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Highly-selective Chemiresistive Sensing and Analysis of Vapors Using Functionalized Nanotubes

Deon Hines
Graduate Center, City University of New York

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Highly-selective Chemiresistive Sensing and Analysis of Vapors Using Functionalized Nanotubes

by

Deon S. Hines

A dissertation submitted to the Graduate Faculty in Chemistry in partial fulfillment of the requirements for the degree of Doctor of Philosophy, The City University of New York

2015
This manuscript has been read and accepted for the Graduate Faculty in Chemistry in satisfaction of the dissertation requirement for the degree of Doctor of Philosophy.

Dr. Daniel L. Akins

________________________

Date

Chair of Examining Committee

Dr. Brian R. Gibney

________________________

Date

Executive Officer

Dr. Daniel L. Akins

Dr. Teresa Bandosz

Dr. Andrei Jitianu

Supervisory Committee

THE CITY UNIVERSITY OF NEW YORK
Abstract

Highly-selective, Chemiresistive Sensing and Analysis of Vapors Using Functionalized Nanotubes

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Deon S. Hines

Advisor: Prof. Daniel L. Akins

Specifically, the project involves the development of a diversified array of nanostructured gas-sensors comprised of selectively, novel surface-functionalized carbon nanotubes (for analyte selectivity by virtue of functionality). Harnessing carbon nanotubes with various electron withdrawing and donating groups help in determining their affinity toward certain prognostic gaseous markers thus increasing specificity of such created sensors. We have devised synthetic routes that have led to the facile production of covalently polyfunctionalized nanotubes in high yield. Seven carbon nanotube analogues were systematically considered and then chemically synthesized, from pristine single-walled nanotubes (SWNT's), for use as the main component of sensory units that was used for this study. The basic chemical structure of these functionalized nanotubes; namely: poly(p-phenol)-co-SWNT [1], poly(p-nitrobenzene)-co-SWNT [2], poly(p-fluorobenzene)-co-SWNT [3], poly(p-aniline)-co-SWNT [4], polybromide-SWNT [5], poly(p-
thiophenol-co-SWNT [6] and poly(p-benzonitrile-co-SWNT [7]. The ability to manufacture total organic sensors was demonstrated using carbon nanotube based architectures.

These derivatized-nanotube-based materials are designed to serve as chemoreceptors that can facilitate the development of highly selective and sensitive chemical and biological sensor arrays through an “electronic nose” approach which mimics the mammalian olfactory system. Functionalized SWNTs (f-SWNTs) were dispersed in dimethyl formamide (DMF) and mCresol and spun-applied to the interdigitated regions of micro-lithographically fabricated, pre-cleaned interdigitated microsensor electrodes (IME 1025-M-Pt and Au). Measured changes in the electrical conductivities of an array of gas sensors upon exposure to selected vapors and inert explosive materials were monitored. These changes are transduced into electrical signals, which are preprocessed and conditioned before identification by a pattern recognition system. Preliminary chemisensory was conducted on four signature vapor components of RDX explosive. Sensor data from these individual detection methods was assessed by their own individual merits, after which they were amalgamate and reclassified to present each vapor as a unique data point on a 2-dimensional map and with a minimum loss of information. Extensive characterizations on the properties of these materials were carried out using various spectroscopic and electrical techniques to assess the usefulness of functionalized single-walled carbon nanotubes. It was found that the conductivity of two functionalized materials (poly(p-aniline)-co-SWNT [4] and polybromide-SWNT [5] ) were more conductive than the pristine SWNT.
The development of consistent and successful functionalization techniques that allows for the construction of CNTs-based species of great usefulness, reversibility and selectivity for the use as sensing element, can be a challenge. We have demonstrated a proof-of-concept by exploring and using the functionalized carbon nanotubes for use as gas sensors, through the utilization of a stochastic fingerprinting methodology. However, further studies into electronic and electrochemical detection methods will provide more unique systems for R&D on the applicability of these materials to future technology.
Acknowledgments

I could not have accomplished the goal of this dissertation without the help, guidance, support and efforts of some wonderful people.

First and foremost, I express my deepest gratitude to my mentor Dr. Daniel Akins, who welcomed me to his lab and provided the opportunity to discover through mentored scientific freedom. Throughout my Ph.D. study, he provided an encouraging, exciting, and a critical environment during our many discussions. Dr. Akins imparted to me the qualities of being a good chemist and an overall good scientist. It was a very enlightening experience and a great pleasure for me to conduct this dissertation under his supervision. I am grateful for his support, inspiration and guidance.

Thanks to my thesis committee members, Dr. Teresa Bandosz and Dr. Andrei Jitianu for their guidance over the years. I sincerely appreciate the time they took to positively discuss and critique this dissertation.

Special thanks to Dr. Bandosz for laying the foundation and guidance during my master's research period, my undergraduate chemistry professors, Dr. John Gibbs, Dr. Stanley Bajue and Dr. John Flowers and all my teachers for their steadfast confidence in my abilities.

I must extend my appreciation and thanks to Dr. David Adebimpe for getting me started on my research programme pathway. We have worked together on many sensing projects and I sincerely appreciate his guidance and support.
It would not have been as fruitful, had it not been for all the talented collaborators; thank you Dr. David Adebimpe of Polymath Interscience, Dr. Mark Rümmeli of Center for Integrated Nanostructure Physics, Institute for Basic Science (IBS), Daejon 305-701, Republic of Korea and Dr. Anthony Guiseppi-Elie of Clemson University (Center for Biochips, Biosensors and Bioelectronics), SC.

I will always remain grateful to my lab colleagues and Diane Beckford for their motivation, support and admirable cooperation. Let me also use this opportunity to thank Kayode for his assistance and training during my time at Center for Biochips, Bioelectronics and Biosensors (C3Bs) at Clemson University. Kayode’s humor and gregarious personality made C3Bs a fun place to work.

My sincere thanks is also extended to my second level proposal committee members, Dr. John Lombardi, Dr. Michael Green and Dr. George John. I also acknowledge Dr. Maria Tamargo, who provided ongoing encouragement during my Ph.D. program. My gratitude is extended to Dr. Jorge Morales for his assistance with SEM/EDAX, to Dr. Andrei Jitianu for the usage of the FTIR-ATR and Dr. Mykola Seredych for assistance with Thermogravimetric Analysis.

Very special gratitude is expressed to my dearest family and friends who have continued to demonstrate immeasurable belief in my ability to achieve my goals. To them I ascribe much of my continued success, especially to my mother - Daisy McCrae, my brother - Recardo Miller, my sister - Charmaine Fletcher, Horace Smith, Lynette Hinds (Mut), Barbara Dawkins,
Euphemia Gordon, Shawndya Simpson, Aileen Stephens, Angela Smith-Gittens, Aunt Gloria, Beverly Smith. Thanks for everything! Let me also acknowledge Nicolette (Nikki), Opal, Andrew, Ian, Deon, Terrence, Rosalyn, Norwyn, Dara, Marva, and Winston, for being great friends and for the support they have given me over these years.

Finally, I must thank the team of doctors, nurses and staff at SUNY Downstate Medical Center for their abilities, with God’s guidance, to help me onto the path of medical recovery, thereby enabling me the opportunity to complete my dissertation. I am sincerely grateful to you all.

TO GOD BE THE GLORY
Dedication

TO MY FAMILY, AND IN MEMORY OF LEONA HURLEY AND MY GRANDMOTHER (MY FIRST CHEMISTRY TEACHER). REST IN HEAVENLY PEACE.
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1.1 CARBON NANOTUBES (CNTS)

Based on what substances naturally occur, Nature has dictated that carbon is a uniquely important element for forming materials that are useful in human exploits as well as for creation of carbon-base living creatures, including humans. At the simplest level, the usefulness of carbon derives in large measure from a combination of its atomic size and its four-electron electronic structure.

Moreover, carbon forms a few allotropes, primarily due to its ability to hybridize, i.e., mixing of orbitals between carbon atoms that leads to different carbon bonding structures. The most popularly known allotropes are diamond and graphite (see Figure 1-1, Panels A and B, respectively). Interestingly, these allotropes possess dramatically different optical, electrical and physical properties; resulting, in the case of graphite and diamond to materials of vastly different esthetic and monetary values. More recently, over the last 2 to 3 decades, other allotropes of carbon resulting from carbon-carbon bonding structures have been discovered, and these new hybridized arrangements have been found to play key roles in leading-edge science and technological pursuits. Examples of the more recently found allotropes include zero-dimensioned C60 (Panel C in Figure. 1-1), discovered via mass spectroscopy of evaporated carbon samples, and one-dimensional carbon nanotubes (CNTs) (discovered by Iijima in 1991 via high resolution electron microscopy (HRTEM) in soot from an arc-discharge experiment.

Carbon nanotubes exist as hollow cylindrical structures of covalently bonded carbon atoms. Nanotubes are found to naturally align themselves into "bundles" held together by van der
Waals forces. Carbon nanotubes come in two different forms; single-walled carbon nanotubes (SWNTs) discovered in 1993 and multi-walled carbon nanotubes (MWNTs), made up of a system of conically encapsulated tubular structures of nanoscale diameter. MWNTs characteristically range in diameters of 5 – 50 nm and are on average several tens of microns in length. SWNTs, on the other hand, have diameters that range between 0.5 and 2 nm, depending on the synthesis method.

More recently, in 2004, another allotrope of carbon (specifically, graphene) has been found and has become the new rave as regards carbon material. Graphene is a covalently connected, single-atom thick arrangement of carbon atoms, forming, if it was completely flat (which typically it is not), the two-dimensional (2D) carbon network in the layered structure of graphite. It is important to discuss graphene because its structural properties are relevant in discussing those of SWNTs.

It is to be noted that, collectively, study of the allotropes of carbon has led to a vast quantity of published interdisciplinary research by scholars in chemistry, physics, engineering, biology and material science. Interest is driven in part from the unique structural, mechanical and electronic properties that the various allotropes exhibit.

In this dissertation, the author focuses on sensing components in an electrochemical system in which single-walled carbon nanotubes (SWNTs) play a key role.
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1.1.1 STRUCTURAL RELATIONSHIP BETWEEN SWNTS AND GRAPHENE

SWNTs can be conceptualized as being formed from a rolled-up graphene sheet that conserves three carbon bonds throughout the resulting structures. SWNTs are differentiated by their chiralities, which are deterministic in term of the nanotubes physical and electronic properties. In terms of chemical bonding, SWNTs are found to consist of sp$^2$ bonded carbon atoms in a 2D hexagonal pattern that has two atoms per unit cell. The structure of a SWNT is illustrated in Figure 1-2(a), which shows a graphene honeycomb structure where $\mathbf{a}_1$ and $\mathbf{a}_2$ are unit vectors; $\mathbf{C}_h$ is the chiral or roll-up vector that specifies how the graphene sheet is rolled into carbon nanotubes, where specific combinations of the scalar indices $n$ and $m$ are found to determine whether the nanotube is metallic or semiconducting in nature. More specific, as regards the indices, it can be shown that if the chiral indices are equal, $n = m$, the nanotube is found to be metallic; if $n - m$ is a multiple of 3, the nanotube is semiconducting, with a very small band gap; while, otherwise, the nanotube is a moderate semiconductor.
Specifically, the chiral vector, $C_h$, is defined as: $C_h = ma_1 + na_2$, where $m$ and $n$ are integers, with the additional requirement that one be greater than or equal to zero and the other integer being greater than or equal to the other (i.e., $0 \leq n \leq m$). As regards naming of unique SWNTs entities, it is to noted that the combination $(n,0)$ of the indices defines what is called a "zigzag" SWNT, while vector the combination $(n,n)$ defines an "armchair" SWNT.

1.1.2 PROPERTIES OF SWNT TYPES:

Conduction happens in armchair (metallic) tubes (because the valence and conduction bands cross each at the Fermi energy (Figure 1-3 below) for a certain wave vector). One dimensional band structure of carbon nanotube expresses a gap at the Fermi energy, and thus exhibit semiconducting properties, which is often seen in majority of the chiral tubes having unit cell with large number of atoms. In other instances where one of the sub-bands extends across
the K point of the two-dimensional structure, zigzag and chiral CNTs are conducting. In this case, the top of the valence band has the same energy as the bottom of the conduction band, and this energy equals the Fermi energy for one special wave vector, the so-called K-point vector.

Figure 1-3: Conduction in carbon nanotube (adapted from Unidym™).  

Once the diameter of the CNT increases, the band gap leans to zero, basically equivalent to a graphene sheet. In general, an \((n, m)\) carbon nanotube will be metallic when \(n - m = 3q\), where \(q\) is an integer. All armchair nanotubes are metallic, as are one-third of all possible zigzag nanotubes. In the case of MWNT, the smallest inner tubes’ electronic structure gets superimposed by the outward, larger planar graphene-like tubes, and it can therefore presumed that any computation on the electronic properties will result in a semi metallic behavior likened to that of graphite.
1.1.3 SYNTHESES METHODS OF SWNTS:

Traditional methods for large scale manufacturing and synthesis of SWNTs have been developed by various researchers around the globe. Such are inclusive of: Laser ablation methods established by R. E. Smalley at Rice University. This procedure involves flowing argon or helium in a tube containing the key component of graphite mixed with cobalt and nickel, within a furnace. Laser pulse and high temperature is used for vaporization. The carbon nanostructures are then collected in an outer trap. SWNTs is obtained by this technique. CNTs also grown by chemical vapor deposition (CVD) method has been achieved by various groups using different approaches to achieve defect-free nanotubes. This technique is widely used because it exploits hydrocarbon decomposition with substrate as, Ni, Fe, Co or alloys of these elements at low temperature, less than 1000 °C. This process resulted in higher defect density, which in turn may impact on the electrical and thermal properties of the tubes produced. Also, further SWNTs synthesis is achieved by floating CO in iron catalyst using high-pressure carbon monoxide (HiPCO) process.

Another technique is the arc discharge, the most commonly used procedure for the producing carbon nanostructures ranging from 4 to 30 nm in diameter and up to 1 um in length. The production of SWNTs is accomplished by changeable pressure and temperature conditions. This procedure includes a system under pressure control with a vacuum and gas line as a DC voltage is applied between two electrodes of graphite. The formation of carbon nanotubes is said to be at the cathode, while at the anode there are catalysts, a source of metal nanoparticle.
The techniques used for growing carbon nanotubes, whether it is arc discharge, laser ablation or CVD, are well-known laboratory procedures that provide tremendous control for a desirable yield, at a lower cost. The easiness of laboratory growth for CNTs, coupled with the unique properties hence makes CNTs exceptional as sensing material for gas sensor applications.

Clearly after these syntheses processes the CNTs produced will be further process in their effort to be used as good sensing elements. Some of these processes involve purification methods, but more importantly for this work, functionalization (as discussed in Chapter 2) is essential to improve the sensing performance, it relates to selectivity, quick response time and sensitivity.

1.1.4 PROPERTIES, FUNCTIONALIZATION AND APPLICATIONS OF SWNTS

Since their discovery in 1993, single-walled carbon nanotubes (SWNTs) have attracted enormous attention from scientists and engineers because of their remarkably high mechanical strength, ballistically-enhanced electrical conductivity and thermal conductivity, which are derived from a unique interplay of quantum confinement associated with the tube's circumference and one-dimensionality along its length. These highly attractive and novel properties almost immediately suggested to many that SWNTs would be ideal candidates for a range of important applications. SWNTs can also serve as active elements in field emission devices, owing to their novel structural properties to emit electrons in the presence of an electromagnetic field. For energy applications, such as hydrogen storage materials, as scanning-probe microscope tips, as catalytic supports (i.e., substrates) for electrocatalysts in proton exchange membrane (PEM) fuel cells, as reinforcing components in high strength composite
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materials, chemical and biological sensing, reinforced composite materials, and in many more areas. While some of the proposed applications remain still a far-off dream, others are close to technical realization. Recent advances in the development of reliable methods for the chemical functionalization of the nanotubes provide an additional impetus towards extending the scope of their application spectrum. In particular, covalent modification schemes allow persistent alteration of the electronic properties of the tubes, as well as to chemically tailor their surface properties, whereby new functions can be implemented that cannot otherwise be acquired by pristine nanotubes, primarily because of their lock of affinity to certain vapors, making them quite inert.

The derivatization or functionalization of the SWNT's sidewalls with active side-groups or organic polymers, which would facilitate the exploitation of the unique chemical properties of SWNTs, allows for enhancing or inducing the electronic properties. This enables the development of highly selective and sensitive chemical- and bio-sensors. SWNTs, chemical functionalization provides an avenue to manipulable chemical sensitivities and reactivities of the resultant composite.

The functionalization efforts of carbon nanotubes have to date, great dependency on wet chemistry\textsuperscript{10-17} or high temperature vapor techniques\textsuperscript{18,19} However, the use of high-temperature may result in damage the nanotubes. Furthermore, the accessibility of various chemistries may not be readily available in the vapor phase. Surface modifications of CNTs have been applied via various approaches, some of which includes: microwave plasma photochemical treatment with
CF₄,²⁰ H₂,²¹ and NH₃,²² with subsequent products being fluorination, hydrogenation and the addition of H, NH, and NH₂ groups to the sidewall of CNTs, just to note a few.

Functionalization of SWNTs allows for an increase in dispersion in organic solvents and water, as dispersion of nanotubes in solvents allows for chemical manipulation of carbon nanotubes. The development of consistent and successful functionalization techniques that allows for the construction of CNTs-based species of great usefulness, reversibility and selectivity for the use as sensing element, can be a challenge. However, success in modifying the framework of SWNTs leads to enhancing the physical and chemical properties,²³,²⁴ which consequently becoming important in the selectivity and specificity needs in various application purposes. Functionalizing SWNTs enables us to exploit to certain degrees, the thermal, mechanical, electronic and optical properties of CNTs⁵ providing tremendous potential for a wide variety of applications in the field of biomedical²⁵-²⁷ and material sciences,²⁸ theses likely to include polymeric solar cells, membrane fuel cells,²⁹ polymer composites,³⁰-³² and sensors.³³,³⁴

1.2 GAS SENSORS

Gas sensors have always played an integral role in industrial applications. They monitor and convey information on selected gases/vapors, which becomes crucial for control and prevention where necessary. In cases they are used to detect gas leaks that could be toxic or of explosive contents. These sensor devices continue to make a significant impact in the daily application of all aspect of life. Some of these devices are used to measure the physical and chemical changes in sensing materials exposed to various conditions, such as, light, and temperature, biological and chemical compounds. Adsorption of gas molecules on a sensing
material is one of the furthermost common sensing principles. For chemiresistor, changes are noted by adjustment in the DC resistance that occurs when sensors are exposed to these various conditions. The extent and character of the change depends on the type of agents that the sensing material has been exposed to. They extensively used in residential and commercial properties. Sensors often classified as electronic noses (e-Noses), have been a part of detection techniques used in the mimicking the mammalian system. This concept has been around for many years. However, since the introduction of Persaud, et al. work,\textsuperscript{35} there has been greater interest in their utilization. However, there are many devices that have been created for use as gas sensors/electronic noses, of which a few are discussed below.

1.2.1 OVERVIEW OF COMMON SENSOR FOR VAPOR DETECTION

Over the years, there has been a variety technologies based gas sensors constructed for use in electronic nose applications. However, a broad analysis is beyond the choice of this discussion, examples of a few are conducting polymers, surface acoustic wave (SAW), metal oxide sensor (MOS), and field effect transistor (FET). Although they have been shown to be effective in their application; the disadvantages of some of these devices ranges from sensitivity, to temperature and humidity, complex interface and reproducibility, and their need for use in controlled environment. Here we will briefly discuss the above noted sensor technologies with respect to their functions, advantages, capabilities and requirements.

1.2.2 CONDUCTING POLYMER BASED SENSOR

Conducting polymers have been used primarily for chemiresistor sensing materials.\textsuperscript{36-40} These sensors may have an array of organic-polymer coated elements with conducting
properties, deposited on an insulating surface, which on exposure to different analytes produce different electrical resistance. Most of the commonly used polymers are those of aniline, pyrrole derivatives. During operation, the adsorption and interaction of vapors with the polymer matrix induce changes in conductivity of the polymer. This therefore leads to the identification and quantification of gaseous vapors. The use of conducting polymers can be advantages because it has a simple sensor structure, it’s functional at room temperature, and it has moderately high sensitivity. However, there is a great concern to the lacking in fabrication reproducibility, and its easy influence to strong humidity and other environmental effects.

1.2.3 SURFACE ACOUSTIC WAVE (SAW)

SAW sensors bellows to the class of micro-electromechanical systems (MEMS) that depends on modulation of surface acoustic waves to detect a physical occurrence. This approach aims mainly at scrutinizing of the effect of the adsorbed gaseous molecules on the acoustic wave propagated pathway. The device structure consists of a piezoelectric substrate (for example quartz, coated for vapor adsorption) with interdigitated transducers and reflectors on its surface. Upon vapor adsorption, there is a conversion between electrical signal and acoustic wave by means of an interdigitated transducer, resulting in changes in frequency, amplitude or phase of the sensor’s response. The type of acoustic wave that gets generated depends primarily on the substrate properties, crystal and the structure of the electrodes. Despite the growth and attributes of low internal loss of signal, uniformity in material density and the mechanical properties, there is still short coming of these sensors. Some disadvantages are that there is a need for more
signal processing with compared to most sensor devices, there is frequency shift and sensitivity to temperature drift. Figure 1-4 provides a schematic of a basic SAW device.

![Diagram of a basic SAW device](image)

**Figure 1-4:** Diagram of a basic SAW device.

### 1.2.4 METAL OXIDE SENSOR (MOS)

Metal oxides, as sensing layer have found use in a wide range of gas sensors. The conductivity of the oxide layer is extremely dependent of its ability to absorb certain gases/vapors to the surface. Conductivity (n-type) is acquired when these layers are doped with metal such as, Pt or Pd. Conductivity is acquired. Gases like oxygen get adsorbed on the layers without difficulty, which leads the transfer of electrons onto the oxygen atoms. This then resulted in a decrease of excess electrons in, for example, SnO₂: Pt layer. As a result, there is a decrease in conductivity, as which is used as the detection signal. Likewise, p-doped MO-layers are mainly used for the detection of easily reducible gases.

Nevertheless, there is a major limitation for this system; one which is due to characteristically low selectivity with respect to particular of gases since all oxidizing gas cause a decrease in conductivity. Additionally, any reducing gas will result in an increase the number of
electrons in the SiO$_2$: Pt layer thus causing an increase in conductivity, providing flawed detection. Also, metal oxides sensors are very sensitive to humidity.

1.3 THE SIGNIFICANCE OF CARBON NANOTUBES AS GAS SENSING ELEMENT

SWNTs have surfaced as a material that finds its way in sensing applications. The recently emergent field of nanotechnology provides a pathway to this goal. Usages of SWNTs in application for electronic device fabrication are significant, owing to their miniature size, ultra-lightweight, and their large surface volume ratio that combines usefulness of their outstanding conductive properties. Functionalized-SWNTs chemiresistors used as gas sensing element can provide the need for more specificity, sensitivity and selectivity to the devices. SWNT-based sensors can provide fast detection of chemicals and other molecules that may be potentially harmful, and even for application in homeland security. This is achieved by utilizing the tube’s fast electron-transfer kinetics capability. In this section, we review other works on carbon nanotubes as sensing element.

Studies of carbon nanotubes as sensing material for detection of gaseous compounds have been realized. The study by Kong et al.\textsuperscript{45} reported drastic changes in the electrical resistance of semiconducting SWNTs upon exposed to gaseous molecules. They observed that gaseous as nitrogen dioxide (NO$_2$) induced an increase in onset voltage because of charge transfer from CNTs and the NO$_2$molecules. While on exposure to ammonia (NH$_3$), there was a decrease in the voltage. Also, the response times of nanotube sensors was detected to be no less than an order of magnitude faster than solid state-based sensors. The semiconducting SWNTs operated at room temperature, showed sensitivity as high as 10$^3$°C. With this experimental data, a basis for
building semiconducting SWNTs-based chemical sensors was established. Liu et al.\textsuperscript{46} study on the band structure of doped SWNTs with NO\textsubscript{2} and NH\textsubscript{3} was modeled after this work.

The use of carbon nanotube as sensing material for vapor detection has quickly advanced. Here, Kong \textit{et al.}\textsuperscript{34} has employed different amine compounds and found similar n-doping effects. Bradley \textit{et al.}\textsuperscript{47} observed through detection of ammonia via charge transfer that sensing is owing to the doping of molecules on nanotubes, rather than effects on contacts.

Huang and Lin\textsuperscript{48} reported a novel type of CNT/Ni-based hydrogen gas sensor that has demonstrated quick response and fast recovery time. The fabricated horizontally aligned carbon nanotube (HACNT) chemoresistor exposed to 200 ppm of various gases, showed remarkable response to H\textsubscript{2},\textsuperscript{48} in comparison to the other gases. Similar report was made in Su \textit{et al.}\textsuperscript{49} work based on flexible H\textsubscript{2} sensor fabricated on MWCNT network.

Hafaiedh \textit{et al.}\textsuperscript{50} fabricated a sensor capable of detecting volatile organic compounds at room temperature by oxygen plasma functionalization of multiwall carbon nanotubes. The advantage of this application showed high sensitivity to certain vapors. However, some levels limitation was shown in baseline recovery for numerous vapors.

While great strides have been made in the efforts of gas sensor application by many research groups, there remain challenges relating to selectivity, sensitivity, and stability.

1.4 CHEMIRESISTOR

These sensor’s systems usually capitalize on the primary benefit of interdigitated electrodes, with increased contact area between the sensing material and the sensor circuitry,
which gets cast with sensing layer formed essentially from conductive materials. As the gases molecules get distributed over sensing array, this stimulate physical and or chemical change in sensing material. As the sensing layer reacts to the presence of an analyte, the conductivity of the film changes, inducing a flow of current through the sensing layer resulting in an analytical measurement. As a result, there are changes in the resistance of the sensor. These changes are processed by a data acquisition system, followed by an incorporated recognition system, used for the interpretation of the patterns. This description is similar to the mammalian olfactory as shown in Figure 1-5, processes and identification of odor. The resistance of a resistive sensor varies as the sensor interacts with different analytes and to different concentrations of analyte. Figure 1-6 is an illustration of a common design for an interdigitated electrode chemical sensor. As the sensing layer in Figure 1-6 reacts to the presence of an analyte there is an increase or decrease its conductivity. The resistance between the interdigitated electrodes will likewise decrease or increase. In this section, we discuss the sensing mechanism that has been proposed.

Figure 1-5: Comparison of the mammalian olfactory system and the electronic nose system.\textsuperscript{51}
This technique can provide an inexpensive pathway to the monitoring of volatile odors, toxic and explosive materials and other agents. For these reasons, extensive research is being done on gas sensors and with the arrival of nanotechnology; there are a lot more possibilities for chemiresistor gas sensor.

To accomplish the aim of acquiring sensitive and specific detection for vapors and gaseous compounds interaction; single-walled carbon nanotubes get functionalized with different groups. At this juncture, the functional group-SWNT matrixes function as the chemical recognition site and electrical readout gets transmitted, based on analyte’s interaction via dispersion or chemical forces.

The desire to achieve specificity has been one of the biggest challenges in nanotube sensors. Our aim to covalently modified SWNTs with these selections of electron donating and withdrawing functional groups for sensing elements may be a conceivable solution.
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Functionalization exploits unique interaction between SWNTs and the specific functional groups causing an enhanced affinity of the functionalized carbon species for aliphatic vapors or small molecular volatile. This is a promising approach for the development of chemiresistor with characteristics of selectivity and specificity for desired applications. This work discusses in future chapters the functionalization of SWNTs and their application as effective chemiresistors for detection of gaseous analytes. In addition to creating and utilizing these devices for common vapors, our objective is to maximize the effort for applications for toxic chemical and explosives.

1.5 CHEMIRESISTOR FOR EXPLOSIVES DETECTION

The ability to detect explosives and explosive related forbidden substances successfully is instrumental to the prevention of terrorist activities, and therefore has great contribution in controlling their harmful effects on our health. Over the years, series of methods have emphasized the different principles that have been employed for explosives detection.

Of all the technological platforms available for vapor and trace detection, canines (K-9s) present the most effective and efficient method. Two dogs can search a 10,000 square feet in about 45 minutes, while it might take a full day for 15 people with trace detectors. On the other hand, little is known today about the real mechanism of biological olfaction. And without this, it will be impossible to lay a realistic blueprint for electronic detection, one based on an understanding of the true science of applied olfaction relating, at least to one organism or specie. An explosive detector with the sensitivity of a Military Working Dogs (canine) will be of invaluable use to the electronic detection community. Supplementary approach has been widely sought, which appear to be the use of mobile robotic systems with sensing capabilities to
minimize the threat to canines as well as their handlers. Presently, there are several other techniques employed for detecting explosives,\textsuperscript{53-57} of which the most commonly used comprise of ion mobility spectrometry (IMS), mass spectrometry (MS), gas chromatography (GC), and detection with sensitive sensors. However, the drawback with some of these devices is bulkiness, cost, and the time required for sampling. These limitations resulted in sparingly deployment of these systems to needed locations as airports and government buildings.\textsuperscript{56}

Therefore, diversified set of nanostructured chemical sensors comprised of novel surface-functionalized carbon nanotubes with high sensitivity, compact size, economical and selectivity to various explosive vapors can be the future device used to combat some of these limitations.

**1.6 SUMMARY AND THESIS OVERVIEW**

In this Chapter 1, we gave a brief background on carbon atoms and the relationship of carbon nanotubes, as theoretical roll-up cylinder of graphene sheets. We review SWNTs inheritance of its structure and properties from graphene, and showed that the folding and the tube curvature SWNTs make it either semiconducting or metallic. A quick review the traditional methods used for large scale manufacturing and synthesis of SWNTs conducted by various researchers around the globe. We looked at gas sensors, and some conventional methods that are still being employed. SWNTs can be made into chemiresistors where the detection techniques used in the mimicking the mammalian system. Such devices are useful for sensing applications. We review some prior sensing work on detection of gaseous species with functionalized carbon nanotube sensors. Also, a look at the need to investigate the use of nanostructured chemical sensors, comprised with selectivity for various explosive vapors. Detection through interaction
with functionalized SWNTs network and selected analytes do present a plausible solution towards developing chemiresistors with high specificity, selectivity and sensitivity.

Chapter 2 provides details on the experimental pathways taken to achieve a cohort of photolytic brominated SWNTs and modified diazonium coupling functionalized SWNTs with electron withdrawing and electron donating groups and the fabrication of chemisensor devices used in sensing applications of various analytes. Chapter 3 reviews some spectroscopic techniques (such as, AFM, SEM, EDAX, Raman, FTIR, and X-Ray), thermal analysis, electrical and electrochemical methods used for a very comprehensive characterization of the functionalized materials synthesized in Chapter 2.

In Chapter 4, we demonstrate through characterization the successful photolytic functionalization with N-Bromosuccinimide to the sidewall of SWNTs and introduce the application of brominated SWNTs as sensing material on platinum interdigitated electrodes for vapor detection. Intriguing results are observed.

Chapters 5 investigates the electrical and electrochemical properties of the functionalized brominated SWNTs material spun cast on Au and platinum interdigitated electrode and their applications as chemisensors for detection of four class of vapors and discuss the obtained results.

Chapter 6 presents information on a cohort of modified diazonium coupling - functionalized SWNTs through the characterization of different methods, and their use as sensing material in chemisensors for the detection of gaseous vapors. These measurements reveal important
interactions between the analytes and SWNT networks. We envisioned these diverse functionalized SWNTs based chemisensors to show sensitivity, unique chemical responses and selectivity to the exposed analyte.

Chapter 7 provided measurement on the electrical properties via impedance spectroscopy and IV characterization and the electrochemical characterization via cyclic voltammetry of pristine and functionalized SWNTs network of materials. These data reveal to some extent; the influence that covalently attached electron donating and withdrawing functional groups have on the sidewall of SWNTs.

Chapter 8 presents data on the preliminary investigation of Au and Pt - brominated SWNTs chemisensors exposed to signature vapor components of explosive Cyclotrimethylene-trinitramine (RDX), which are cyclohexanol, cyclohexanone, octane and 2,3-dimethyl-2,3-dinitrobutane (DMDNB). The sensor/vapor interactions show promising use for explosive detection and will be examined further. While Chapter 9 summarizes our work and discussed suggestions for future work.
1.7 REFERENCES


(4) In *Boundless Chemistry* Boundless:


(5) Saitô, R.; Dresselhaus, G.; Dresselhaus, M. **1998**.


(7) Electronics, U. C. f.


(26) Bianco, A.; Kostarelos, K.; Prato, M. **2008**.


(40) Huang, X.-J.; Choi, Y.-K. *Sensors and Actuators B: Chemical* 2007, 122, 659.

(41) Hoummady, M.; Campitelli, A.; Wlodarski, W. *Smart materials and structures* 1997, 6, 647.


(44) Electronics Bus.


(49) Su, P.-G.; Chuang, Y.-S. Sensors and Actuators B: Chemical 2010, 145, 521.

(50) Hafaiedh, I.; Elleuch, W.; Clement, P.; Llobet, E.; Abdelghani, A. Sensors and Actuators B: Chemical 2013, 182, 344.


(53) Yinon, J. Counterterrorist detection techniques of explosives; Elsevier, 2011.


CHAPTER 2: Syntheses Pathways of Functionalized SWNTs and Device Fabrication

2.1 JUSTIFICATION FOR CHOICE OF FUNCTIONALIZED NANOTUBES

The functionalized nanotubes chosen for this research exercise are themselves special. To our knowledge, thus far, no other groups have characterized them in this form, and further explored their use as sensors. Furthermore, these functionalized nanotubes provide the full spectrum of the possible photonic and optoelectronic properties that could be expected from carbon nanotubes. The functionalized nanotubes are poly(p-phenol)-co-SWNT [1], poly(p-nitrobenzene)-co-SWNT [2], poly(p-fluorobenzene)-co-SWNT [3], poly(p-aniline)-co-SWNT [4], polybromide-SWNT [5], poly(p-thiophenol)-co-SWNT, [6], and poly(p-benzonitrile)-co-SWNT [7]. Their basic chemical structures are shown below in Scheme 2.1.

![Chemical structures of functionalized nanotubes](image)

**Figure 2-1:** Chemical structures of functionalized nanotubes are poly(p-phenol)-co-SWNT [1], poly(p-nitrobenzene)-co-SWNT [2], poly(p-fluorobenzene)-co-SWNT [3], poly(p-aniline)-co-SWNT [4], polybromide-SWNT [5], poly(p-thiophenol)-co-SWNT [6], and poly(p-benzonitrile)-co-SWNT [7]. For reasons of clarity only one benzenoid substituent is shown per nanotube.

Nanotubes [1] and [4] are grafted with electron donating moieties while [2], [3], [5] – [7] are grafted with electron withdrawing moieties. However, the electron withdrawing moiety in [2] is
deactivated while the moiety in [3] (and also [1] and [4]) is activated towards reactions with
gaseous analytes, particularly those that are electrophilic by nature. The heteroatoms within [1]
(oxygen), [2] (nitrogen and oxygen), [4] (nitrogen), and [7] (nitrogen) are capable of hydrogen
bonding, charge stabilization and charge transfer processes with gaseous analytes. Also, The vast
surface area of the outer surfaces of [1],[2], [4], [6] and [7], which are covered by a sea pi-
electrons from both sp\(^2\)-bonded carbon (the benzenoid moiety) and of heteroatoms lone pairs
allows for sensitive interaction with gaseous analytes. Furthermore, the engineering of
compound [3] is challenged by the inclusion of fluorine, the most electronegative of all the elements. It is supposed that the addition of this element will simulate material polarization capable of bringing about such electronic effects that will induce selectivity to the compound's association with gaseous analytes. Fluorine also has effects within a material as well as a β-
cation-destabilizing effect (α-cation stabilizing), an β-anion stabilizing effect (α-anion
destabilizing) due to its lone pairs, and being a superb leaving group (as a fluoride ion). Also
engineered into the materials as a case of chemical curiosity (and a potentially critical observation window) is an opportunity to follow the interaction of material hydrogen with the volatile vapors it encounters, when it has different chemical characters. Progressing from [1] and then to [4] hydrogen is portrayed in 2 different chemical environments. Unlike the C-H bond, where available hydrogen atoms are only removable with difficulty, some of these protons in [1] have been rendered quite mobile (as in O-H) and while in [4] and [6] some have further been rendered very reactive (as in N-H, and S-H).
2.2 CHEMICALS AND REAGENTS

The N-Bromosuccinimide (99 %) and mCresol (98+ %), were obtained from Sigma-Aldrich. Dichloromethane (ACS: 99.5% stab. with amylene), chloroform (HPLC grade: 99.5% min) and Diethyl ether (99+%), 4-aminothiophenol (97%), p-Aminobenzonitrile (98%), Acetonitrile (99.8+%), 1, 2-dimethoxyethane (99+% stab. with 0.01% BHT), Diethylene glycol dimethyl ether (99%, stab. with BHT), also known as Diglyme, 4-Aminophenol (98%), 4-Nitroaniline (98%), and 4-Fluoroaniline (99%) were purchased from Alfa Aesar. The SWNTs (in black dry powder), which was purchased from Unidym™ Inc., Sunnyvale, CA, consisted of tubes with diameters from 0.8 to 1.2 nm, lengths from 100 to 1000 nm and was bundled in ropes. Purity of tubes is 95 wt. % with moisture content of >5 wt.%, and have a maximum density of 1.6 g/cm³. The nanotubes were used without any further purification.

2.3 FUNCTIONALIZATION OF SWNTS WITH BROMINE BY PHOTOLYTIC PROCESS

Brominated (i.e., functionalized polybromide-SWNT) nanotubes were chemically synthesized from pristine single-walled nanotubes (SWNTs). Product was formed from the reaction of pristine nanotubes with radicalized bromine. The use of the electron-withdrawing, covalently bonded bromine substituents attached to the surface of SWNTs is used to fine-tune electronic properties. With this approach, one can expect dilute networks of interconnected brominated SWNTs. The basic chemical structure of functionalized nanotubes, represented as polybromide-SWNT [5].
Polybrominated-SWNT nanotubes were fabricated by photolytic decomposition of N-Bromosuccinimide (yellow in color) in the presence of pristine nanotubes. Typically, 20 mg of the SWNT sample was sonicated in 15 mL of dichloromethane for 20 minutes. The dispersed mixture was then poured into a 100 mL round bottom flask. N-Bromosuccinimide (11 mg) was then added, which resulted in the formation of dark orange-color dispersion. The dispersion was then refluxed while irradiated through the bottom of the flask with light from a conventional 100 watt incandescent light bulb (General Electric, A19 incandescent bulb). Though the majority of the emission from an incandescent light bulb is in the visible region, a small fraction of UV radiation does emit in the UV-A region. This is sufficient to drive the homolytic cleavage of N-Bromosuccinimide.

The radiating heat from the light bulb might also contribute to the process. Exposure of the dispersion to the radiation promotes the formation of free bromine radicals. The reaction was allowed to run for about 15 minutes during which time out-gassing of gaseous components (oxides of nitrogen, oxides of carbon, hydrogen bromide). Then, 21 mg of N-Bromosuccinimide was added to the dispersion to drive the reaction further. The reaction was allowed to continue uninterrupted for another 90 minutes, after which a bright yellow dispersion formed with a phase separated suspension on top. At this point, the radiation source was lowered below the reaction flask (from 5 mm to 40 mm) to reduce the reaction rate. The reaction was allowed to proceed for another 10 hours. For other syntheses studies, the reaction procedure was modified by allowing the final step to occur for durations of 24 and 48 hours. In all cases, after the reaction, a light yellowish dispersion was obtained with no heterogeneous suspension. The dispersion was cooled
and filtered through a PTFE membrane (0.45 μm, 25mm), and the resulting precipitate was washed thoroughly with chloroform followed by numerous washing with diethyl ether. The resultant product was dried overnight at 60 °C in a Napco 5861 vacuum oven.

The resultant product underwent series of sample preparations for extensive characterization techniques (as discussed in Chapter 3) and is used to formulate a polymeric sensing element for use in an electronic nose configuration. Scheme 2-2 illustrates the mechanism to achieve Poly-bromination.

**Initiation**

**Step [1]** Cleavage of the N-Br bond forms Br radical.

**Propogation**

**Step [2]** Br radical reacts with sonicated SWNTs to form Brominated-SWNTs

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**Figure 2-2:** Formation of brominated SWNT using N-Bromosuccinimide (NBS) for bromine radical formation via photolysis in dichloromethane
2.4 FUNCTIONALIZATION OF SWNTS BY DIAZONIUM COUPLING

A typical synthesis for 6 cohorts of functionalized SWNTs was realized through modified diazonium coupling\(^1\) and aryl diazonium functionalization\(^2\) reactions using aniline derivatives, which leads to the formation of diazonium ions. Further synthesis pathways promote functionalized nanotubes such as; poly(p-phenol)-co-SWNT, poly(p-nitrobenzene)-co-SWNT, poly(p-fluorobenzene)-co-SWNT, poly(p-thiophenol)-co-SWNT, poly(p-benzonitrile)-co-SWNT and poly(p-aniline)-co-SWNT. A typical synthesis process was as follow: ca. 6 mg of SWNTs was sonicated in 10 mL of diglyme (bp: 162°C; MW: 134.2) for 10 minutes and added to a 100 mL 3-neck round bottom flask, immersed in a cold bath (crushed ice) to maintain a temperature of solution of 0°C. The apparatus was set for reflux condensation with bubbler containing mineral oil and a dry block thermometer: range -15 to 105°C was connected to one neck of the flask to measure temperature of solution. The temperature was monitored and crushed ice added, as needed, to ensure that the temperature did not fall below 0°C or above 5°C. If the temperature goes above 5°C, the diazonium ions will react to form phenol. On the other hand, if temperature dropped below 0°C, the rate of diazotization will be very slow.

2.4.1 FOR POLY(P-THIOPHENOL)-CO-SWNTS:

The addition of 0.2505g (2 mmol/ 4 equivalent of carbon) of Amino-thiophenol solution, made to dissolve in 5 mL of acetonitrile, to the SWNTs suspension was done. Ca. 0.5008 g (2 equivalent to amino-thiophenol) of isoamyl nitrite was quickly added via an addition funnel to the cold mixture and stirred to form diazonium salt. After 2 minutes, the cold bath was replaced by hot oil bath on a hot plate set at 60°C (heat source) with continued stirring to promote the
functionalization proceeding of SWNTs. The temperature was maintained at approximately 60°C, and reflux condensation occurred 24 hours in an inert environment of nitrogen gas.

Additionally, for other syntheses studies, the reaction procedure was modified by allowing the final step to occur for durations of 48 hours. In all cases, upon completion of the reaction, oil in the bubbler was pale yellow, confirming emission of gases. The final suspension was cooled and filtered through a PTFE membrane filter (0.45 um, 25mm). The filtrate was thoroughly washed with chloroform followed by diethyl ether. The resultant product was dried overnight at 60°C under vacuum (Napco E-Series vacuum oven). The resultant product underwent series sample preparations for extensive characterization techniques (as discussed in Chapter 3) and used to formulate a polymeric sensing element for use in an electronic nose application. Figure 2-3 illustrates the experimental setup of the reaction processes.

2.4.2 FOR POLY(P-PHENOL)-CO-SWNTS:

6 mg of HiPCo SWNTs was sonicated in 10 mL of diglyme (bp: 162°C; MW: 134.2) for 10 minutes and added to a 100 mL 3-neck round bottom flask, immersed in a cold bath (crushed ice) to maintain a temperature of solution of 0°C. The apparatus was set for reflux condensation with bubbler containing mineral oil and a dry block thermometer: range -15 to 105°C was connected to one neck of the flask to measure temperature of solution. The temperature was monitored and crushed ice added, as needed, to ensure that the temperature did not fall below 0°C or above 5°C. If the temperature goes above 5°C, the diazonium ions will react to form phenol. On the other hand, if temperature dropped below 0°C, the rate of diazotization will be very slow. Following was the addition of 0.2183g (2 mmol/ 4 equivalent of carbon) of 4-
Aminophenol solution, made to dissolve in 5 mL of acetonitrile. 0.4366 g (2 equivalent to 4-aminophenol) of Isoamyl nitrite was quickly added via an addition funnel to the above cold mixture as it was stirred to form diazonium salt. After 2 minutes, the cold bath was replaced by hot oil bath on a hot plate set at 60°C (heat source) with continued stirring to promote the functionalization proceeding of SWNTs. The temperature was maintained at approximately 60°C and reflux condensation occurred 24 hours in an inert environment of nitrogen gas. The reaction went as further detailed for poly(p-thiophenol)-co-SWNTs above.

2.4.3 FOR POLY(P-NITROBENZENE)-CO-SWNTS:

6 mg of HiPCO SWNTs was sonicated in 10 mL of diglyme (bp: 162°C; MW: 134.2) for 10 minutes and added to a 100 mL 3-neck-round bottom flask, which was setup for reflux condensation with bubbler containing mineral oil. Following was the addition of 0.2763 g (2 mmol/4 equivalent of carbon) of p-Aminonitrobenzene solution, made to dissolve in 5 mL of acetonitrile. 0.5525 g (2 equivalent to p-Aminonitrobenzene) of Isoamyl nitrite was quickly added via an addition funnel to the cold mixture as it was stirred to form diazonium salt. The reaction went as further detailed for poly(p-thiophenol)-co-SWNTs above.

2.4.4 FOR POLY(P-FLUOROBENZENE)-CO-SWNTS:

6 mg of HiPCO SWNTs was sonicated in 10 mL of diglyme (bp: 162°C; MW: 134.2) for 10 minutes and added to a 100 mL 3-neck round bottom flask. Following was the addition of 0.1482 g (2 mmol/4 equivalent of carbon) of 4-Fluoroaniline solution, made to dissolve in 5 mL of acetonitrile. 0.2964 g (2 equivalent to 4-Fluoroaniline) of Isoamyl nitrite was quickly added
via an addition funnel to the cold mixture as it was stirred to form diazonium salt. The reaction went as further detailed for poly(p-thiophenol)-co-SWNTs above.

2.4.5 FOR POLY(P-ANILINE)-CO-SWNT:

Synthesis of poly(p-aniline)-co-SWNTs was produced following the preparation poly(p-nitrobenzene)-co-SWNTs by the reducing the nitro group to an amine group. The use of stannous chloride with the solvent, ethanol is one of the model used the most for the reduction of nitro groups to an amine group, without the use of the more “classic” reagent, acid. In this work, a typical experimental procedure included: the treatment of ca. 12 mg of poly(p-nitrobenzene)-co-SWNT (contains ca. 0.004 mole of p-nitroaniline) and 3.793 g (0.02 moles) of SnCl₂ in 20 mL in refluxing ethanol for 2 hrs., at 70°C under nitrogen atmosphere. The solution was allowed to cool down and then filtered and washed with deionized water to remove any inorganic salts. The solid was treated with aqueous sodium bicarbonate, followed by the extraction with 40 mL of ethyl acetate. The organic phase was thoroughly washed with brine and dried over sodium sulfate to afford poly(p-aniline)-co-SWNTs.

2.4.6 FOR POLY(P-BENZONITRILE)-CO-SWNT:

In a typical procedure, 6 mg of HiPco SWNTs was sonicated in 10 mL of diglyme (bp: 162°C; MW: 134.2) for 10 minutes and added to a 100 mL 3-neck round bottom flask, which was setup for reflux condensation with bubbler containing mineral oil. Following was the addition of 0.2363g (2 mmol/ 4 equivalent of carbon) of Amino-benzonitrile solution, made to dissolve in 5 mL of acetonitrile. 0.4726 g (2 equivalent to amino-benzonitrile) of Isoamyl nitrite
was quickly added via an addition funnel to the above cold mixture as it was stirred to form diazonium salt. The reaction went as further detailed for poly(p-thiophenol)-co-SWNTs above.

2.5 MECHANISM OF DIAZOTIZATION PROCESS

Diazonium salt is an essential intermediate in the process diazotization. The diazonium ion is produced through the reaction of an arylamine with cold nitrous acid (in situ formation from isoamyl nitrite). The coupling of aryl diazonium ion involves a radical intermediate which then binds to single-walled carbon nanotube to form the functionalized-co-SWNTs compounds. Scheme 2-3 shows the conversion of an aniline derivative into the positive diazonium ion, then to aryl radical.

Figure 2-3: Illustrates the mechanism of diazotization.
Figure 2-4: Illustration of chemical structures formed from the functionalization reactions of SWNTs with in situ generated aryl diazonium compounds to form compounds of [1] to [3], [6] and [7]. Compound [4] formed by reduction of [2] using stannous chloride as a reducing agent.

This suite of derivatized-nanotube-based materials serve as chemoreceptors and facilitate the development of highly selective and sensitive chemical and biological sensor arrays by an approach that mimics the mammalian olfactory system – “electronic nose.” Functionalized SWNTs (f-SWNTs) were dispersed in dimethylformamide (DMF) and cast onto the interdigit space of microlithographically fabricated interdigitated microsensor electrodes (IME 1025-M-Pt. and IME 1025-M-Au), purchased from ABTECH Scientific, Inc., Richmond, Virginia.
2.6 DEVICE FABRICATION

2.6.1 PREPARATION OF IME 1025. 3-M Pt DEVICES:

The Interdigitated region of IMEs, used for electrical and electronic characterization during this work, were dipped into photoresist for protection and allowed to cure before applying epoxy to the contact region. Gold pins were then mounted onto IMEs and soldered at 700°F. Epoxy was used to cover soldered region, which was then allowed to cure at 150°C for 2 hours. Following these steps, the devices were entered for cleaning.

![Diagram of IME device preparation](image)

**Figure 2-5:** Illustrates the preparation stages of the IME device

2.6.2 CLEANING OF INTERDIGITATED ELECTRODES

The IME-1025-3.M Pt and Au electrodes underwent solvent cleaning to remove grease and other residue from the devices’ surface. Using Branson 1510, the devices were first ultrasonicated in 2-propanol, ethanol, and Milli-Q® deionized water for 3 minutes each, respectively. Next, the devices were blown with 0.22 micron filtered compressed air to remove
any remaining residue from IMEs. The devices were placed in a UV-ozone cleaner (Boekel Industries) and irradiated for 10 minutes. This method removes organic compounds that were not removed during the solvent cleaning processes. UV cleaned devices were subsequently ultrasonicated with 2-propanol for 1 minute and then placed in the plasma chamber for treatment of 5 minutes. Following cleaning of the bare platinum and gold IMEs, they then underwent surface modification.

2.6.3 SURFACE MODIFICATION OF IME DEVICES

The IME devices were chemically modified with octadecyltrichlorosilane (OTS) (C18H37Cl3Si; MW: 387.93; Bp: 160 °C; Vp: 5mm Hg @ 20°C). The objective is to introduce hydrophobic methyl groups on the surface to create a neutral glass surface and the possibility of improving the stability of the devices. 0.1 wt. % solution of OTS in anhydrous toluene was prepared in a glass vial. IMEs were immersed in a glass vial with OTS solution and placed in a convection oven for 45 minutes at 40°C for the initial silanization process. Vial was covered with foil to avoid evaporation of the solution. IMEs were removed from solution and rinsed in isopropyl alcohol for 3 minutes. This was followed by curing in a vacuum oven at 40°C for 20 minutes, then at 110°C for 20 minutes and finally 40°C for 20 minutes. Immediately following the surface modification, IMEs underwent cathodic treatment.

2.6.4 CATHODIC TREATMENT IN PHOSPHOROUS BUFFERED SILANE (PBS) FOR OTS MODIFIED DEVICES

This procedure is useful in removing OTS layer from working platinum electrodes (Pt. or Au). IMEs underwent an application of 20 cleaning cycles over the range of 0 - 1.2 V vs.
Ag/AgCl, 3 M KCl at 100 mV/s until highly reproducible cyclic voltammograms (CVs) were obtained. Treatment took place in 1M phosphorus buffered saline (PBS). Devices were removed from the electrochemical setup and rinsed with ultrapure deionized water and dried by blowing with 0.22 micron filtered compressed air. **Figure 2-1** shows series voltammograms obtained from the repeated electrochemical cathodic treatment of surface modified IMEs.

**Figure 2-6**: Cyclic voltammograms of four Pt-based IMEs (panels A, B, C and D) after cathodically treated for 20 cycles at 0 - 1.2 V vs. Ag/AgCl, 3 M KCl at 100 mV/s in 1M PBS at pH 7.38 being surface modified with OTS. (A) IME_1-Pt, (B) IME_2-t, (C) IME_3-Pt and (D) IME_4-Pt. are a comparison of cleaned Pt-electrode (Black, 1st cycle, Red, 18th cycle and Blue, 20th cycle.)
All Panels show the result of the electrochemical cleaning protocol to return the Pt. electrodes on the IMEs to a condition similar to the originally cleaned state while OTS stayed on the glass spacings between the working electrodes. As observed, for each first cycle, the redox curve differs from the 20th cycle. However, as the cleaning process continues, the electrodes get cleaner, and the cycles follow the same pathway. Examples are that of cycles 18th and 20th for each panel. Removing the OTS from the working electrodes provide a surface, where the expectation for interaction (charge transfer) occurs primarily between the interface of functionalized SWNTs and the metal electrodes. Such is examined through characterization techniques, including electrical impedance spectroscopy, IV characterization, multiple scan rate cyclic voltammetry (MSRCV) (discussed in Chapter 3), and electronic application demonstrated.
2.7 REFERENCES


CHAPTER 3: CHARACTERIZATION TECHNIQUES

3.1 OVERVIEW

Functionalized nanotubes can exhibit an extensive range of potential photonic and optoelectronic properties whose changes can be measured. For example, Raman spectroscopy samples can be assessed from functional group presence and sp$^3$ content (the latter based principally on D-mode intensity). For this research, Raman spectra were acquired using a Raman microscope system (Olympus BX41, Jobin Yvon Horiba) with the application of 632.5 nm laser radiation. By applying the scanning electron microscope (SEM – Zeiss Supra 55VP) technique, coupled with Genesis EDAX; the surfaces of the functionalized SWNTs were examined, and the presences of functional moieties measured. Additional assessments for characterization of functional groups included thermogravimetric analysis (TGA/DTA) and FT-IR measurements (Varian 7000 FTIR). Also, surface topographical imaging of devices, using TopoMetrix Explorer AFM was taken; mainly to show the bridging of SWNTs with interdigitated electrodes. The electrical conductivity of the materials were realized with Electrical Impedance Spectroscopy (Solartron 1260A Gain-Phase Analyzer) and Keithley 4200 S used for IV characterization. The electrochemical research was done with a PAR 283 Potentiostat/Galvanostat (Princeton Applied Research) equipped with PowerSuite® software.

3.2 IMAGING MICROSCOPY: AFM, SEM AND EDX

In this segment, a brief discussion on the imaging of SWNTs on interdigitated electrode devices and blank-IME with AFM and SEM is undertaken. AFM allows for the formation of high-resolution topographic image of a surface by taking the measurement of the force (attractive
or repulsive) that oscillates between the scanning tip and the sample. This measurement can show the height of the sample surface, as in this case, that of the nanotubes and electrodes. Binnig et al. invented the AFM in 1986,\textsuperscript{1,2} as part of the Scanning Probe Microscopy (SPM) family. Since then, AFM has become an important and useful method for surface scanning probe investigation that senses forces as Pauli, electrostatic, Van der Waals, on so forth. Fig. 3-1 illustrates the basic idea of the AFM. The cantilever has a sharp tip, usually made of silicon, with a radius relating to few nanometers. By the cantilever interaction with the sample surface, the force acting on the tip causes a deflection the cantilever (\textit{Eq. 3.1}). This deflection is measured by a laser beam that is reflected from the mirrored surface on the back of the cantilever onto a split photodiode, thus revealing information about the topography of the sample.

\begin{equation}
F = ks; \quad \textit{Eq. 3.1}
\end{equation}

Where, $F$ is the force from the cantilever spring, $k$ is the cantilever spring constant, and $s$ is the deflection of the cantilever.

\textbf{Figure 3-1:} Schematic diagram of AFM setup apparatus basic components; adapted from ref. \textsuperscript{3}
For the investigation of carbon nanotubes and devices, the TopoMetrix Explorer Scanning Probe Microscope (SPM) was employed. The system resides on an active air vibration table. All measurements were carried out at the room temperature. The TopoMetrix scanning tip method is a unique feature that allows for the imaging of any diameter or thickness. In the contact AFM mode, silicon nitride cantilevers (AFM #1520) were used. The nominal resonance frequency of the cantilevers is 17 kHz, with force constant of 0.32 - 0.064 N/m in thickness and the probe curvature radius of < 50 nm. The measuring tip with the attached cantilever detection system was mounted on the piezotube scanner. The AFM permits high-resolution scanning topography images in ranges of 200-µm x-y with 10-µm z range and 2-µm x-y with 0.8-µm z in air.

For topographical images of single-walled carbon nanotubes placed on interdigitated electrodes mounted on borosilicate glass substrate, the contact AFM method was selected. The reason for selecting this technique is that it is proven to be advantageous for characterizing solid, stable samples like carbon nanotubes. The main focus of the AFM technique applied to Blank-IME and decorated SWNTs devices is to confirm the cathodic cleaning of the Blank digits and that the placement of SWNTs samples bridged the fingers of the IME device. Topographic imaging of the surfaces was produced by rastering the tip over the SWNT-device, capturing the displacement of the x, y, z-piezo mechanism as a function of position. The amplitude of oscillation from 100 nm to 200 nm, cantilever oscillated at the resonance frequency of 100 kHz were used. The AFM provided two and three-dimensional topographic images of the sample
surface, including height of SWNTs on the surface of interdigitated device with a high degree of accuracy and precision.

Electron microscopy (EM) is the dominant technique use to view carbon tubes and nanodevices. Electron microscope uses electron beams to illuminate the sample; providing a magnified image. Electron microscopy is associated to the scientific revolution of electrons discovery (1897). However, its electron imaging was achieved by German engineers Ernst Ruska and Maximillion Knoll in 1931, having the competence of magnification to the 400th power. Nevertheless, the first prototype was constructed by Ruska in 1933 with a revolving capability to 50 nm. With continued progress to the evolution of the electron microscope, the first practical EM was built in 1938 at the University of Toronto by Burton and his group. EM is similar to a light microscope. However, EM produces greater resolution. All electron microscopes use electrostatic and electromagnetic lenses to control the electron pathway for image focusing. As electron beam travels in the direction of the sample, down the central component, the column of the electron microscope, it is exposed to apertures, electron gun, the acceleration field and focusing lens, which influenced the size of the beam. For SEM to operate, a vacuum is required. As the beam interacts with the sample, several signals get generated due the emission of secondary electrons from the sample surface and other sensor signals, producing a different image.
Figure 3-2: Schematic of an SEM, adapted from ref. 5

SEM is a type of EM applied in this thesis for surface characterization of materials. With the use of Zeiss Supra-55 VP SEM, images of SWNTs and its devices were acquired more quickly than AFM. However, dissimilar to the AFM, the SEM does not provide quantitative information about the tubes’ height. Also with SEM, some charging effects at high resolution were experienced during some study. High energy electron beam gets focused on the sample surface. With the interaction of the electron beam and sample, the emission of electrons across
the sample surface provide detailed image that is produced by signals of secondary electrons (SE), backscattered electrons (BSE), and characteristic X-rays.

Secondary electrons, the most common imaging mode, which rely on the interactions of the electron beam interacting with the atoms close to the sample surface and is the result of inelastic scattering. SE imaging can be achieved at high resolution with less than 1 nm. The brightness of signal output for SE is greatly dependent on the amount of electrons that are detected. Backscattered electrons are of higher energy, elastic scattering, which originate from the beam electrons that are reflected from the sample. BSE is important for investigating the chemical compositional contrast the sample surface as BSE signals are strongly related to the atomic number of sample. SEM is used for surface characterization, alongside energy dispersive X-ray analyzer (EDX), which provides elemental identification and quantitative compositional data. This technique relies on the interaction of X-ray excitation and the sample. Here, X-ray beams get focused into the sample causing excitation of an electron on the inner shell of the atom. Electron is then emitted, leaving electron hole. The electron from the outer shell fills the hole. During the process, the energy of emitted X-rays from the sample is measured by an energy-dispersive spectrometer. Since the energy of the X-rays is distinctive to different energy shells and the atomic structure of elements, the elemental composition of the sample is calculated. The samples used for SEM/EDX characterization were dispersed in ethanol, followed by ultrasonic vibration with Branson 2510 sonicator for 5 min. Suspension was then pipetted (a drop) with disposable glass pipette onto a copper grid for analysis. SEM analysis
was conducted using 5kV with working distance of 6 to 8.5 mm. For EDX analysis, the voltage of 15kV and working distance of 8.5 mm were engaged.

### 3.3 RAMAN SPECTROSCOPY

To characterize single-walled carbon nanotubes, Raman scattering is a valuable technique that has been employed. It is said to be the most sensitive characterization tool for CNTs and requires very little, to no sample preparation.\textsuperscript{7,8} This technique is used to observe vibrational and rotational excitations and low-frequency modes within a system and is dependent on inelastic scattering of monochromatic light, typically from a laser source. Herein work, Raman spectroscopy is also used to characterize covalently functionalized SWNTs.

Typically, monochromatic laser beam illuminates a sample. The illuminated light from the sample is collected with a lens and is then directed through a wavelength selector, from which Raman spectrum of the sample is obtained. A fraction of the scattered light is the elastic, intense Rayleigh scattering while another fraction is the inelastic, weak Raman scattering. For Raman scattering procedure, the incident photon energy excites the vibrational modes of the molecules producing scattered photons with energy than that of the incident photons. These scattered lights show lines that are below the Rayleigh scattering peak. This outcome leads to Stokes scattering (lower frequencies) and anti-Stokes scattering (higher frequencies) as seen in Figure 3-3.
Raman spectroscopy is measured by shifts in wavenumbers, which is due to the Raman effect or scattering.

\[ \text{Raman shift} = \bar{\nu} \pm \nu_m \quad \text{Eq (3.2)} \]

where \( \bar{\nu} \) represents the wavenumber (cm\(^{-1}\)) of the incident rays, and \( \nu_m \) is the wavenumber (cm\(^{-1}\)) for the difference in energy amid the lowest and first excited vibrational energy levels.

The two important Raman modes observed when characterizing SWNTs are radial breathing mode (RBM) and tangential G band mode. The RBM is unique to CNTs, not seen in other carbon materials. The frequency of the RBM mode is proportional to the inverse of carbon nanotube’s diameter. Typically, RBM frequencies are in the range of 100 to 500 cm\(^{-1}\). For the G band of SWNTs, there are primarily two strong peaks around 1580 cm\(^{-1}\). Another significant peak, mainly for characterizing the functionalization of SWNTs is the second-order scattering D-
band, observed at about 1350 cm\(^{-1}\). This peak is referred to as, disorder band and is related to sp\(^3\) hybridization of carbon in the hexagonal structure of carbon nanotubes.\(^{10}\) Another feature in Raman spectra of CNT is the G’ band, which is also a second order scattering mode observed at a frequency around 2700 cm\(^{-1}\). In this experiment, the RBM and the relationship between the D/G-band modes are important features seen for the functionalization of SWNTs. The collection of Raman spectra was accomplished by using an HR800 Horiba Jobin Yvon Raman Microprobe. Solid samples were placed on a cover glass and excited with 632.8 nm HeNe laser radiation; magnification of x100 obje lens was used, and the spectrum was recorded from 100 to 3500 cm\(^{-1}\).

### 3.4 FOURIER TRANSFORM INFRARED (FTIR) SPECTROSCOPY

FTIR is a spectroscopic procedure used for the determination the presence of functional groups and structural analysis of materials. The first spectrophotometer used for taking an infrared spectrum was created in 1957 by Perkin-Elmer.\(^{11}\) However, the first commercialized FTIR spectrometer was established by the then Digilab.\(^{12}\) The theory of Fourier transform is to shine a beam of infrared light covering a broad wavelength onto the sample by way of an interferometer. The wavelength of light gets filtered by beamsplitter, generating different spectrum. The objective is to measure how much light transmitted light gets absorbed at each wavelength by the sample. The study of absorption features reveals information of the molecular structure of the sample.

Contrasting Raman scattering, IR needs that the vibrational mode of the molecule has a change in dipole moment. At this junction, the radiation of the same frequency will interact with
the molecule causing promotion to an excited state. The vibrational mode of a molecule can be either linear (3N-5 degrees of freedom) or nonlinear (3N-6 degrees of freedom).

In this work, Fourier-transform infrared (FTIR) spectra were visualized using Varian 7000 spectrometer (Figure 3-4) in the range of 400-4000 cm\(^{-1}\) with a resolution of up to 8 cm\(^{-1}\). Both KBr pressed pellet and the attached MIRacle single horizontal reflection Attenuated Total Reflectance (ATR) accessory were used for identifying the functional groups on the sidewall of SWNTs. For immediate sample analyzer with FTIR-ATR with Varian 7000, SWNTs samples were placed directly onto the germanium crystal for data acquisition. For KBr method; samples were prepared with the use of KBr pellet kit. Functionalized SWNTs sample of 1mg was thoroughly ground with a mortar and pestle. 100mg of anhydrous KBr was added and carefully mixed. Portion of a mixed sample was added to bolt and pressed into a pellet for analysis.

![Varian FTS 7000 FTIR spectrometer and UMA 600 Microscope (Dr. Akins’s lab).](image)

**Figure 3-4:** Varian FTS 7000 FTIR spectrometer and UMA 600 Microscope (Dr. Akins’s lab).
3.5 X-RAY PHOTOELECTRON SPECTROSCOPY

X-ray photoelectron spectroscopy (XPS) is closely related to the methods of EDS. The emitted electrons are employed in a manner similar to that of Auger Electron Spectroscopy (AES). The technique of XPS is based on Einstein’s idea of the photoelectric effect, founded in 1905. However, the XPS technique was developed by Dr. Kai Siegbahn (awarded the noble prize in Physics, 1981) and his research group during the mid-1960. XPS is now one of the most widely used surface analytical techniques. Its use is to penetrate the depth of 1 to 10 nm of the sample surface, measuring its elemental composition. The basic mechanism of XPS occurs, the electronic stated of atoms below the surface of the sample get excited by X-ray beams of specific energy and core electrons get ejected. Information on the emitted electrons, such as, the kinetic energy (KE) and the amount of electrons is used to calculate the binding energy (BE), which is the element used in the chemical characterization of the sample by XPS equipment. The unit for binding energies is electron volts (eV). The binding energy is defined by means of Equation 3.3, which illustrates the energy required to remove an electron from its neutral level to the vacuum level.

\[
BE = h\nu - (KE + \phi) \quad Eq \ (3.3)
\]

Where, \( KE = \) Kinetic Energy (measure in the XPS spectrometer), \( h\nu = \) photon energy from the X-Ray source (controlled), \( \phi = \) spectrometer work function and \( BE = \) is the unknown variable.

The main components of XPS system are illustrated in Scheme 3-5. Chemical structure of the functionalized SWNTS was observed by the X-ray photoelectron spectroscopy (PHI5600 at
Leibniz Institute for Solid State and Material Research, Dresden, Germany) equipped with a monochromatic AlKα source (1486.6 eV). The Monochromatic X-ray beam irradiated the photoelectrons from a limited depth of 10 nm of the sample surface. In an ultra-high vacuum condition, the base pressure of $5 \times 10^{-10}$ mbar was applied to avoid excessive surface contamination. The kinetic energy of emitted photoelectrons from the sample was measured by the Cylindrical Mirror Analyzer (CMA). Spectral resolution of 0.5 eV was applied as the spectrum plotted by the computer from the analyzer signal. The binding energies determined from the peak positions and the for C 1s, N 1s, F 1s, and S 2s edges of the samples were identified.

**Figure 3-5:** illustrates the sketch of the side view of XPS system (Dr. Rümmeli’s Lab)

### 3.6 THERMOGRAVIMETRIC ANALYSIS

Thermogravimetric Analysis (TGA) is a technique used in studying the properties of the material as it relates to temperature increase at a constant rate. This sensitive technique characterizes the material by measuring the weight change of the sample as the temperature
increases. These changes in weight are often due to loss of volatile compounds, decomposition and oxidation processes. It is specifically useful in determining the organic components in a sample as it is commonly used to determine the functional groups attached to the side wall of carbon nanotubes.

All TGA experiments were performed on a combined TGA/DSC (TA Q600). Around 12 mg of SWNTs sample was loaded into the alumina crucible while the reference cell was kept empty. The sample and reference cells were maintained at 25 °C for 5 minutes, after which they were heated from 30 to 1000 °C at a rate of 10°C/min under an inert atmosphere with nitrogen gas, with a flow rate of 100 mL/min. As the temperature increases, the detection material’s weight loss is recorded. This loss is a result of emitted moisture and decomposed functional groups at a particular temperature. In general, this technique helps in determining some degree of functionalization to the SWNTs; confirming functional moieties on the sidewall of the tubes.

3.7 ELECTRICAL IMPEDANCE SPECTROSCOPY & IV CHARACTERIZATION

Electrical Impedance measures the resistance induces by a circuit to the current when a voltage is applied. The introduction of electrical impedance was by Oliver Heaviside around the mid-1880s. This theory was thereafter developed in the form of vector diagrams and complex image by Arthur Kennelly in 1983. The two most common plots to understand the results of electrical impedance analysis and relate them to physical properties of the sample are the Nyquist plot and the Bode plot. The Nyquist plot displays $Z''$ against $Z'$. This is often used as it allows an easier prediction of the equivalent electronic circuit. The Bode plot displays the phase angle against the frequency, which allows for the determination of the absolute value of the magnitude
of impedance $|Z|$ and the phase shift. The magnitude $|Z|$ of impedance is related to the ratioed of
the amplitude for both voltage and current at a particular frequency ($\omega$). The phase angle ($\phi$) of
impedance relates to the current lagging the voltage.

Unlike a resistance that relates only magnitude, impedance communicates both
magnitude and phase, making it an important model for electrical engineering. Ohm’s law as it
applies to resistors in DC circuits, states that, $R = V/I$; $R$ being the resistance; $V$ is the applied
voltage, and $I$ equals the current. The alternate quantity for AC is the impedance $Z$ which is a
more complex quantity than $R$. For a complex system, the magnitude and phase impedance is
determined by resistance and reactance (capacitors and inductors) as shown in the modulus:

$$|Z| = \sqrt{ZZ^*} = \sqrt{\text{Real}^2 + \text{Imaginary}^2}; \theta = \text{arc tan}(Z^*/Z)$$

Impedance of an ideal resistor, that is, the resistance forms the real part of the impedance
as shown in the electrical conductivity analysis for the functionalized SWNTs. The data illustrate
different levels of real resistors. Here, one can state that the voltage and current waveforms to be
proportional and in phase as shown in Figure 3-6, exhibiting no phase shift, making $Z = R$.

![Voltage & Current in phase](image)

**Figure 3-6:** AC circuits the phase angle $\phi$ between the voltage and the current is zero.\textsuperscript{17}
For AC circuit: The voltage across the resistor and the current flowing in the resistor can be written as \( V_R = V_{\text{max}} \sin \omega t \) and \( I_R = I_{\text{max}} \sin \omega t \), respectively; where \( \omega = 2\pi f \), \( \omega \) is the frequency in \( \text{s}^{-1} \), and \( f \) is the frequency in Hz, \( V_m \) is the maximum peak to peak voltage, and \( V_R \) is the voltage at any point in time.

Reported works\textsuperscript{18,19} have shown electrical impedance spectroscopy to be a useful technique for exploring the electrical behavior of polymer film and solid state devices as it relates an alternating current with an adaptable frequency. In this work, electrical impedance spectroscopy was performed using a Solartron 1260 Frequency Response Analyzer (Solartron Analytical). All impedance experiments were carried out in a co-planar, two-electrode mode to measure the impedance between the digits of the interdigitated microsensor electrodes. Devices were studied at RT in Air and, in 1 mL of PBS buffer at pH = 7.38. The analysis of peak-to-peak sine wave at 40 mV was conducted over the frequency range of \( 10^{-1}-10^{6} \text{ Hz} \). The impedance analysis presented in this work resulted in standard electronic circuits composed of different levels of SWNTs resistors.

I-V Characterization was performed in air (-1.0 to +1.0 V) using a Keithley 4200 Semiconductor Characterization System connected to a probe station via a switching matrix and was run using the Keithley Interactive Test Environment (KITE) software.

3.8 ELECTROCHEMICAL METHOD: CYCLIC VOLTAMMETRY

Electrochemistry studies the chemical reactions that take place in a solution at the interface of the electrode and the electrolyte. This process includes the application of an external
potential difference across the interface, resulting in the current response. Electrochemical reaction\textsuperscript{20,21} involves the transfer of charge by way of an electron or ion. An example of such process is oxidation/reduction (redox reaction). This involves the transfer of at least one electron from a chemical species to another, which induces a change in the oxidation state of the species. The method of the redox reaction is guided by Faraday’s law, which states, the quantity of reacted species is directly proportional to the current passing through the cell. The two processes in a redox reaction involve the loss of electrons (oxidation) and the gain of electrons (reduction).

The electrochemical process executed in this work is the cyclic voltammetry (CV). Cyclic voltammetry\textsuperscript{22} is a potential-controlled technique and usually consist of a three electrode system. The current measured between the counter and working electrodes is a function of potential difference that is applied amid the reference and working electrodes. The current response is plotted as a function of voltage. In the event of a reversible reaction, the species is sequentially being oxidized and reduced. During CV, a cyclic potential waveform is applied. In this case, the voltage is swept in two parts, a forward and reverse sweep. In the IUPAC convention, these sweeps are either increasing potential (anodic), with a reverse decreasing potential (cathodic) or vice versa (in other conventions). Figure 3-7 illustrates a typical cyclic voltammogram that is achieved from redox couple system and how to calculate the anodic and cathodic peak currents ($I_{p_a}$ and $I_{p_c}$, respectively). $E_{p_a}$ and $E_{p_c}$ are the peaks potentials at the anode and cathode, respectively.
**Figure 3-7:** Schematic representation of a cyclic voltammogram in an electrochemical reaction.

For a reversible system, the ratio of the anode peak current ($I_{pa}$) and the cathode peak current is equal to one: $I_{pa}/I_{pc} = 1$. Randles-Sevcik equation: governs this:

$$i_{pa} = 2.687 \times 10^5 n^{3/2} \sqrt{v} D^{1/2} A C_{red} \quad Eq. 3.4$$

Where $n$ represents the number of electrons associated with the charge transfer, $v$ is the scan rate, $D$ is the diffusion coefficient of the redox species in the electrolyte, $A$ is the electrode surface area and $C$ is the concentration.

In this work, investigation for multiple scan rate voltammetry (MSRCV) was conducted using a three-electrode system, which includes working, counter and reference. This electrochemical setup was connected to a PAR 283 Potentiostat/Galvanostat (Princeton Applied Research) equipped with PowerSuite® software. MSRCV was carried out in freshly prepared 1X PBS (pH = 7.38) containing 50 mM [Fe(CN)$_6$]$_{3-4}^-$ at room temperature. The platinum and gold interdigitated microsensor electrodes (IME 1025-M-Pt-U and IME 1025-M-Au-U), and micro Ag/AgCl electrode (3 M Cl$^-$) were used. During this process, voltammograms were
accomplished by scanning through potential range of 10 to 300 mV with given scan rates of 10, 25, 50, 100, 150, 200, and 300 mV/s, for three sweeps potential between 0V and 0.5V vs. Ag/AgCl.

3.9 SUMMARY

In this chapter, we have explained the principle of the experimental techniques used in the characterization processes of our functionalization SWNTs materials. Discussions on how functionalized SWNTs can be imaged using SEM were presented. Also, where the use of EDX determines the chemical distribution of functionalized elements attached to the sidewall of the tubes. The AFM is presented to be a dominant used in exploring the topography of carbon nanotubes and its electronic devices.

Spectroscopic techniques as Raman scattering, FT-IR, and XPS were also discussed, along with thermogravimetric analysis for their applicable use in identifying levels of functionalization of various groups to the sidewall of the SWNTs.

Introduction on the electrical characterization techniques, which include electrical impedance spectroscopy and IV characterization that were used to study the electrical conductivity of the pristine and functionalized SWNTs were discussed.

Finally, discussion on the electrochemical process and the use of multiple scan rate cyclic voltammetry to examined the effect of our functionalized SWNTs samples 50 mM [Fe(CN)_6]^{3-/4} was presented.
3.10 REFERENCES


(3) Goertz, M. P.; Moore, N. W. Progress in Surface Science 2010, 85, 347.


(9) Moxfyre 2009.


(11) Anal. Chem. 1957, 29, 94A.


(15) Heaviside, O. Electrical papers; Cambridge University Press, 2011; Vol. 2.

(16) Kennelly, A. American Institute of Electrical Engineers, Transactions of the 1893, 10, 172.
(17) Storr, W.; Basic Electronics Tutorials.


4.1 INTRODUCTION

Single-walled carbon nanotubes (SWNTs) are exciting candidates to use as active constituents in devices and sensors because of their nanoscale dimensions, high aspect ratios, large specific surface areas, and outstanding mechanical and electronic properties.\(^1\text{-}^8\) However, use of SWNTs for actual applications in devices and sensors has proven problematic due to their intrinsic chemical inertness, the difficulty to control their chirality (which imbues them with semiconductor or metallic electronic properties), and especially their extremely low solubility in most common solvents.

Other researchers have attempted to fine-tune the properties of carbon nanotubes through chemical functionalization in order to overcome the solubility challenge.\(^9\text{-}^{10}\) In general, it has been found that chemical functionalization of carbon nanotubes for solubility purposes also impacts chemical interaction specificity and sensitivity, as well as significantly alters a nanotube's physical, electronic and optical properties.\(^3\) Such alterations, in fact, can enhance the application potential for nanotubes as active agents in sensors and devices.\(^{11\text{-}20}\)

In this paper, we report results for an initial effort (with bromine atoms as the SWNTs adduct) that we have undertaken to modify the interaction affinity of SWNTs for sensing of a number of single component analyte vapors. Subsequent efforts will deal with other covalent adducts, with the aim of creating a finger-print response matrix for a given vapor component in a multicomponent vapor with the various covalently modified SWNT coated electrodes. The sensing system that we seek to develop would be able to measure, with high accuracy, the fractional
composition of the various components in a complex vapor, thus aiding in identifying the source of
the vapor. Such a system is broadly referred to as an e-nose.

4.1.1 BACKGROUND

Efforts at developing CNT-based gas sensors have centered primarily on two approaches to
transduce an analyte's signal (e.g., concentration) directly into an electrical signal. One involves
incorporation into a chemical field-effect transistor (ChemFET) configuration. The second involves
creation of a chemical resistor (Chemiresistor) element. In the ChemFET configuration the CNT or
an ensemble of CNT are electrically contacted across a source and drain. The conductance across the
CNT is then modulated using a gate, where, in essence, the gate is a third electrode capacitavely
coupled through a thin dielectric layer to the CNT or CNT ensemble.

In the Chemiresistor configuration, the conductance of a single tube or an ensemble is
measured across two electrodes. Obviously, creation of a Chemiresistor is simpler and cheaper to
produce, as well as requires less complex ancillary electronics to operate.\textsuperscript{21} Both the Chemiresistor
and ChemFET configurations can operate with either pristine or functionalized tubes. However, as
mentioned \textit{vide supra}, the use of functionalized tubes can lead to improved sensing performance
since, for example, the chemical affinity can be tuned to enhance sensitivity. The two main surface
functionalization approaches for CNTs involve noncovalent or covalent interactions. Noncovalent
functionalization is typically based on supramolecular complexation through van der Waals,
electrostatic and $\pi$-stacking interactions, that result in surface adsorption of molecules.\textsuperscript{22,23} Covalent
functionalization of CNT, as the name suggests, involves a covalent bond between the CNT and the
molecule or atom being attached, and is hence the more stable functionalization approach.
Typically, covalent functionalization is achieved by the esterification or amidation of carboxylic acid groups. Another useful functionalization strategy involves creation of halogen radicals. Usually the functionalization of carbon nanotubes with halogens is achieved by oxidizing F₂ gas, followed by electrochemical treatment with Br₂ and Cl₂, or using elemental iodine—through a modified Hunsdiecker-type reaction. Functionalization with halogens, which are electron-withdrawing entities, leads to the formation of carbon-halogen bonds, which create defect sites in the sidewalls of CNTs, resulting mainly in changes in the tubes' electronic properties. For example, Bahr et al. reported changes in the electronic conductivity of fluorine-functionalized SWNTs; they found a resistance > 20 MΩ as compared to 10 - 15 Ω for pristine SWNT.

In terms of bromine-based functionalization of CNT, the literature is quite sparse. A small number of publications have reported the bromination of the sidewall of a carbon nanotube. Mazov et al. have reported studies on multiwall CNT halogenation by means of direct vapor-phase bromination, and demonstrated a 2.5 wt.% yield, while Bulusheva et al. via XPS data obtained from the direct chemical vapor deposition synthesis of nanotubes show very high yields reaching 35 wt%. Colomer et al. have reported studies dealing with the bromination of doubled-walled carbon nanotubes through the use of a microwave-assisted, bromination technique.

To our knowledge, no studies have been reported that utilize photobromination to form bromine radicals from N-bromosuccinimide to promote the addition of bromine to the sidewall of SWNTs. Here, in pursuit of developing a platform for chemical sensing, we have identified a facile and efficient photobromination technique for the covalent sidewall functionalization of SWNT with
bromine. In this process the radiation source cleaves the bromine molecule into radicals by photolysis, *viz.*, homolytic cleaving induced by light. Specifically, the photons are able to break a molecular bond between molecular fragments in which the bonding electrons are evenly shared between the bonded atoms. After cleavage each of the previously bonded atoms receives one electron from the electron bond, resulting in the formation of bromine free radicals. The generated free radicals can then be expected to attack the CNT wall much like radicals do in diazotization that leads to conjugation with benzene.\(^{35}\) The process is illustrated in Scheme 4-1 below.

![Scheme 4-1](image)

**Figure 4-1:** Formation of brominated SWNT using N-bromosuccinamide (NBS) for bromine radical formation via photolysis in dichloromethane.

Remarkably high functionalization yields of between 15 - 25 wt.% are found for this photolysis reaction. To our knowledge, this is the highest reported bromination level of CNT. Herein, the as-produced brominated SWNT have been used as active agents for an electronic nose-type (e-Nose) applications aimed at vapor compositional analysis (*i.e.*, vapor analysis).

4.2 EXPERIMENTAL SECTION

4.2.1 SYNTHESIS TECHNIQUE AND SENSOR PREPARATION

The N-bromosuccinamide (99 %) was purchased from Sigma Aldrich. Dichloromethane (ACS: 99.5% stab. with amylene), chloroform (HPLC grade: 99.5% min) and diethyl ether (99+ %) were purchased from Alfa Aesar. Single-walled carbon nanotubes (purity: 95 wt.%) were purchased
from UnidymTM Inc., Sunnyvale, CA, with diameters and lengths quoted as ranging, respectively, from 0.1 to 1.2 nm and 100 to 1000 nm. They were used without further purification. The individual SWNTs diameters ranged from ca. 0.8 to 1.2 nm; with individual lengths of ca.100 to 1000 nm. The nanotubes are bundled as ropes; maximum density of 1.6 g/cm³. The moisture content for SWNTs dry powder was <5 wt.%. The synthesis procedure was conducted as detailed in Chapter 2 (see – Experimental section, 2.3).

4.2.2 CHARACTERIZATION TECHNIQUES

Raman spectra were collected using a HR800 Horiba Jobin Yvon Raman Microprobe spectrometer. Solid samples were placed on a cover glass and excited with a 632.8 nm HeNe laser radiation (x100 objective lens). Low voltage scanning transmission electron microscopy (SEM) measurements were accomplished using a Zeiss Supra 55VP Scanning Electron Microscope coupled with a Genesis EDX system. For surface topographical imaging of the SWNT mats created for the gas sensing electrodes, a TopoMetrix Explorer AFM was used in the contact mode. Fourier-transform infrared (FTIR) measurements were conducted using a Varian 7000 FTIR. For the FTIR investigations, the SWNT samples (ca. 1 mg) were mixed with KBr and pressed into pellets using standard procedures. Thermogravimetric investigations were accomplished on a TA Instruments Thermogravimetric Analyzer / Differential Scanning Calorimeter (Q600). For this latter system, ca. 12 mg of SWNT samples, pristine or Br-SWNT, were loaded into the sample cell with the reference cell left empty. The sample and reference cells were maintained at 25 °C for 5 minutes, after which they were heated at a rate of 100 °C/min in a nitrogen atmosphere, with a flow rate of 100 mL/min.
4.2.3 GAS SENSOR FABRICATION AND EVALUATION

To fabricate the gas sensors, the SWNT functionalized with bromine sample was first dispersed in mCresol (Sigma Aldrich: 98+ %), then spin-coated via WS-650S-6NPP/LTTE Laurell Technologies Co. spin coater onto a commercially prepared substrate consisting of an array of interdigitated, microstructured gold electrodes (see Chapter 2.6 for more detailed information on device fabrication). 3uL drops of f-SWCNTs in DMF were spun cast onto the interdigitated region of the IME chips spun at 2000 rpm for 3 min and followed by an added application of 6uL which was spun at 1000 rpm for 3 min. The SWNT mat coated electrode apparatus was then dried at 60 °C in a conventional oven for 10 to 15 minutes. The resulting electrically contacted SWNT mat served as the active sensing element. The device fabrication process is schematically represented in Scheme 4-2, while the AFM of SWNT-Bromine cross-linking on electrodes is illustrated in Figure 4-1.

![Schematic illustration of dispersed Br-SWNT, spin casting onto interdigitated Au electrodes (IDE), and IDE decorated with Br-SWNT.](image)

**Figure 4-2:** Schematic illustration of (a) dispersed Br-SWNT, (b) spin casting onto interdigitated Au electrodes (IDE), and (c) IDE decorated with Br-SWNT.
Figure 4-3: AFM images: (A) Br-SWNT mat bridging adjacent electrodes (acquired at scan rate: 32 μm/s). (B) 3D image showing scan of highlighted region in (A); note the presence of Br-SWNTs on electrode as well as in the channel between electrodes. (C) Highlighted Au electrode using semitransparent color.

The experimental setup for the sensor is provided in Scheme 4-3. It consists of two main subsystems: (a) The vapor delivery and distribution system, which allows one to initially purge the sensor environmental chamber with an inert gas and then to deliver selected quantities of analyte vapor and carrier gas (N₂, 0.025 l/min.) to the sensing chamber; (b) the response monitoring and data acquisition subsystem, which detects variations in the resistance of the brominated-SWNT mat that changes due to vapor molecule adsorption. In essence, analytes interact with the brominated-SWNT mat through weak dispersive or chemical forces. The interactions, which are related to the surface concentration of the analyte, perturb the electronic system of the mat, resulting in resistance changes, which are monitored and recorded using a lab built PXI-platform from National Instruments (NI), Model 1042.
4.3 RESULT AND DISCUSSION

4.3.1 CHARACTERIZATION OF THE BROMINATED-SWNTS

We compared the Raman spectra of pristine SWNTs and Br functionalized SWNTs (see panel A of Figure 4-5). In general, three key Raman bands are used as the fingerprint pattern of sp² bonds in carbon materials. These are the D-band (defect) at ca. 1350 cm⁻¹, the G-band (graphitic) at ca. 1600 cm⁻¹, and the 2D-band (second-order band) at ca. 2700 cm⁻¹. These bands are observed for all our samples, but with variations between the functionalized and pristine specimens. The G-band, which exhibits a Breit-Wigner-Fano line profile, broadens and upshifts (14 cm⁻¹) upon Br functionalization. Such a change is expected with bromine functionalization of SWNTs, indicating electron transfer between Br atoms and SWNTs.³⁸⁻⁴¹ The D-band is found to increase in intensity
relative to the G-band and to exhibit broadening and upshifting; the latter, as in the case of the G-band, arise from charge transfer. The increase in relative intensity exhibited by the D-band indicates a decrease in structural order of the SWNT, and can be attributes to the formation of vacancies and the loss of some sp² character on the nanotube's surface resulting from bond formation with the functional groups. And, since the photolysis reaction is not particularly harsh, the above changes are expected to be due to bromination alone. The radial breathing modes (RBMs), which lay between ca. 150 cm⁻¹ and 300 cm⁻¹, are found to be considerably weaker after the functionalization, consistent with the impact expected when mass is attached to the nanotubes surface.

Figure 4-5: Green and black traces in all panels refer to functionalized and pristine SWNT samples, respectively. (A) Raman spectra using 632-nm excitation for functionalized Br-SWT and pristine SWNT samples. (B) FTIR-KBr spectra of samples. (C) TGA and (D) DTA measurements conducted under pure nitrogen at heating rate of 10 °C per minute for the same samples.
FTIR measurements also show clear differences between pristine and functionalized samples (see panel B of Figure 4-5). The FTIR spectrum of the pristine sample shows a band at ca. 1590 cm\(^{-1}\) that is attributable to C=C vibration. This band is slightly upshifted in the brominated sample, consistent with stiffening associated with doping. In addition, a relatively intense new band appears at ca. 650 cm\(^{-1}\), which is attributed to a C-Br vibration\(^{43}\) and suggests the successful incorporation of Br atoms to the SWNT.

We also employed thermogravimetric analysis on samples prepared using a 24 hr photolysis reaction period. The data was compared to the pristine samples, as shown in panel C of Figure 4-5. The pyrolysis was conducted in a N\(_2\) atmosphere up to a temperature of 1000 °C. The pristine SWNT are relatively stable and thermogravimetric analysis resulted in a weight loss of 10% at 1000 °C. In the case of the brominated SWNT samples, the weight loss rate changed significantly at ca. 210 °C, followed by a further loss at ca. 350 °C (see the derivative data in panel D of Figure 4-5). The weight loss between the two regions can be attributed to thermal decomposition involving Br atoms and suggests a 15 wt.% (± 2 wt.%) loss, in good agreement of the EDX data (ca. 17 wt.%). A further decomposition step occurs between 510 and 600 °C, attributable to the decomposition of the SWNT.

SEM investigations of the specimens showed no discernible differences between the pristine and Br-functionalized samples in terms of their morpholog (e.g., see Figure 4-6A), but elemental analysis data presents the elements on the surface of the nanotubes (see Figure 4-6B). Energy dispersive spectroscopy (EDX) was also used as this can show the level of bromine species present in the samples. Measurements were made for multiple samples that underwent the photolysis reaction for 12, 24 and 48 hrs (Table 1); the EDX measurements indicated values of 7, 17 and 15
wt.% (± 4 wt.%), respectively. In Table 1, the data shows that the incorporation of Br species reaches a saturation limit that does not increase for reaction times longer than 24 hrs. The above levels of Br incorporation substantially exceed previously reported values that reached yields only up to 8 wt.% 27,36

Figure 4-6: (A) SEM surface and (B) elemental analysis of Br-SWNT sample.

Table 4-1: EDX elemental data for different Br-SWNT samples and their synthesis times

<table>
<thead>
<tr>
<th>Wt.%</th>
<th>At.%</th>
<th>Synthesis Time (hrs.)</th>
<th>Br-SWNT Samples (†)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.80</td>
<td>2.21</td>
<td>48</td>
<td>C</td>
</tr>
<tr>
<td>14.47</td>
<td>2.54</td>
<td>48</td>
<td>C</td>
</tr>
<tr>
<td>18.27</td>
<td>3.36</td>
<td>48</td>
<td>C</td>
</tr>
<tr>
<td>19.85</td>
<td>3.68</td>
<td>24</td>
<td>B</td>
</tr>
<tr>
<td>16.95</td>
<td>3.22</td>
<td>24</td>
<td>B</td>
</tr>
<tr>
<td>15.81</td>
<td>2.87</td>
<td>24</td>
<td>B</td>
</tr>
<tr>
<td>7.52</td>
<td>1.24</td>
<td>12</td>
<td>A</td>
</tr>
</tbody>
</table>

† Sample A was brominated for 12 hrs.; 3 different representative samples B were each brominated for 24 hrs.; 3 different representative samples C were each brominated for 48 hrs.
4.4 GAS SENSING WITH BR-SWNT

Because of the polar nature of halogen-carbon bonds, the hydrogen bonding capacity of halogen functionalized sp³ carbon is improved resulting in enhanced affinity of the functionalized carbon species for aliphatic vapors or small molecular volatiles. To assess the gas sensing potential of Br-SWNT, we exposed Br-SWNT sensors to various one component vapors independently. The vapors used were HCl, NH₃, HNO₃, C₃H₆O, C₂H₃N, C₂H₄O₂, H₂SO₄ and N,N-dimethylacetamide.

To conduct a measurement, initially, a baseline was established under a pure N₂ flow for at least 1 min. Then the sensor was exposed in periodic cycles of pure N₂ followed by carrier gas N₂ containing a selected analyte vapor and the sensor's response was measured. The sensor showed high sensitivity to the eight volatile compounds mentioned above for concentrations varying from ca. 286 to 1645 ppb. The concentrations calculated primarily from the measurement volume, specific density at 20 °C, the flow rate of the carrier gas, and molecular weights of compounds. Table 4-2 provides the calculated concentration for each analyte mixture. Injection of the analyte vapor was externally controlled by a solenoid driven valve and a flow meter.
Table 4-2: Concentration of analytes exposed to Br-SWNT gas sensor element

<table>
<thead>
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<td>1.284 x 10^6</td>
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Figure 4-7 shows the resistance response of the brominated SWNT sensors to the various vapors, as ethanol, HCl, ammonia and sulfuric acid (A comprehensive set of responses for all the vapors investigated is provided Figure 4-7). The shapes of resistance response curves differ for the various analytes. The simplest interpretation of the shape of the response to the presence or absence of analyte in the flow mixture is that adsorption buildup occurs when the analyte is flowing, while when the flow of analyte is terminated, desorption occurs, as the carrier gas sweeps the analyte off of the electrode. This model suggests the possibility to differentiate between analytes based on measurement of their different response curves. Our analysis scheme is to determine the ratios of the response function areas when the analyte was present in the vapor (i.e., the "on-time" area) to that when the flow of analyte is not present (i.e., the "off-time" area) as a function of the percentage change in resistance (R); i.e., $\Delta R\% = (R-R_o/R_o)\times100$, as shown in Figure 4-8.
Figure 4-7: Sensing profiles for the Br-SWNT coated electrodes. Analytes used for panels (A) through (D) are, respectively, ethanol, HCl, ammonia and sulfuric acid. Response data in panel B has been amplified by a factor of 6 for easier viewing, but true signal magnitude is provided by lower smaller response.

Figure 4-8: Represents schematic for parameters ΔR and "vapor-on" and "vapor-off" areas, whose values are used for determining parameters used in Figure 4-9 below.

Figure 4-9 represents random response cycles of area ratios for several cycles of the various response curves (for the different analytes) shown in Figure 4-7 and Figure 4-10 as a function of
ΔR%. The net effect of choosing different cycles for a given analyte is to define the inherent uncertainty to be anticipated for any given measurement. Additionally, when the random cycle measurements cluster together, as depicted in panel B of Figure 4 for several of the analytes, one can conclude that if a subsequent measurement of an area ratio for a single cycle (or the average of several cycles) for an unknown analyte falls within the cluster region, then the identity of the analyte can be inferred to a high level of confidence.

![Graph showing clustering of area ratios for 7 analytes vapors exposed to SWNT-bromine sensor. The dashed ellipsoids enclose suggested clusters. The vapors used were A- ethanol, B- HCl, C- acetonitrile, D- N,N-dimethylacetamide, E- ammonia, F- acetic acid and G- nitric acid.]

**Figure 4-9:** One finds clustering of area ratios for 7 analytes vapors exposed to SWNT-bromine sensor; the dashed ellipsoids enclose suggested clusters. The vapors used were A- ethanol, B- HCl, C- acetonitrile, D- N,N-dimethylacetamide, E- ammonia, F- acetic acid and G- nitric acid.

In addition to analyte profiles presented in Figure 4-7, Figure 4-10 below shows a more comprehensive exposure curves with additional analytes that is also represented in the clustering illustration (see Figure 4-9). Added sensing curves are for instance, that of acetonitrile, N,N-dimethylacetamide, acetic acid, nitric acid, and 2-propanal. With our covalently functionalized
technique of adding bromine to the side walled of single-walled carbon nanotubes and its exposure to analytes, a range of analyte affinity to SWNT-Br based sensor was observed. Once more, from a series of data resulting from a number of experimental runs, we were able to identify, what might be termed, a number of individual "data vector components" based on their repeatability and the uniqueness of the analysis information that they engender. Fig. 4-10A through 4-10l show the typical response time profiles of a SWNT-Br sensor during six cycles of On/Off exposures to various vapors. The resistance of the sensor changes during the absorption and desorption processes. The observed response patterns vary, with the response showing strong correlation to physisorption and/or chemisorption of the sensing material for a particular vapor. The covalently functionalized process with bromine maybe induce and or enhance reactivity to various analytes, simply by shifting the Fermi level and thus changing the nanotubes’ electronic properties. This maybe as a result related the cause of –ve (n-type) or +ve (p-type) charge doping of electronic bands with is due to added moiety to the side wall of the nanotubes. In our case, the formation of covalent bond between bromine and the sidewall of nanotubes may resulted in the formation on n-type semiconducting system, with bromine being an enriched dopant due to its excess valence electrons compared to carbon’s (4) valence electrons causing shift of the Fermi level toward the conduction bands. With that, there is the expectation for interaction between the π covalently functionalized sensing layer and the different exposed analytes. This will cause changes in the conductivity of the material, and as a result, induce an increase or decrease in resistance. These experimental exposures of sensing layers to analytes show significant changes in the resistance values, with rapid adsorption and desorption kinetics, unique patterns, and other characteristics such as reversibility, reproducibility, sensitivity and selectivity towards analyte. The changes in resistance
of all sensors show diversity from one vapor to another, which maybe the result of interactions involving weak surface van der Waal forces, and or the interpolation of vapors, thus creating chemisorption with the sensing layer. As a result, some vapor interactions show very good baseline recovery, while, for others, a saturation phenomenon is suggesting, and thus, the signal does not show full baseline recovery. The SWNT-Br sensor upon exposure to some vapors, show substantial relative baseline recovery after each cycle as in the case of HCl (4-10B), ammonia (4-10C) and acetonitrile (4-10E) vapors, while for the other vapors, the desorption process (Off cycles) experienced an incomplete baseline recovery, which maybe the outcome of a chemisorption or the need for a longer desorption period (Off) to enable baseline recovery; in future work, the investigation of this view point will be conducted. Upon scrutiny of Fig. 4-10A, noticeable difference based on vapor/sensor interaction response is observed for HCl, nitric and acetic acid. The sensor exhibits lowered resistances when exposed to these three acids, possibly revealing the formation of a higher electron conducting material. This perhaps owing to change of the density current carriers in the nanotubes, this therefore caused an increase in the electrical conductivity. Vapors that induce an increase in resistance of the SWNT-Br sensor, perhaps through an adsorption process, where the vapor caused expansion of material,\(^{46}\) which change the percolation and consequently reduce the conductivity. Overall, SWNT-Br shows crucial sensitivity to a series of vapors, measurements illustrated that absorption and desorption rates of exposed analytes show levels of reversibility and repeatability. Observed also is the distinctiveness of each sensor/vapor profile, which indicates the capability to differentiate a vapor based on the shape of the response curve.
Figure 4-10: Sensor response data of the gas sensor using Br-SWNT as sensing agent for (A) ethanol, (B) HCl, (C) ammonia, (D) sulfuric acid, (E) acetonitrile, (F) N,N-dimethylacetamide, (G) acetic acid, (H) nitric acid, and (I) 2-propanol.

4.5 CONCLUSION

We have demonstrated a facile and efficient means of functionalizing SWNT with Br based on a UV photolysis synthesis route. The functionalization yield is significantly improved compared to those reported using other approaches. In addition, we show for the first time, that the profile of the response curves for gas chemiresistor sensors could provide a means for analyte selectivity, in other words, gas identification. The paper presents interesting data on bromination of SWNTs and their utilization as gas sensors. The developed approaches on functionalization and sensing are rather
original and can be expanded on other carbon materials, as the studies on covalently functionalized brominated carbon materials, and also their demonstration of possible application are rare.
4.6 REFERENCES


CHAPTER 5: Chemiresistive Responses of Brominated SWNTs on Au and Pt Electrode Arrays

5.1 INTRODUCTION

The need is there for advanced synthetic molecular chemoreceptors, both in the design and development of all electronic natural olfactory sensor emulators (e-NOSEs).\(^1\) The e-nose uses a combination of diverse, non-specific gas/vapor sensors that respond to a wide range of odorants, resulting in identification and quantitation of the agent that gives rise to a specific vapor.\(^2\) Various e-nose sensor technologies have been developed and are characterized by their selectivity, sensitivity, sample consumption, composition, fabrication method, sensing mechanisms, types of vapor-sensor interaction, response and recovery times, response to temperature and humidity influences, reproducibility, lifespan, and signal processing system.\(^3\) The e-nose sensor architecture most often uses an array of 8 to 32 cross-specific sensor elements of varying-sensitivity. Thus, an odorant’s signature consists of a pattern of responses from a group of such sensors, not just one sensor. E-nose sensor array elements typically comprise a chemically-sensitive material (i.e., one that reversibly interacts with the volatile organic compounds of an odor) on a chip consisting of a pattern of electrodes on a glass or silicon substrate. Both piezoelectric\(^4\) and conductivity\(^5\) technologies have been shown to be good e-nose transducers. The piezoelectric sensor family includes quartz crystal microbalance (QCM) and surface acoustic wave (SAW) type systems. In the former, odorant adsorption changes sensor mass and dielectric properties, respectively causing changes in oscillation frequency. On the other hand, the conductivity sensor family, which involves metal oxide and polymer materials, function as follows: for the metal oxide sensors, odorants interact with a heated sensor (generally
above 300°C) to increase response time and reduce moisture effects—they deliver high sensitivity and are fast but their power requirements may limit their feasibility for field use; for the conducting polymer sensors, adsorption of odorant molecules causes swelling of the polymer surface material, which increases resistance. These sensors have widespread use and, in fact, were used in the first commercially available e-noses. They respond to a range of substances, exhibiting high sensitivity to alcohols, ketones, fatty acids and esters. They respond quickly (typically 2-20 s), operate at ambient temperature, and are reversible. A key plus is their ease of fabrication and flexibility in choice of substrate, as many different monomers may be polymerized. The latter are also small, inexpensive, reproducible, and have low power requirements. Polymer sensing materials have the disadvantages of low sensitivity to fully oxidized compounds such as CO₂ and NO₂, susceptibility to sensor drift, high sensitivity to humidity, and, due to consumption, require large samples.

Specific chemiresistive materials for use in e-nose applications include conductive electroactive polymers (CEPs) or their composites and carbon black or metal-filled composites operating near the percolation threshold. Carbon nanotubes with the novel properties presents an attractive opportunity for use as active elements for thin films in integrated circuits transistor devices due to their high mobility (20,000 cm²/V.s at room temperature), and their low resistivity, and thermal properties, when use for gas vapor, temperature, and humidity detection. Also, carbon nanotubes with their range of semiconducting and metallic properties and relative ease of non-covalent and covalent functionalization are well suited for chemoreceptor use in e-Noses. However, in most applications, modification of CNTs surfaces
or structural framework is essential for more effective responses, since the pristine CNTs do have low affinity or sensitivity, when associated to vapor detection.\textsuperscript{13,14} To overcome such challenges, researchers have fine-tuned CNTs’ properties through chemical functionalization. In this regard, halogens do represent a useful class of intermediates as they can act as precursors in the functionalization processes by adding to the sidewall of the carbon nanotube.\textsuperscript{15,16} Hu et al. have shown that functionalization with halogens creates changes in the SWNTs’ electronic properties as a result of shifting of the Fermi Level.\textsuperscript{17} Through fluorination of SWNTs, Bahr et al.\textsuperscript{18} established a resistance > 20 MΩ when compared to that of pristine SWNTs, which has a resistance in the range of 10 - 15 Ω. Also, the polar nature of halogen-carbon bonds causes the hydrogen bonding capacity to improved, which enhances vapor affinity of the carbon network.

A series of functionalized SWNTs, rationalized on the basis of covalent chemical modification that impart electron-donating or electron-withdrawing functionalities at defect sites have been synthesized and characterized.\textsuperscript{19} These derivatized-nanotube-based materials are designed to serve as chemoreceptors that can facilitate the development of highly selective and sensitive chemical and biological sensor arrays through an “electronic nose” approach that mimics the mammalian olfactory system.\textsuperscript{20} In the discussion, functionalized SWNTs (f-SWNTs) were synthesized using photobromination approach,\textsuperscript{21} then dispersed in m-Cresol, and spun-applied onto the interdigitated regions of microlithographically fabricated, pre-cleaned microsensor electrodes (IME 1025-M-Pt and -Au).\textsuperscript{22} Devices were 10 µm line and space with 25 fingers of e-gun deposited Au or Pt (100nm)/TiW (20nm) patterned on borosilicate glass. Prior to deposition of functionalized SWNTs, devices were solvent cleaned and chemically modified.
with octadecyltrichlorosilane (OTS), cathodically cleaned (20 cycles, 100 mV/s, PBS 7.38) to remove the silane from the metallic digits, rinsed with isopropyl alcohol and dried in flowing argon. The resulting individual devices (sensory receptors) were characterized by two–electrode impedance spectroscopy (40 mV p-t-p; $10^{-1} – 10^6$ Hz; RT) and equivalent circuit modeling in various gases/vapors.\textsuperscript{22} The devices were also characterized by I-V in air (-1.0 to +1.0 V).

We have demonstration of an efficient synthesis route for high-yield brominated-SWNT via UV photolysis. In this paper we report on the performance of a single chemoreceptor fabricated from brominated SWNT (SWNT-Br) that was spun-deposited onto an IME device that had been chemically modified with octadecyltrichlorosilane (OTS). A number of characterization techniques have been used to analyze the material. Surface topographical imaging of devices, using TopoMetrix Explorer AFM was taken; mainly to show the bridging of SWNTs with interdigitated electrodes. By applying the scanning electron microscope (SEM – Zeiss Supra 55VP) technique, coupled with Genesis EDAX; the surfaces of the functionalized SWNTs were examined to evaluate the presences of functionalized moieties. The Electrical Impedance Spectroscopy (EIS) profile, the I-V characteristics, and the response to vapors when the same chemiresistive f-SWNT layer was cast onto gold vs. platinum IME devices were evaluated. We compare the EIS profiles and the I-V characteristics when the same SWNT-Br layer was cast onto IME devices where only the interdigit spaces chemically modified with -OTS-, but were fabricated from gold or platinum.\textsuperscript{23} We have also; seek to classify the f-SWNTs through temperature dependency and the effect of electrochemistry using Au and Pt electrodes. The impedimetric responses of the chemoreceptors were also measured for four vapors: ethanol,
methyl isoamyl ketone (MIAK), toluene, and octane—representing the four basic classes of vapors, alcohols, ketones, aromatic and aliphatic.

5.2 EXPERIMENTAL

5.2.1 MATERIALS AND METHODS

Reagents: Chemicals and washing solvents were purchased from Sigma Aldrich and Alfa Aesar, while pristine single-walled carbon nanotubes (purity, 95 wt. %) were purchased from Unidym™ Inc, Sunnyvale, CA and used without further purification. A Branson Ultrasonic 2510 was used for dispersion of SWNTs in various solvents. Interdigitated microsensor electrodes (IME 1025-M-Au-U and IME 1025-M-Pt-U) were purchased from ABTECH Scientific, Inc. (Richmond, VA) and phosphate buffered saline (PBS) solution was prepared with PBS tablets from MP Biomedicals (Cat. No. 2810305, Lot M6305, pH 7.38, without calcium and magnesium; Solon, OH). Deionized (DI) water generated by a Milli-Q® Ultrapure Water Purification System was used in preparation of solution and washing of glassware.

Preparation of Covalently Brominated-SWNTs: Poly-brominated SWNTs were synthesized through a novel approach of photobromination of pristine nanotubes using N-Bromosuccinamide (NBS). Typically, ca. 20 mg of SWNTs was sonicated in 15 mL of dichloromethane for 20 minutes and then dispersed mixture was poured into a 100 mL round bottom flask, and NBS (0.5 equivalent) was added to the dispersion. The reaction was conducted under reflux conditions with a GE, 100 watt incandescent light bulb, which promoted generation of free bromine radicals. The reaction was allowed to run for about 15 minutes,
during which time gaseous components were evolved, and the final produce was a light yellowish liquid suspension. Next, ca. 1.0 equivalent of NBS was added in order to drive the reaction toward complete utilization of all bromine formed. The reaction was allowed to continue uninterrupted for another 90 minutes. At this point, the heat source was lowered (≈ 40 mm) below the reaction flask to reduce the reaction rate. The reaction was allowed to proceed to completion for another 10 hours. Additionally, for other syntheses studies, the reaction procedure was modified by allowing the final step to occur for durations of 24 and 48 hours. The final suspension was cooled and filtered through a PTFE membrane filter (0.45 um, 25mm). The filtrate was thoroughly washed with chloroform followed by diethyl ether. The resultant product was dried overnight at 60°C under vacuum.

Preparation of IME-Devices: The functionalized CNTs were deposited onto substrates consisting of an array of microstructured interdigitated platinum or gold electrodes via spin coating using a model WS-650S-6NPP/LTTE Laurell Technologies Co. spin coater. The IME devices were each first cleaned using ethanol, isopropyl alcohol, and deionized water, and then chemically modified with octadecyltrichlorosilane (OTS), to introduce hydrophobic methyl groups on the surface. Cathodic cleaning was applied to remove the OTS from the Pt and Au electrodes. 3µL drops of f-SWNTs in m-Cresol were spun cast onto the interdigitated region of the IME chips spun at 2000 rpm for 3 min, and followed by an added application of 6µL which was spun at 1000 rpm for 3 min.
5.2.2 ELECTRICAL IMPEDANCE AND IV CHARACTERIZATION

I-V Characterization was performed in air (-1.0 to +1.0 V) using a Keithley 4200 Semiconductor Characterization System connected to a probe station via a switching matrix and was run using the Keithley Interactive Test Environment (KITE) software.

Electrical Impedance Spectroscopy (EIS) was performed in freshly prepared 1X phosphorous buffered saline (PBS) and in air (40 mV p-t-p, $10^{-1} - 10^{6}$ Hz, RT and temperature dependence in the range 290.2 to 333.3 K) using a Solartron 1260 Frequency Response Analyzer (FRA) equipped with ZView and ZPlot software.

5.2.3 ELECTROCHEMICAL CHARACTERIZATION

Multiple Scan Rate Cyclic Voltammetry (MSRCV) was performed in a three electrode arrangement of working (WE), counter (CE) and reference (RE) electrodes in freshly prepared 1X PBS (pH = 7.38) and in 1X PBS containing 50 mM [Fe(CN)$_6$]$_{3/4}$- at RT. For MSRCV, a PAR 283 Potentiostat/Galvanostat (Princeton Applied Research) equipped with PowerSuite® software was used. The platinum interdigitated microsensor electrode (IME 1025-M-Pt-U) and micro Ag/AgCl electrode (3 M Cl-) purchased from ABTECH Scientific, Inc. (Richmond, VA), were used as working and reference electrodes, respectively. The two arms of the IME were shorted to constitute the W.E. and nitrogen was bubbled into the solution to remove dissolved oxygen. MSRCV was studied by scanning the potential range of 0 to 500 mV vs. Ag/AgCl at scan rates of 10, 25, 50, 100, 150, 200, and 300mV/s for 3 cycles. The third cycle was captured and reported.
5.2.4 CHEMORESISTIVE GAS /VAPOR RESPONSES

Chemiresistive response to vapor was studied using the Solartron 1260 FRA to measure temporal changes to the impedance magnitude, $|Z|$, upon vapor exposure. The brominated SWNT sample was spun-applied to OTS-modified Pt and Au IME devices, and then exposed to very low concentration of static, headspace vapors emanating from a specific condensed sample of solvent (100 uL) contained in a closed (1 mL) vial. Vapors studied were ethanol (EtOH), methyl isoamyl ketone (MIAK), octane (Oct) and toluene (Tol). Vapor exposure proceeded for 60 s (hereinafter referred to as "On" period) followed by 60 s exposure to air (herein referred to as "Off" period) at room temperature. Each run time was 3 min with an On-Off-On cycle of 1 min each. It is to be emphasized that the durations used were completely arbitrary. Both sensor systems, in general, exhibited rapid adsorption and desorption kinetics at room temperature.

5.3 RESULTS AND DISCUSSION

5.3.1 ROLE OF THE OTS SURFACE MODIFICATION

OTS was used for surface modification of the IME devices as a way to introduce hydrophobic methyl groups to the interdigit space of the glass’ surface. This process replaces the highly polar, water-rich, and hydrogen-bonding surface of the unmodified glass (-Si-OH groups) with the purely dispersive, self-assembled, hydrophobic layer with terminal methyl (-CH$_3$) groups. This effectively changes the surface energy of the device in order to; i) favor a uniform distribution of the SWNT dispersion when spun-applied to the IME devices, and ii) eliminate the interaction of the –Si-OH groups of the glass with the SWNT. In this regard, cathodic cleaning of the metallic electrodes of the IME chip following surface modification was crucial to the
removal of the silane ad-layer from the metal electrodes. Thus, electrical characteristics and vapor responses of the sensor element are expected to be derived from the SWNTs and their electrical coupling to the metallic electrodes of the IME devices.

5.3.2 ELECTRICAL CHARACTERISTICS OF THE PRISTINE AND BROMINATED SWNTS

Electrical impedance characteristics of functionalized SWNT (specifically SWNT-Br) that was cast onto OTS-modified IME devices of Au and Pt were measured at RT in air by electrical impedance spectroscopy (40 mV p-t-p, 10⁻¹ – 10⁶ Hz, RT) (Figure 5-1A) and by I-V characterization (-1.0 to +1.0 V) (Figure 5-1B). Impedance spectra showed the blank OTS-modified device to be a classic Randles equivalent circuit similar to that previously reported by Hang and Guiseppi-Elie, 23 wherein it was shown that an OTS-modified IME device had impedance characteristics that were more stable and higher than that of the un-modified counterpart. Once decorated with the spun-applied SWNT-Br, the impedance spectrum converted to a flat line characteristic of a pure resistor. The I-V data compliments that of EIS, where the resistance values for the SWNT-Br were obtained from the slope of linear responses over the range -1.0 to +1.0 V. Over this range the blank OTS-modified device exhibits a flat line, while the SWNT decorated devices of Au and Pt are both linear but demonstrate dramatically different positive slopes.
Figure 5-1A and 5-1B: Electrical characteristics of pristine (SWNT-p) and functionalized SWNT (SWNT-Br) cast onto OTS-modified IME devices of Au and Pt measured at RT in air by:
(A) electrical impedance spectroscopy (40 mV p-t-p, 10^{-1} – 10^{6} Hz, RT) and (B) I-V characterization (-1.0 to +1.0 V).

Figure 5-2A summarizes the electrical properties as measured on the Au and Pt devices and shows the similarity of the AC and DC results, confirming resistor-like behavior; however, there was significant difference between results measured on Au and Pt devices. The data may
reflect the influence of the different work function (wf) of each metal, which are 5.10 eV and 6.35eV, respectively, or the differences in the resistivity of the metals, which are $2.44 \times 10^{-8}$ and $1.06 \times 10^{-7}$ at 20 °C, respectively. To evaluate the relative importance of these two possibilities, we compared the temperature dependence of the magnitude of the impedance as measured on Au and Pt devices (Figure 5-2B) (below). The impedance analysis with respect to applied temperature ranging from 290K to 333K for Au and Pt devices shows that the resistance of the sensing element increases with increasing temperature and is linear with $1/T$ (Figure 5-2B). IME-Au-SWNT-Br shows a lower rate of increase in magnitude when compared to IME-Pt-SWNT-Br. As reflected in the slopes, the temperature dependence of the Au device was $2.44 \times 10^{-3}$ OhmK$^{-1}$ ($R^2 = 0.950$) and of the Pt device was $13.78 \times 10^{-3}$ OhmK$^{-1}$ ($R^2 = 0.994$). These values may be compared with the known temperature dependence of the resistance of Au and Pt, which are $3.40 \times 10^{-3}$ OhmK$^{-1}$ and $3.927 \times 10^{-3}$ OhmK$^{-1}$, respectively. While gold devices show quite similar values, the platinum devices are one full order of magnitude larger, indicating that
interfacial effects between the platinum and SWNT dominate the measured impedance of the device under test conditions, and that gold devices are therefore better suited for e-NOSE applications.

**Figure 5-2A.** Summary of the electrical properties of the SWNT-Br as measured by (A) EIS and I-V characterization of platinum (gray) and gold (yellow) brominated devices.
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Figure 5-2B: Summary of the temperature dependence of the magnitude of the impedance, |Z|, measured over the range 290K to 333K (17-60 °C) for brominated platinum and gold chemiresistors.

5.3.3 ELECTROCHEMICAL CHARACTERISTICS OF THE PRISTINE AND BROMINATED SWNTS

Cyclic voltammograms, shown in Figures 5-3 were recorded in 50 mM [Fe(CN)₆]³⁻/⁴⁻ prepared in phosphate buffered saline solution at potential scan rates from 10 to 300 mV/s. Shown in Figures 5-3A to 5-3C are the voltammograms for OTS-modified but otherwise uncoated Pt-IME, pristine-SWNT coated Pt-IME and brominated-SWNT coated Pt-IME respectively. Figure 5-3D illustrates the three electrode setup used to obtain the MSRCV measurements and illustrates that the two electrodes of the IME device were shorted for the MSRCV measurements. The use of ferri/ferrocyanide one-electron redox couple (Eq. 5-1) serves as an electrochemical probe for studying the possible participation of the SWNT network in the redox reaction.
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\[ \text{Fe}^{(III)}\text{(CN)}_6^{3-} \rightleftharpoons \text{Fe}^{(II)}\text{(CN)}_6^{4-} \quad \text{Eq. 5-1} \]

Similarly, cyclic voltammograms measurements were carried out for IME-Au devices and shown in Figures 5-3E- 5-3G as OTS-modified uncoated Au-IME, pristine-SWNT coated Au-IME and brominated-SWNT coated Au-IME respectively.

**Figure 5-3a:** MSRCV of (A) an OTS-modified but otherwise IME-Pt-Blank, (B) an OTS-modified IME-Pt decorated with pristine SWNT (SWNT-p), (C) an OTS-modified IME-Pt device decorated with a functionalized SWNT (SWNT-Br) and (D) a schematic of the electrode arrangement. Voltammograms were obtained over the range 0 to 500 mV vs. Ag/AgCl at scan rates of 10, 25, 50, 100, 150, 200, and 300 mV/s for 3 cycles in 1X PBS containing 50 mM [Fe(CN)₆]³⁻/⁴⁻ at RT. The third cycle is reported.
As expected, in all cases there was a corresponding increase in the peak current with the increase in scan rate for each electrode type. Figure 5-4 is a plot of the anodic peak current, $i_{pa}$, as a function of the square root of scan rate in accordance with the familiar Randles–Sevcik equation for reversible redox reactions at large area electrodes that support semi-infinite linear diffusion at room temperature (Eq. 5-2).

$$i_{pa} = 2.687 \times 10^5 n^{\frac{3}{2}} v^{\frac{1}{2}} D^{\frac{1}{2}} A^{\frac{1}{2}} C_{\text{red}}$$  

\textit{Eq. 5-2}
Examination of the MSRCV plots reveals that the brominated SWNT (IME-Pt-SWNT-Br) produced the lowest current relative to the uncoated (IME-Pt-Blank) and pristine SWNT modified array electrodes (IME-Pt-SWNT-p) and that the pristine SWNT electrodes was similar in performance to the blank electrode. The blank device shows the characteristic curvature reflective of a transport contribution from radial diffusion due to the microelectrode array format\(^{24}\) and this is accentuated for the pristine SWNT modified array electrodes (IME-Pt-SWNT-p). This curvature is enhanced for the IME-Pt-SWNT-p although the magnitude of the currents is not appreciably increased. This suggests a role for the pristine SWNTs in influencing the microarray character of the electrode. The IME-Pt-SWNT-Br displays considerably reduced current and a smaller slope. A fully contiguous network of conductive and electroactive SWNT formed between the interdigitated electrodes should support an increase in the apparent surface area of the electrode and a corresponding expectation of an approximately 1.5-fold increase in current relative to the blank. This is not substantiated by the observed electrochemical characteristics. In fact the pristine SWNT modification supports an equivalent electrode area while the SWNT-Br supports what could be considered, a reduction in apparent surface area or the formation of monolayer. This suggests that while highly conductive, the SWNT-Br does not support efficient charge injection from the \([\text{Fe(CN)}_6]^{3-/4-}\) redox couple.

Similar to the IME-Pt devices, the IME-Au chemisensors demonstrate that corresponding increase in the peak current is relative to the increase in scan rate for each sensor type. With the exception of IME-Au-SWNT-p, the magnitude of the currents increased relative those of IME-
Pt-Blank and IME-Pt-SWNT-Br devices. In this electrochemical system, the lower current for IME-Au-SWNT-p does not support overall observation for gold devices being more suitable for sensor application than platinum devices. This result could be the effect of other factors and therefore will be reviewed before any further discussion. Again, the IME-Au-Blank device displays curvature which is likened to that of classic transport impact, while the IME-Au-SWNT-Br does not sustain proficient charge injection from the redox system.

![Graph](image)

**Figure 5-4.** Comparison of the oxidation peak current, $i_{pa}$, vs. the square root of scan rate obtained from MSRCV for an OTS-modified but otherwise IME-Au-Blank, IME-Pt-Blank, an OTS-modified IME-Au decorated with pristine SWNT (SWNT-p), an OTS-modified IME-Pt decorated with pristine SWNT (SWNT-p), an OTS-modified IME-Au device decorated with a functionalized SWNT (SWNT-Br) and an OTS-modified IME-Pt device decorated with a functionalized SWNT (SWNT-Br). Obtained in 1X PBS containing 50 mM [Fe(CN)$_6$]$^{3/-4}$ at RT on Au and Pt Electrodes.

A direct comparison of the electrochemical characteristics of the three device structures at scan rates of 10 and 100 mV/s (Figure 5-5) clearly illustrates that the redox coupling of
[Fe(CN)₆]³⁻/⁴⁻ with the platinum and gold electrodes vary with the different SWNT surface modifications. For Figure 5-5A (10 mV/s), the IME-Pt-Blank produces, for the of [Fe(CN)₆]³⁻/⁴⁻ redox couple, an $E^{o'}$ of 251.5 mV vs. Ag/AgCl. This value was increased to 294.5 and 313.1 mV vs. Ag/AgCl for the IME-Pt-SWNT-p and IME-Pt-SWNT-Br devices, respectively. This shift to higher values suggests a less facile charge transfer reaction. The change is $\Delta E_p$, established as 129.6 mV at the blank Pt device, was reduced to 116.7 at the IME-Pt-SWNT-p device and increased to 153.8 for the IME-Pt-SWNT-Br device. The shift to a larger $E^{o'}$ value and corresponding narrowing of the $E^{o'}$ implies a less facile but more reversible charge transfer reaction at the pristine SWNT modified interface. The shift to a larger $E^{o'}$ value and corresponding broadening of the $E^{o'}$ implies a less facile and quasi-reversible charge transfer reaction at the brominated SWNT modified interface. This confirms that there is a fundamental difference in the HOMO and LUMO energy levels of SWNT-Br when compared to SWNT-p. There is also a decrease of ca. 10% and 74% in the peak oxidation current, $i_{pa}$, of the [Fe(CN)₆]³⁻/⁴⁻ redox couple at the IME-Pt-SWNT-p and IME-Pt-SWNT-Br devices, respectively. It is also clear that oxidation of Fe(CN)₆³⁻/Fe(CN)₆⁴⁻ takes place at a lower potential for pristine SWNT in comparison to functionalized SWNT. The same is observed at 100mV/s for each device (Figure 5-5B) and the results are presented in Table 5-1. These data trends are similar to that is reported with modified MWNT on GCE.
Figure 5-5A and 5-5B. Comparison of voltammograms obtained using an OTS-modified but otherwise IME-Pt-Blank, an OTS-modified IME-Pt decorated with pristine SWNT (SWNT-p) and an OTS-modified IME-Pt device decorated with a functionalized SWNT (SWNT-Br). Obtained using (A) 10 mV/s and (B) 100 mV/s in 1X PBS containing 50 mM [Fe(CN)₆]³⁻/⁴⁻ at RT.

According to Figure 5C (10 mV/s) the IME-Au-Blank yields, for the of [Fe(CN)₆]³⁻/⁴⁻ redox couple, an $E^{o'}$ of 254.51 mV vs. Ag/AgCl. This value was slightly increased to 256.97 and then produced 254.59 mV vs. Ag/AgCl for the IME-Au-SWNT-p and IME-Au-SWNT-Br devices, respectively. This shift to slightly higher values suggests a marginally less simplistic charge transfer reaction for IME-Au-SWNT-p, but a similar charger transfer reaction for IME-Au-SWNT-Br. The change in $\Delta E_p$, is established to be 107.25 mV at the IME-Au-Blank device, was slightly increased to 115.63 mV at the IME-Au-SWNT-p device and further increased to 221.32 mV at the IME-Au-SWNT-Br device. The observed shift to a little larger $E^{o'}$ value and the corresponding $E^{o'}$ implies a similar reversible charge transfer reaction at the IME-Au-SWNT-p modified interface. A comparable behavior is observed at 100mV/s for each device (Figure 5-5D) and results are presented in Table 5-1. Comparable to the observation for the Pt devices at 10 mV/s, there is also a decrease in the peak oxidation current, $i_{pa}$, of the [Fe(CN)₆]³⁻/⁴⁻ redox couple at ca. 22% and 76% at the IME-Au-SWNT-p and IME-Au-SWNT-Br devices,
respectively. This reveals that there are major differences in the energy levels of the functionalized SWNT-Br in comparison to its pristine counterpart. To better understand and discuss the dynamics of these devices in the electrochemical system, further analyses are been undertaken. Overall, the display ratio of oxidation and reduction peak currents reveal that the IME-Au devices produces a more unified reversible coupling, as their waves ratios \( \left( \frac{i_{pa}}{i_{pc}} \right) \) are more reflective of 1.

**Figure 5-5C and 5-5D:** Comparison of voltammograms obtained using an OTS-modified but otherwise IME-Au-Blank, an OTS-modified IME-Au decorated with pristine SWNT (SWNT-p) and an OTS-modified IME-Au device decorated with a functionalized SWNT (SWNT-Br). Obtained using (C) 10 mV/s & (D) 100 mV/s in 1X PBS containing 50 mM \([\text{Fe(CN)}_6]^{3+/4-}\) at RT.
### Table 5-1: Electrochemical characteristics of Au and Pt OTS-modified IME-Blank, OTS-modified IME decorated with pristine SWNT (SWNT-p) and OTS-modified IME device decorated with a functionalized SWNT (SWNT-Br). Obtained using (A) 10 mV/s and (B) 100 mV/s in 1X PBS containing 50 mM [Fe(CN)₆]³⁻⁻/⁴⁻ at RT.

<table>
<thead>
<tr>
<th></th>
<th>IME-Pt</th>
<th>IME-Au</th>
<th>IME-Pt</th>
<th>IME-Au</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ΔEₚ</td>
<td>E°'</td>
<td>Iₚ/Iₚ.rawValue</td>
<td>ΔEₚ</td>
</tr>
<tr>
<td>BLANK</td>
<td>129.60</td>
<td>251.50</td>
<td>-1.289</td>
<td>107.25</td>
</tr>
<tr>
<td>SWNT-pristine</td>
<td>116.72</td>
<td>294.49</td>
<td>-1.306</td>
<td>115.63</td>
</tr>
<tr>
<td>SWNT-Br</td>
<td>153.84</td>
<td>313.05</td>
<td>-1.147</td>
<td>221.32</td>
</tr>
</tbody>
</table>

ΔEₚ is the difference between the anodic and cathodic peak potentials

E°' is the average of the anodic and cathodic peak potentials

Iₚ/Iₚ.rawValue is the ratio of the anodic and cathodic peak currents

### 5.4 CHEMORESISTIVE RESPONSE TO VAPORS

The response of the sensor elements to vapor may arise from the sorption and partitioning of vapor into the underlying OTS organic layer leading to swelling and a change in percolation of the SWNT network. An alternative possibility is that the vapor may adsorb onto the surfaces of the functionalized SWNT, and acting though the purposefully introduced defects (bromination), produce a change in electron density within the tubes thereby altering the apparent conductivity. The first model would result in vapors such as toluene having the most dramatic response as these would readily partition into (i.e., mix with) and effectively swell the...
OTS layer. The second model suggests that vapors such as ethanol, being more polar, will produce a larger response than MIAK, or octane. Using an IME-Pt-SWNT-Br device, the responses to these vapors were obtained and compared and are shown in Figure 5-6A. The largest response (Figure 5-6B) was to ethanol ($\Delta = 0.4\%$) over MIAK ($\Delta = 0.12\%$) and toluene ($\Delta = 0.01\%$). This confirms that the likely basis for the response of the sensor element is an interaction of the vapor with the f-SWNT. It can be stated that our highly conductive functionalized network of SWNT-Br, casted as a mat on both Pt and Au interdigitated electrodes to form chemisensors demonstrated the capability of sensitivity, reversibility and unique resistance changes upon interaction with signature components of RDX; that is ethanol, MIAK, and toluene.

Figure 5-6A and 5-6B: (A - left) Chemiresistive adsorption isotherm (responses) of IME-Pt-SWNT-Br statically exposed to the head space vapor of ethanol, MIAK and toluene for 1 cycle each of 30 min OFF/ON at RT. (B - right) Comparison of the magnitude of the 4-point resistance changes after 6 min of exposure to the head space vapor of ethanol, MIAK and toluene.
5.4.1 CHEMIRESISTIVE RESPONSE TO CLASSES OF VAPOR FOR THE SWNT-BR DEVICES

The normalized chemiresistive adsorption and desorption profiles (responses) of IME-Au-SWNT-Br (Figure 5-7A) and IME-Pt-SWNT-Br (Figure 5-7B) were obtained following exposure of the devices to the head space organic vapor of four distinct classes of odorants followed by exposure to air in an ON-OFF-ON cycle at RT. The organic vapors of ethanol, methyl isoamyl ketone (MIAK), toluene and octane therefore served as analytes. Figure 5-7A/B shows the responses of the sensor elements to be immediate sharp rises followed by slow approach to an asymptotic limit. The magnitude of the response is dictated by the character of the vapor and the nature of the metal of the device. All responses appear fully reproducible; returning to baseline following exposure to air. The magnitude of the change in impedance expressed as \( \% \Delta \) was determined using equation 5-3 and is presented as bar chart in Figure 5-8.

\[
-|Z|^{Au/Pt}_{SWNT-Br} = 100 \left( \frac{|Z|^{Pt}_{SWNT-Br} - |Z|^{Au}_{SWNT-Br}}{|Z|^{Au}_{SWNT-Br}} \right)
\]

Eq. 5.3

Two things are clearly apparent: firstly, that the magnitude of the responses is in all cases larger for Au devices than they are for Pt devices. Secondly, there is a more complete recovery to the baseline following exposure to vapor.
**Figure 5-7A and 5-7B:** Normalized chemiresistive adsorption and desorption profiles responses of (A) IME-Au-SWNT-Br and (B) IME-Pt-SWNT-Br statically exposed to 4 classes of chemical vapors and to air in ON-OFF-ON cycles at RT. Vapors are Ethanol, Methyl Isoamyl Ketone (MIAK), Toluene and Octane.

**Figure 5-8:** Percent change ($\% \Delta$) in the chemiresistive responses of IME-Au-SWNT-Br and IME-Pt-SWNT-Br statically exposed to 4 classes of chemical vapors and to air in ON-OFF-ON cycles at RT. Vapors are Ethanol, Methyl Isoamyl Ketone (MIAK), Toluene and Octane.
5.5 CONCLUSION

The role of the choice of metal, Au or Pt, in the fabrication of impedimetric receptors for chemiresistive arrays that use functionalized SWNTs for an e-NOSE has been investigated. It is fair to note that the work function and the metal’s resistivity have great influence on the sensory receptor’s responses to impedance, I-V, temperature and vapor response characterization. Electrical and electronic characterization confirm a role for the Pt-to-SWNT interface in testing the performance of the sensor element, but for Au devices the measured resistance more faithfully reflects the interactions of the vapor with the SWNTs; i.e., the vapor response of the sensor elements are larger and more reproducible when gold is used. The present study clearly confirms that Au devices are better suited than Pt devices in the construction of chemiresistive receptor elements for an e-NOSE array.
5.6 REFERENCES


(2) Wilson, A. Sensors 2013, 13, 2295.


(13) Kelvin M. Frazier, T. M. S. Analytical Chemistry 2013, 85, 7154.


(20) David Adebimpe.


CHAPTER 6: Functionalized SWNTs and their Application as Chemosensors

6.1 INTRODUCTION

As previously mentioned, pristine carbon nanotubes are chemically inert, extremely low solubility in universal solvents and, no affinity to vapors, especially when no defects are present. These properties make their application in sensing devices as inadequate. In order to overcome this obstacle, functionalization of the nanotubes becomes essential to improving the wetting and dispersion of the nanotubes. Functionalization the SWNT sidewall will overcome the π-π stacking interactions and dispersive forces amid the SWNTs in the bundles and matter dramatically increase the accessibility to individual SWNTs.

The approach aims mainly at controlling, but does not degrade the electrical integrity of nanotubes of SWNTs coated on the sensors. Diazonium coupling functionalized the carbon nanotubes with various electron donating and drawing groups with the goal to provide different binding properties of each chemiresistor element on exposure to a specific analyte. These functional groups can directly influence the response pattern for a vapor, and thus create a platform for selectivity and specificity. Conducting organic matrices get spin cast onto micro-interdigitated gold electrodes, which on exposure to different analytes produce different electrical resistance.

In this project, we developed e-nose sensors for vapor detection using a diversified set of nanostructured chemical sensors comprised of novel surface-functionalized carbon nanotubes, aim at enhancing specific responses. Such gas sensing materials was spun coated to form SWNT mats onto interdigitated electrodes —the interdigitated electrodes create contact between the
sensing materials and the sensor circuitry. Initial studies involve measuring changes in the electrical conductivities of an array of sensing materials upon exposure to selected vapors. These changes transduced into electrical signals, which are preprocessed and identified by a pattern recognition system.

An array of engineered SWNT films produces a signal pattern for specific analytes, and hence, identification is possible. The sensor has been tested with various vapors as: acetic acid, ethanol, chloroform, ammonia, HCl, nitric acid, sulfuric acid, cyclohexanone, hexanal, acetone, N, N-dimethylacetamide, acetonitrile and ethyl acetate. Of these, ten vapors repeatedly evaluated on our chemosensors are discussed in this chapter. The results of these evaluations show that these sensors can classify each vapor from the others.

6.2 Experimental

6.2.1 MATERIALS AND METHODS

Reagents and chemicals were purchased from Sigma Aldrich and Alfa Aesar (see Chapter section 2.2). Single-walled carbon nanotubes with purity of 95 wt. % and synthesized by HiPCo method was purchased from Unidym\textsuperscript{TM} Inc, Sunnyvale, CA., and used without further purification. The nanotubes were up 10 um in lengths, with diameters ranging from ca. 0.8 to 1.2 nm

6.2.2 PREPARATION OF COVALENTLY FUNCTIONALIZED-SWNTS

The syntheses were achieved using diazonium precursors with slight modifications to the wet chemistry methods already established by Tour; \textit{et al.}\textsuperscript{4-6} Illustrated in Scheme 2.4 (Chapter 2). Typically, sequence of ca. 6 mg of HiPCO SWNTs were sonicated; each in 15.0 mL of glyme
or diglyme for 20 minutes. Each resulting aqueous suspension of SWNTs was placed in a 100 mL three-neck, round bottom flask in a solution of derivatives of aniline (2mmol) in 5 mL of acetonitrile. With a reflux condenser in one neck of the flask, as the flask was immersed in a cold bath, the mixture was stirred for 10 minutes with nitrogen bubbling through. Isoamyl nitrite (2 equivalents) was quickly added to the mix. The cooling bath was replaced with oil bath heated to 60°C and kept for 12 to 48 hours with continuous stirring. After duration, the experimental mixture was set to cool by removing oil bath. Mixture was diluted with chloroform, filtered over PTFE (0.45 um) membrane and washed extensively with chloroform and rinsed with ether. The samples were placed in a vacuum oven to dry overnight at 65°C. More details on the synthesis of SWNTs can be found Chapter 2 (section 2.4). Extensive spectroscopic characterization was conducted for proof of functionalization to the sidewall of SWNTs.

These functionalized nanotubes are; p-phenol-SWNT (SWNT-p-OH), p-nitrobenzene-SWNT (SWNT-p-NO₂), p-fluorobenzene-SWNT (SWNT-p-F), p-aniline-SWNT (SWNT-p-NH₂) and p-thiophenol-SWNT (SWNT-p-SH) and p-benzonitrile-SWNT (SWNT-p-CN). In this chapter, more comprehensive discussion will be on samples of SWNT-pristine, SWNT-p-NO₂, SWNT-p-F and SWNT-p-SH. This suite of derivatized-nanotube-based materials serve as chemoreceptors and facilitate the development of highly selective and sensitive chemical and biological sensor arrays by an approach that mimics the mammalian olfactory system – “electronic nose.”
6.3 CHARACTERIZATION METHODS

The nanotubes arrays were characterized by Raman spectroscopy with an HR800 Horiba Jobin Yvon Raman Microprobe spectrometer, to confirm the presence of functionalized groups on the SWNTs matrix. Solid samples were placed on a cover glass and excited with a 632.8 nm HeNe laser radiation (x100 objective lens). The morphology of the SWNTs mats, formed upon deposition of SWNT network onto the substrates was investigated by means a low voltage, scanning transmission electron microscopy (SEM). SEM measurements were performed using a Zeiss Supra 55VP Scanning Electron Microscope coupled with a Genesis EDX system. For surface topographical imaging of the SWNT mats created for the gas sensing electrodes, a TopoMetrix Explorer AFM was used in the contact mode. Chemical structure of the functionalized SWNTS was observed by the X-ray photoelectron spectroscopy (PHI5600) equipped with a monochromatic AlKα source (1486.6 eV). Fourier-transform infrared (FTIR) measurements were conducted using a Varian 7000 FTIR. For the FTIR investigations, the SWNT samples (ca. 1 mg) were mixed with KBr and pressed into pellets using standard procedures. Thermogravimetric investigations were accomplished on a TA Instruments Thermogravimetric Analyzer / Differential Scanning Calorimeter (Q600). For this latter system, ca. 12 mg of SWNT samples, pristine or functionalized-SWNTs, were loaded into the sample cell with a reference cell left empty. The sample and reference cells were maintained at 25 °C for 5 minutes, after which they were heated at a rate of 100 °C/min in a nitrogen atmosphere, with a flow rate of 100 mL/min. More detail on instrumentation and techniques are found in Chapter 3.
CHAPTER 6 Functionalized SWNTs and …

6.4 GAS SENSOR FABRICATION AND EVALUATION

6.4.1 FABRICATION OF DEVICES

At this junction, the functionalized SWNTs were individually dispersed in organic dimethylformamide (DMF) by ultrasonically stirred for 20 minutes at room temperature. Substrates consisting of an array of microstructured gold interdigitated electrodes (IME) devices first underwent solvent cleaning using 3 minutes each in ethanol, isopropyl alcohol and deionized water. Samples were subsequent; 3uL drops of functionalized-SWNTs in DMF were spun cast onto interdigitated region of the cleaned IME chips at 2000 rpm for 3 min and followed by an added application of 6uL, which was spun at 1000 rpm for 3 min. The device was placed in a conventional oven for 10 minutes at 60 °C to warrant the evaporation of the solvent in which functionalized SWNTs was dispersed.

6.3.2 EVALUATION SETUP

Our aim is to test whether the sensing system being investigated, might represent a useful technique to identify potentially harmful agents that are invariably introduced into our environment; providing sensitivity and selectivity that are beyond the capacities shown for gas chromatographic (GC) and mass spectroscopic (MS) analytical techniques. It has been reported that the sensitivities of electronic noses are almost 40 times greater than that of headspace/GC measurements.7

The sensor evaluation system is schematically illustrated in Scheme 4-3 in Chapter 4. The network consists of two main subsystems: (a) the vapor delivery and distribution system, this region allows for the initially purging of the sensing chamber with nitrogen (N2) and then the
delivery of selected analyte vapor diluted with the carrier gas. A mass flow controller is used for mixing a carrier gas (flow rate, 0.025 l/min.) and the selected vapor and subsequently feed them into the sensing chamber. The concentration of mixed gases varied based on the analyte’s vapor pressure/ specific density (calculated concentration seen in Table 4-1 of Chapter 4); (b) the response monitoring and data acquisition subsystem, which detects variations in the resistance of the functionalized-SWNT network due to its interaction with gaseous molecules. In essence, the analytes interact with the functionalized-SWNT mat through weak dispersion or chemical forces. The interactions, which are related to the surface concentration of the analyte, perturb the electronic system of the SWNT based conducting network, resulting in resistance changes, which are monitored and recorded using a lab built PXI-platform from National Instruments (NI), Model 1042.

The signal collection utilized, involved determining a baseline for a measurement, followed by the measurement itself; specifically, 60-sec baseline period was defined. The sensor was exposed to zero-grade nitrogen gas flowing at 0.025 liters/min; this baseline measurement was followed by a 30-sec exposure to a mixture of N₂ and selected solvent/vapor (i.e., herein called "On" period); and then a 60-sec exposure to only N₂ at 0.2 liters/min (herein referred to as "Off" period). It is to be emphasized that the durations used were to observe the sensor’s ability to produce quick responses profile and a recovery baseline, which may provide more selectivity data. The On/Off process was cycled six times (6 cycles), followed by a 60-sec rest period. Interaction between a functionalized nanotube–based sensor and an analyte is measured by an increase or decrease in the amount of analyte interacting (through adsorption/desorption
processes) via a physisorption or chemisorption process. This process causes a change in the chemical or physical properties of the sensing element and resultant change in the electrical resistance of the sensing element. The resistance of the sensor was automatically recorded before, during and after exposure to the different vapors. The process of nitrogen/vapor injection into the sensing chamber is accomplished via electronically controlled solenoid valves (specifically, Parker® PTFE (polytetrafluoroethylene) valves). The system, also equipped with a Parker® PTFE flow meter/controller in order to control the amount of analyte vapor that was mixed with an inert carrier gas. The vapor/carrier-gas mixture then carried into the chamber containing the sensor chip (i.e., the interdigitated electrode assembly) that was electrically connected to the above mentioned NI-PXI measuring system.

6.5 RESULTS AND DISCUSSION

6.5.1 CHARACTERIZATION OF THE FUNCTIONALIZED-SWNTS

The functionalization of SWNTs with various groups is undeniably confirmed by the Raman spectra, collected with excitation at 632.8 nm, of SWNTs treated under reaction condition of diazonium coupling (Figure 6-1. There are three key modes in the Raman spectra of CNTs, of which are the radial breathing mode (RBM), the disorder (D) mode and the tangential or G mode. Characteristic peaks of pristine and functionalized SWNTs appear at around 160 to 300 cm\(^{-1}\), and it due to the RBM, which is a vibration mode of CNTs in the radial direction and representative of the diameter sizes of SWNTs. Raman spectra suggest that the functionalized tubes lose structural uniformity, evidenced by the sizable decrease in intensity of the RBM band. Observed mainly for the SWNT-p-NO\(_2\) sample is the practical eradicated of the RBM,
with downshifted and little intensity in the remains at 160 to 180 cm\(^{-1}\). This observation may be the result of etching of the smallest diameter tubes in this sample, as smaller tubes are more susceptible to strain, and thus led to more unstable carbon-carbon bonds.\(^8\,^9\)

Also, comparison of spectra reveals a weaker band near 1296 cm\(^{-1}\), which show increase in intensity for the functionalized samples relative to the pristine SWNT. The band is attributable to the D-band, associated with an increase in disorder in the SWNT lattice.\(^10\) Both the changes in RBM and D-band suggest that the nanotubes have become functionalized.\(^11\) Another strong tangential mode for SWNTs observed at (≈1575 cm\(^{-1}\)) is the G band. The intensity of spectra is normalized using the G-band, and is found that the functionalized spectra differs substantially from their pristine sample. In particular, the relative intensity of the disorder mode is much larger than that existing for pristine SWNTs, which produce a noticeably smaller ratio of the D to G band for functionalized tubes to that of the pristine nanotube (Table 6.1). The ratio \(I_D/I_G\) for pristine SWNT is calculated to be ca 1: 8.8 compared to 1:2.4, which can be stated to have most defective lattice of functionalized samples. The higher the degree of functionalization, the higher is the intensity of D band in the Raman spectra, which means the introduction of more sp\(^3\) carbon atoms onto the SWNTs. The spectra also show variations in the shifting of D and G bands after SWNTs functionalization. Moreover, the Raman spectra provided a clear indication that covalent functionalization to the sidewall of SWNTs is accomplished.
Figure 6-1: Panel A shows Raman spectra using 632-nm excitation for functionalized SWNTs and pristine SWNT samples: Pristine SWNT (black solid line), SWNT-p-NO$_2$ (red solid line), SWNT-p-F (blue solid line) and SWNT-p-SH (violet dot-dash line). Panel B (bottom left), the RBMs show decrease and shift in intensities as it relates to the tubes diameters, while Panel C (Bottom right), shows visible increase of the disorder (D-band).
Table 6-1: Ratios of D and G modes for the pristine SWNTs, and nitrobenzene (SWNT-p-NO₂), fluorobenzene (SWNT-p-F) and thiophenol (SWNT-p-SH) functionalized samples

<table>
<thead>
<tr>
<th>Samples</th>
<th>Ratio of D/ G band</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWNT-Pristine</td>
<td>1: 8.8 ≈ 0.11 ± 0.01</td>
</tr>
<tr>
<td>SWNT-p-NO₂</td>
<td>1: 5.9 ≈ 0.17 ± 0.02</td>
</tr>
<tr>
<td>SWNT-p-F</td>
<td>1: 3.2 ≈ 0.31 ± 0.01</td>
</tr>
<tr>
<td>SWNT-p-SH</td>
<td>1: 2.4 ≈ 0.42 ± 0.04</td>
</tr>
</tbody>
</table>

Thermogravimetric is one of the most commonly used analytical techniques for the determination of functional groups attached to the sidewall of SWNTs. Figure 6-2 reported respectively the TGA and DTA analyses; that enables us to evaluate to a certain degree of functionalization of SWNTs with nitrobenzene, fluorobenzene and thiophenol, primarily by the mass loss upon decomposition by pyrolysis.

We have employed thermogravimetric analysis on diazonium coupling samples. The data was compared to the pristine samples as shown in panel A of Figure 6-2. The pyrolysis was conducted in a N₂ atmosphere up to a temperature of 1000 °C. The pristine SWNTs are relatively stable, and thermogravimetric analysis bring about a weight loss of 10% at 1000 °C. In the case of the functionalized SWNT-p-NO₂ samples, the decomposition takes place in 3 stages. The significant weight loss occurs at the beginning of ca. 140 to 240 °C and 260 to 450 °C, followed by a further weight loss onset at ca. 500 °C (also see the derivative data in panel B of Figure 6-2),
which maybe attributed to the decomposition of the SWNT. The weight loss within the second region can be attributed to thermal decomposition involving NO$_2$, as reported by Brills et al., which states that decomposition of NO$_2$ from nitrobenzene occurs at 275 °C.$^{12}$ Total weight loss account for an estimated total of 27% (± 4.6 wt.%) loss, which is relatively in good agreement with the EDX data of nitrogen. (mean value of ca. 22.4 wt.%, see Table 6-1).

Pyrolysis study of SWNT-p-F showed mass loss of ca. 27% (Figure 6-2) with major mass loss between 100 to 500 °C. This correspond with TGA study$^{13}$ on thermal fluorination of SWNTs, where defluorination is nearly accomplished at 400 °C; having most of the fluorine decomposed between 200 to 300 °C. Similar evidence of weight loss from fluorinated CNTs is shown in the work of Bulusheva et al.,$^{14}$ where decomposition of fluorine atoms is said to be completed at 455 °C, while Pulikkathara et al. reported a DTA peak in the range of 400–600 °C for confirmation in removal of fluorine from SWNTs.$^{15}$

The thermal decomposition of SWNT-p-SH showed the largest weight loss when compared to that of the pristine and all the functionalized samples ca. 37%. This observation is evident to the Raman spectrum of SWNT-p-SH, revealing the highest intensity in D band, resulting in the highest degree of defect to the sidewall of the SWNTs (Figure 6-2). The presence of sulfur in the SWNT network was determined TGA/DTA data. Three peaks (DTA) is observed for SWNT-p-SH sample at approximately 300, 500 and 660 °C, which are likely the contribution of processes that include melting, burning and decomposition of sulfur and possible byproducts, as reported by Attar et al.$^{16}$ that the transformation of sulfur may change during pyrolysis. Baker et al.$^{17}$ work on removal of pyritic sulfur (FeS$_2$) from coal showed the evolution of sulfur with a
steady increase between 375 and 550 °C, while Powell’s work\textsuperscript{18} concluded that sulfur decomposition began at 300 °C and was completed at 600 °C, which is close to our last observed peak at 660 °C.

\textbf{Figure 6-2:} (A) Thermogravimetric analysis conducted under pure nitrogen at heating rate of 10 °C per minute for SWNT-Pristine (black line) and functionalized SWNT-p-NO\textsubscript{2} (red line), SWNT-p-F (blue line) and SWNT-p-SH (purple line).
Figure 6-2: (B) differential thermal analysis measurements conducted under pure nitrogen at heating rate of 10 °C per minute for SWNT-Pristine (black line) and functionalized SWNT-p-NO2 (red line), SWNT-p-F (blue line) and SWNT-p-SH (purple line).

FTIR measurements also show clear differences between pristine and functionalized samples as illustrated in Figure 6-3. The Infrared spectroscopy of the pristine sample showed adsorption signal at ca. 1500 to 1600 cm⁻¹, corresponding to C=C vibration is in agreement with IR characterization data on functionalized SWNTs.¹⁹-²² This band showed a slight shift in the reported range of 1500 – 1700 cm⁻¹ for the nitro, fluoro and thiol samples, which is associated to the effect of the functional group on doping. In addition, the presence of benzene ring is seen for SWNT-p-NO2, SWNT-p-F and SWNT-p-SH samples through absorption signal for aromatic C-H in the range of 790 – 840 cm⁻¹. The result is consistent with Coates’ reported range for aromatic ring with 1,4-disubstitution (para).²³ For these samples through synthesis method,
SWNTs and the different functional groups created the para substitution to benzene ring. This band is not observed in the pristine SWNTs, which again confirmed functionalization for nitro, fluoro and thiol samples.

Further evidence on the structure of functionalized SWNTs for each group is also seen in IR spectra of samples. Absorption signal for SWNT-p-NO$_2$ reveals nitro group attached to aromatic ring, which correspond to the N-O stretching at ca. 1360 – 1290 cm$^{-1}$. For SWNT-p-F sample, the peak appearance at ca. 1245 cm$^{-1}$, said to represent to C-F bonds, and a smaller feature at 1160 cm$^{-1}$, similar values showed for C-F peaks in Pehrsson et al. work on the fluorination of SWNTs$^{13}$ and Lee et al. fluorinated SWNTs.$^{24}$ IR spectrum shows a peak at ca. 620 cm$^{-1}$ that is attributed to an S-H vibration and suggests the successful incorporation of thiophenol group to the sidewall of SWNTs. During this process, Infrared spectroscopy (KBr pellet technique) confirmed the existence of functional moieties covalently attached to the sidewall of SWNTs.
Figure 6-3: FTIR-KBr spectra of SWNT-pristine (black line), and functionalized samples of SWNT-p-NO2 (red line), SWNT-p-F (blue line), and SWNT-p-SH (purple line).

Electron microscope investigations (SEM/EDX) were used to characterize the structural features, and morphology of pristine and functionalized SWNTs (see low magnifications images in Panel A of Figures 6-4, 6-5 and 6-6). Panel A of Figure 6-4 shows 1 um morphology of SWNT-p-NO2 sample B. Energy dispersive spectroscopy (see Panel B) with elemental mapping (Panel C) was also used as this can show the level of nitrogen species present in the surface of the samples. Measurements were made for multiple samples that underwent the photolysis reaction 24 hrs (Table 6-1); the EDX analyses indicated values of 22.54, 24.86, 21.93 and 20.33 wt.% (standard deviation, s = 1.88 wt.%), respectively. In Table 6-2, the data shows that the incorporation of nitrogen species on specimens investigated to have a value of ca. 24.10 At% (s = 1.49) for two syntheses of 24 hrs.
SEM images and elemental mapping of SWNT-p-F and SWNT-p-SH are shown in Figures 6-5 and 6-6, respectively. Measurements were made for multiple samples that underwent the photolysis reaction for 12, 24 and 48 hours. For SWNT-p-F, Table 6-3 shows the EDX measurements indicated elemental values of fluorine atoms as 7.73, 5.85 and 2.95 wt.% for syntheses periods of 24 and 12 hours, respectively. An increase reaction time exhibited an increase of fluorine atoms to the SWNT matrix of more than ca. 50 wt %. This synthesis technique contributes a greater yield of ca. 5.2 At % of fluorine atoms, when compared to Bahr et al. work on the electrochemical reduction to yield 3.6 At %. In Table 6-4, the data shows that the incorporation of sulfur species after photolysis reaction at 12, 24 and 48 hours reaches a mean value ca. 4 At % of the sulfur atom.

**Figure 6-4:** shows Panel A SEM surface, Panel B elemental analysis and Panel C, mapping of elements carbon (red), oxygen (blue) and nitrogen (green) for SWNT-p-NO₂ sample #B2.
EDX conducted is qualitative analysis. A statistical error is measured by Gaussian distribution with a standard deviation ($\sigma$) of $n^{1/2}/n$ was used to calculate error %. For a single measurement, error is $\pm 2\sigma$; $n$ is equal # of counts collected, which equals $\pm 2\%$.

Table 6-2: EDX elemental data for two syntheses (A & B) of SWNT-p-NO$_2$ samples

<table>
<thead>
<tr>
<th>Element</th>
<th>Wt%</th>
<th>At%</th>
<th>Synthesis Time (hrs.)</th>
<th>SWNT-p-NO$_2$ Samples (†)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>22.54</td>
<td>23.64</td>
<td>24</td>
<td>A1</td>
</tr>
<tr>
<td>N</td>
<td>24.86</td>
<td>26.26</td>
<td>24</td>
<td>A2</td>
</tr>
<tr>
<td>N</td>
<td>21.93</td>
<td>23.51</td>
<td>24</td>
<td>B1</td>
</tr>
<tr>
<td>N</td>
<td>20.33</td>
<td>22.91</td>
<td>24</td>
<td>B2</td>
</tr>
</tbody>
</table>

† Sample A and B are representatives 2 different diazonium coupling reactions undertaken for 24 hours to achieve SWNT-p-NO$_2$ samples.

Figure 6-5 shows Panel A SEM surface, Panel B elemental analysis and Panel C, mapping of elements carbon (red), oxygen (blue) and fluorine (green) for SWNT-p-F sample #B1.
Table 6-3: EDX elemental data for different SWNT-p-F samples and synthesis times

<table>
<thead>
<tr>
<th>Element</th>
<th>Wt%</th>
<th>At%</th>
<th>Synthesis Time (hrs.)</th>
<th>SWNT-p-NO₂ Samples (†)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>0.265</td>
<td>01.76</td>
<td>12</td>
<td>A1</td>
</tr>
<tr>
<td>F</td>
<td>02.95</td>
<td>01.99</td>
<td>12</td>
<td>A2</td>
</tr>
<tr>
<td>F</td>
<td>07.73</td>
<td>05.19</td>
<td>24</td>
<td>B1</td>
</tr>
<tr>
<td>F</td>
<td>05.85</td>
<td>03.99</td>
<td>24</td>
<td>B2</td>
</tr>
</tbody>
</table>

† Sample A underwent diazonium coupling reaction 12 hours; 2 different representative samples. Samples B were each reacted for 24 hours; 2 different representative samples.

**Figure 6-6:** shows Panel A SEM surface, Panel B elemental analysis and Panel C, mapping of elements carbon (red), oxygen (blue) and sulfur (green) for SWNT-p-SH sample #B2.
Table 6-4: EDX elemental data for two syntheses (A, B &C) of SWNT-p-SH samples

<table>
<thead>
<tr>
<th>Element</th>
<th>Wt%</th>
<th>At%</th>
<th>Synthesis Time (hrs)</th>
<th>SWNT-p-SH Sample (†)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>13.39</td>
<td>05.63</td>
<td>48</td>
<td>C1</td>
</tr>
<tr>
<td>S</td>
<td>07.43</td>
<td>03.04</td>
<td>24</td>
<td>B1</td>
</tr>
<tr>
<td>S</td>
<td>07.45</td>
<td>03.32</td>
<td>24</td>
<td>B2</td>
</tr>
<tr>
<td>S</td>
<td>05.13</td>
<td>02.67</td>
<td>12</td>
<td>A1</td>
</tr>
</tbody>
</table>

† Sample A underwent diazonium coupling reaction 12 hours; Sample B for 24 hours; 2 different representative samples and Sample C for 48 hours.

Additional evidence on the structure of the functionalized SWNTs was obtained from the X-ray photoelectron spectroscopy (XPS) of the functionalized SWNTs, achieved via diazonium coupling reaction. XPS technique applied during this process (discussed in detail in chapter 3) was used to analyze all samples to afford elemental and chemical state and on the top surface of the samples. Analyses were conducted by Dr. Ruemmelli (Dresden, Germany) using PHI5600 instrument, with a focus displayed signals for carbon, nitrogen, fluorine, sulfur and oxygen atoms. The resulting spectra show electron counts/intensity versus their binding energy, as revealed in Figures below for four samples of SWNT-pristine, SWNT-p-NO₂, SWNT-p-F and SWNT-p-SH. However, no quantitative peak analysis for surface element concentrations was done.

High-resolution spectra of the samples generated by XPS are shown with raw data, curve fitting of spectra for chemical state analysis. The curve fitting was accomplished through the use
of student version software provided by Magic Plot for deconvolution of C 1s peaks. The curve fitting was carried out using Gaussian/Lorentzian function. The full width half maximum (FWHM) process has an associated error of about ± 0.2 eV. The colors in the curve fitting spectral profile represent the different groups identified by their binding energies, which are assigned with the aid of NIST X-ray Photoelectron Spectroscopy Database\textsuperscript{26} and the referencing of similar data reported by other researchers. The dotted purple lines represent the C 1s raw data of the actual spectra.

SWNT-pristine sample was analyzed by XPS and showed spectrum of C and O 1s core level. The peaks identified at 284.5 and 533.3 eV, illustrate the presence of surface carbon and oxygen atoms\textsuperscript{27}, respectively (Figure 6-7). The signal for oxygen may originate from the 5% impurities of the acquired nanotubes (95 % purity) as they were used without further purification or is attributed to sample exposure to the atmosphere.

![XPS elemental survey scans of SWNT-pristine sample showing surface elements of oxygen (O 1s) and carbon (C 1s).](image)

**Figure 6-7a:** XPS elemental survey scans of SWNT-pristine sample showing surface elements of oxygen (O 1s) and carbon (C 1s).
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Figure 6-7b shows the deconvolution of C 1s for SWNT-pristine, revealing the chemical state of the surface. The primary peak identified at 284.5 eV resulting from the carbon; carbon double bond dominates the spectra, but complex spectral features due to carbon-oxygen bonding (286.4 eV\textsuperscript{28,29} is evident at higher binding energy (O 1s, ca. 533.0 eV). Also appearing at 291.9 eV is the binding energy peak structure, assigned to be satellite peak due to the π – π* transition\textsuperscript{30,31} which is an indication of the considerable amount of aromatic character from SWNTs.

![Figure 6-7b: Chemical state of elements for SWNT-pristine sample showing the dashed lines for raw data and solid color lines are the corresponding curve fit component of C 1s.](image)

Figure 6-7b: Chemical state of elements for SWNT-pristine sample showing the dashed lines for raw data and solid color lines are the corresponding curve fit component of C 1s.
XPS is utilized to analyze the nitrobenzene functionalized sample, SWNT-p-NO₂. The spectrum of Figure 6-8 revealed SWNT-p-NO₂ comprised of carbon (C 1s), oxygen (O 1s) and nitrogen (N 1s).

Figure 6-8: XPS elemental survey scans of SWNT-p-NO₂ sample showing surface elements of oxygen (O 1s), nitrogen (N 1s) and carbon (C 1s).

The C 1s for SWNT-p-NO₂ was deconvoluted into four peaks with binding energies (Panel A of Figure 6.9). The peak at ca. 284.5 eV corresponds to sp² C-C bond, peak at 285.8 eV agrees to C-NO₂ domain, while 286.0 and 290.6 eV are assigned to carbon to oxygen atom (C-O) and C=C satellite peak, respectively. The two latter peaks show a slight shift when compared to the values for the pristine sample, and may be the effect charge transfer due to functionalization. Panel B of Figure 6-9 shows the deconvolution components of N 1s. The deconvolution peaks identified at 399.5 and 406.1 eV are in agreement with corresponding binding energy reported for nitrogen attached to a carbon domain, where the assignment was
made to carbon-nitrogen and nitrogen-oxygen bonds, respectively. XPS analysis of the surface chemistry of SWNT-p-NO₂ confirmed levels of functionalized with the nitro group (C-NO) to the SWNT network.

**Figure 6-9:** XPS chemical state of elements for SWNT-p-NO₂ sample showing the dashed purple lines for the actual data and the color lines are the corresponding curve fitting components of the C 1s (Panel A) and the spectra of N 1s identifying carbon-nitrogen and nitrogen-oxygen atoms bonding (Panel B).

Figure 6-10 The XPS study on SWNT-p-F sample shows energies matching atoms as carbon at 284.5 eV, a match for oxygen at 533 eV and, 687.5 eV for fluorine. The intensity of each peak is relative to the number of atoms for the particular element.
Figure 6-10: shows elemental survey scans for SWNT-p-F sample showing surface elements of fluorine (F 1s), oxygen (O 1s) and carbon (C 1s).

The XPS high resolution of C 1s structure for sample SWNT-p-F as shown in Panel A of Figure 6-10 with the assignment of deconvoluted complex features. This sample exhibited three peaks corresponding to different chemical states. Firstly at 284.5 eV, assigned to carbon bonded to carbon, secondly peak at 286.0 eV, attributed to carbon bonded to oxygen atom, corresponding to NIST Database\(^\text{26}\) and similar reported peak\(^\text{28,29}\), and thirdly, a broad peak at 287.3 eV is allotted to carbon bonded to a fluorine atom (C-F), in agreement with similar peaks for carbon – fluorine bonding.\(^\text{13,24,29,34,35}\) The F 1s binding energy reveals two peaks (Panel B in Figure 6-11); a very small peak of 682.5eV and a strong, narrow peak at 687.5 eV, both of which are either exact or within the range of binding energy values reported by other works on fluorinated carbon nanotubes.\(^\text{13,24,29,35}\)
Figure 6-11: XPS chemical state of SWNT-p-F sample showing the dashed purple lines for the actual data and the color lines are the corresponding curve fitting components of the C 1s (Panel A) and the spectra of F 1s (Panel B).

Figure 6-12a displays the binding energies of O 1s, C 1s, S 2s, S 2p, Al 2s and Al 2p obtained from XPS for SWNT-p-SH. The binding energies in thiol group appear at 228.0 eV for S 2s, and at 164.5 eV for S 2p, consistent with value reported in Lu et al. polythiophene nanotube composites.\textsuperscript{36} Similar to the other discussed functionalized samples, the O 1s peak around 532.0 eV appears to be shifted to a lower binding energy when compared to the pristine sample (533.3 eV). This may be due to electron transfer from the functional groups.\textsuperscript{36} The presence of the XPS peaks for Al 2s and Al 2p is results of the monochromatic source (AlK\textalpha) used during analysis. The XPS peak for C 1s (Figure 6-12b) is deconvoluted showing different chemical states.
Figure 6-12a: XPS elemental survey scans of SWNT-p-NO₂ sample, showing elements of oxygen (O 1s), carbon (C 1s), sulfur (S 2s and S 2p), and aluminum (Al 2s and Al 2p).

Figure 6-13 spectra show deconvoluted XPS peak of C 1s for SWNT-p-SH where three chemical states are revealed. One appears at the binding energy of 284.6 eV attributed to the sp² carbon as referenced at same binding energy for previously discussed SWNT-pristine, SWNT-p-NO₂, and SWNT-p-SH. Likewise, there is the similar displayed broader carbon bonded peak at 290.7 eV, which is energy loss satellite feature, commonly described as the “shake-up” of the hybridized sp² carbon atoms. The third peak at 285.9 eV is carbon sulfur related. The appearance of S 2p in elemental scan and C-S in curve fit for SWNT-p-SH spectra (Figure 6-12a and 6-12b) show the SWNT-p-SH was accomplished.
The incorporation of different functional moieties to the sidewall of SWNTs was confirmed by characterization via TGA/DTA, IR, EDX and XPS analyses. These functionalized SWNTs were then used as sensing elements for sensor devices.

6.6 GAS SENSING WITH SWNT-P-NO$_2$, SWNT-P-F AND SWNT-P-OH

To evaluate the conductance response of the diazonium reaction based functionalized-SWNTs devices (for SWNT-p-NO$_2$, SWNT-F and SWNT-p-OH), we exposed these sensors to various one component vapors independently. The gases used were C$_2$H$_5$OH, HCl, NH$_3$, H$_2$SO$_4$, C$_2$H$_3$N, N, N-dimethylacetamide, C$_2$H$_5$O$_2$, HNO$_3$, C$_3$H$_7$OH, cyclohexanone, hexanal and acetone. The performance of the sensors conduct was evaluated as baseline established under a pure...
N₂ flow for at least 1 min. After which, each sensor was exposed to alternate cycles of mixed carrier gas N₂ and a selected analyte vapor (Vapor ON), followed by pure N₂ (Vapor OFF), each lasting for 30 and 60 seconds, respectively, for a total of 5 to 6 cycles. The sensor showed high sensitivity to the eight volatile compounds mentioned above for concentrations varying from ca. 286 to 1645 ppb. As mentioned in Chapter 4, the concentrations of exposed mixture are calculated primarily from the measured volume of solvents, their specific density at 20 °C, the flow rate of the carrier gas, and molecular weights of compounds. Table 4.2 provides the calculated concentration for each analyte mixture. Injection of the analyte vapor was externally controlled by a solenoid driven valve and a flow meter.

The sensors responses depend not only on the ambient concentration of analytes, but also on the influence of chemical susceptibilities of the functional groups, the high surface area of functionalized SWNT composites, and the chemical composition of the interacting analytes. The linear solvation energy relationship (LSER) reveal how adsorption is affected by a specific chemical properties. LSER communicates the chemical properties of the materials in combination with polarizability, dipolarity and acidity of basicity of hydrogen bond.

When functionalized SWNT sensor networks are exposed to volatile analytes, sensor-vapor interaction may result in the swelling of sensing material due to the percolation of vapor within matrix layers, vapor adsorption to the surface, which influence the conductivity of the SWNTs network. Upon exposure to the gaseous vapors (Vapor ON), changes in the electrical resistance of each sensing element showed an increase in the profiles. This stage can be qualified as adsorption of gaseous molecules to the surface layers of the SWNT functionalized network,
resulting in changes in the conductivity. In the course of purging with N\textsubscript{2} (Vapor OFF), the resistance decreases as the gas molecules desorbed, and in some case desorption occurred very slowly.

The resulting data shows different profile behavior as the sensors interact with each vapor. The resistance versus time plot of the sensors (SWNT-p-OH, SWNT-p-NO\textsubscript{2} and SWNT-p-F), as they are exposure to the vapors are illustrated in Figure 6-13A, 6-13B and 6-13C, respectively. This demonstrates the effect of the sensing materials as conductors, on the resistance of the devices against time, as it relates to the vapor and non-vapor exposure.

The resistance of the sensing devices, SWNT-p-NO\textsubscript{2}, SWNT-p-F and SWNT-p-OH change during the absorption and desorption processes to the nine analytes. The patterns vary from sensor to sensor as the interactions show a strong association with the chemisorption and or physisorption processes of the sensing materials and the vapors. We exposed our sensors to common in laboratory vapors to test the sensitivity, reversibility and individuality of the sensing materials. From our preliminary evaluation of sensor/vapor interaction, Figures 6-13 (Panels A-C) show detection response profiles for all sensors as they are exposed to the different vapors during the experimental periods. The individual induced changes in resistance for all sensors show diversity with one vapor to another. Differences with the interactions are the basis for the unique patterns detected. For some sensor/vapor, the interactions have produced fairly good baseline recovery, and for other the saturation state during these experimental cycles does not allow for full baseline recovery. For example, in the case of HCl, all sensors experienced a drastic decrease in resistance, thereby revealed an increasing effect on the conductive properties
CHAPTER 6 Functionalized SWNTs and …

of the sensing materials. The doping effect of HCl shows very low change in resistance during
the adsorption/ desorption processes; as fairly good baseline recoveries are observed. In some
cases, sensor/vapor interactions show incomplete recovery of baseline, which resulted in an
increase in gradient. In these instances, this may be due to the accumulation of vapor buildup
during adsorption and thus would require longer desorption time (vapor off) for particular
vapors. Also, chemisorption interaction might have taken place. Despite the lack of baseline
recovery in some sensor/vapor profiles, the compared adsorption/desorption per cycle illustrate
uniform resistance changes. The shape and magnitude of the sensing response depend on
functionalized group on the SWNTs and the analyte being sensed.

Noted also, while individual vapor interaction demonstrated variation in their shapes to
the sensor’s response, levels of uniqueness can also be observed in when comparing sensor to
sensor relations with the same vapors. In Figure 6-13, the sulfuric acid vapor interaction with
sensors SWNT-p-NO₂, SWNT-p-F and SWNT-p-OH portray distinct difference in contours,
resistance intensities and cycle’s direction. This aids in pointing out the influence the functional
groups in the SWNT network.
Figure 6-13: shows resistance verses time plot profiles for sensors SWNT-p-NO₂ (Panel A), SWNT-p-F (Panel B) and SWNT-p-OH (Panel C) upon exposure to various vapors. Different color lines are used to represent the 9 analytes; ethanol (blue), HCl (red), ammonia (purple), sulfuric acid (magenta), acetonitrile (brown), N,N-dimethylacetamide (orange), acetic acid (green), nitric acid (black) and 2-propanal (grey).

The shapes of resistance response curves differ for the various analytes and from one sensor to another. To further extrapolate the sensor/vapor interaction, we extract data points from the shape of the sensor response data (using Figure 6-14 - also used in Chapter 4). This
model proposes the opportunity to differentiate between analytes based on measurement of their different response curves. Here we determine the ratios of the response function areas when the analyte was present (i.e., the "on-time" area) to that when the flow of analyte is absent (i.e., the "off-time" area) as a function of the percentage change in resistance (\(R\)); i.e.,

\[
\Delta R\% = \left(\frac{(R_{\text{max}} - R_0)}{R_0}\right) \times 100,
\]

as shown in Figure 6-14.

**Figure 6-14:** represents schematic for parameters \(\Delta R\%\) and "vapor-on" and "vapor-off" areas, whose values are used for determining parameters used in clustering plots in Figure 6-15 below.

Figure 6-15 show random response cycles area ratios for several cycles of the various response curves (for the different analytes) some of which are realized in Figure 6-13, as a function of \(\Delta R\%\). The overall effect of choosing different cycles for a given analyte is to define the inherent uncertainty to be anticipated for any given measurement. Additionally, when random cycle measurements cluster together, as depicted in panels A, B and C of Figure 6-15 for several of the analytes, one can conclude that if a subsequent measurement of an area ratio for a single cycle (or the average of several cycles) for an unknown analyte falls within the cluster region. At that point, the identity of the analyte can be inferred to a high level of confidence.
With clarity, we observe that the analytes are only discriminated by an individual sensor, but we can also identify a vapor based on its interaction with one sensor to the other. The area ratio plotted against ΔR% clusters give a fair indication, as to how the analytes influence each functionalized SWNT network.

Figure 6-15: shows clustering of area ratios verses ΔR% for 10 analytes vapors exposed to SWNT-p-NO₂, SWNT-p-F and SWNT-p-OH sensors; the dashed ellipsoids enclose suggested clusters. The vapors used were cyclohexanone, hexanal, 2-propanol, HCl, ethanol, acetic acid, acetonitrile, acetone, and N,N-dimethylacetamide.
6.7 CONCLUSION

In summary, we report on preliminary efforts that we have undertaken to modify the interaction affinity of SWNTs with a range of analytes. In this chapter we have discussed direct functionalization to the sidewall of SWNTs with various chemical groups, such as nitrobenzene, fluorobenzene, thiophenol, phenol and benzonitrile by way of diazonium coupling. Apparently the presence of these functional groups attached to the side wall of the nanotubes was demonstrated by our characterization techniques noted above. As compared to other approaches, the functionalization yield is improved. We have found that a mesh formed of these SWNT moieties when deposited across electrodes can serve as a conduction medium that detects with high efficiency the presence of a range of vapor analytes. In addition, we have shown that the profile of the response curves for gas chemiresistor sensors could provide a means for analyte selectivity, in other words, gas identification. Our broader effort is the utilization of a number of different covalent adducts on SWNT surfaces, with the idea of developing a highly discriminating chemical sensing platform. Such cohort of functionalized SWNTs has never been characterized in this format. Our exploratory studies on the gas sensing capabilities of these functionalized SWNTs are shown to be very promising.
6.8 REFERENCES


(23) Coates, J. *Interpretation of infrared spectra, a practical approach*, 2000.


CHAPTER 7: Electrical and electrochemical Characterization of Covalently Functionalized SWNTs on Platinum electrodes

7.1 INTRODUCTION

Single-walled carbon nanotubes (SWNTs) are a one-dimensional nanomaterial with advantageous electrical conductivity, mechanical, optical properties. Due to their unique properties, they are finding increasing application in numerous areas of science, engineering and technology. They are great interest of use in applications for batteries, chemical sensors (as demonstrated in chapter 6) and electrode materials\(^1\),\(^2\) as the tubes high surface area enhance the conductivity. Carbon nanotubes are often used as conductive fillings in composite materials since their low resistance and stability make them an appropriate material for contribution in the areas of electrical conductance and electrochemical sensing.\(^3\),\(^4\) However, carbon nanotubes surface is by nature inert and in its pristine state does not favors reactivity or dispersion, but supports agglomeration, thereby preventing a homogeneous solution. As a result, an effective method for dispersing nanotubes in aqueous solution or for chemical sensing is through covalent functionalization of SWNTs, as discussed in the synthesis processes in Chapter 3.

A supporting factor to prove the addition of functional groups, for example, (bromine (Br), aniline (pNH\(_2\)) phenol (pOH), thiophenol (pSH), nitrobenzene (pNO\(_2\)), fluorobenzene (pF), and benzonitrile (pCN)) to the sidewall of SWNTs is the modification to the electronic structure of CNTs. Owing to the sp\(^2\) hybridization of carbon atoms that give rise to a highly conjugated aromatic system, with the regular atomic distribution and formation, sp\(^3\) bonding is made possible. Introduction of groups (defects) caused the Fermi level of carbon nanotubes, an energy level to likely be occupied by an electron or vacant.\(^5\) This induced different electronic
characteristics from CNTs as it relates to their valence band, occupying electrons and empty conduction band, allowing for different degree of functionalized SWNT network.

To study the structures of the resulting functionalized SWNT; Br, pNH₂, pOH, pSH, pNO₂, pF, and pCN, a series of characterization techniques was employed as discussed in the previous chapters. The incorporation of these functional moieties to the sidewall of SWNTs was confirmed by characterization via TGA/DTA, FTIR, SEM/EDX and XPS analyses. Qualitatively, the results showed that functional groups are attached to the sidewall of the SWNTs. Also, demonstration of the usefulness functionalization of SWNTs in relationship to chemical sensing and the ability to create sensing devices with selectivity was conducted.

As part of a continuing effort to distinguish this group of chemically doped SWNTs, investigation on the conductance and state of electron transfer reaction of these SWNTs was facilitated. In this chapter, we attempt to combine this study with the assessment of the usefulness of the electrical and electrochemical properties of functionalized SWNTs. We observed through electrical impedance spectroscopy (EIS), IV characterization and multiple scan rate cyclic voltammetry the influence that functionalization had on the electrical and electronic properties of SWNTs. To study the cohort of functionalized SWNTs impedance spectroscopy was performed in at room temperature in air at 40 mV peak to peak with a frequency range of 10⁻¹ to 10⁶, using Solartron 1260 Frequency Response Analyzer. IV characterization was conducted using Keithley 4200 SCS system, while a simple electrochemical method was employed with multiple scan rate cyclic voltammetry (MSRCV) of 10 - 300 mV/s in 50 mM phosphate buffered saline and ferri/ferrocyanide solution.
Overall, changes in the physical properties of carbon nanotubes were established upon functionalization. Other researches indicated that the band-to-band transition of pristine SWNTs underwent disruption due to covalent functionalization.\textsuperscript{7-9} The impedance and IV characterization data showed the resistance of functionalized SWNTs changes (in some cases dramatically) with respect to that of the pristine samples.\textsuperscript{7,10-13} Cyclic voltammograms exhibited evidence of interference with charge transfer for the functional group of SWNTs, as the produced current flow is smaller than that of the pristine’s higher current flow. Data showed that functionalization of SWNTs can produce good conductors with resistance as low as ca. 65 ohms. The resistance of the functionalized carbon nanotubes is shown to increase relatively to the strength of each electron withdrawing group.

7.2 EXPERIMENTAL

7.2.1 MATERIALS AND METHODS

Reagents and chemicals were purchased from Sigma Aldrich and Alfa Aesar (see Chapter section 2.2). Single-walled carbon nanotubes with purity, 95 wt. % and synthesized by HiPCO method was purchased from Unidym\textsuperscript{TM} Inc, Sunnyvale, CA., and used without further purification. The nanotubes were up 10 um in lengths, with diameters ranging from ca. 0.8 to 1.2 nm.

7.2.2 CHARACTERIZATION OF DEVICES ELECTRICAL IMPEDANCE SPECTROSCOPY AND IV CHARACTERIZATION

Electrical impedance spectroscopy of the various functionalized SWNTs matrix, control and blank measurements were accomplished using Solartron 1260 Frequency Response Analyzer (FRA) equipped with Zview and Zplot software. The test frequency range stretches from $10^{-1}$ -
10^6 Hz with an oscillator voltage level of 40 mV p-t-p. Two-point measurements were taken at room temperature in freshly prepared 1X phosphorous buffered saline (PBS) and in air. I-V characterization was performed in air (-1.0 to +1.0 V), using a Keithley 4200 semiconductor characterization system connected to a probe station via a switching matrix and was run using the Keithley Interactive Test Environment (KITE) software.

### 7.2.3 CHARACTERIZATION OF DEVICES VIA ELECTROCHEMICAL METHOD: CYCLIC VOLTAMMETRY

The electrochemical characterization of the various functionalized SWNTs matrix, control and blank was investigated through multiple scan rate cyclic voltammetry (MSRCV) using three-electrode system, which includes working, counter and reference. This electrochemical setup was connected to a PAR 283 Potentiostat/Galvanostat (Princeton Applied Research) equipped with PowerSuite® software. The platinum interdigitated microsensor electrode (IME 1025-M-Pt-U) and micro Ag/AgCl electrode (3 M Cl⁻) purchased from ABTECH Scientific, Inc. (Richmond, VA) were used as working and reference electrodes, respectively. MSRCV was carried out within 50 mM [Fe(CN)_6]^{3/-4-} prepared in freshly prepared 1X PBS (pH = 7.38), at room temperature. Nitrogen gas was bubbled through solution to remove any possible oxygen. During this process, voltammetry was accomplished by scanning through potential range of 10 to 300 mV with given scan rates of 10, 25, 50, 100, 150, 200, and 300 mV/s, with three sweeps between 0V and 0.5V vs. Ag/AgCl.
7.3 RESULT AND DISCUSSION

7.3.1 ELECTRICAL IMPEDANCE AND IV CHARACTERIZATION OF THE BLANK, PRISTINE AND FUNCTIONALIZED SWNTS DEVICES

The blank (IME-Blank), pristine SWNTs (IME-SWNT-p) and functionalized SWNTs (IME-SWNT-Br, IME-SWNT-p-NO₂, IME-SWNT-p-F, IME-SWNT-p-SH, IME-SWNT-p-NH₂, IME-SWNT-p-OH and IME-SWNT-p-CN were tested using electrical impedance spectroscopy at frequencies from $10^1 - 10^6$ Hz and 40 mV peak to peak and room temperature in air, Figure 7-1. As seen from the Solartron 1260 (Figure 7-1A), the bare OTS-modified device is shown to be a classic Randles equivalent circuit, which is similar to that previously reported by Hang and Guiseppi-Elie.¹⁴ Wherein the IME-SWNT-p and all functionalized-SWNTs samples produced flat line characteristic of ideal resistors (purely real, where $Z = R$), of varied impedance magnitude, $|Z|$. Figure 7-1B displayed a phase of approximately 0, observed for all the resistors inclusive of pristine SWNT. On the other hand, the blank device showed capacitive phase response (-20 – 90degree), again classical Randles circuit with a capacitive element. As explained in the discussion of previous chapters (4, 5 and 6), with applied characterization techniques and application showing that these diverse suite of functional groups does impart different effect on the overall network of the cohort of covalently functionalized SWNTs. Likewise for EIS, the evidence on the impact that each functional group had on the SWNTs is established based on the different levels of resistors categorized. The data showed various magnitude of impedance for the SWNTs/electrode interface. The decorated IME SWNT-Br, SWNT-pNH₂ and SWNT-p delivered highest conductivities of SWNT networks, with the magnitude of impedance values of ca. 65.24 ($±0.05$)Ω, 79.22 ($±0.22$) Ω and 92.01 ($±0.10$) Ω,
respectively. Both of the IME-SWNT-Br and IME-SWNT-pNH₂ proved to be more conductive than the pristine SWNT (IME-SWNT-p). Material displaying lower conductivity (higher magnitude of impedance) than the pristine sample are IME-SWNT-pOH, IME-SWNT-pSH, IME-SWNT-pNO₂, IME-SWNT-pF and IME-SWNT-pCN at ca. 221.79 (±0.10) Ω, 269.19 (±0.65) Ω, 1.9 (±0.25) MΩ, 3.81 (±0.68) MΩ and 4.98 (±0.85) MΩ, respectively. All of which are have electron withdrawing moieties attachment to the sidewall of SWNTs, except that of phenyl sample (IME-SWNT-pOH). The result indicates that electron donating groups have a conductive impact on SWNTs compared to electron withdrawing groups. Bar chart (Figure 7-1C) illustrated the magnitude of impedance |Z| in correspondent to each sample.

![Figure 7-1A](image)

**Figure 7-1A:** Magnitude of impedance, |Z| vs frequency for electrical characterization of Blank, pristine (IME-SWNT-p) and functionalized SWNTs (IME-SWNT-p-SH, IME-SWNT-Br, IME-SWNT-p-NO₂, IME-SWNT-p-NH₂, IME-SWNT-p-OH and IME-SWNT-p-CN) cast onto OTS-modified IME devices of Pt measured at RT in air by electrical impedance spectroscopy (40 mV p-t-p, 10⁻¹ – 10⁶ Hz, RT); magnified region below.
**Figure 7-1B:** Phase angle, $\theta$ (degree) of EIS for Blank, pristine (IME-SWNT-p) and functionalized SWNTs (IME-SWNT-p-SH, IME-SWNT-p-Br, IME-SWNT-p-NO$_2$, IME-SWNT-p-NH$_2$, IME-SWNT-p-OH and IME-SWNT-p-CN) cast onto OTS-modified IME devices of Pt measured at RT in air by electrical impedance spectroscopy (40 mV p-t-p, $10^{-1}$ – $10^6$ Hz, RT).
CHAPTER 7 Electrical and Electrochemical…

Figure 7-1C: Bar Chart illustration of measured electrical impedance data vs pristine SWNT (IME-SWNT-p), IME-SWNT-p-Br, IME-SWNT-NH₂, IME-SWNT-p-OH, IME-SWNT-p-SH, IME-SWNT-p-NO₂, IME-SWNT-p-F and IME-SWNT-p-CN decorated onto electrodes of IME 1025.3M Pt.

IV Characterization of the said samples was conducted at -1.0 to +1.0 V. The resistance values derived from the Keithley 4200 system were determined by dividing the observed current by the applied voltage, Figure 7-2. I-V data compliments that of EIS, where the resistance of the materials are determined from the slope of linear responses over the experimental range (-1.0 to +1.0 V). Over this range the blank OTS-modified device exhibits a flat line, which characteristic capacitive behavior. For SWNT decorated devices of IME-SWNT-p, IME-SWNT-p-NH₂ and IME-SWNT-Br, sharp slopes are identified; with the most conductive, IME-SWNT-Br having the sharpest slope. In the meantime, IME-SWNT-p-OH and IME-SWNT-p-SH both displayed linear responses, but with dramatically different positive slopes, indicating lesser conductivities.
7.3.2 THE CORRELATION OF ELECTRICAL IMPEDANCE $|Z|$ AND IV CHARACTERIZATION TO HAMMETT SUBSTITUENT CONSTANTS OF FUNCTIONAL GROUPS

In order to understand the reaction influence that the functional groups may have on SWNTs properties, which resulted in the characterization of data gather during this experimental processes. We visualize Table 7-1 to provide a connection with the electrical impedance and IV characterization data to the Hammett substituent constants of these groups. Hammett constant is derived from Hammett equation; $\sigma \rho = \log (K/K_H)$ (linear free energy relationship, $K/K_H$ is equilibrium constant, $\sigma$ is substituent constant), which provides a quantitative measurement of substituent effects on chemical reactivity. The Hammett constant $\sigma \rho$ is used because all
substituents are attached at the para positions of the benzene ring, with the exception of bromine (no phenyl component). The implication of this equation states that, when $\sigma = $ negative, electron donating properties exist and for $\sigma = $ positive value, electron withdrawing effect. Hammett $\sigma$ Constants have been conventionally used to represent substituent electronic effects, and therefore, shown relatively good correlations to the electrical state of these functionalized SWNT materials.

It being so; we seek to associate the relative effects that the electron donating and electron withdrawing properties may have on the resulting conductivity of the cohort of covalently functionalized SWNTs by means of the electrical characterization data. As seen in Table 7-1, the conductivities obtained for the electron donating group-SWNTs matrix showed relative agreement to the Hammett substituent constants for the said functional groups; as these group are more conductive (with negative $\sigma$ values) than electron withdrawing groups (with positive $\sigma$ values). A quantitative way to describe the effect of functional groups’ EDG and EWG properties on the range of conductivity of samples was derived. Equation was 7-1 envisioned and calculation to the normalized magnitude of impedance with reference to pristine SWNT ($|Z|_{\text{p-SWNT}}$) was performed. The calculated $|Z|^{f_{-\text{SWNT}}}$ for each sample was plotted against Hammett constant for each functional group (Figure 7-3). Resulting data in
Figure 7-3 showed negative Hammett’s on the LHS, positive Hammett’s on the RHS, which representing electron donating and electron withdrawing, respectively, thus complimenting the conductivity data (levels of resistors) produced upon functionalization.

Based on the conductance of functionalized SWNTs relative to the pristine SWNT (Figure 7-1), it is apparent that the electrical properties of SWNTs are sensitive to the chemical modification processes undertaken with the electron donating and withdrawing substituents. As mentioned in Chapter 4, the functionalized process may have induce or enhance reactivity of the nanotubes, simply by shifting the Fermi level and thus changing the nanotubes’ electronic properties. In this case, the doping with bromine to the sidewall of SWNTs may have caused the Fermi level to shift toward the conduction band, relative to the initial position of the pristine nanotube. This therefore is the resultant of an electrical conduction boost with bromine, which now creates a semiconductor system that is more conductive than the pristine SWNT. The same can be concurred for aniline and phenol modified SWNTs as electron donating groups (NH₂ and OH) donate into the benzene ring and delocalized the negative charge. However, like bromine, the effect of aniline on the SWNTs resulted in SWNT material that is more conductive than the pristine, while phenol contributes a lesser conducting material. Functionalization of SWNTs with thiophenol (pSH), nitrobenzene (pNO₂), fluorobenzene (pF), and benzonitrile (pCN), all of which have electron withdrawing influence to the sidewall of SWNTs. The use of electron-withdrawing substituent attached to the primary molecular structure of SWNT is to fine-tune the molecule properties. Consequently, this produced diluted networks of interconnected-SWNTs that behave like a p-type semiconducting network. This evidently showed decrease in the
conductivity of the nanotube complexes, as other properties of the functionalized groups induced impedance in the overall materials, a show drop in conductivity as related to the pristine SWNTs (Table 7-1).

Table 7-1: Correlation of electrical impedance $|Z|$, IV characterization, and Hammett’s constant for functionalized groups

<table>
<thead>
<tr>
<th>Electron Donating/ withdraving substituents</th>
<th>SWNT-Pristine</th>
<th>SWNT-Br</th>
<th>SWNT-pNH$_2$</th>
<th>SWNT-pOH</th>
<th>SWNT-pSH</th>
<th>SWNT-pNO$_2$</th>
<th>SWNT-pF</th>
<th>SWNT-pCN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hammett’s Constant ($\sigma_p$) &amp; Bond Value</td>
<td>Zero or Low affinity</td>
<td>weakly withdrawing (no phenyl group)</td>
<td>donating</td>
<td>donating</td>
<td>withdrawing</td>
<td>withdrawing</td>
<td>withdrawing</td>
<td>withdrawing</td>
</tr>
<tr>
<td>$</td>
<td>Z</td>
<td>$ (Ohms)</td>
<td>92.07</td>
<td>65.19</td>
<td>79.22</td>
<td>222.59</td>
<td>269.29</td>
<td>1,905.51</td>
</tr>
<tr>
<td>$R = \frac{V}{I}$ (Ohms)</td>
<td>72.39</td>
<td>65.51</td>
<td>79.09</td>
<td>214.30</td>
<td>587.89</td>
<td>1,542.01</td>
<td>5,105.42</td>
<td>5248.50</td>
</tr>
</tbody>
</table>
7.3.3 ELECTROCHEMICAL CHARACTERISTICS OF THE BLANK, PRISTINE AND FUNCTIONALIZED SWNTS DEVICES

As another method of characterization, the oxidation or reduction of the analyte molecules were studied through the electrochemical technique of cyclic voltammetry (CV). CV was employed to evaluate how these modified SWNTs matrix undergoes redox reaction relative to blank and pristine SWNTs sample. Since there are different functional groups were used in the modification to the sidewall of SWNTs, varied levels of redox couple is anticipated. In the present work, CV is performed on aqueous solutions with phosphate buffered saline serving as supporting electrolyte in a three-electrode cell.

Cyclic voltammograms of the uncoated electrode, pristine-SWNTs and functionalized-SWNTs films casted on OTS-modified electrodes were investigated in a redox system. Figure 7-
4 shows cyclic voltammograms for electrochemically redox reaction conducted in 50 mM Fe$^{III}$(CN)$_6^{3-}$/Fe$^{II}$(CN)$_6^{4-}$ coupling, prepared in phosphate buffered saline at potential scan rates of 10 to 300 mV/s. The CVs were recorded for (A) uncoated OTS modified-Pt IME-Blank, OTS-modified IME-Pt device decorated with pristine SWNT (B) IME-SWNT-p, devices decorated with functionalized SWNTs; (C) IME-SWNT-Br, (D) IME-SWNT-p-NO$_2$, (E) IME-SWNT-p-F, (F) IME-SWNT-p-SH, (G) IME-SWNT-p-NH$_2$, (H) IME-SWNT-p-OH and (I) IME-SWNT-p-CN. The use of ferro/ferricyanide couple (Eq. 7-2 and 7-3) serves as an electrochemical probe for studying these devices; the possible participation of the SWNTs and the effect of the attached functional groups may have in the redox reaction. This coupled system provides a simple pathway as the reduction and oxidation processes progress by way of a one-electron transfer redox system. The resulting cyclic voltammograms produce plots of the response current at each working electrodes vs. the applied excitation potential.

\[
\begin{align*}
\text{Fe}^{II}(\text{CN})_6^{-4} & \rightarrow \text{Fe}^{III}(\text{CN})_6^{3-} + e \\
\text{Fe}^{III}(\text{CN})_6^{3-} + e & \rightarrow \text{Fe}^{II}(\text{CN})_6^{-4}
\end{align*}
\]

Eq. 7-2

Eq. 7-3

As illustrated in CVs (Figure 7-4), all devices experienced some levels of the redox reaction. As working electrodes for uncoated IME-Blank and coated IME-SWNT-p and all functionalized-SWNTs were scanned with a potential of 0V toward a more positive potential of 5V (forward scan, the potential was made more positive, which causes oxidation of ferrocyanide at the electrode surface (Eq. 7-2). During this process, the anodic current gets generated and gradually increases to anodic peak current (Ipa). As the concentration of ferrocyanide at the electrode surface gets depleted, the anodic current drops. A switch occurs in the scanning
direction, towards a lower potential. At this phase, the electrode becomes a reductant and reduces ferricyanide (Eq. 7-3) resulting in cathodic peak current (Ipc), which peaks and gradually decays.

Each device (Panel 7-4A – 7-4I) showed pronounced peak separation between anodic peak potential and cathodic peak potential values, and a corresponding increase in the peak current with the increase in scan rates (10 - 300 mV/s) for each electrode type. In this work, the switch for reversible redox reactions depends on the effect of scan rate and the material coated on the working electrodes. As observed the shape and the current flow varies with devices, which indicate that the functional groups impact the redox system. Blank IME (Panel A) show the highest peak currents for clearly defined anodic and cathodic peaks (with the exception of IME-SWNT-p-CN), which support the fact that there is no interruption to one electron transfer process. Panel B (IME-SWNT-p), with the existence of pristine carbon nanotubes, cast on the platinum electrode showed some level impedance to the electron transfer as the peak currents is lowered in comparison to the IME-Blank device. Panels C to I show the MSRCVs of ferri/ferrocyanide measured over the potential range of 0-500 mV at IME-SWNT-p-NO₂, IME-SWNT-p-F, IME-SWNT-NH₂, and IME-SWNT-p-OH illustrate lower peak currents in comparison to that of Blank-IME. Pristine SWNTs (IME-SWNT-p) compared to its functionalized counterparts demonstrate that its pristine form can support faster electron transfer with the redox couples.¹⁷ Based on the shape of the redox reaction voltammograms, these electrodes demonstrated there was little or no adsorption to the surfaces, making non-Faradaic charge unimportant. There is a noticeable change in the CVs of IME-SWNT-Br and IME-SWNT-p-CN for all scan rates, as the anodic and cathodic peaks are not clearly identified and could be attributed to hindrance of the functional group components (bromine and benzonitrile).
It’s possible that these functional moieties generate changes in the interfacial double layer structure\(^{18}\) between the electrode and the solution, which then create an overall change in the electric field across the boundary, thereby affecting the rate of electron transfer.

Figure 7.4 illustrates the conditional behavior of oxidation peaks of each device to scan rate by plotting of peak current versus square root of scan rate. Plot of the anodic current peaks (I\(_{pa}\))

\[
i_{pa} = 2.687 \times 10^5 n^{3/2} v^{1/2} D^{1/2} A C_{red}
\]

by means of a function of the square root of scan rate is in accordance with the known Randles–Sevcik equation for reversible redox reactions at large area electrodes, which support semi-infinite linear diffusion at room temperature (Eq. 7-4 above).
Figure 7-4: MSRCV of (A) an OTS-modified but otherwise IME-Blank, OTS-modified IME-Pt device decorated with pristine SWNT (B) IME-SWNT-p, devices decorated with functionalized SWNTs; (C) IME-SWNT-Br, (D) IME-SWNT-p-NO$_2$, (E) IME-SWNT-p-F, (F) IME-SWNT-p-SH, (G) IME-SWNT-p-NH$_2$ and (H) IME-SWNT-p-CN, Voltammograms were obtained over the range 0 to 300 mV/s vs. Ag/AgCl at scan rates of 10, 25, 50, 100, 150, 200, and 300 mV/s for 3 cycles in 1X PBS containing 50 mM [Fe(CN)$_6$]$^{3+/4-}$ at RT. The third cycle is reported.
Our investigation the effect of functionalized-SWNTs on MSRCV with ferri/ferrocyanide reveals (Figure 7-5) that the aniline functionalized SWNTs (IME-SWNT-p-NH$_2$) generated the lowest current relative to the uncoated (IME-Blank) and pristine SWNT modified array electrodes (IME-SWNT-p), and all the other functionalized SWNTs. Compared with pristine SWNT electrode, the curve showed similarities in performance to the blank electrode (IME-Blank). The particular curve for the blank device is reflective of a transport contribution from radial diffusion due to the microelectrode array format, and this is accentuated for the pristine SWNT modified array electrodes (IME-SWNT-p). This curvature is greater for the IME-SWNT-p although the magnitude of the currents is not appreciably increased. This suggests a role for the pristine SWNTs in influencing the microarray character of the electrode. The IME-SWNT-pNH$_2$ displays considerably reduced current with a linear diffusion behavior. The current is heightened for IME-SWNT-pNO$_2$, IME-SWNT-pOH and IME-SWNT-Br with relatively small slopes (IME-SWNT-Br displaying the smallest slope). An abundantly connecting network of conductive and electroactive SWNTs formed between the interdigitated electrodes should create a surface area the electrode, thereby enhancing the electron transfer, which should resulted in an increase in current relative to the blank. This is not demonstrated by the observed electrochemical characteristics, except for that of IME-SWNT-pF electrode, where the current is higher relative to that of the blank electrode. If this theory applies, then pristine SWNT modification supports an equivalent electrode area while the SWNT-pNH$_2$, SWNT-Br, SWNT-pOH and SWNT-pNO$_2$ may suggest a reduction in apparent surface area. An alternative view could be that redox coupled system caused a decrease in the conductivity of these functionalized-SWNTs at electrode surfaces, resulting in the resistance to electron transfer processes.
However, the observation from this investigation proposed that, highly conductive functionalized-SWNTs (SWNT-pNH₂, SWNT-Br), lower conductive (SWNT-OH, SWNT-p-NO₂) do not support efficient charge injection from the [Fe(CN)]₆³⁻/⁴⁻ redox couple. While, amongst the least conductive SWNTs (SWNT-pF), efficient charge injection of the redox couple ferri/ferrocyanide was achieved. These results showed that the decorated electrodes with modified SWNTs influenced ion incorporation as well as charge transfer. This development may be a reflection the variation with size of the functionalized SWNT band gap in these redox processes, where the smaller the band gap energies, the slower the reduction rate. Also, there may be the formation of self-assembly monolayer, which may slow down the electron transfer process for the IME- SWNT-Br and IME-SWNT-pNH₂.
Figure 7-5: Comparison of the oxidation peak current, $i_{pa}$, vs. the square root of scan rate obtained from MSRCV for an OTS-modified but otherwise, IME-Pt-Blank, an OTS-modified IME-Pt decorated with pristine SWNT (SWNT-p), an OTS-modified IME-Pt device decorated with a functionalized SWNTs; SWNT-pNH$_2$, SWNT-Br, SWNT-pOH, SWNT-pNO$_2$ and SWNT-p . Obtained in 1X PBS containing 50 mM [Fe(CN)$_6$]$^{3-}$/4$^-$ at RT.

7.4 CONCLUSION

Evidence exists to demonstration that functionalization altered the inherent electrical conductivity of the tubes. However, the characteristics and nature of the resulting materials showed the effect of the modification to the electronic properties of nanotubes is dependent on the kind of functional group used. As shown, electrical and electrochemical studies on different functional molecules (Br, pNH$_2$, pOH, pSH, pNO$_2$, pF, and pCN), attached to the sidewall of SWNTs, showed diverse results. The correlation of Hammett constant is complimentary to the
resulting electrical data owed to the electron donating and withdrawing groups influence on functionalization.

Based on observations of the electrochemical characterization of these functionalized SWNTs (especially that of IME-SWNT-Br and IME-SWNT-pNH₂), in future studies, their capabilities as super capacitors will be investigated.
7.5 REFERENCES


CHAPTER 8: Preliminary Detection of Vapor Components of RDX Explosives with Functionalized Brominated-SWNTs on Au and Pt Chemosensors

8.1 INTRODUCTION

The primary aim of this chapter is to mimic the behavior of canine olfaction and odor detection as a foundation for scientific enquiry aimed towards gaining a better understanding of data acquired from interdigitated-electrode (IDE) based gas sensors that use intrinsically conducting composites as sensory elements. The particular objective is the production of a device comprising a diversified array of nanostructured gas-analyzing sensors containing selectively carbon nanotube composites. Upon exposure of such sensors to any material (to an explosive for example), or to environmental odors of interest (as discussed in previous chapters), electrical signals (reflecting changes in sensor transduction mechanism as a function of time) will be obtained as the diversified array of nanostructured electronic sensory units within the array/network independently interact with headspace odors.

During this reporting period, we have established a comprehensive knowledge on a cohort of functionalized SWNTs through characterizations of different methods. These methods include; spectroscopic, electrical, and sensors operation ranging from electrochemical to chemosensors (illustrated for detection of gaseous vapors). We envisioned the use of such diverse functionalized SWNTs based chemosensors to be ideal in producing unique chemical responses and selectivity to the exposure of explosives components.

For almost 100 years, the world has witnessed the terror and destruction that explosives can cause on the battlefield and in noncombatant communities. Today, no one, worldwide, is
safe from being caught up in a terrorist bombings event. Despite the U.S. military assets and experiences in dealing with explosive devices, there is still a crucial need to heighten the protection of its war fighters, especially with the growing use of improvised explosive devices (IEDs) by terrorists and militants alike. Moreover, the gratuitous violence visited on innocent, noncombatant communities by bombings, which leaves broken bodies and paralyzing fear, cannot be tolerated by society, and must be challenged wherever it occurs. In this chapter, we have conducted preliminary work in the development of electronic-noses (i.e., e-noses) with application in the detection of signature components explosives (for example RDX), as they have posed a threat for both health and security of the nation.

8.2 DETECTION OF EXPLOSIVES

The detection of explosives and explosive related banned substances has played a vital role in the prevention of terrorist activities\textsuperscript{1} and thus, contribute to the monitoring of their harmful effects on health. There are numerous methods with emphasis on different principles that have been explored over the years for usage in explosives detection. Microsensors play a vital role in current research device application aimed at environmental monitoring chemical vapor and explosives detection.\textsuperscript{2-8} Extensive discussions have been made through research, books and conferences, which deal with approaches to explosives detection. Although there have been several developments in recent years to improve on the approach and detection of explosives, no ideal sensor has yet been identified\textsuperscript{9} beyond the use of canines.
8.2.1 CANINES

Since World War II, canines have been trained and used for explosive demining purposes.\textsuperscript{10} Unmoving, thus far, canines are still said to be the dominant system in the field for the detection explosives. Canines surpassed the competence of current sampling techniques, and so find the explosive source in their discovery. However, A critical issue that is commonly stated for training of canines with explosive vapors includes, cross contamination,\textsuperscript{11} the explosive vapor pressure, the size exposed to, temperature, and the different component vapors,\textsuperscript{12} which primarily has to do with the manufacturing source of the explosive. Also, canines are limited to the compound being detected,\textsuperscript{13} which is nominally dependent on the atmospheric pressure conditions. It is reported that canines’ positive responses are primarily based solvents used in the explosive production processes, by-products and other volatiles, rather than the explosive signature vapor.\textsuperscript{10} With certainty, there is a need for a system that has the capabilities to address these concerns; one that can identify and characterize signature odor//vapor stemming from explosive compounds. Therefore, our research on the use of functionalized carbon nanotubes based chemosensors, which will provide sensitivity, vapor selectivity and discrimination is ideal to the future of explosive detection.\textsuperscript{14}

8.2.2 CARBON NANOTUBES BASED EXPLOSIVE DETECTION

Great interests have been shown with the development of nanotube based sensors for explosives detection due to its electrical properties, surface area and the unique ability to tune the properties.\textsuperscript{8,14} Surface modification can promote the accumulation of the analyte to the electrodes. Kelvin et al. have employed the use of SWNT chemosensors in the detection
explosives signature cyclohexanone,\textsuperscript{11,15,16} a component of RDX used in the recrystallization process.\textsuperscript{17,18} Wang \textit{et al.} reported the surface modification of multi-walled carbon nanotubes (MWCNT) on glassy carbon for the detection of TNT. \textsuperscript{19} An SWNT based chemiresistors was described by Park \textit{et al.} as sensitive and selective technique for detection of nitro-aromatic explosives.\textsuperscript{20} Here SWNTs-based chemiresistors were applied for environmental monitoring of water samples. Senesac \textit{et al.} discuss the possibility for nanosensors, such as carbon nanotubes as a platform for trace explosive detection.\textsuperscript{14} Amongst other, theses sensing devices are fabricated to improve selectivity with the interaction/affinity of nanotube-based network with the trace vapors.

In this dissertation, we have developed e-nose sensors for vapors using a diversified set of nanostructured chemical sensors comprised of novel surface-functionalized carbon to enhance specific responses. The gas sensing materials have been spun coated as a film onto interdigitated electrodes made of different electrode materials (platinum and gold). This study involves measuring changes in the electrical conductivities of the decorated electrodes upon exposure to selected vapors, with the intention for analyte discrimination and fingerprinting. Prior to the identification of vapors by pattern recognition system, these changes are converted into electrical signals, which are tempered and preprocessed. In this chapter, we discussed briefly our preliminary investigation of signature components of Cyclotrimethylene trinitramine (RDX) under static exposure to the brominated SWNT sample (IME-SWNT-Br) spun casted on gold and platinum interdigitated electrodes.
8.3 PROPERTIES OF EXPLOSIVES – COMPONENTS OF EXPLOSIVES

During World War II, the usage of RDX was reckoned to be the second most widely used explosive and today, it is observed to be one of the most popular.\textsuperscript{1} Detection of trace explosive with a high degree of sensitivity and selectivity employed by various sensors has been a challenge due to a number of factors; these are inclusive of the small amount of explosive molecules that get absorbed in a practical exposure period due to their extremely low vapor pressure at room temperature.\textsuperscript{21} There is also an issue with the range of chemical components and combinations that has used in the production explosives worldwide. In this chapter, we employed an alternate approach to lessen these concerns; a direct usage of reported inert chemical components of RDX explosive system for detection is studied. These components are reported in Adebimpe \textit{et al.} \textsuperscript{22,23} fabrication of pseudoscents of explosive, which comprised of non-energetic signature chemical components for use as training aids for explosive detecting dog (EDD). These pseudo-components are inclusive of cyclohexanol, cyclohexanone, octane and 2,3-dimethyl-2,3-dinitrobutane\textsuperscript{22,24} and are noted with respect to their equilibrium vapor pressure at room temperature.

In this study, brief discussion on the use of pristine SWNTs and functionalized nanotubes as the RDX explosive sensing network is embarked on. The functionalized SWNTs will allow for an increase in sensitivity due to the high surface area and selectivity, owing to the attached functional moieties. As reported in earlier chapters and Zhang \textit{et al.}\textsuperscript{25}, pristine carbon nanotubes have very little affinity to analytes and therefore would not be reasonable for sensing application. However, the hope to demonstrate that functionalized nanotube-based chemosensors have a great
future as extreme sensitivity and selective signal transduction platform for an explosive sensing system is envisioned.

8.4 EXPERIMENTAL

8.4.1 MATERIALS AND METHODS

Reagents: Chemicals and washing solvents were purchased from Sigma Aldrich and Alfa Aesar, while pristine single-walled carbon nanotubes (purity, 95 wt. %) were purchased from Unidym Inc, Sunnyvale, CA and used without further purification. Interdigitated microsensor electrodes (IME 1025-M-Au-U and IME 1025-M-Pt-U) were purchased from ABTECH Scientific, Inc. (Richmond, VA).

Preparation of Covalently Brominated-SWCNTs: Poly-brominated SWNTs were achieved through a novel approach of photolysis of bromine to the side-wall of pristine nanotubes using N-Bromosuccinamide (NBS). Typically, ca. 20 mg of HiPco SWNTs was sonicated in 15 mL of dichloromethane for 20 minutes. The dispersed mixture was poured into a 100 mL round bottom flask. NBS (0.5 equivalent) was then added to the dispersion. The reaction was conducted under reflux conditions with a GE, 60 watt incandescent light bulb as a UV/heat source, which promoted generation of free bromine radicals. The reaction was allowed to run for about 15 minutes, during which gaseous components were emitted, resulting in a light yellowish liquid suspension. Next, ca. 1.0 equivalent of N-Bromosuccinamide was added in order to drive the reaction toward complete utilization of all bromine formed. The reaction was allowed to continue uninterrupted for another 90 minutes. At this point, the heat source was lowered (≈ 40 mm) below the reaction flask to reduce the reaction rate. The reaction was allowed to proceed to
CHAPTER 8: Preliminary Detection of …

completion for another 10 hours. Additionally, for other syntheses studies, the reaction procedure was modified by allowing the final step to occur for durations of 24 and 48 hours. The final suspension was cooled and filtered through a PTFE membrane filter (0.45 μm, 25mm). The filtrate was thoroughly washed with chloroform followed by diethyl ether. The resultant product was dried overnight at 60°C under vacuum. Device preparation is as discussed in Chapter 2 (section 2.6).

Observation revealed that the functionalization of SWNT by photolytic with N-Bromosuccinimamide does produce conductive nanotube-based chemiresistors; as discussed in previous chapters, the conductivity of the network has improved when compared to the pristine SWNT. With the ionic nature of halogen-carbon bonds (C-Br), the hydrogen bonding capacity of halogen functionalized sp² carbon is improved resulting in enhanced affinity of the functionalized carbon species (SWNT-Br) to aliphatic vapors or small molecular volatile. In photolysis, photons can break the molecular bond between molecular fragments in which the bonding electrons are evenly shared between the bonded atoms. After cleavage each of the previously bonded atoms receives one electron from the electron bond and thus free radicals are formed. The generated Br free radicals can then be expected to attack the CNT wall much like radicals do in diazotization that leads to conjugation with benzene.

8.4.2 CHEMORESISTIVE GAS /VAPOR RESPONSES

Chemoresistive response to RDX vapor components was studied using the Solartron 1260 FRA to measure progressive changes in the magnitude of impedance |Z|, upon exposure. Brominated SWNT was spun-applied to OTS-modified Pt and Au IME devices, which then gets
inserted into the vial (via its cap) with very low concentration of static, headspace vapors emanating from a specific condensed sample of solvent (50 µL) contained in a closed (1 mL) vial. Explosive chemical components considered are cyclohexanol, cyclohexanone, 2,3-dimethyl-2,3-dinitrobutane (DMDNB) and octane. Vapor exposure proceeded for 60 s (herein referred to as "On" period) followed by 60 s exposure to air (herein referred to as "Off" period) at room temperature. Each run time was 3 min with an On-Off-On cycle of 1 min each. The durations used were entirely arbitrary. In general, both sensor systems exhibited rapid adsorption and desorption kinetics at room temperature.

8.5 RESULTS AND DISCUSSION

8.5.1 CHEMORESISTIVE RESPONSE TO VAPORS

Similar occurrence to our discussion in Chapter 5; as the response of the sensing elements to the vapors, as seen in Figure 8.1, may have resulted from the incorporation of vapor into the underlying OTS organic layer, which leads to swelling and changes in percolation of the SWNT network. A more fundamental alternative is that the vapor may adsorb onto the surfaces of the functionalized SWNT, and interaction with the introduced bromine, thus producing changes in electron density within the tubes thereby altering the resistance. The first hypotheses would favor favorable vapors such as octane having the most dramatic response as these would readily partition into (i.e., mix with) and effectively swell the OTS layer. The second choice suggests that vapors such as cyclohexanol, being more polar, will produce a larger response than cyclohexanone, octane and DMDNB. Using an IME-Pt-SWNT-Br device, real time the resistance responses to these vapor components of RDX are shown in Figure 8-1A. The largest
response was to cyclohexanol, over cyclohexanone and octane, while DMDNB did not reveal and significant resistance change. This confirms that the furthermost possible basis for the response of the sensor element is the interaction of the vapor with the f-SWNTs by manner of surface adsorption. In each instance, the electric resistance increased when chemosensor gets exposed to the surrounding vapor (On state) and decreased in air atmosphere (off state). Apparently the sensing response to each component varies, which is likely due to the dipole interaction of the analyte to the sensors system. Cyclohexanol having the highest relative polarity demonstrated the supreme effect on the monitored resistance changes during exposure to the SWNT-Br chemosensor. The chemosensor has shown little to no response to the DMDNB analyte, as DMDNB (described as a taggant in RDX) exude the lowest vapor pressure, thus providing little vapor for effective interaction within the sampling time used. Despite the intensity of resistance changes, the average maximum upon exposure appears to be uniform for each analyte. In other words, we can refer to the “on state” as having a good recovery baseline (recovery upon vapor exposure).
Figure 8-1A: Chemiresistive adsorption and desorption profiles (responses) of IME-Pt-SWNT-Br statically exposed to 4 signature vapor components of RDX explosive and to air in ON-OFF-ON cycles at RT. Vapors are cyclohexanol, cyclohexanone, octane and DMDNB.

Similar to Figure 8-1A, Figure 8-1B shows vapor response to IME-Au-SWNT-Br as adsorption to the surface of the SWNT network, with reversibility. However, there are distinct differences in the intensity of resistance changes upon exposure when compared to the IME-Pt-SWNT-Br sensor. As discussed in Chapter 5, Au electrode is a more conductive metal than Pt and therefore suits for casting on interdigitated electrodes for sensing application. The order of sensitivity of the signature vapors (in reference to magnitude of resistance changes - cyclohexanol > cyclohexanone > octane > DMDNB) is similar to that of the Pt device.

However, the Au device response showed higher resistance changes to that of the IME-Pt-SWNT-Br device for cyclohexanone and octane; exhibiting roughly 2-fold increase in
sensitivity. Again, DMDNB does exhibit the same negligible interaction with the IME-Au-SWNT-Br device. Owing to the relative polarity and vapor pressure of the signature vapors, it seems likely that would cyclohexanol have a greater influence on interacting with the devices. This adsorption causes the greatest increase in the resistance of the functionalized SWNT network.

**Figure 8-1B:** Chemiresistive adsorption and desorption profiles (responses) of IME-Au-SWNT-Br statically exposed to 4 signature vapor components of RDX explosive and to air in ON-OFF-ON cycles at RT. Vapors are cyclohexanol, cyclohexanone, octane and DMDNB.

**8.6 CONCLUSION**

A network of brominated SWNTs has been used to construct thin-film chemosensors on gold and platinum interdigitated electrodes for detecting signature components of RDX. With
preliminary experimentation, the sensors responses based on static operation demonstrated the capabilities of sensitivity, reversibility and the ability of detecting low concentration levels of cyclohexanol, cyclohexanone and octane with uniqueness. With future work, we will be able elaborate more on the unique and discriminative responses of our chemosensor for explosive detection.
8.7 REFERENCES


(10) Osborn, T.; Burns, W. A.; Green, J.; Reeve, S. W. **2011**.


(15) Kelvin M. Frazier, T. M. S. *Analytical Chemistry**2013**, 85, 7154.


CHAPTER 9: Conclusion

9.1 SUMMARY

We have demonstrated that the electronic structure of singled walled carbon nanotubes (SWNTs) is tunable by means of covalent functionalization with electron donating and electron withdrawing groups. The resulting characterized materials were then exposed as sensing elements for vapor detection and have the potential for further investigation as super capacitors.

In Chapter 4, we present a facile and efficient photobromination technique for the covalent sidewall functionalization of SWNT using N-bromosuccinamide as the bromine radical source. The modified bromine functionalized SWNTs are used as active agents in a resistance measuring electrode system for sensing of analyte vapors. We have deduced that covalently brominated single-walled carbon nanotubes may function as one sensing element, in a more complex multisensing platform that involves a number of different covalent adducts on SWNT surfaces, for the determination of the compositional makeup of a complex vapor emanating from an unknown sample. We found in Chapter 5 were this chemiresistor fabricated on Au and Pt interdigitated electrodes, revealed that the metals’ work function and the resistivity have pronounced impact on the sensory receptor’s responses to IV, impedance, temperature and vapor characterization.

In exploring the diazonium coupling functionalized SWNT materials, Chapter 6 proves through various qualitative characterization techniques, the successful incorporation of functional moieties on the sidewall of the nanotubes. Our discussion with the comparisons of the characterized data and vapor/ sensor interaction attest that the functionalized groups have a
diverse effect on the electronic structure of the SWNTs. The impact that functionalized had on the electrical properties of the SWNTs displayed remarkable differences in the levels of resistors presented in Chapter 7. Covalent Functionalization is known to disrupt the electronic structure of carbon nanotubes. However, with this cohort of functionalization, we have showed in two instances (SWMT-Br and SWNT-NH$_2$) where the conductivities were superior to that of the pristine SWNTs. Chapter 8 reveals great potential for these chemisensors/chemiresistors for use in the application of the detection of signature components of various explosives.

9.2 SUGGESTION OF FUTURE WORK

In reference to Chapter 7, more investigation will be conducted to qualify these chemisensors/chemiresistors for effect use super capacitors.

In Chapter 8, we present an area for continued research with regards to explosives detection. There are a number of possibilities for further research as it relates to functionalized SWNT based network devices and specifically chemisensors using interdigitated electrodes. The primary goal for future work on the detection of signature vapor components of explosives will be the continued investigative approaches to proving selectivity to vapor components of RDX. Other important efforts include exposing other nanotube-based chemisensors (as presented in Chapter 6; IME-SWNT-NO$_2$, IME-SWNT-SH, IME-SWNT-F, IME-SWNT-OH, IME-SWNT-NH$_2$ and IME-SWNT-CN) to vapor components of RDX, TNT, Dynamite, TATP, PETN and other high-level explosives that are of threat to society.
During this period, we will seek to optimize this new generation of diverse chemisensors for detection of explosive vapors, with the hope of providing high sensitivity, vapor selectivity, sensor reversibility, stability and overall, superior performance. The results obtained from these detection will be then amalgamated, classified—using multivariate analytical methods such as linear discriminant analysis (LDA), which can map multidimensional data onto 2 or 3 dimensions with a minimum loss of information —and thereafter compared against target odors and/or scent signatures exuded by explosives, which would have been previously determined, classified, and programmed within our devices.
Bibliography

Chapter 1


(4) In Boundless Chemistry Boundless:


(7) Electronics, U. C. f.


(40) Huang, X.-J.; Choi, Y.-K. Sensors and Actuators B: Chemical 2007, 122, 659.

(41) Hoummady, M.; Campitelli, A.; Wlodarski, W. Smart materials and structures 1997, 6, 647.


(44) Electronics Bus.


(49) Su, P.-G.; Chuang, Y.-S. Sensors and Actuators B: Chemical 2010, 145, 521.

(50) Hafaiedh, I.; Elleuch, W.; Clement, P.; Llobet, E.; Abdelghani, A. Sensors and Actuators B: Chemical 2013, 182, 344.


(53) Yinon, J. Counterterrorist detection techniques of explosives; Elsevier, 2011.


Chapter 2


Chapter 3


(3) Goertz, M. P.; Moore, N. W. Progress in Surface Science 2010, 85, 347.


(5) Gheorghe, M.; Guinea-Pi-Elie, A. Biosensors & Bioelectronics 2003, 19, 95.


(9) Moxfyre 2009.


(11) Anal. Chem. 1957, 29, 94A.


(15) Heaviside, O. Electrical papers; Cambridge University Press, 2011; Vol. 2.

(16) Kennelly, A. American Institute of Electrical Engineers, Transactions of the 1893, 10, 172.
(17) Storr, W.; Basic Electronics Tutorial.


(21) Rubenstein, I. Physical electrochemistry: principles, methods, and applications; CRC Press, 1995; Vol. 7.


Chapter 4


(14) Zhou, O.; H. Shimoda; B. Gao; S. Oh; L. Fleming; G. Yue, Accounts of chemical research. 2002. 35(12): 1045-1053.


(37) Bulusheva, L.G.; A.V. Okotrub; E. Flahaut; I.P. Asanov; P.N. Gevko; V. Koroteev; V.V. Fedoseeva; A. Yaya; C.P. Ewels, Chemistry of Materials. 2012. 24(14): 2708-2715.


(45) Dommelen, L.V., Semiconductors: Quantum Mechanics of Engineers. 6.23.

Chapter 5


Chapter 6


(18) Powell, A. R. Industrial & Engineering Chemistry. 1920, 12, 1077.


(23) Coates, J. Interpretation of infrared spectra, a practical approach, 2000.


Chapter 7


(14) Hang, T. C.; Guiseppi-Elie, A. Biosensors and Bioelectronics 2004, 19 1537.


Chapter 8


(9) Tourné, M. J Forensic Res S2013, 12, 2.

(10) Osborn, T.; Burns, W. A.; Green, J.; Reeve, S. W. 2011.


(15) Kelvin M. Frazier, T. M. S. Analytical Chemistry2013, 85, 7154.


