materials evaluated under similar electrolyte conditions. The correlation between capacitance and nitrogen doping in Figure 4.2B strongly agrees with the increase in edge plane density as shown by Raman spectroscopy in Chapter 3.

4.3.2 Heterogeneous Electron Transfer

Unless stated otherwise, the N-CNTs used for direct comparisons with non-doped graphitic carbons throughout the rest of the chapter are doped with 4.0 ± 0.5 at. % nitrogen.
4.3.2.1 Outer-sphere Electron Transfer

The voltammetric responses of non-doped CNT and N-CNT electrodes immersed in an aqueous solution of 1 mM Ru(NH$_3$)$_6$Cl$_3$ and 1 M KNO$_3$ are shown in Figure 4.3. The observance of a single set of peaks for both CNT types is significant because it offers insight on the spatial dispersion of electrochemically active sites on the CNT electrodes. Large spatial separation of higher activity electron transfer sites in between much lower activity sites on an electrode leads to multiple sets of peaks in the cyclic voltammetry for a given diffusional redox couple. The single set of peaks in both voltammograms in Figure 4.3 implies that facile electron transfer sites are sized and spaced far less than $\sqrt{D \tau}$ (~20 µm for $v = 0.1$ V s$^{-1}$) for both non-doped CNT and N-CNT electrodes. Also, the facile electron transfer, i.e. peak splitting ($\Delta E_p$) exhibited at both non-doped CNT and N-CNT electrodes in Figure 4.3 (60 ± 4 and 58 ± 3 mV) highlights two powerful features of the floating catalyst chemical vapor deposition methodology discussed in Chapter 2. First, the CNT films from this preparation route do not show appreciable ‘iR’ drop, indicating a very low contact resistance between the carbon and the underlying nickel support. In contrast, similar CNT materials have shown ‘poor’ electrochemical properties when grown on semi-conductor supports because of poor ohmic contact. For example, Marken et. al. reported slow heterogeneous electron transfer ($\Delta E_p \sim 170$ mV for Ru(NH$_3$)$_6^{3+/2+}$) at CNTs deposited on ceramic substrates.$^{32}$ Second, this preparation method results in CNT electrodes that are free of surface impurities/adsorbents which arise from processing steps (e.g. polishing) or
Figure 4.3 Voltammetric responses of non-doped CNT (blue) and N-CNT (red) electrodes immersed in deaerated 1 M KNO$_3$ with 1 mM Ru(NH$_3$)$_6^{3+/2+}$. Scan rate: 0.1 V s$^{-1}$
binders/paste, as typically the case with glassy carbon or carbon paste electrodes. For example, the preparation and pretreatments steps described Li et al. 33 and Dodelet et al. 34 for their CNT electrodes may have contributed to their poor electron transfer kinetics ($\Delta E_p \sim 170$ and 110 mV, respectively) for Fe(CN)$_6$$^{3-/4-}$. While Fe(CN)$_6$$^{3-/4-}$ is not a simple outer-sphere redox probe like Ru(NH$_3$)$_6$$^{3+/2+}$ given its partial sensitivity to electrode surface conditions, 35-37 large $\Delta E_p$ values for Fe(CN)$_6$$^{3-/4-}$ voltammetry are suggestive of fouling of glassy carbon surfaces. 35 Correspondingly, nearly nernstian $\Delta E_p$ values for Fe(CN)$_6$$^{3-/4-}$ at both non-doped CNTs and N-CNT electrodes ($\Delta E_p = 72 \pm 1$ and 67 $\pm 2$, respectively, Table 4.1) are demonstrative of their pristine surfaces.

The voltammograms in Figure 4.3 for both non-doped CNTs and N-CNTs demonstrate fast heterogeneous electron transfer. Curiously, Ajayan et al. 38 have attributed facile electron transfer at carbon nanotubes as evidence of high crystallinity and absence of defects in their wall structure. That assertion is counter to the overwhelming contradictory evidence that defect-free basal plane graphite electrodes exhibit anomalously suppressed electron transfer rates ($\Delta E_p \sim 700$ mV). 36,39 McCreery et al. have proposed in highly ordered graphitic carbon electrode, the semi-metal character of graphitic carbon, i.e. the low local density of states (LDOS) at the Fermi level, causes abnormally slower electron transfer rates for Ru(NH$_3$)$_6$$^{3+/2+}$ than expected by self-exchange. 36 Experimentally, it was shown that when edge-plane defects are introduced into the same graphitic carbon electrodes, the electron transfer rate for Ru(NH$_3$)$_6$$^{3+/2+}$ was greatly accelerated, suggesting a substantial increase in the density of states in disordered graphitic
Table 4.1 $\Delta E_p$ and $E_p$ for Selected Redox Couples$^{a,b}$

<table>
<thead>
<tr>
<th>Redox Probe</th>
<th>CNT</th>
<th>N-CNT (4.0 at. % N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Ru(NH_3)_6^{3+/2+}$</td>
<td>$0.060 \pm 0.004$</td>
<td>$-0.651 \pm 0.007$</td>
</tr>
<tr>
<td>$Fe(CN)_6^{2-/3-}$</td>
<td>$0.072 \pm 0.001$</td>
<td>$-0.248 \pm 0.003$</td>
</tr>
<tr>
<td>$O_2$</td>
<td>--</td>
<td>$-0.767 \pm 0.007$</td>
</tr>
<tr>
<td>Dopamine</td>
<td>$0.146 \pm 0.006$</td>
<td>$-0.086 \pm 0.005$</td>
</tr>
<tr>
<td>Norepinephrine</td>
<td>$0.11 \pm 0.01$</td>
<td>$-0.097 \pm 0.007$</td>
</tr>
<tr>
<td>Epinephrine</td>
<td>$0.50 \pm 0.04$</td>
<td>$-0.08 \pm 0.02$</td>
</tr>
<tr>
<td>DOPAC</td>
<td>$0.21 \pm 0.08$</td>
<td>$-0.14 \pm 0.02$</td>
</tr>
</tbody>
</table>

$^a$ Scan Rate 0.1 V s$^{-1}$, V vs. Hg/Hg$_2$SO$_4$
$^b$ $N = 3$
$^c$ 1 M KNO$_3$
$^d$ irreversible
$^e$ 0.1 M, pH = 5.8 acetate buffer
carbons. In that regard, the voltammetry in Figure 4.3 is in accord with the significant structural disorder in both non-doped CNTs and N-CNTs that was detailed by TEM, Raman, and XPS analyses in both non-doped CNTs and N-CNTs in Chapter 3, i.e. nearly nernstian $\Delta E_p$ should be expected for the moderately to heavily disordered non-doped CNTs and N-CNTs, provided the surfaces are clean and iR drops are minimal. Any increased population in the LDOS of graphitic carbon doped with nitrogen (as intimated by C1s XPS spectra in Chapter 3) apparently has minimal influence on the ability of these CNTs to support fast outer-sphere redox processes as the values for Ru(NH$_3$)$_6^{3+/2+}$ and Fe(CN)$_6^{2-/3-}$ are nominally the same.

### 4.3.2.2 Inner-sphere Electron Transfer: Catechol Oxidation

The redox behavior of catechols have been studied extensively because of their importance in neurochemistry.\textsuperscript{40-43} The stoichiometry of the generic catechol/orthoquinone system is given by Eq 1,

$$\begin{align*}
\text{OH}^-\text{R} \xrightleftharpoons[k_1^0]{k_4^0} \text{O}^+\text{R} + 2\text{H}^+ + 2\text{e}^-
\end{align*}$$

(1)

where $R$ represents the defining alkyl branch of the catechol. The process is an overall two electron oxidation involving multiple deprotonation and electron transfer steps.\textsuperscript{44} The system is quasireversible for most catechols, including dopamine ($R = \text{C}_4\text{NH}_2$), a catechol whose electrochemistry at carbon surfaces has been thoroughly investigated. Cyclic voltammograms for dopamine oxidation at
non-doped CNT and N-CNT electrodes are shown in Figure 4.4. For both electrode types, the onset of oxidation current is $\sim -0.25$ V. As indicated in Chapter 3, N-CNTs with 4.0 at. % nitrogen possess more edge plane defects per unit area than non-doped CNTs, by a factor of 2.4. The association between electrochemically active sites and edge plane graphite$^{42,45,46}$ is consistent with the larger observed current densities for N-CNT than for non-doped CNT electrodes. The more edge plane character for N-CNTs is more clearly illustrated by the respective semiintegrals for dopamine oxidation in Figure 4.4B. Following the analysis of Bowling et. al.$^{47}$ the semiintegrals for both non-doped and N-CNTs show evidence of weak adsorption, i.e. both semiintegrals show evidence of peaks. The relative differences in semiintegral peak heights for the two CNT varieties indicate that the surface coverage, $\Gamma$ (mol cm$^{-2}$), of dopamine adsorption is at least double for the N-CNTs, suggestive that more edge plane sites promote adsorption of dopamine. While increased current density and surface coverage for N-CNTs are consistent with a carbon surface that has a higher density of dopamine adsorption sites, the larger $\Delta E_p$ at N-CNT electrodes for the 2e$^-$ dopamine/ dopamine orthoquinone couple ($141 \pm 6$ and $190 \pm 6$ mV for non-doped CNTs and N-CNTs, respectively) suggests that the oxidation process is less facile at the N-CNTs ($k_1^0$ is smaller by roughly an order of magnitude). Kuwana et. al.$^{48}$ and McCreery et. al.$^{49,50}$ have shown that favorable dopamine oxidation is not observed unless the surface is carefully cleaned of adsorbed impurities that block adsorption sites. We have also noted that unless the polishing procedure for GC electrodes is scrupulously kept clean, $k_1^0$ for dopamine oxidation can be
Figure 4.4  (A) Voltammograms of 1.5 mM dopamine in 0.1 M acetate buffer (pH = 5.8) at N-CNT and CNT electrodes. Scan rate = 0.1 V s\(^{-1}\) (B) Semiintegrals of oxidative portion of corresponding voltammograms in A. (C) Voltammograms of 1.3 mM norepinephrine in 0.1 M acetate buffer (pH = 5.8) at N-CNT and CNT electrodes. Scan rate = 0.1 V s\(^{-1}\) (D) Semiintegrals of oxidative portion of corresponding voltammograms in C.
suppressed ~ 2 orders of magnitude (data not shown). Since no cleaning or pre-
treatment procedures were performed on either type of CNT electrodes, it is again
evident that the CNTs are clean of surface fouling impurities. The cyclic
voltammetry in Figure 4.4C for the oxidation of norepinephrine (R = CH(OH)CH2NH2), a catecholamine with similar size and pKa as dopamine (cf. 8.92 and 8.88 for dopamine and norepinephrine, respectively), also shows both a larger $\Delta E_p$ and a more peak-shaped semiintegral for N-CNTs relative to the non-
doped CNTs and GC (Figure 4.4A). Again, the difference in $\Delta E_p$ values for the
N-CNT and non-doped CNT norepinephrine voltammetry denotes slightly less
than an order of magnitude decrease in $k_1^0$ for N-CNTs. The smaller $k_1^0$ at N-
CNTs for both the dopamine and norepinephrine orthoquinone couples may be
rationalized considering that both dopamine and norepinephrine as well as the N-
CNTs are positively charged at pH 5.8 due to their respective pK_a and pH_pzc
values, resulting in an unfavorable ionic interaction that can influence protonation
and/or electron transfer steps in the catecholamine oxidation mechanism. Similar
arguments have been made for the observation of negatively charged carbon
surfaces showing increased dopamine oxidation kinetics but decreased oxidation
kinetics for DOPAC, a structurally similar catechol (R = CH2CO2H).49,51,52 For
N-CNTs, this suggests that cyclic voltammetry for negatively charged DOPAC at
neutral pH (pK_a ~ 4), should exhibit more narrow peak splitting. Cyclic
voltammograms for the DOPAC/DOPAC orthoquinone couple are shown in
Figure 4.5. The N-CNTs demonstrate good reversibility ($\Delta E_p = 140 \pm 20$ mV) for
DOPAC oxidation, slightly improved relative to the reversibility of dopamine and
Figure 4.5  Voltammetric responses of non-doped CNT (blue) and N-CNT (red) electrodes immersed in 1.0 mM DOPAC in 0.1 M acetate buffer (pH = 5.8). Scan rate: 0.1 V s⁻¹
norepinephrine voltammetry in Figures 4.4. Conversely, both the non-doped CNTs (Figure 4.5) and glassy carbon ($\Delta E_p = 141$ mV, data not shown) electrodes exhibit much poorer DOPAC oxidation reversibility, approximately 2 orders of magnitude smaller values of $k_1^0$ than the N-CNTs. We attribute the increased $k_1^0$ at N-CNTs to the favorable attraction of the positive surface charge of the N-CNTs and the negative charge of DOPAC at pH 5.8. It may also be important that the strong Bronsted-Lowry base character of the N-CNTs further facilitates catecholamine and catechol oxidation, as N-CNTs have shown an increased sensitivity to the acid/base character of the supporting electrolyte for oxygen reduction relative to other carbon materials. While it is premature to identify specific mechanistic step(s) that affect the voltammetry at N-CNTs from only Figures 4.4 and 4.5, it is clear that in both cases of either cationic (dopamine and norepinephrine) and anionic (DOPAC) redox probes N-CNTs demonstrate electrochemical responses that are unlike ‘typical,’ clean graphitic electrode materials (non-doped CNTs and glassy carbon). To our knowledge, this is the first report of an inherently electrocatalytic carbon surface that demonstrates favorable anionic catechol electrooxidation.

4.3.2.3 Inner-sphere Electron Transfer: $O_2$ Reduction

Initially interested in the native sensitivity of as-prepared N-CNT electrodes towards dissolved $O_2$, using potential step techniques. The advantages of chronocoulometry over chronoamperometry for our CNT electrodes are the increase in signal to noise with longer measurement times and the separation of
the faradaic and capacitive components of the measured charge, as indicated in
the integrated form of the Cottrell equation (Eq 2),

\[ Q = 2nFAD_{O_2}C_{O_2} \pi^{-1/2}t^{1/2} + nF\Gamma_{O_2} + Q_{DL} \]  

(2)

where \( Q \) is the measured charge, \( F \) is Faraday's constant, \( A \) is the geometric area
of the electrode, \( D_{O_2} \) and \( C_{O_2} \) are the diffusion coefficient and concentration of
dissolved \( O_2 \), respectively, and \( t \) is time. A plot of the total charge passed vs. \( t^{1/2} \)
is linear, purely a result of the faradaic reduction process, and directly
proportional to the concentrations of dissolved \( O_2 \). Figure 4.6 shows the
coulometric response of an as-prepared N-CNT electrode following a potential
step from -0.2 V to -0.7 V for the reduction of \( O_2 \) in solutions with varied partial
pressures of \( O_2 \) above the 0.5 M KNO\(_3\) solution. As the partial pressure was
increased to raise the \( O_2 \) concentration in solution, the slopes increased
accordingly. Figures 4.6B and 4.6C verify the electrode response is linear over
the studied concentration ranges (1-40 ppm \( O_2 \)). The interesting feature of these
N-CNT electrodes was that they demonstrated reproducible behavior at low
overpotentials as prepared. A comparison of the linear sweep voltammograms for
\( O_2 \) reduction in 1 M KNO\(_3\) at a rigorously cleaned and polished glassy carbon
electrode and an N-CNT (1.0 at. \%) electrode made via the pyrolysis of iron (II)
phthalocyanine is shown in Figure 4.7. The oxygen reduction peak potential, \( E_p \),
at -0.65 V for the N-CNT electrode is shifted ca. 0.37 V more positive relative to
the peak for the glassy carbon electrode. Neither voltammetric waves occur at
Figure 4.6 Chronocoulometric responses of a N-CNT electrode immersed in a solution containing 1 M KNO₃ and indicated amounts of O₂. (A) Plot of charge vs $t^{1/2}$ measured for solutions under various partial pressures of O₂. (B) and (C) Plots of slopes determined from chronocoulometric plots vs. dissolved O₂ concentration obtained over two different concentration ranges.
Figure 4.7 Voltammetric responses of N-CNT and glassy carbon (GC) electrodes immersed in a 1 mM O₂ saturated solution containing 1 M KNO₃. Scan rate: 0.005 V s⁻¹
potentials suggestive of a direct 4e$^-$ reduction pathway, the case at platinum electrodes.$^2$ As with all other untreated carbon electrodes, the oxygen reduction processes in Figure 4.7 correspond to the 2e$^-$ O$_2$ reduction and subsequent generation of hydroperoxide, HO$_2^-$.

$$O_2 + H_2O + 2e^- \Leftrightarrow HO_2^- + OH^- \quad E^0 = -0.065 \text{ V (vs. NHE)} \quad (3)$$

The positive shift in Figure 4.7 demonstrates that N-CNTs are more electrocatalytic for the 2e$^-$ O$_2$ reduction process relative to conventional glassy carbon. To compare more directly the mechanistic influence of nitrogen doping on O$_2$ reduction, we focused our attention towards O$_2$ reduction at similarly prepared non-doped and N-CNT electrodes. For the following discussion both CNT types were produced from ferrocene and either xylene or pyridine, as detailed in Chapters 2.

The background-corrected voltammetric responses for O$_2$ reduction at non-doped and N-CNT electrodes in an O$_2$ saturated 1 M KNO$_3$ solution (pH = 6.4) are shown in Figure 4.8. Two marked differences between the two CNT variants can be seen. The O$_2$ reduction peak for N-CNTs is shifted significantly positive (ca. 0.07 V) relative to the response for non-doped CNT. This positive potential shift implies that O$_2$ reduction is more kinetically facile at the N-CNT electrode. Additionally, only a single reduction peak at $E_{p1} = -0.69 \text{ V}$ (vs. Hg/Hg$_2$SO$_4$) for O$_2$ reduction is observed for N-CNT electrodes, whereas two reductive peaks at $E_{p1} = -0.76 \text{ V}$ and $E_{p2} = -0.97 \text{ V}$ are seen for non-doped
**Figure 4.8** Background subtracted voltammetric responses of a non-doped CNT electrode (blue) and a N-CNT electrode (4.0 at. % N, red) immersed in an O₂ saturated 1 M KNO₃ solution. Scan rate: 0.1 V s⁻¹
electrodes. Figure 4.9 displays voltammetric responses for the reduction of O\textsubscript{2} in more basic 1 M KOH oxygen saturated solutions. In alkaline conditions, $> \text{pH} 10$, the voltammograms for non-doped and N-CNTs are now remarkably similar, i.e. only slightly shifted and both with two well separated peaks. The first peak at $\sim E_{p1} = -0.71 \text{ V}$ for the N-CNTs and at $E_{p1} = -0.75 \text{ V}$ for the non-doped CNTs. The second peaks in Figure 4.8 and 4.9 correspond to a second two electron reduction process, Eq 4, for the reduction of the generated $\text{HO}_2^-$ to $\text{OH}^-$. 

$$\text{HO}_2^- + \text{H}_2\text{O} + 2\text{e}^- \rightleftharpoons 3\text{OH}^- \quad E^0 = 0.867 \text{ V (vs. NHE)} \quad (4)$$

Figure 4.10 overlays the voltammograms for O\textsubscript{2} reduction and H\textsubscript{2}O\textsubscript{2} reduction at a non-doped CNT electrode. The potential of the wave for H\textsubscript{2}O\textsubscript{2} reduction is commensurate with the second wave in the O\textsubscript{2} reduction voltammogram. The absence of the second wave at N-CNTs (Figure 4.8) is suggestive of either an inability of N-CNTs to reduce $\text{HO}_2^-$ or a significant difference between non-doped CNTs and N-CNTs in the rate of heterogeneous decomposition of $\text{HO}_2^-$ to regenerate O\textsubscript{2}, Eq 5.

$$\text{HO}_2^- \rightleftharpoons \frac{K_5}{2} \text{O}_2 + \text{OH}^- \quad (5)$$

Whether the hydroperoxide species undergoes further electrochemical reduction (Eq 4) or decomposes (Eq 5), O\textsubscript{2} reduction at sufficiently negative
Figure 4.9 Background subtracted voltammetric responses of a non-doped CNT electrode (blue) and a N-CNT electrode (4.0 at. % N, red) immersed in an O₂ saturated 1 M KOH. Scan rate: 0.1 V s⁻¹
Figure 4.10 Voltammetric responses of a non-doped CNT electrode immersed in (TOP) a solution containing 1 mM O₂ and 1 M KNO₃ and (BOTTOM) a deaerated solution containing 4 mM H₂O₂. Scan rate = 0.1 V s⁻¹
potentials involves four electrons per oxygen molecule. For our CNT electrodes, quantitative assessment of the number of electrons, n, involved in O₂ reduction was performed using chronocoulometry. Determination of n is possible from the slopes of the chronocoulometric plots shown in Figure 4.11 using Eq 2.桥梁
Non-doped and N-CNT electrodes in 1 M KNO₃ give similar values of 3.7 ± 0.4 and 3.6 ± 0.4 electrons at -1.10V, respectively, indicating that the electrochemical process of the broad single wave for N-CNTs is identical to the sum process of the sharp two waves for non-doped CNTs, where one equivalent of O₂ undergoes a net four electron reduction at -1.10 V for both CNT types. For conventional graphitic electrodes in the absence of additional catalysts (e.g. Pt), both successive two electron reductions of O₂ (Eq 3 and Eq 4) are observed since the slow kinetics of the chemical decomposition step (Eq 5) make hydroperoxide a stable intermediate.桥梁

Hence, the rate constant for Eq 5 must be so large at N-CNT surfaces that HO₂⁻ is not a stable intermediate under these conditions.

Although exhaustive mechanistic analysis of O₂ reduction is difficult given the numerous possible pathways, linear sweep voltammetry can provide insight on the rate determining step (RDS) and whether an outer sphere (non-adsorptive) or inner sphere (adsorptive) pathway is observed.桥梁

Many investigators, including Mrha⁷, Yeager², and McCreery⁸ have proposed that at metal-free carbon surfaces, O₂ reduction involves surface adsorption, (Eq 6) with the initial electron transfer step consisting of O₂ being reduced to superoxide (Eq 7), followed by protonation to form hydroperoxide radical (Eq 8) and subsequent reduction to hydroperoxide (Eq 9).
Figure 4.11 Chronocoulometric response of non-doped CNT (open symbols) and N-CNT (dark symbols) electrodes immersed in 1 M KNO₃ and 1 M KOH. The electrodes were stepped from -0.30 V to -1.10 V in 1 M KNO₃ (○,●) and from -0.40 V to -1.00 V in 1 M KOH (□,□).
McCreery et al\textsuperscript{57} have argued that since the pK\textsubscript{A} of the superoxide species likely shifts from \(~4\) to \(~9\) when it is adsorbed rather than when it is free in solution, the protonation step (Eq 8) at all pH values less than the pK\textsubscript{A,\textsubscript{O_2}} should be fast. Hence, for \textit{O}_2 reduction in solutions with the pH < pK\textsubscript{A,\textsubscript{O_2}}, the RDS is the initial electron transfer rather than the protonation of \textit{O}_2\textsuperscript{−}.\textsuperscript{57} Technically, the RDS should shift from Eq 7 to Eq 8 for \textit{O}_2 reduction proceeding via the adsorptive pathway, yielding a value of \(\alpha_{\text{obs}} = 0.5\) at neutral pH and increasing to a value near \(\alpha_{\text{obs}} = 1\) in very alkaline conditions. From the voltammetry shown in Figures 4.7 and 4.8, \(\alpha_{\text{obs}}\) can be estimated from the measured width of the waves (Eq 10),
\[ \alpha_{\text{obs}} = \frac{1.875RT}{(E_{p/2} - E_p)} F \]  

(10)

where \( E_{p/2} \) is the potential at exactly one-half the total peak current.\(^{18} \) At pH = 6.7, \( \alpha_{\text{obs}} \) is 0.4 for N-CNT electrodes and is 0.8 for non-doped CNT electrodes. In pH = 14 solutions, the values for \( \alpha_{\text{obs}} \) are 0.8 and 1.0 for N-CNT and non-doped CNTs electrodes, respectively, and are demonstrated in Figure 4.12. The N-CNTs exhibit a change in charge transfer coefficient, \( \alpha_{\text{obs}} \), as the pH becomes more alkaline, consistent with a strongly adsorptive pathway while the non-doped CNTs show voltammetry and a respective \( \alpha_{\text{obs}} \) that is invariant to solution pH, suggestive that O\(_2\) is not strongly absorbed at the non-doped CNTs in the studied pH range.

In addition to the different \( \alpha_{\text{obs}} \) dependences, the dissimilarities in the voltammograms in Figure 4.8 (shift and occurrence of a 2\(^{\text{nd}}\) wave) also indicate that the rates for some mechanistic steps in O\(_2\) reduction are different, especially in pH <10 solutions. In particular, the positive shift is consistent with the idea that the electron transfer rate for reduction of O\(_2\) to O\(_2^-\) (Eq 7) is accelerated when adsorbed.\(^{57} \) To better assess this behavior, a commercial simulations package was used to model the observed voltammetry. The appendix describes the parameters used for the simulation in more detail. Although the simulation package only models outer-sphere electron transfers, it can be used in this context to mimic the effect of adsorption of O\(_2\), assuming adsorption significantly impacts the electron transfer rate of the 1e\(^-\) reduction of O\(_2\) to O\(_2^-\), as discussed by McCreery et al.\(^{57} \) Figure 4.13 shows the effect of the rate constant associated
Figure 4.12 Plot of the apparent charge transfer coefficient, $\alpha_{\text{obs}}$, of non-doped CNT (□) and N-CNT (●) electrodes immersed in various O$_2$ saturated KNO$_3$/borate buffered solutions. Individual data points represent a pooled set of five electrodes measured 10 times each as a function of pH.
Figure 4.13  Simulated O$_2$ reduction voltammograms with varied first electron-transfer step (Reaction 7) rate constant, $k_7^o$. Scan rate: 0.1 V s$^{-1}$
with the first electron transfer step (\(O_2\) to \(O_2^-\), \(k_7^0\), (Eq 7)) on \(E_{p/2}\) for \(O_2\) reduction. Variations in the value of \(k_7^0\) over a small range of orders of magnitude shift \(E_{p/2}\) of the first reduction peak by several tenths of a volt, indicating a strong sensitivity of the position of the oxygen reduction peak towards the rate of the initial electron transfer step. The 125 mV difference in \(E_{p/2}\) between the voltammograms in Figure 4.8 reflects a 10-fold increase in \(k_7^0\). This is consistent with the idea that \(O_2\) reduction to \(O_2^-\) with \(pH < 10\) is limited by the first electron transfer step (Eq 7) rather than the proton transfer step (Eq 8). Interestingly, Figure 4.13 suggests that if nitrogen doping accelerates the initial reduction of \(O_2\) to \(O_2^-\), then additional nitrogen doping should shift the observed \(E_p\) further positive. Figure 4.14 shows a plot of \(E_p\) for \(O_2\) reduction in 1 M KNO\(_3\) vs. total nitrogen content. At the N-CNTs with the highest nitrogen content, \(E_p\) is shifted \(\sim +300\) mV relative to the non-doped CNTs, demonstrating the electrocatalytic effect nitrogen doping has on the reduction of \(O_2\) to \(O_2^-\).

As discussed above, the lack of a second voltammetric peak for N-CNT electrodes indicates the intermediate, \(HO_2^-\), is much less stable at the CNT/solution interface. McIntyre has previously reported modeling studies that show the influence of \(k_{5,f}\) on hydrodynamic voltammetry for \(O_2\) reduction.\(^{59,60}\) Following McIntyre’s approach, the influence of the rate of the observed heterogeneous hydroperoxide decomposition (Eq 5) on \(O_2\) reduction voltammetry was also simulated. (see Appendix A for simulation parameters).\(^{59,61,62}\) Figure 4.15 shows the influence of \(k_{5,f}\) on the observed voltammetry. With small values (< 10\(^{-4}\) cm s\(^{-1}\)), \(O_2\) regeneration (recycling) is negligible and two separate
Figure 4.14  Plot of the voltammetric peak potential, $E_p$, of N-CNT electrodes for O$_2$ reduction (same conditions as in Figure 8) as a function nitrogen content.
Figure 4.15 Simulated voltammograms of the peroxide pathway reduction of O$_2$ with varied values for the heterogeneous hydroperoxide decomposition rate constant, $k_{5,f}$. The effect of $k_{5,f}$ on the normalized hydroperoxide reduction currents is shown in the inset. Scan rate: 0.1 V s$^{-1}$. 
reduction peaks are observed. With larger values of ($> 10^{-3}$ cm s$^{-1}$), a transition from two observed peaks to only one observed peak is seen. The second reduction peak disappears because electrochemically generated hydroperoxide chemically decomposes to $O_2$ at a rate faster than the rate at which it is electrochemically reduced to $OH^-$. The key feature of this simulation is that the transition between the two extreme conditions occurs within a small range encompassing three orders of magnitude of $k_{5,f}$, as indicated in the inset of Figure 4.15.

To assess experimentally the magnitude of difference in the chemical decomposition rates of hydroperoxide at non-doped CNTs and N-CNTs, bulk measurements of the decomposition of $H_2O_2$ in aqueous suspensions of carbon nanotubes were performed. Figure 4.16 shows representative results for the measured hydroperoxide decomposition rates at N-doped and non-doped CNTs. For N-CNTs, $k_{5,f}$ was found to be $5.1 \pm 0.7 \times 10^{-6}$ cm s$^{-1}$ and for non-doped CNTs, was $3.0 \pm 0.4 \times 10^{-8}$ cm s$^{-1}$. In 1 M KOH, the $k_{5,f}$ values for N-doped and non-doped CNTs were determined to be $1.8 \pm 0.5 \times 10^{-5}$ cm s$^{-1}$ and $1.0 \pm 0.4 \times 10^{-7}$ cm s$^{-1}$, respectively. In both neutral and alkaline pHs, the N-CNTs demonstrate over a 100-fold increase in catalytic activity. Our observations are also in agreement with studies of other nitrogenated carbons showing similar hydroperoxide decomposition activity.$^{10}$ Surprisingly, these values are within an order of magnitude of decomposition rates reported for most active catalysts, e.g. Pt-black.$^{63}$ The slight increase of $k_{5,f}$ in alkaline solutions has been reported for other peroxide decomposition catalysts and is most likely attributable towards a
Figure 4.16  Gasometric analysis of the heterogeneous decomposition of hydroperoxide at non-doped CNFs (○) and N-doped CNFs (■) in 1 M KNO₃.
greater instability of hydroperoxide with increasing pH alkaline solutions. Irrespective of the solution pH, the heterogeneous decomposition of hydroperoxide appeared to be first order (cm s\(^{-1}\)) at both CNT types, in agreement with reported first order behaviors of other graphitic carbons and most metal oxide based catalysts. A question that must be addressed is why \( k_{5,f} \) values measured for the N-CNTs in neutral and alkaline pH media are three orders of magnitude smaller than those values predicted by our electrochemical simulations. This discrepancy may be rationalized by the limitations of the model and simplified simulation parameters, i.e. the exclusion of the influence of reactant adsorption and decomposition reaction intermediates. The simulation presented here follows McIntyre's approach and treats the hydroperoxide decomposition as one uncomplicated chemical step that is confined to the surface but with no reactants as adsorbed species. As discussed by Appleby et al, the actual catalytic regeneration of oxygen from hydroperoxide likely involves numerous adsorbed reactive intermediates such as \( O_2^-, HO_2^+ \), and \( HO^+ \). The absence of such intermediates in the decomposition step oversimplifies the potential dependence of the hydroperoxide decomposition reaction as the aforementioned intermediates are all likely reduced at the potentials necessary for oxygen reduction. Further, the relevant rate limiting step for the simulation may not be the same as for the gasometric or RDE bulk measurements conducted at open circuit conditions. The observance of a first order rate behavior in the experimental data suggests that the rate limiting step in reactions measured by bulk measurements is unimolecular, possibly involving an initial adsorption of
hydroperoxide. Subsequent bimolecular surface bound reactions, as in the homogeneous case,\textsuperscript{65} are likely rapid. Hence, if the hydroperoxide species is already adsorbed, as is the case in the in-situ generation of hydroperoxide during O\textsubscript{2} reduction, the decomposition of the hydroperoxide species is not limited by adsorption but instead proceeds at the rate of the slowest subsequent step, which is likely to be several orders of magnitude faster than an initial adsorption step(s). This may also explain the observance of the second peak in the O\textsubscript{2} reduction voltammetry for N-CNTs in strongly alkaline solutions. Although bulk measurements show the $k_{5,6}$ value for N-CNTs remains two orders of magnitude greater than the value for non-doped CNTs in 1 M KOH, the second peak corresponding to the electrochemical reduction of hydroperoxide to OH\textsuperscript{-} is not suppressed. Alkaline solutions may favor an initial adsorptive step for hydroperoxide, as suggested by the RDE measurements. However, the greater stability of intermediates like O\textsubscript{2}^{-}, HO\textsuperscript{2}^{-}, and HO\textsuperscript{*} in alkaline solutions could impede subsequent steps in the disproportionation relative to the rates observed in 1 M KNO\textsubscript{3}. If the decomposition steps of the hydroperoxide species have slowed by only two orders of magnitude, the electrochemical reduction of hydroperoxide should be observed. While the specific cause for the reappearance of the peroxide reduction peak in more alkaline solutions at N-CNTs is unclear, the dissimilarity of the voltammograms of Figure 4.8 and the similarity in Figure 4.9 strongly indicate that the mechanism for oxygen adsorption and hydroperoxide decomposition at N-CNTs is strongly dependent on pH.
The possible participation of iron in the observed activity must be addressed. While many have speculated that iron species may participate in the observed catalytic activity in as many as three ways (as exposed solid iron on the carbon surface, as dissolved iron species leaching out of the CNTs into solution, or as nitrogen-chelated Fe$^{2+/3+}$ sites), the evidence suggests that none of these scenarios are operative. In particular, no voltammetric peaks commensurate with the oxidation of metallic iron or reduction of iron oxide on the surface of the CNTs were observed. This is consistent with our TEM observations that all iron particles are encased by at least 2-3 graphene layers. Moreover, since TGA and XPS results demonstrate nominally equivalent loadings of iron for both CNT types, it seems unlikely that solid-phase surface iron species could be catalytically active for only the N-CNTs and not the non-doped variety. Tseung et al$^{66}$ hypothesized that dissolved transition metal hydroxides leached from metal surfaces can act as aqueous, Fenton-like peroxide decomposition catalysts (i.e., Fe$^{+2/+3}$ redox mediated peroxide decomposition). As detailed in Chapter 3, iron leaching rates were extremely slow ($< 10$ femtomoles L$^{-1}$ s$^{-1}$). Additionally, we see no evidence for the presence of iron-chelated surface sites (i.e., FeN$_2$/C or FeN$_4$/C) that could act as fenton-type catalysts and/or as facile O$_2$ adsorption sites as proposed by Dodelet et al$^{14}$ and Schulenburg et al.$^{67}$ If iron coordination sites were operative, then exposure to agents that bind strongly with iron centers (e.g. CO and CN$^{-1}$) should change the shape and position of the O$_2$ reduction wave. As demonstrated in Figure 4.17, the O$_2$ reduction voltammetry at N-CNTs is unaffected, i.e., the peak position and absence of a second reductive peak, when
Figure 4.17 Effect of poisoning agents on O₂ reduction at N-CNT electrodes. (A) Background subtracted voltammograms for O₂ reduction in (black) 1 M KNO₃ and (green) 1 M KNO₃/2 mM KCN. Scan rate: 0.1 V s⁻¹ (B) Background subtracted voltammograms for O₂ reduction in 1 M KNO₃ (black) before and (green) after exposure to 1 M KNO₃/1 mM CO. Scan rate: 0.05 V s⁻¹ (C) Background subtracted voltammograms for O₂ reduction in 1 M KNO₃ (black) before and (green) after 10 minute soak in 1mM BMB in acetone. Scan rate: 0.1 V s⁻¹
the solution has been saturated with either CO or CN\(^{-}\) at high poisoning concentrations (1 mM). Figures 4.17A and 4.17B clearly indicate that active sites are not iron-chelated based. Interestingly, exposure of the N-CNT electrodes to an adsorbent like bis-methylstyryl benzene (BMB)\(^{68}\) which has a strong affinity for basal and edge plane sites noticeably alters O\(_2\) reduction voltammetry (Figure 4.17C), with the onset of reduction current shifting to a more negative potential and the emergence of the hydrogen peroxide reduction wave. When compared to Figures 4.17A and 4.17B, the dramatic changes seen in Figure 4.17C strongly suggest that the catalytic sites for O\(_2\) reduction on N-CNTs are related to carbon-nitrogen surface functionalities rather than iron-related sites.

As our electrochemical simulations qualitatively demonstrate, we believe that the increased catalytic activity and more positive O\(_2\) reduction potential observed for N-CNT electrodes is predominantly a result of enhanced adsorption which proceeds to accelerate O\(_2\) reduction and to advance heterogeneous hydroperoxide decomposition. This idea supports the original position of Yeager\(^{2}\) and Wiesener\(^{69,70}\) that the transition metal (iron in this case) serves primarily to facilitate the stable incorporation of nitrogen into the graphitic structure during the CNT growth. This hypothesis is consistent with the ability of iron to alloy with carbon and nitrogen,\(^{71}\) where at elevated temperatures the supersaturation of iron particles is relieved by the precipitation of both carbon and nitrogen, as detailed by Baker et al.\(^{72}\) Hence, iron acts as a secondary participant in the formation of active carbon, i.e. as an agent to stabilize the incorporation of nitrogen within the graphene matrix. Increased nitrogen doping has repeatedly
been noted to increase the basic nature\textsuperscript{10,58,73} and catalytic activity\textsuperscript{10,74} of the graphitic carbon. As indicated by Radovic et al.\textsuperscript{75} the enhanced basicity of the carbons is a consequence of strong $\pi$ electron delocalization. Delocalized $\pi$ electrons are capable of nucleophilic attack, giving a Lewis basicity independent of basic heteroatom functionalities. The basic nature imparted on the N-CNTs may stem from both the existence of electron rich nitrogen sites (e.g. pyridinic nitrogen possess one lone pair of electrons in addition to the one electron donated to the conjugated $\pi$ bond system) and from the stability against oxidation of the carbon which generally forms acidic oxygen functionalities. This is in accord with $pH_{pzc}$ measurements (the pH where the net surface charge is zero) by Biniak et al\textsuperscript{10} of nitrogenated carbons and our aforementioned preliminary $pH_{pzc}$ observations of N-CNTs that exhibit a basic nature.

The importance of the basic nature of N-CNTs is supported by earlier conclusions of Marsh et al.\textsuperscript{73} which indicate that nitrogen incorporation produces activated carbons with increased stability towards oxidation. This nitrogen-induced stability is also reflected in the difference in the Fe2p XPS data between our CNT varieties, as discussed in Chapter 3. The observance of only metallic (zero-valent) iron in N-CNTs intimates these carbons have a more reducing nature that prevents oxidation. As suggested by Strelko et al.\textsuperscript{74} the strong Lewis basicity of N-doped carbons acts to facilitate reductive $O_2$ adsorption at open circuit conditions without the irreversible formation of oxygen functionalities. This has been experimentally verified by Boehm et al\textsuperscript{76} through observations of adsorbed on NH$_3$-treated carbons that showed enhanced catalytic activity for oxidative
reactions (i.e. NO₂, SO₂). A similar prevalence of adsorbed on the surface of the N-CNTs which serves as the active species for driving the heterogeneous decomposition of hydroperoxide is likely. Adsorbed O₂⁻ can react with HO₂⁻ to form more reactive species (e.g. HO₂⁺ and HO⁺) that proceed to decompose hydroperoxide via surface analogues of chemical steps described by Bielski. Biniak et al¹⁰ have noted a decreased O₂ reduction overpotential for nitrogenated carbons that demonstrate faster rates of hydrogen peroxide decomposition rates. In light of the presented evidence, the strong adsorptive nature of the N-CNTs drives the more facile oxygen reduction observed at neutral pH. At more alkaline pH, it is unclear what determines the shift of N-CNT electrodes to O₂ reduction behavior similar to that observed at non-doped CNTs. Likely, the specific interplay of O₂ reduction intermediates determines the fate of in situ generated hydroperoxide.

4.4 CONCLUSIONS

Analyses of the electrochemical responses for Ru(NH₃)₆³+/²⁺, Fe(CN)₆³⁻/⁴⁻, dopamine, DOPAC, and O₂ of these materials illustrated similarities and differences in electrocatalytic activity between nitrogen doped carbons and non-doped carbons. No discernable difference between non-doped CNT and N-CNT electrodes was noted in the voltammetric responses for outer-sphere redox couples. Catechol oxidation at non-doped CNT and N-CNT electrodes occurred with different overall rates, with N-CNTs showing more favorable kinetics for anionic catechols. As-prepared N-CNT electrodes demonstrated more facile adsorption of O₂ and a greater activity for heterogeneous HO₂⁻ decomposition. A
mechanism was proposed where the reduction of \( \text{O}_2 \) in pH <10 solutions proceeds by a two-electron process with the rate-limiting step controlled by adsorbed \( \text{O}_2^- \). In pH >10 solutions, the adsorption process is partially hindered at the N-CNTs, and is limited by rate of protonation of \( \text{O}_2^- \). Digital simulations of the observed voltammetry support the proposed mechanism for N-CNTs. The \( \text{O}_2 \) reduction wave position, \( E_{p/2} \), shifted to more positive potentials with increasing total nitrogen content.

4.4 REFERENCES


CHAPTER 5

Future Directions

5.1 INTRODUCTION

The previous three chapters were devoted to detailing and elucidating the intimate relationship between the physicochemical and electrochemical properties of N-CNTs. Through the course of this study, several critical points related to the further characterization and application of the CNT materials arose. For example, the presented work focused on the influence of nitrogen doping on resultant properties of CNTs. The possible advantages from controllably doping other heteroatoms into CNTs are unexplored. Also, it is presently unclear in what ways N-CNTs made under identical conditions but with different metal growth catalysts are similar. A need for more sophisticated analytical procedures for assessing reactivities was noted. Methods exist to interrogate the physical properties of CNTs with high spatial resolution, e.g. TEM, but specific analytical methodologies for probing the localized chemical and electrochemical reactivities of N-CNTs with high spatial resolution are not common.

The contents of this chapter focus on continuing topics of research that address some of these fundamental and applied issues. In the first half of the discussion contained herein, electrochemical results from CNT/Nafion composite films are presented as further evidence against the role of iron-related active sites in the electrocatalytic activity of N-CNTs. In addition, two sets of preliminary
experiments are presented that illustrate potential methods for measuring the heterogeneous decomposition of hydrogen peroxide at CNT/solution interfaces. Finally, the second half of this discussion describes the plausibility of directly applying the CNT electrode architectures to zinc-air battery designs. Where noted, the presented results were acquired in collaboration with various members of the Stevenson and Bard groups.

5.2 EXPERIMENTAL

5.2.1 N-CNTs from Nickel Graphitization Catalysts

5.2.1.1 Preparation of N-CNTs

The ‘wet’ floating catalyst system was used as described in Chapter 2 (section 2.2.1.2), except for the following changes. Butyronitrile (99+%, Aldrich) and nickelocene (99.5%, Strem Chemicals) were used as the solvent and organometallic precursors, respectively, and solutions were prepared with a concentration of 15 mg ml\(^{-1}\). The change in solvent (from pyridine to butyronitrile) was necessary to match the solubility and stability of the air-sensitive nickelocene. The gas feed stream composition was 2.5 % NH\(_3\) and 97.5 % Ar. The evaporation temperature of Furnace 1 was 130 °C but the pyrolysis temperature of Furnace 2 was maintained at 800 °C. N-CNTs yields were much lower than with ferrocene and coverages on nickel mesh substrates were incomplete. However, sufficient quantities (~1 mg) of N-CNTs were collected from the interior the quartz process tube.
5.2.1.2 Casting of N-CNT/Nafion Films on Glassy Carbon Electrodes

A standard protocol for the casting of Nafion films from suspensions of CNTs onto glassy carbon electrodes was followed. Briefly, N-CNTs were pulverized for 10 minutes with an agate mortar and pestle. 1 mg of crushed N-CNTs were suspended in 10 ml water/methanol (50 % vol/vol) with 0.1 % vol/vol Nafion (5%, Aldrich). The suspensions were sonicated for at least 30 minutes until the suspensions were a uniform consistency. 0.8 µL were pipetted onto a glassy carbon electrode (AFE2M050GC, Pine Instruments) and allowed to dry in air. The N-CNT modified glassy carbon electrodes were then immersed in O2 saturated 0.1 M H2SO4. Electrochemical measurements were conducted at room temperature (23 ± 2 °C) and recorded with an EG&G PAR 263A potentiostat. These measurements were taken in collaboration with Mr. Ganesh Vijayaraghavan.

5.2.2 Measurements for the Heterogeneous Decomposition of Hydrogen Peroxide

5.2.2.1 Scanning Electrochemical Microscopy

Non-doped CNT films and N-CNT (4.0 at. % N) films were prepared on 1 cm² silicon wafers with ca. 100 nm oxide coating. Separately, each substrate was placed in a Teflon cell filled with O2 saturated 0.85 M KOH. Gold wire and a Hg/Hg2SO4 electrode (CHI Instruments) were used as the counter and reference electrodes, respectively. The working electrode was a gold wire (d = 12.5 µm) embedded in a sharpened glass capillary. SECM approach curves were conducted with a tip approach speed of 1 µm s⁻¹, \( E_{app} = -1.0 \) V vs. Hg/Hg2SO4, and recorded with a CHI Instruments 900 potentiostat. The interrogated substrates were left at
open circuit. All electrochemical measurements were recorded at room temperature (23 ± 2 °C). 2D arrays of CNT films were prepared through the confined dewetting lithographic patterning of iron oxide (NANOCAT) colloidal particle solutions. Briefly, a 20 µl aliquot of an acetone iron oxide colloidal solution was applied to a cleaned silicon wafer covered by a 100 nm oxide layer. A metal microgrid (PELCO 8 GN, Ted Pella, Inc.) was placed over the droplet. During the evaporation of solvent, particles were drawn into the interior voids of the microgrid and an array of patterned square (l = 10 µm) iron oxide deposits was leftover after complete solvent evaporation. Substrates were then used for CNT growth. Electrochemical measurements were taken in collaboration with Dr. Jose Fernandez, Dr. Cedric Hurth, and Dr. Allen J. Bard. Patterned CNT films were prepared in collaboration with Ms. Emily Barton.

5.2.2.2 Potential-Dependent Measurement of the Decomposition of Hydrogen Peroxide through Fluorescence Quenching

N-CNT electrodes were prepared without NH₃ as described in Chapter 2, except the mesh was cut in smaller sections (0.25 cm²). Tris(2,2’-bipyridyl)ruthenium(II) chloride (Ru(bpy)₃Cl₂, Strem Chemicals) and KNO₃ were used as received as the fluorescent probe and supporting electrolyte, respectively. Individual N-CNT electrodes and a micro stir bar were placed in a disposable plastic cuvette filled with 3.50 ml of aqueous solution (1 µM Ru(bpy)₃Cl₂, 1 M KNO₃). Gold wire and a Hg/Hg₂SO₄ electrode were used as the counter and reference electrodes, respectively. Both were immersed in a separate cell filled with 1 M KNO₃ connected to the cuvette through a ceramic junction. The set-up is depicted in Figure 5.1. The system was placed in a spectrofluorometer (QM-
Figure 5.1 Arrangement of the reference, counter, and working electrodes in a cuvette for potential-dependent measurement of the H$_2$O$_2$ decomposition rate by fluorescence quenching detection of O$_2$. 
4/2005, Photon Technology International) and the cuvette solution was stirred continuously before and during all measurements. The sensitivity of this system for dissolved O₂ concentrations was determined by measuring the quenched fluorescence of Ru(bpy)_3²⁺ at various concentrations of O₂. O₂ concentrations were varied by varying the fraction of O₂ in the sparging gas. After saturation at each O₂ concentration, fluorescence spectra were recorded for each O₂ concentration (Figure 5.2A). The Stern-Volmer plot in Figure 5.2B demonstrates the linearity of the fluorescence quenching at λ_ex = 600 nm. Following calibration, the cuvette solution was thoroughly purged with argon gas for ~30 minutes. Fluorescence emissions of Ru(bpy)_3²⁺ at 600 nm (excitation 455 nm) were monitored continuously until further purging resulted in no additional increase in signal. 40 µl of 1 M H₂O₂ were then added to the cuvette and a potential was applied (E_app) to the N-CNT working electrode. The steady-state current and decaying fluorescence emissions were recorded continuously for 20 minutes. Following, the N-CNT electrodes were thoroughly rinsed in NANOpure water (18 MΩ cm, Barnstead) and then the measurement process was repeated with a different E_app.

5.2.3 Half-Cell O₂ Reduction Cathode Comparison

N-CNT electrodes were prepared without NH₃ as described in Chapter 2 and placed in a half cell testing cell (QC200, Fuelcellstore.com) filled with 1 M KOH and equipped with a polyethylene O₂ membrane. A bias potential of -0.8 V vs. Hg/Hg₂SO₄ was applied and corresponding steady-state currents were recorded after 30 seconds with an Autolab PGSTAT 30 potentiostat. Measurements were repeated with a commercial zinc-air battery (ZA 675,
Figure 5.2  (A) Representative fluorescence emission spectra for 1 µM Ru(bpy)$_3^{2+}$ solutions containing various dissolved O$_2$ concentrations. Excitation wavelength = 455 nm  (B) Stern-Volmer plot of reciprocal normalized fluorescence emission intensities at 600 nm as a function of dissolved O$_2$ concentrations.
All electrochemical measurements were recorded at room temperature (23 ± 2 °C). These measurements were taken in collaboration with Mr. Ryan Williams.

5.3 DISCUSSION

5.3.1 Fundamental Studies

5.3.1.1 Nickel-catalyzed N-CNTs

The potential for a variety of useful enhancements to the physicochemical and electrochemical properties of graphitic carbon exists through heteroatom doping of elements other than nitrogen. For example, Rolison et al.\(^3\) have reportedly recently that sulfur-containing surface functionalities on graphitic carbons increases their binding capacity for platinum particles. Preliminary attempts to demonstrate similar effects in CNTs doped with specified levels of sulfur have thus far proven difficult. Sulfur containing solvents like thiophene and thioanisole have been used in the ‘wet’ floating catalyst CVD methodology, but the low decomposition temperature of these solvents apparently inhibits the formation of CNTs. Ongoing work is being conducted to optimize process conditions for producing sulfur doped CNTs.

Another opportunity afforded by the CVD preparation methods involves the use of non-iron metal CNT growth catalysts. CNTs made without iron seed particles offers the opportunity to further disseminate the relevance of iron-related active sites in N-CNTs. Although it was demonstrated in Chapter 2 that residual iron contents could be minimized, a significant portion of residual metal is unavoidable since the metal catalysts are inherent to the CVD growth process.
Therefore, rather than minimize iron contents or attempt acid leaching to remove the iron and risk damage to the N-CNT structure, an effective alternative approach is to use another metal catalyst instead of iron that is not known to be electrocatalytic in any form. In that regard, nickel species are known to be efficient catalysts for CNT growth\(^4\) but poor catalysts for O\(_2\) reduction.\(^5\) The preparation of N-CNTs with organometallics that contain metals other than iron is generally not as efficient in terms of collected yields. For example, the yields of N-CNTs produced from the pyrolysis of either nickelocene or ferrocene (two metalloccenes that differ only in their metal center) are very different. The use of nickelocene as a precursor results in \(< 0.01\) % molar efficiency as compared to the 0.1 % molar efficiency seen for ferrocene (Chapter 2, section 2.3.1). Unfortunately, complete coverages of nickel mesh substrates through nickelocene pyrolysis have thus far been unachievable under a variety of process conditions, prohibiting the direct comparison of voltammetric responses of N-CNTs made with nickelocene to those discussed in Chapter 4. However, N-CNT deposits on the interior of the quartz tube are sufficiently large for a secondary electrochemical analysis. A popular method\(^1,6\) for evaluating the activity of O\(_2\) reduction catalysts involves modification of a poorly electrocatalytic electrode (e.g. glassy carbon) with a composite film of Nafion and the catalyst material. Equivalent Nafion/ N-CNT films were prepared for N-CNTs made from either nickelocene or ferrocene. Although a detailed mechanistic analysis as discussed in Chapter 4 is not valid in this way, direct comparisons of the inherent electrocatalytic natures of the different N-CNTs is still possible. Figure 5.3 compares voltammograms for O\(_2\) reduction in 1 M H\(_2\)SO\(_4\) at glassy carbon.
Figure 5.3 Voltammetric responses of CNT/Nafion films cast on a polished glassy carbon electrode immersed in O₂ saturated 0.1 M H₂SO₄. Scan rate: 0.02 V s⁻¹
electrodes modified with non-doped CNTs, N-CNTs prepared from nickelocene, and N-CNTs prepared from ferrocene. The peak potential, $E_p$, for the voltammogram for non-doped CNTs is shifted 400 mV more negative than the voltammogram for N-CNTs prepared from nickelocene. As before, this large shift indicates that O$_2$ reduction is much more facile at the N-CNTs. The critical aspect in Figure 5.3 is that the observed shift of the N-CNTs made from nickelocene cannot be attributed to either an iron-coordinated or nickel-coordinate site. Hence, the catalytic effect seen in Figure 5.3 for the N-CNTs must stem directly from the nitrogen doping. Interestingly, the N-CNTs made from ferrocene show an additional shift of $E_p$ of nearly 250 mV relative to the N-CNTs made from nickelocene. In this preliminary work, it is assumed that the nitrogen contents for both N-CNT types are nominally equivalent since identical pyrolysis temperatures and NH$_3$ contents were used. However, this assumption is likely not valid as subtle differences in the solvent decomposition (pyridine vs. butyronitrile) and in the abilities of iron and nickel to generate nitrogenated carbons may result in non-equivalent nitrogen coordinations and contents. Work is underway to quantitatively determine the nitrogen doping of the nickel-derived N-CNTs. Nevertheless, Figure 5.3 qualitatively verifies that the influential aspect for O$_2$ reduction is nitrogen doping and not the identity of the residual metal.

5.3.1.2 Advanced Methods for Measuring the Heterogeneous Decomposition of Hydrogen Peroxide

In Chapter 4, values were reported for the heterogeneous disproportionation of hydrogen peroxide (Eq 1) at N-CNTs as measured by standard analyses of aqueous suspensions of bulk quantities of CNTs.
\[ \text{HO}_2 \xrightarrow{k_{f,1}} \frac{1}{2}\text{O}_2 + \text{OH}^- \] 

Those standard methods are limited in several important respects. First, these methods are sample intensive, usually requiring 10 – 100 mg of material for an accurate analysis. Second, they must be conducted at open circuit conditions, i.e. no potential control of the tested material. Third, they are not amenable for rapid analysis of multiple materials. The following discussion centers on two proposed analytical schemes that address and overcome these issues.

5.3.1.2.1 Scanning Electrochemical Microscopy

Scanning electrochemical microscopy (SECM) has been used to measure the kinetics at solid surfaces of simple heterogeneous electron transfers and heterogeneous electron transfers coupled with chemical reactions.\(^7\) Recent work by Bard et. al.\(^8\) has shown measurements of rate constants for heterogeneous chemical reactions at solid/liquid interfaces are also possible through SECM approach curves. Hence, SECM is an attractive method for measuring the rate of Eq 1 at CNT films because quantitative analysis can be conducted on as-prepared films.

The feedback system used for the measurement of \(k_{f,1}\) is illustrated in Figure 5.4A. Briefly, the current at a tip generating hydroperoxide, \(\text{HO}_2^-\), from the \(2e^-\) reduction of \(\text{O}_2\) (Eq 2) is affected by the approach of the tip towards a surface that is catalytic for the heterogeneous decomposition of hydroperoxide (Eq 1).
Figure 5.4 (A) Representation of the feedback process at a gold tip consuming O$_2$ approaching a surface that regenerates O$_2$ (B) Experimental approach curves for a 12.5 µm radius gold tip in O$_2$ sat. 0.85 M KOH for non-doped CNTs (blue) and N-CNTs (4.0 at. % N, red). $E_{app} = -1.0$ V vs. Hg/Hg$_2$SO$_4$, approach speed: 1 µm s$^{-1}$. 

\[ \text{O}_2 + \text{H}_2\text{O} + 2e^- \rightarrow \text{HO}_2^- + \text{OH}^- \]

\[ \frac{1}{2}\text{O}_2 + \text{OH}^- \rightarrow \text{HO}_2^- \]
\[
O_2 + H_2O + 2e^- \rightleftharpoons HO_2^- + OH^- \quad (2)
\]

If the surface does not promote Eq 1, then a completely negative feedback will be observed for the approach curve. If the surface supports fast catalytic rates for Eq 1, then the approach curve assumes a partial positive feedback form that is in between a totally negative and totally positive feedback response.8

Approach curves taken over bare SiO₂, where the rate of Eq 1 was negligible, gave an ideal negative feedback response. Figure 5.4B illustrates representative approach curves at non-doped CNTs and N-CNTs films (4.0 at. % N) grown on SiO₂. A clear difference between the two approach curves is evident, with the curve for non-doped CNTs possessing an entirely negative feedback that matched the response over bare SiO₂. In contrast, the approach curve for N-CNTs had a clear positive feedback response, with the tip current increasing as it approached the N-CNT film. Qualitatively, Figure 5.4B agrees with the earlier findings from gasometric analyses that N-CNTs demonstrate a large value for \( k_{het} \). However, quantitative interpretation of this approach curve is complicated by convolution from side processes. Fernandez et al.8 modeled the expected shapes of approach curves for this system and concluded that even the fastest possible rates for the heterogeneous decomposition of hydroperoxide will not support a totally positive feedback response, since the stoichiometry of the feedback system results in a net loss of \( \frac{1}{2}O_2 \), i.e. the heterogeneous decomposition of hydroperoxide only regenerates \( \frac{1}{2}O_2 \) for every \( 1 \ O_2 \) consumed at the tip. Instead, Fernandez and co-workers determined that positive feedback shapes like
that shown in Figure 5.4B occur when Eq 1 is separated spatially into two component half reactions, i.e. the reduction of $\text{O}_2$ (Eq 2) and the oxidation of $\text{HO}_2^-$ (Eq 3).

\[
\text{HO}_2^- + \text{OH}^- \rightleftharpoons \text{O}_2 + \text{H}_2\text{O} + 2e^- \quad (3)
\]

The localized concentration gradient of hydroperoxide at the N-CNT film underneath the tip polarizes the potential of the film such that Eq 3 occurs under the SECM tip while Eq 2 occurs far away from the tip, with electrons conducted laterally through the film to connect the half reactions. Since each $\text{O}_2$ consumed at the tip is now regenerated in full at the substrate by Eq 3, a fully positive feedback response for approach curves is possible. Unfortunately, since the feedback response of the substrate then becomes a complex function of the geometric surface area, conductivity, and electrocatalytic ability of the substrate to support Eq 2 and Eq 3, the direct quantitation of $k_{f,1}$ is not possible from the curves in Figure 5.4B. Hence, the total negative feedback response seen for non-doped CNT films in Figure 5.4B is illustrative of the inability of non-doped CNTs to support Eq 2 and Eq 3 in addition to Eq 1. For conductive substrates that not under potential control, this convolution is always possible when the footprint of the interrogated film is much larger than the tip area.

To avoid convolution, efforts are underway to prepare regulated CNT films with areas on the order of the probe tip. Figure 5.5A illustrates a methodology for producing CNT films with small footprints on the order of a typical SECM probe tip diameter. Each spot consists of quantities with total
Figure 5.5 (A) SEM micrographs showing a 2D array of regions of iron particles on SiO₂. Following CVD growth, the result is a 2D array of spatially separated CNT film spots. (B) Illustration of SECM analysis on distinct array elements.
masses less than 10 µg. An attractive advantage of such arrays are that CNTs with varied properties (e.g. N content, residual metal, nanotube density) may be prepared on the same substrate and readily analyzed by approach curves in a high-throughput fashion (Figure 5.5B), as demonstrated for catalyst screening by Fernandez et al.\(^9\) This type of fast quantitative analysis would provide a rapid method for assessing the values of \(k_{f,1}\) for a series of N-CNT films with varied nitrogen contents while requiring negligible quantities of material. This approach is not limited to only the study of Eq 1 but may be utilized for quantifying the activity of CNTs in other respects. For example, an array of CNT film spots could be prepared where each array element has different sulfur contents, as alluded to in Section 5.3.1 Exposure of the array to a suspension of catalyst materials (e.g. platinum) will result in varied sequestration of the catalyst at the sulfur-containing CNT film spots. SECM feedback analysis for O\(_2\) reduction over each film spot as described by Fernandez et al.\(^{10}\) would allow direct assessment of the loading and activity of each sulfur doping level. In this way, the amount and type of sulfur coordination that is most beneficial for binding metals could be quantitatively determined. Using the bulk-quantity techniques discussed in Chapter 4, an analogous set of analyses would require three orders of magnitude more material (~100 mg vs. ~100 µg for 10 samples). Moreover, for patterned CNT films on conductive substrates, the potential dependence of \(k_{f,1}\) can be assessed. The opportunity exists with this SECM approach to rapidly assess the chemical nature of as-prepared CNT films doped with heteroatoms.

5.3.1.2.2 Potential-Dependent Measurement of the Decomposition of Hydrogen Peroxide through Fluorescence Quenching
An alternative method for assessing the potential dependence of Eq 1 which involves the detection of O₂ from fluorescence quenching was developed by the Stevenson group.¹¹ Fluorescence quenching by dissolved O₂ has been used as an effective method for real-time measurement of the concentration of O₂.¹² The approach taken by the Stevenson group centers around the fluorescence quenching of Ru(bpy)₃²⁺ by O₂ (Eq 4 - 6).

\[
\text{Ru(bpy)}_3^{2+} + \text{hv} \rightarrow \text{Ru(bpy)}_3^{2+*} \quad (4)
\]

\[
\text{Ru(bpy)}_3^{2+*} \rightarrow \text{Ru(bpy)}_3^{2+} + \text{hv'} \quad (5)
\]

\[
\text{Ru(bpy)}_3^{2+*} + \text{O}_2 \rightarrow \text{Ru(bpy)}_3^{2+} + \text{O}_2^* \quad (6)
\]

In deoxygenated solutions containing hydrogen peroxide and a hydrogen peroxide decomposition catalyst, the O₂ in Eq 6 comes from the extent of reaction for Eq 1. Hence, the time dependent quenching of Ru(bpy)₃²⁺ fluorescence tracks the rate of Eq 1. Ru(bpy)₃²⁺ is an excellent fluorescent probe for O₂ since it has a high quenching constant by O₂ (3.3 x 10⁹ M⁻¹ s⁻¹),¹³ is not a catalyst for Eq 1, and is electroinactive in the range of potentials for O₂ reduction at N-CNT electrodes.

Reciprocal fluorescence emissions (I₀/I) at 600 nm for solutions with an immersed N-CNT electrode under potential control are shown in Figure 5.6. Larger values of (I₀/I) report increased quenching of Ru(bpy)₃²⁺ by O₂. As purging of the solution eliminated any dissolved O₂ from air, the sole source of O₂ was from the decomposition of H₂O₂ at the N-CNT electrode surface. As can be
**Figure 5.6** Reciprocal fluorescence emission intensities at 600 nm as a function of time after injection of H$_2$O$_2$ for several values of applied potentials of N-CNT electrode. Excitation wavelength = 455 nm.
seen from Figure 5.6, the rate of increased quenching with time following the injection of \( \text{H}_2\text{O}_2 \) and changed as the applied bias of the N-CNT electrode was varied. From calibrations of solutions with known amounts of \( \text{O}_2 \), each value of \( (I_0/I) \) corresponds to the concentration of generated \( \text{O}_2 \) at time \( t \), and, using the stoichiometry of Eq 1, \( \text{H}_2\text{O}_2 \) concentrations for all times could be determined. Plots of \( \ln[\text{H}_2\text{O}_2] \) vs. time were linear (data not shown) and the slopes were taken as the apparent homogeneous rate constant, \( k_{\text{app}} \) (\( s^{-1} \)) for the decomposition of \( \text{H}_2\text{O}_2 \). Homogeneous rate constants rather than heterogeneous rate constants, \( k_{\text{f,1}} \), are reported because of the mass transfer convolution between the position of the electrode and position of the probed solution volume. The results from Figure 5.6 are presented in Figure 5.7 as a function of applied potential to the N-CNT electrode.

The measured homogeneous decomposition rate constants, \( k_{\text{app}} \), show a modest increase with potentials in the range of -0.3 V to -0.45 V vs. Hg/Hg\(_2\text{SO}_4\). Beyond -0.45 V vs. Hg/Hg\(_2\text{SO}_4\), there is a sharp decrease in the measured values of \( k_{\text{app}} \). The demonstrated potential dependence of \( k_{\text{app}} \) was consistent for multiple N-CNT electrodes. The drastic decrease can be attributed to an increase in the rate of electrochemical reduction of \( \text{H}_2\text{O}_2 \) to \( \text{OH}^- \) at these more negative potentials, i.e. the \( \text{H}_2\text{O}_2 \) is electrochemically reduced at the surface of the N-CNTs before it can be chemically decomposed to \( \text{O}_2 \). When this occurs, fluorescence quenching decreases since the amount of \( \text{O}_2 \) generated decreases. The first range of more positive potentials contains the more interesting information, as the electrochemical reduction of both \( \text{O}_2 \) and \( \text{H}_2\text{O}_2 \) are negligible at these potentials (Chapter 4, Figure 4.8). The correlation between an increase in \( k_{\text{app}} \) and the
Figure 5.7  Apparent homogeneous rate constants of the decomposition of hydrogen peroxide as a function of applied potentials of the N-CNT electrode.
applied bias in Figure 5.7 represent the first reported evidence for the potential dependence of Eq 1 for any electrode material. As discussed in Chapter 4, the likelihood of such a potential dependence is reasonable since the likely intermediate species (e.g. $\text{O}_2^-$, $\text{HO}_2^*$, and $\text{HO}^*$) are all electroactive at these potentials. A strong potential dependence of Eq 1 may help to rationalize why the measured rate constant for the heterogeneous decomposition of hydrogen peroxide at N-CNTs by gasometric analyses in Chapter 4 were several orders of magnitude smaller than those predicted values predicted by the voltammetric simulations in Chapter 4.

This method of assessment of $k_{app}$ is limited by the mass transport of solution species from the electrode to the volume probed by the excitation light. As such, the specific methodology described here can only be used to assess qualitative trends in the potential dependence of Eq 1. However, this set of experiments demonstrates that in principle this detection scheme is sensitive to the changes in reaction rate of a heterogeneous process. If the probed volume is moved closer to the electrode/solution interface, then direct estimates of $k_{het}$ can be evaluated with high spatial resolution. Such localized placements of the fluorescent volumes may be envisioned through either a total internal reflection setup or the use of a near field scanning optical microscopy (NSOM) probe tip. As the case with the SECM approach, these two variants of the methodology presented here would allow analysis of small quantities of material.

### 5.3.2 Industrial Applications

Zinc-air batteries ideally consist of the following half reactions at the zinc and carbon electrodes (anode and cathode), respectively.
Since zinc-air batteries are typically employed in low power density applications (e.g. hearing aids), O₂ reduction occurs in the absence of additional transition metal catalysts, i.e. at the carbon electrode itself. However, although current densities are small, significant concentrations of HO₂⁻ can accumulate from the 2e⁻ pathway (Eq 2). Substantial HO₂⁻ contents are problematic because they hasten the corrosion of the battery housing and shorten device lifetimes. To overcome this problem, the standard designs for zinc-air battery cathodes consist of graphitic carbon powders mixed with substantial MnO₂ (5-10 wt. % of the device weight) pressed onto a nickel mesh current collector (Figure 5.8).¹⁵ There are two disadvantages in this type of cathode design. It involves multiple cathode components and it requires several preparation steps. The N-CNT film electrodes are an attractive alternative cathode design because they are prepared in a single step and are active for O₂ reduction without any additional binders or catalytic materials. Figure 5.8 demonstrates that for half cell tests, the performance of an as-prepared N-CNT electrode (4.0 at. % N) is comparable with that for a commercial zinc-air battery cathode. Since the N-CNT electrode is inherently active towards HO₂⁻ decomposition, Figure 5.8 suggests that N-CNT electrodes prepared as described in Chapter 2 may be readily and directly applied to existing zinc-air battery technologies.
**Figure 5.8**  (Left) A schematic of a commercial zinc-air battery design highlighting the architecture of the air cathode.17  (Right) Tafel plots for the comparison of O\textsubscript{2} reduction half-cell measurements for commercial air cathodes(*) and as-prepared N-CNT electrodes (4.0 at. % N, ●).
A similar direct application of nickel mesh-supported CNT film electrodes may be possible in flow-through reactions such as the abatement of pollutant species in industrial chemical processes. Sheintuch has recently summarized the advantages and advancements of fibrous catalyst architectures for flow-through chemical processes, e.g. H₂ reduction, N₂H₄ reduction, and CH₃OH oxidation. For flow through reactions, catalytic materials are more efficient when presented on open mesh (fibrous) supports than when in packed beds due to higher active surface areas, zero pressure drops from flows of reactant gases/liquids, and shorter reactant diffusion distances. As the case with zinc-air battery cathodes, the catalyst/fibrous support architectures described by Sheintuch are morphologically identical to the nickel-mesh supported CNT films described in Chapter 2, i.e. chemically active materials in direct contact with a metallic mesh substrate. This direct preparation methodology would eliminate costly and intensive existing preparation methods like thermal spray deposition and electrophoretic deposition, which suffer from poor adhesion of the catalytic material onto the mesh support. Hence, the CNT mesh electrodes detailed in Chapter 2 could also be directly applied to a flow-through chemical process, where the activity of the catalyst (i.e. CNT film) and the void volume of the mesh support are both optimized for the highest reactivity.

5.4 CONCLUSIONS

Several continuing experiments were presented for the continuing study of CNT materials. Voltammetric experiments of N-CNT electrodes prepared from nickelocene illustrated the identity of the residual metal is not important for the observation of significant O₂ reduction activity. SECM measurements
demonstrated an alternative technique for measuring chemical process at CNT films that required minimal sample and offered the possibility of high-throughput analysis. The distinct catalytic natures of non-doped CNTs and N-CNTs for the decomposition of H₂O₂ were demonstrated by approach curves. A preliminary scheme involving measurements of the quenching of Ru(bpy)₃²⁺ fluorescence by O₂ generated from the decomposition of H₂O₂ was demonstrated as a novel way for observing potential-dependent rates for the heterogeneous decomposition of H₂O₂. An increase in the heterogeneous rate of H₂O₂ decomposition with increasingly negative applied biases was noted. Finally, the direct application of nickel-mesh supported CNT films in industrial processes was discussed. A comparison between the performance of a commercial zinc-air battery cathode and an as-prepared N-CNT electrode demonstrated the possible ease of implementation of these electrode architectures in existing technologies.

5.3 REFERENCES


17. http://hometown.aol.com/watchbatteries/page6.html on 11/20/05
APPENDIX A

O₂ Reduction Simulation *

A.1 INTRODUCTION

A detailed description of the simulation used to model the influence of the rate constants for the first electron transfer step and the catalytic decomposition of hydrogen peroxide on the observed O₂ reduction voltammetry is presented here.

A.2 SIMULATION DETAILS

The following reaction scheme was entered into Digisim 3.05 (Bioanalytical Systems). General simulation parameters were \( v = 0.1 \, \text{V s}^{-1} \), \( C_{O_2} = 1 \, \text{mM} \), \( D = 1 \times 10^{-5} \, \text{cm s}^{-1} \) (for all species). The pH was set to 7.

\[
\begin{align*}
\text{O}_2 + e^- & \overset{k_{A1}^o}{\rightleftharpoons} \text{O}_2^- \quad (A.1) \\
\text{O}_2^- + \text{H}_2\text{O} & \overset{K_{A2}}{\rightleftharpoons} \text{HO}_2^- + \text{OH}^- \quad (A.2) \\
\text{HO}_2^- + e^- & \overset{k_{A3}^o}{\rightleftharpoons} \text{HO}_2^- \quad (A.3)
\end{align*}
\]

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Steps A.1 and A.3 were set with the following conditions: $E_{A,1}^0$ and $E_{A,3}^0$ were -0.6 V and 1.0 V, respectively. $\alpha$ for both steps was 0.5. The electron transfer rate constant for step A.3 ($k_{A,3}^o$) was $1 \times 10^6$ cm s$^{-1}$. Assuming superoxide in step 2 is adsorbed with a pK$_A$ ~ 9,$^1$ the equilibrium constant for step A.2 was set to $1 \times 10^{-5}$ (pK$_w$ – pK$_A$) with a rapid forward rate constant ($k_{A,2,f}^o = 1 \times 10^3$).

The catalytic regeneration of oxygen from hydroperoxide was simulated as a heterogeneous chemical reaction with a simplified O$_2$ reduction scheme.

\[ \ce{O_2 + 2e^- + H_2O &<=> [K_{A,4}] \rightarrow HO_2^-} \]  
\[ \text{(A.4)} \]

\[ \ce{HO_2^- + e^- &<=> [K_{A,5}] \rightarrow iHO_2^{2-}} \]  
\[ \text{(A.5)} \]

\[ \ce{iHO_2^{2-} &<=> [K_{A,6}] \rightarrow P + e^-} \]  
\[ \text{(A.6)} \]

\[ \ce{2P &<=> [K_{A,7}] \rightarrow O_2} \]  
\[ \text{(A.7)} \]

\[ \ce{HO_2^- + 2e^- &<=> [K_{A,8}] \rightarrow OH^-} \]  
\[ \text{(A.8)} \]

Reactions A.7 and A.8 were set with the following conditions; $E_{A,4}^0 = -0.3$ V, $\alpha_{A,4} = 0.5$, $k_{A,4}^o = 1 \times 10^{-9}$ cm s$^{-1}$ and $E_{A,8}^0 = 0.75$ V, $\alpha_{A,8} = 0.5$, and $k_{A,8}^o = 1 \times 10^{-30}$ cm s$^{-1}$, respectively. The net sum of reactions A.5 - A.7 is the chemical decomposition of hydroperoxide, but separating the chemical reaction into faux electron transfer half reactions pinned the regeneration of oxygen at the electrode.
surface rather than the bulk solution. By setting $\alpha_{A.5} = 0$ and the rates for steps A.6 and A.7 fast, $k_{A.5}^o$ exhibits no potential dependence and becomes equivalent to the first order heterogeneous decomposition rate constant, with units of cm s$^{-1}$. Parameters for steps A.6 and A.7 were $E_{A.6}^0 = -2V$, $\alpha = 0.5$, $k_{A.6}^o = 1 \times 10^3$ cm s$^{-1}$ and $K_{A.7} = 1 \times 10^{12}$, $k_{A.7,f} = 1 \times 10^{12}$ M$^{-1}$ s$^{-1}$, respectively.

A.3 REFERENCES

VITA

Stephen Maldonado, the son of Dr. Alfredo and Myriam Maldonado, was born in Des Moines, Iowa on October 10, 1978. After completing his work at Knoxville High School, Knoxville, Iowa, in 1997, he enrolled at the University of Iowa in Iowa City, Iowa. He graduated with a Bachelor of Science degree with Honors from the University of Iowa in May 2001. In September 2001 he entered the University of Texas at Austin to pursue his Doctorate in Chemistry under the guidance of Prof. Keith J. Stevenson

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