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To my wife, Caitlin

In memory of Lola,
November 15, 2006 to
February 25, 2017
In this thesis, chemiresistive devices for the detection of volatile organic compounds to include chemical warfare agents are developed. Active sensing materials were produced by crafting composites of synthetic polymers and single walled carbon nanotubes. Sensitivity to and selectivity for target analytes were augmented by the introduction of molecular recognition elements into polymer side chains or by the addition of additives into a polymer/single walled nanotube composite. Additionally, methods to create n-type single walled carbon nanotubes through covalent side wall functionalization were explored.

Chapter 1: Chemiresistive sensors are becoming increasingly important as they offer an inexpensive option to conventional analytical instrumentation, they can be readily integrated into electronic devices, and they have low power requirements. Nanowires (NWs) are a major theme in chemosensor development. High surface area, inter-wire junctions, and restricted conduction pathways give intrinsically high sensitivity and new mechanisms to transduce binding or action of analytes. This chapter details the status of NW chemosensors with selected examples from the literature. We begin by proposing a framework for understanding electrical transport and transduction mechanisms in NW sensors. Next, we offer the reader a review of device performance parameters. Then, we consider the different NW types followed by a summary of NW assembly and different device platform architectures. Subsequently, we discuss NW functionalization strategies. Finally, we propose a roadmap for future developments in NW sensing that addresses selectivity, sensor drift, sensitivity, response analysis, and emerging applications. The NW field is still in its infancy, and continuing advances present abundant opportunities.

Chapter 2: Chemical warfare agents (CWA) continue to present a threat to civilian populations and military personnel in operational areas all over the world. Reliable measurements of CWAs are critical to contamination detection, avoidance, and remediation. The current deployed systems in United States and foreign militaries, as well as those in the private sector offer accurate detection of CWAs, but are still limited by size, portability and fabrication cost. Herein,
we report a chemiresistive CWA sensor using single-walled carbon nanotubes (SWCNTs) wrapped with poly(3,4-ethylenedioxythiophene) (PEDOT) derivatives. We demonstrate that a pendant hexafluoroisopropanol group on the polymer that enhances sensitivity to a nerve agent mimic, dimethyl methylphosphonate, in both nitrogen and air environments to concentrations as low as 5 ppm and 11 ppm, respectively. Additionally, these PEDOT/SWCNT derivative sensor systems experience negligible device performance over the course of two weeks under ambient conditions.

Chapter 3: The detection of alkylating agents using carbon nanotube chemiresistive devices has confounded researchers in the sensor field for quite some time. In this work, we address this quandary by fabricating a chemiresistive device consisting of poly(4-vinylpyridine)/single walled carbon nanotube/lithium bromide composites that is able to detect gaseous ethylene oxide (EtO) and a mustard agent simulant, 2-chloroethyl ethylsulfide (CEES). Our devices were sensitive to EtO and CEES down to 1048 ppm and 33 ppm, respectively. We calculated theoretical detection limits of 212 ppm for EtO and 10 ppm for CEES. These results should encourage researchers in the field to tackle analytes once thought to be undetectable via carbon nanotube chemiresistive devices, as they offer a low cost and low power alternative to current options.

Chapter 4: The covalent functionalization and characterization of single walled carbon nanotubes (SWCNTs) by dihalocarbenes and the trifluoromethylation Togni’s reagent is explored in this chapter. Covalent functionalization reactions were performed to increase the SWCNT solubility, imparting n-type semiconducting behavior while maintaining the native conductivity of the conjugated sp² network. Previous computational studies predicted the conservation of the electrical conductivity of SWCNTS after carbene additions, but experimental work to verify the electrical properties has not been performed. In the studies presented herein, we utilized five different covalent functionalization methods to modify SWCNTs and utilized X-ray photoelectron spectroscopy (XPS) in tandem with Resonance Raman spectroscopy to characterize our products. Though electrical characterization was not performed, we improved upon literature methods concerning the dichlorocarbene addition of –CCl₂ groups to pristine SWCNTs.

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<th>Description</th>
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<tr>
<td>CWA</td>
<td>Chemical warfare agent</td>
</tr>
<tr>
<td>CEES</td>
<td>2-chloroethyl ethylsulfide</td>
</tr>
<tr>
<td>DMF</td>
<td>N,N-dimethylformamide</td>
</tr>
<tr>
<td>DMMP</td>
<td>Dimethyl methylphosphonate</td>
</tr>
<tr>
<td>EDOT</td>
<td>3,4 Ethylenedioxythiophene</td>
</tr>
<tr>
<td>EtO</td>
<td>Ethylene oxide</td>
</tr>
<tr>
<td>FTIR-ATR</td>
<td>Fourier transform infrared-attenuated total reflectance</td>
</tr>
<tr>
<td>GPC</td>
<td>Gel permeation chromatography</td>
</tr>
<tr>
<td>HFIP</td>
<td>Hexafluoroisopropanol</td>
</tr>
<tr>
<td>KCTP</td>
<td>Kumada catalyst transfer polycondensation</td>
</tr>
<tr>
<td>MM</td>
<td>Mechanical milling</td>
</tr>
<tr>
<td>NBS</td>
<td>N-bromosuccinimide</td>
</tr>
<tr>
<td>NIR</td>
<td>Near infrared</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance</td>
</tr>
<tr>
<td>o-DCB</td>
<td>ortho-dichlorobenzene</td>
</tr>
<tr>
<td>m-SWCNT</td>
<td>Metallic single walled carbon nanotube</td>
</tr>
<tr>
<td>PEDOT</td>
<td>Poly(3,4 ethylenedioxythiophene)</td>
</tr>
<tr>
<td>PTFE</td>
<td>Poly(tetrafluoroethylene)</td>
</tr>
<tr>
<td>p-SWCNT</td>
<td>Pristine single walled carbon nanotube</td>
</tr>
<tr>
<td>RBM</td>
<td>Radial breathing mode</td>
</tr>
<tr>
<td>RH</td>
<td>Relative humidity</td>
</tr>
<tr>
<td>SWCNT</td>
<td>Single walled carbon nanotube</td>
</tr>
<tr>
<td>sc-SWCNT</td>
<td>Semi-conducting single walled carbon nanotube</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric analysis</td>
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<tr>
<td>VOC</td>
<td>Volatile organic compound</td>
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<td>XPS</td>
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CHAPTER 1

Nanowire Chemical/Biological Sensors: Status and a Roadmap for the Future

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1.1 Abstract

Chemiresistive sensors are becoming increasingly important as they offer an inexpensive option to conventional analytical instrumentation, they can be readily integrated into electronic devices, and they have low power requirements. Nanowires (NWs) are a major theme in chemo sensor development. High surface area, inter-wire junctions, and restricted conduction pathways give intrinsically high sensitivity and new mechanisms to transduce binding or action of analytes. This chapter details the status of NW chemo sensors with selected examples from the literature. We begin by proposing a framework for understanding electrical transport and transduction mechanisms in NW sensors. Next, we offer the reader a review of device performance parameters. Then, we consider the different NW types followed by a summary of NW assembly and different device platform architectures. Subsequently, we discuss NW functionalization strategies. Finally, we propose a roadmap for future developments in NW sensing that addresses selectivity, sensor drift, sensitivity, response analysis, and emerging applications. The NW field is still in its infancy, and continuing advances present abundant opportunities.

1.2 Introduction

The omnipresence of wireless devices, cloud data, and printable electronics is an extraordinary opportunity for electronic chemical sensors. These sensors enable governments, businesses, and individuals satisfy an ever-expanding appetite to measure chemical and biological processes as well as physical quantities. Over the last decade, the electronic chemical sensor du jour contains nanowires (NWs). The assertion that NWs offer advantages in sensors is often made without justification. However, we contend that it is generally warranted. The simplest reason is their high surface area-to-volume ratios, which allows for more interactions with analytes. However, monolayers of 2-D materials such as graphene

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and MoS$_2$\textsuperscript{3-7} also have high surface areas. The most important difference between 1-D NWs and 2-D materials is how they transport current.

In a NW, electrical transport is primarily along the NW axis. If the NW is small enough in diameter, high sensitivity is achieved because analytes could bind anywhere along the NW to perturb its entire conductivity. This effect is similar to what our group reported with semiconducting polymers, where we demonstrated signal gain by wiring receptors in series.\textsuperscript{8} Although this principle was studied for exciton rather than charge transport, there was a correlation between carrier path length and signal amplification. Thus, long single NWs are attractive because sensitivity increases with length available for interacting with analytes. However, they are difficult to fabricate.

Alternatively, disordered NW networks can be readily deposited by solid transfer, printing, spraying, or drop-casting a dispersion. Random networks of NWs, as opposed to densely packed aligned networks, have the advantage of porosity with high surface area and limited contact between NWs to give restricted pathways that preserve 1-D character. The inter-NW contacts are critical: For NWs with high carrier mobilities, these junctions are conductivity-limiting. Various intra- and inter-NW mechanisms of transduction are illustrated for single-walled carbon nanotubes (SWCNTs) in Figure 1.1. Amongst all NWs, our group favors SWCNTs due to their excellent conductivity, exceptional aspect ratios, and numerous methods available for functionalization.

For many systems, reductions in conductivity are observed; coherence in electronic transport is destabilized by heterogeneous potentials that result from analytes. However, analytes can also enhance conductivity by facilitating charge transfer across resistive interfaces, lowering barriers, or injecting carriers through doping.
A chemiresistor comprising a percolative, randomly oriented network of SWCNTs spanning two metallic electrodes has a current (yellow cloud) flowing through it when a voltage is applied. The presence of analyte (red sphere) can inhibit current flow (red cloud) via (B) Schottky barrier modulation at electrode–SWCNT junctions, (C) charge transfer between analyte and SWCNT, or (D) increasing SWCNT–SWCNT junction distance by intercalation or swelling of the SWCNT network.

That a “turn-on” response is more sensitive than “turn-off” is often stated in fluorescence; however, this assertion is only true with zero background fluorescence in the absence of analyte and emission only in presence of analyte. The analogy for NWs is an insulating device that becomes conductive upon exposure to analyte. If this activation is achieved by carrier injection, high sensitivity is obtained when the NW has very low carrier density in the absence of analyte. Alternatively, NW networks could be assembled slightly below a percolation threshold such that they are highly resistive, and analyte-triggered formation of new conduction pathways can produce a large turn-on response.

Sensitivity without selectivity, however, is simply noise. Systems should respond strongly only to desired analytes. Coupling molecular processes to conductivity changes for selectivity
often involves careful molecular constructions. Chemistry has provided decades of innovations in molecular recognition to guide development of chemical sensors. The challenge is how to produce specific electronic perturbations by analyte binding.

In this article, we survey the NW sensor landscape. First, we lay out performance parameters employed to evaluate progress. We then move on to compositions, fabrication methods, device architectures, and operational modalities. Rather than a comprehensive review, we discuss selected examples to highlight advantages of NW sensors, the status of the field, and opportunities for going forward, which we hope provides a roadmap for future innovations.

1.3 Sensory device performance parameters

The performance of a chemical sensor is a product of the physical form of the sensor material, strength of the analyte transduction event, selectivity of the response to a given analyte, and the sensor’s stability. Figure 1.2 is a representative sensing trace that may assist in graphically visualizing key terms.

1.3.1 Sensitivity, dynamic range, limit of detection

The limit of detection (LOD) is the minimum amount of analyte that can be detected at a known confidence level. The target LODs in sensors for environmental safety are driven by regulation. Representative values are published by the United States Environmental Protection Agency, the National Institute of Occupational Safety and Health (NIOSH), and the European Union Agency for Safety and Health at Work.
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Figure 1.2 Graphical representation of selected device performance parameters in a device successively exposed to increasing concentrations of analyte.

The LOD can be influenced by receptor–analyte interactions, surface area, functionalization, and signal amplification. A low LOD is closely tied to high sensitivity (response per unit concentration). In chemiresistors and chemicapacitors, the extent to which analyte influences the electronic properties of NWs is a major factor in the LOD.

Chu et al. demonstrated that alignment of receptors can be used to improve the LOD. A surface-modified Si-NW field effect transistor (FET) achieved LODs of 0.1 fM for ssDNA and 0.5 ppm for alcohols. The authors deduced that the field creates structural order to increase the efficiency of molecular reactions, strengthen the molecular dipoles, and consequently improve sensitivity. The reorganizations are likely more complicated than shown in Figure 1.3 (b, c), as APTES generally produces multilayer, polymerized coatings.

An increase in surface area offers more sites for analyte–sensor interactions and lowers LOD. Yue et al. obtained high surface areas in ZnO NW devices by growing them on 3-D graphene foam, resulting in an increased surface area from 6 to 33 m$^2$/g and a LOD of 1 nM for uric acid and dopamine, indicators of Parkinson’s disease.
Figure 1.3 Electric field alignment of aminopropyltriethoxysilane (APTES) on SiNW FETs. (a) SEM image of a SiNW-FET. (b, c) Schematic illustrations of the possible APTES molecular structures before and after the alignment process. (Reprinted from Ref. [16] with permission. Copyright 2013 American Chemical Society.)

**Figure 1.4** Illustration of formation of metalized wires from stretched rolling circle amplification (RCA) products to generate an electrical signal. (Reprinted from Ref. [18] with permission.) (Copyright 2014 American Chemical Society.)

Signal amplification of molecular interactions can reveal otherwise undetectable events. Russell et al.\(^8\) employed a rolling circle amplification (RCA) technique to create DNA strands to template the formation of NWs between two electrodes (Figure 1.4). This turn-on method detected synthetic and bacterial DNA at 100 pM and 66 fM, respectively.
Bounded by the LOD and limit of linearity, dynamic range is the range of analyte concentrations that can be accurately measured by a sensor. NWs can improve sensor dynamic ranges by increasing the limit of linearity (e.g., by increasing the surface area of the sensor to prevent saturation) and by lowering the LOD.

1.3.2 Selectivity

Figure 1.5 Creation of a highly stable SWCNT sensor by polymerization of functional selector around the deposited NW network (Reprinted from Ref. [23] with permission.) (Copyright 2013 American Chemical Society.)
Selectivity is measured as the ratios of sensitivity of the target analyte to that of interferents. *Specificity* should be reserved for cases of ultimate selectivity. Researchers must choose relevant interferents to effectively demonstrate selectivity.

Membrane coatings can exclude interferents based on analyte size, affinity, or permeation time.\(^9\) The operating temperature of a sensor will also affect selectivity. Increased selectivity can also be achieved by using a separate device to bind and pre-concentrate an analyte followed by thermal desorption to the sensor.\(^{20-22}\) Many sensors derive selectivity from functionalization with recognition elements that interact selectively with an analyte. In Section 6, we discuss how functionalization can impart selectivity.

### 1.3.3 Stability

Stability is determined by the sensor’s ability to produce the same output for an identical input over time, quantified as a ratio of the aged device’s response relative to a new device’s response. A stable sensor should remain unchanged over the lifespan of the device.

NW functionalization has been explored to improve stability. Our group demonstrated how SWCNTs functionalized with trialkoxysilane moieties exhibit increased robustness (Figure 1.5). Hydrolytic polymerization affixes the SWCNTs in place on the glass substrate. These sensors can survive sonication in methanol.\(^{23}\) Alternatively, coatings can be used to stabilize devices by functioning as a barrier to reactive chemicals or by immobilizing NWs.\(^{23-27}\)

### 1.3.4 Drift
Drift is the stimuli-independent change of a measurable output over time. It can lead to uncertain results, false alarms, and the need for frequent recalibration or replacement of sensors. Furthermore, there is a dearth of discussion on drift in the literature. There can be both short- and long-term drift, and the difference between the two can in some cases allow one to deconvolute specific contributions. Some potential causes include reorientation of particles and domains, segregation of mixtures, sublimation/evaporation of components, adsorption of species, doping/de-doping, and charge migration. The high surface area of NWs creates a challenge for drift, and how to mitigate these factors without passivation needs further exploration.

Drift can be addressed either by in-device recalibration or algorithmically during data processing and/or workup, for instance, by using principal component analysis (PCA). However, many applications cannot sustain intensive computational solutions to sensor drift. Therefore, the challenge of drift must be addressed at the device level.

1.3.5. Hysteresis

Hysteresis is the difference between outputs when an analyte concentration is approached from an increasing and decreasing range. It is important to minimize as a result of the challenges it poses to reversibility and dynamic range. When this suppression is not possible, the best one can do is characterize the hysteresis of the sensor.

1.3.6. Response time, dead time, rise time

Response time is determined at 90% of its final amplitude after analyte exposure, dead time is the time it takes to reach the first 10% of its final signal, and rise time is the difference. Response time is critical as many applications employ sensors to activate
systems in response to changing analyte levels. The factors that govern response time mirror those of reaction kinetics: surface area, temperature, and catalysis.

1.3.7. Reversibility and recovery time

Reversibility is the extent to which signal is restored to its initial state prior to analyte exposure. The recovery time is the time to decrease to 10% of the peak amplitude after removing the analyte. Although irreversibility can be exploited in dosimetry, incomplete, sluggish recovery is often undesirable.

Remedies to promote complete recovery include heating the sensor or exposing the sensor to ultraviolet (UV) light. However, heat and UV treatment create more complex systems with difficulties such as baseline noise and attenuated device lifetimes. Further investigations into alternate solutions for irreversibility are needed.

1.4 Nanowire types

We define a NW as a high aspect ratio nanostructure capable of charge transport. Wire does not imply an intrinsic metallic electronic state; most NWs in chemical sensors are in fact semiconductors. Semiconducting polymers, which can be considered molecular wires, were first recognized as affording signal amplification prior to the extensive NW sensor efforts. However, we will restrict ourselves to a more conventional description of NWs: high aspect ratio materials that are larger than a conventional polymer chain and often polydisperse in terms of length, diameter, and composition.

1.4.1 Elemental semiconductor NWs
NWs fabricated from Si and Ge have been extensively studied in sensors, especially in FETs. Si NWs are popular as a result of their compatibility with Si electronics and because Si doping and functionalization are mature technologies. However, they have limited stability and oxidize quickly, resulting in surface passivation. Silica NWs (SiO₂ NWs), however, have been substantially documented as an excellent material for sensing applications because of their ease of modification, functionalization, and biocompatibility.

Si/Ge NW synthesis can be accomplished through methods such as thermal evaporation. A common technique for growing various inorganic NWs is the vapor-liquid-solid (VLS) method using chemical vapor deposition (CVD) processes. Laser ablation can be used with VLS. Si/Ge NWs can also be grown from solution using a supercritical fluid-liquid-solid growth method.

1.4.2. Metal chalcogenide or pnictide NWs

NWs of chalcogenides such as SnO₂, ZnO, TiO₂, In₂O₃, WO₃, V₂O₅, CuO, Cr₂O₃, Nb₂O₅ and Fe₂O₃ and pnictides such as GaN or AlGaN, have been used extensively in chemiresistive gas sensors and FETs. Their sensing often relies on redox reactions between the analyte and the surface, generating variations in carrier concentrations, or surface trapping. They are inexpensive, robust to temperature and resistant to caustic environments, easily integrated into electronic circuits, and give high sensitivity. However, their use in sensing is often hampered by poor selectivity and high operating temperatures.

Nitrogen oxides (NOₓ) have been analytes of choice to assess the performance of metal oxide-based devices. NWs of oxides can be synthesized by methods that are variations on VLS in CVD or catalyst-free thermal oxidation.

1.4.3 Carbon nanotubes (CNTs)
CNTs are excellent sensor candidates due to their mechanical and electrical properties. Since Iijima and co-workers significantly raised the profile of CNTs in 1991, there has been a widespread effort to exploit their properties. CNTs can be considered as long hollow tubes of rolled-up graphene sheets. The angles at which they are rolled (the chiral vector) and the tube diameter determine whether a CNT is semiconducting or metallic. CNTs are either single-walled (SWCNT) or multi-walled (MWCNT). MWCNTs consist of multiple concentric layers of SWCNTs. In defect-free tubes, the bonds between carbons in the sidewalls are sp\(^2\) hybridized, and non-covalent van der Waals forces or π-stacking dominate intermolecular interactions. CNTs are synthesized via laser ablation, arc discharge, CVD, and combustion. CVD is the premier method with mild conditions, high yield, simplicity, and facile mediation of physical characteristics. Recent reviews can be found on CNTs in biotechnology and drug delivery, electronics, energy production and storage, and catalysis.

CNTs have found a special place in the sensor community because of aforementioned properties, compatibility with organic chemistry for functionalization, and easy integration into electronic circuits. CNTs have been used to sense biological molecules and vapors of industrial gases and explosives.

1.4.4 Transition metal NWs

Metal-based NWs such as Ni, Pt, Pd, Au, Ag, Pb, and Co have found limited applications in chemical sensing compared to their semiconducting counterparts, but they excel in the use of group 10 NWs in \(\text{H}_2\) sensing, Ag NWs for \(\text{NH}_3\) sensing, Au NWs for alkanethiol sensing, Ni and Cu NWs for carbohydrate sensing, and organothiol-functionalized Au NWs for biosensing. Metal NWs can be synthesized from chemical
etching\textsuperscript{105} or reductive cation electrodeposition.\textsuperscript{103,107} Metal NWs can be synthesized by bulk solution phase methods where a polyol is used as both solvent and reducing agent for metal cations.

### 1.4.5 Conducting Polymer NWs

Conducting (or conjugated) polymers (CPs) are a class of materials that are semiconducting upon oxidation or reduction (doping).\textsuperscript{108} Their molecular construction allows for intimate integration of receptor units into the backbone. Sensing relies on inducing modification of band structure or structure, resulting in changes in electronic properties.\textsuperscript{108} Many reviews exist on these materials as sensors.\textsuperscript{109-112} We restrict this discussion to NW constructions created from CPs.

Polymers in 1-D assemblies are formed by oxidative polymerization and can have improved electrochemical capacities.\textsuperscript{113,114} Templated synthesis relies on physical supports (hard template) to create nanostructures or on molecular self-assembly to guide growth of CP-based NWs (soft template). Template-free syntheses also exist.\textsuperscript{115} Electrospinning of nanofibers allows control over size, alignment, morphology and surface functionalization.\textsuperscript{116,117} Nanolithography methods allow reproduction of a pattern on a surface.\textsuperscript{118,119} CP NW films can also be deposited by layer-by-layer (LbL), Langmuir-Blodgett (LB), inkjet printing, dip-coating and spin-coating, drop-casting, electrophoretic deposition and thermal evaporation.\textsuperscript{120,121}

Sensors based on FETs (organic field-effect transistors, OFETs, and organic electrochemical transistors, OECTs) and chemiresistor architectures have revolutionized sensing using CPs with short response times, high sensitivity, easy device integration,\textsuperscript{108,120} and room-temperature operation.\textsuperscript{120} CPs can serve as a receptor layer, transducer, protective
coating, or electronic circuit. Sensing with non-functionalized CPs is mostly limited to small molecules (e.g., HCl, NH₃, hydrazine, chloroform, acetone, acetonitrile, alcohols, and benzene) and cations (e.g., Cu²⁺, Ag⁺, Pb²⁺, and Cd²⁺) in solution and reactive gases (e.g., H₂, N₂H₄, NH₃, H₂S, HCl). CPs can be functionalized and included in formulations to improve sensor properties. Long-term instability, irreversibility, and poor selectivity are the main drawbacks of CPs in sensing.

1.5 NW assembly and sensor fabrication

NW devices can be classified by the number of NWs (one or many) and orientation (aligned, not aligned). Single NW devices have a NW bridging the gap between two electrodes (Figure 1.6a, 1.6b) and offer high sensitivity, fast response to changing analyte concentrations, and high spatial resolution. However, single NW devices require specialized equipment to fabricate, and the low yield of functional devices increases cost. The Leiber group has used single crystalline NWs, n- and p-doped Si and Ge nanowires, in FETs for detection of DNA, single viruses, cancer markers, and small molecule-protein interactions. The Nuckolls group (Figure 1.7) has shown novel NW junctions where SWCNTs are cut and then reconnected by small molecules with probes to observe binding events such as methylation of DNA. They also bridged SWCNT-SWCNT junctions with DNA, thus illustrating the ability of DNA-nanowire devices to serve as sensors for biochemical events.
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Figure 1.6 Types of NW devices (schematics and images). [Figure 1.6b provided by reference 143 with the permission of 2006 Nature Publishing Group; Figure 1.6d provided by reference 144 with the permission of American Chemical Society 2003; Figure 1.6f provided by reference 145 with the permission of the Royal Society of Chemistry 2014]

Aligned multi-NW devices (Figure 1.6c, 1.6d) have multiple NWs arranged in a single orientation. Compared to NW networks, aligned NW devices have longer mean free paths for conducting electrons and meet percolation thresholds for connectivity with fewer inter-NW contacts. Accordingly, aligned NW devices can have lower resistance and greater current density but require complicated assembly processes.

Network NW devices (Figure 1.6e, 1.6f) are those in which the orientation of NWs is random. Because of the sheer number of NWs, statistics mitigate effects of electronic heterogeneity arising from polydispersity in NW length, diameter, and structure. Network devices diminish the need for precise position or orientation of any individual NW, which lowers the difficulty of fabricating devices. On the other hand, network devices have shorter mean free paths for electrons, leading to higher resistance and lower current density. Networks contain resistive NW-NW junctions that offer prospects for innovative integration of molecular switches.
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Figure 1.7 Electrical detection of methyl transferase (M.SssI) binding at a DNA-bridged CNT device. (Reprinted from Ref. [142] with permission.) (Copyright 2012 Royal Society of Chemistry.)

1.6 Platform architectures for sensor devices

The electronic properties of NWs are sensitive to changes in their chemical environment. These changes can be electrically evaluated using simple device architectures. A resistor (chemiresistor) is the simplest device with two electrodes (source and drain) on an insulating support connected by NWs (Figure 1.8A). The resistance can be measured by monitoring changes in current with a fixed voltage bias across the electrodes.

Figure 1.8 Graphical representation of chemiresistor, FET, and chemicapacitor devices and corresponding circuit diagrams and data readouts.
It can be advantageous to control the carrier concentration when transduction results from charge transfer interactions between a semiconducting NW and analyte. An additional electrode (gate) underneath the support converts a resistor into a FET and introduces additional control of carrier densities through modulation of the applied gate voltage and insight into the sensory mechanism (Figure 1.8B).

Changes in capacitance can also be analyte-specific. The high surface area and prospects for polarizing interfaces are well suited to creating large capacitive signals (Figure 1.8C). The use of AC field for measurements in chemicapacitors can reduce 1/f noise, ensure rapid response, and avoid electrophoretic effects from an applied directional voltage, which can reduce drift and enhance reversibility. Moreover, simultaneously examining changes in conductance and capacitance can help increase specificity.

The analog nature of chemiresponsive circuit components allows for facile integration into wireless devices such as resonant circuits and radio-frequency identification (RFID) antennas. Resonant circuits are comprised of inductive, resistive, and capacitive elements, so chemiresponsive elements directly influence their resonant frequency and Q-factor. Our group leveraged these features and developed SWCNT sensors that are wirelessly powered and read by smartphones (Figure 1.9). This method uses the smartphone's near field communication (NFC) by cutting the circuit of a passive sensor tag and reconnecting it with chemiresponsive SWCNTs.
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Figure 1.9 Illustration of a smartphone wirelessly powering and communicating with a passive RFID tag. (Reprinted from Ref. [146] with permission.) (Copyright 2014 Proceedings of the National Academies of Science.)

1.7 Functionalization methods for applications

NWs display useful intrinsic sensor properties, but functionalization is generally necessary to improve processability, sensitivity, selectivity, operating conditions, and stability.

1.7.1 Functionalization of inorganic semiconductor NWs

1.7.1.1 Non-covalent Functionalization of Inorganic Semiconductor NWs

Typical NW functionalization involves sputtering of metal films (Pt or Pd, typically 100 Å) on top of GaN,\(^{147}\) InN,\(^{148}\) or Si.\(^{149}\) In the presence of catalytic Pt or Pd on NWs, H\(_2\) binds and dissociates, modifying the carrier concentrations as evidenced by FET measurements.\(^{150}\) Coating NWs with metals allows for faster, enhanced response and shortened recovery time. Au nanoparticles (AuNPs) were deposited onto GaN NWs by plasma-enhanced chemical vapor deposition (PECVD), and physisorption of gases such as N\(_2\) and CH\(_4\) reduced conductivity of the NW network.\(^{151}\) CO\(_2\) sensing was achieved by coating GaN NW transistors with poly(ethyleneimine) (PEI). In the presence of CO\(_2\) and humidity, carbamic acid groups form and ionize to create new charges that affect the transport of the NWs.\(^{152}\)
Specific detection of biological species is achieved by functionalization of NWs with receptors possessing high selectivity (enzymes or antibodies). Glucose oxidase was immobilized in a ZnO NW matrix on top of a GaN transistor. In the presence of glucose, the enzyme catalyzes formation of gluconic acid and peroxide, which translates into a change in charge on the NWs, allowing for real-time glucose monitoring and a 0.5 nM LOD. Approaches have also been reported for detection of biomarkers such as prostate-specific antigen (PSA) using In$_2$O$_3$ NWs functionalized with antibodies via phosphonic acid binding. DNA sensing was achieved at 10 pM detection limit by electrostatically adsorbed complementary ssDNA onto Si NWs functionalized with amine side chains.

1.7.1. Covalent functionalization of inorganic semiconductor NWs

If an oxide layer is present, silane chemistry allows for functionalization of Si NWs with functional groups (amines, aldehydes) for further functionalization. However, the passivating oxide layer lowers sensitivity, so the SiO$_2$ is often etched away, and the exposed surface is covalently functionalized by hydrosilylation, halogenation, alkylation, thiolation, or arylation.

One of the earliest reports in Si-based FET sensing described pH monitoring by APTES-functionalized NWs, and the same type of NWs were found to respond to TNT in sub-fM amounts in solution and sub-ppt concentrations in air through formation of Meisenheimer complexes. Si NWs modified with thiol groups showed response to Cd$^{2+}$ and Hg$^{2+}$. Peptides were attached to Si NWs and used in an array to detect Cu$^{2+}$ and Pb$^{2+}$ in low nM concentrations, and Na$^+$ was detected by crown ether-functionalized Si NWs. Volatile organic compounds (VOCs) and small molecules (NH$_3$, acetone, NMe$_3$, acetic acid) were detected orthogonally by oligopeptides appended to Si NWs. Many biosensors were
developed by appending receptors to Si NWs\textsuperscript{162,163} such as biotin for streptavidin recognition,\textsuperscript{164} antigens for recognition of their respective antibody,\textsuperscript{137,165} and DNA strands for recognition of complementary oligonucleotides.\textsuperscript{166}

1.7.2 Functionalization of metal oxide NWs

1.7.2.1 Compositional mixtures with metal oxide NWs

Metal oxides possess many desired properties, but rarely does one exhibit all desired attributes.\textsuperscript{167} Work function and carrier density can be modulated by preparing mixed metal oxides. There has been considerable effort in the functionalization of SnO\textsubscript{2}.\textsuperscript{58} Gaseous analytes such as H\textsubscript{2}S,\textsuperscript{168} EtOH,\textsuperscript{169-172} CO,\textsuperscript{173} H\textsubscript{2}\textsuperscript{174} and formaldehyde\textsuperscript{175-177} have been detected using mixed metal oxides. Integrating SnO\textsubscript{2} nanocrystals with CuO-NWs allows for detection of NH\textsubscript{3} at room temperature.\textsuperscript{178} The presence of highly environment-sensitive nanosized p-n junctions was given as an explanation for the sensitivity. Copper oxide NWs have garnered attention as a non-enzymatic determination of biologically important molecules. CuO-NWs have been used as the active sensing component to determine glucose concentration in concert with a Nafion film\textsuperscript{179} and in a Cu-CuO NW composition.\textsuperscript{180} In both cases, the NWs electrocatalyze the oxidation of glucose; both devices display high sensitivity and linearity in the biological range of blood glucose (3-50 mM) and environmental stability. Electrochemically synthesized Cu\textsubscript{2}O-NWs have been employed with Nafion to determine H\textsubscript{2}O\textsubscript{2} concentration over a wide and relevant range (0.25 \textmu M to 5.0 mM) and a low LOD (0.12 \textmu M).\textsuperscript{181}

AuNP-decorated SnO\textsubscript{2} NWs provide enhanced sensing performance for NO\textsubscript{2}\textsuperscript{182} and aromatic gases (i.e., benzene, toluene).\textsuperscript{183} Similarly, SnO\textsubscript{2} NWs decorated with AgNPs displayed improved sensitivity and selectivity for ethanol over other gaseous analytes,\textsuperscript{184} and
PtNP-decorated SnO$_2$ nanofibers detected acetone in sub-ppm concentrations.$^{185}$ More complex functionalization schemes exist where the (doped or mixed) metal oxide is decorated with other nanostructures. A recent example reported Mg-doped In$_2$O$_3$ NWs functionalized with metal NPs (Au, Ag, or Pt). Used in an array at room temperature, the sensors were able to discriminate vapors of CO, ethanol, and H$_2$ at 100 ppm, and the LOD for CO was 0.5 ppm.$^{186}$

1.7.2.2 Covalent functionalization of metal oxide NWs

Covalent functionalization has been investigated mostly for biofunctionalization. ZnO can be modified with carboxylic acid or amine functions for further functionalization.$^{148}$ APTES was used to functionalize ZnO NWs with uricase in order to develop a FET sensor for uric acid in aqueous solution.$^{187}$ GaN NWs are also amenable to organosilane chemistry, allowing covalent functionalization to afford sensors with high stability.$^{188}$

1.7.3. Functionalization of carbon nanotubes

CNTs offer some of the best opportunities for precise molecular assembly; however, they have considerable imprecision in structure and are mixtures with different diameters, chiralities, and lengths. They also have aperiodic functional groups (defects) that influence their properties. There is still much to learn in how to best functionalize SWCNTs in order to create optimal NW sensors.

1.7.3.1 Physical mixtures containing CNTs

Functionalization can be achieved by mixing CNTs with selectors, which often leads to composites of lower stability than covalent modification. The fabrication of metal–CNT composites is achieved through sputtering$^{189,190}$ or electrodeposition.$^{191}$ Physical mixtures of
MWCNTs and PMMA have also been used for sensing CH₂Cl₂ and CHCl₃, where the response was ascribed to a swelling mechanism. Solution mixing was used to fabricate SWCNT mixtures with a copper(I) scorpionate for the detection of ethylene. In this case, the copper(I) was modelled as binding to the CNT (Figure 1.10). Finally, physical mixtures of small molecule selectors and either MWCNTs or SWCNTs have been produced via solid-state mechanical mixing for chemiresistors. This rapid prototyping method allows for screening of CNT composites as sensor materials.

1.7.3.2 Non-covalent functionalization of CNTs

Non-covalent modification is less invasive than covalent functionalization as it relies on π (π)-interactions and van der Waals interactions between molecules and CNTs. Non-covalent interactions are often integral to dispersing CNTs, achieved through solution-based mixing, in situ polymerization, or melt mixing. Wei et al. showed detection of trinitrotoluene (TNT) using aminopyrene as a selector. For the detection of cyclohexanone by Frazier and Swager (Figure 1.5), a trifunctional molecule containing an aromatic unit (hexafluoroxylene), a selector unit (a thiourea), and an anchoring unit (a silane) gave non-covalently functionalized CNTs with superior durability and good sensitivity.

Figure 1.10 Optimized structure of copper(I) scorpionate bound to 6,5-SWCNT. (Reprinted from Ref. [193].)
A common strategy is to use polymers. The active materials are typically obtained by drop-casting, dip-coating, solution mixing or in situ polymerization. CPs are excellent for dispersion of SWCNTs. Polythiophenes with receptor-based sidechains have been used in sensors to discriminate between different xylenes (Figure 1.11).

Figure 1.11 Schematic view of the SWCNT/polymer sensor that selectively adsorbs p-xylene. (Reprinted from Ref. [203].)

1.7.3.3 Covalent functionalization of CNTs

Covalent modification disturbs the π-electron system and adds defects but can increase the stability of dispersions. Common sidewall reactions include azomethine ylide dipolar cycloadditions and reductive reactions with diazonium ions. Covalent functionalization can also be conducted at CNT termini. A common strategy relies on oxidation to produce carboxylic acid moieties at defect sites, which can be further functionalized. Weizmann et al. demonstrated exclusive regioselective functionalization SWCNT termini for the detection of single-stranded DNA (ssDNA) using a chemiresistor with detection limits of 10 fM and discrimination of single, double, and triple base pair mismatches (Figure 1.12). End-of-tube oxidation followed by polymer modification has also been used to build FET sensors with ppb-level detection limits for NH₃ and NO₂.
Using phenyl radical addition, Vlandas et al. demonstrated covalent functionalization of SWCNT sidewalls with boronic acids for detection of glucose at 5–30 mM.\textsuperscript{209} Huang et al. utilized a similar approach to functionalize double-walled CNTs (DWCNTs) with aromatic carboxylic acids as a selective sensor for NH\textsubscript{3}.\textsuperscript{210} DWCNTs allowed for higher degrees of functionalization compared to SWCNTs. Our group has demonstrated covalent functionalization of SWCNTs via thermal aziridination to introduce amino groups that were further functionalized with hydrogen bond donors for the detection of cyclohexanone and nitromethane.\textsuperscript{96} The covalent functionalization of MWCNTs using a modular zwitterionic functionalization strategy allowed for formation of diverse densely functionalized materials. Arrays of these materials were used in detection of a number of volatile organic compounds.\textsuperscript{211}

### 1.7.4 Functionalization of conducting polymer NWs

As discussed earlier, by our definition CPs are not intrinsically NWs. However, they can be used to create NWs by templated synthesis or assembled in composite structures with nanofibers or CNTs.
1.7.4.1 Physical mixtures of CP NWs

Composites with CPs can produce materials with superior properties such as high selectivity and sensitivity, enhanced resistance to humidity, low detection limits, low sensing temperatures, and enhanced stability. Rational design of materials combining CPs with non-conductive polymers, carbon-based materials, metal nanoparticles and oxides, or biological materials has been reported. CPs can serve as a matrix for a secondary material or can be decorated with nanostructures in an organized manner.

Polyaniline (PANI) was widely investigated and combined with carbon-based materials such as CNTs or metal oxides. "One-pot" procedures are used where aniline is oxidatively polymerized in the presence of CNTs. For example, PANI-SWCNT composites are sensors for NH$_3$ and HCl. Compared to chemically modified polymers, blending materials together avoids complex syntheses, and composite materials may have improved morphology, partition coefficients toward analytes, swelling behavior, mechanical or conductive properties. An additive can also help maintain properties of the polymer and increase lifetime. Polymers enable the production electrospun high surface area nanofibers for gas sensors with enhanced sensitivity and reversibility over bulk films.

1.7.4.2 Non-covalent functionalization of CP NWs

Non-covalent functionalization can be accomplished by deposition of NPs onto the surface of CP fibers. For example, AgNP-decorated PEDOT NWs were found to detect NH$_3$ with a detection limit (1 ppm) fivefold lower than that of pristine PEDOT NWs, and AuNP-decorated PANI NWs show excellent response to H$_2$S.

1.7.4.3 Covalent functionalization of CP NWs
Covalent modifications have been used to improve solubility, processability and sensing. These modifications include side-chain, co-polymer, or graft functionalization.\textsuperscript{120} Many schemes have been developed to immobilize biocompatible receptors onto polymers in order to enhance stability under aqueous conditions.\textsuperscript{230} Polypyrrole (PPy) is particularly amenable to covalent functionalization because the nitrogen atom can be functionalized. PPy-NTA (nitrilotriacetic acid) chelator NWs were found to detect Cu\textsuperscript{2+} cations at sub-ppt concentrations, and the Cu\textsuperscript{2+} complex could be used to detect His-tagged proteins.\textsuperscript{231} Carboxylic acid-functionalized polypyrrole (CPPy) NWs were found to improve immobilization onto APTES-functionalized surfaces through covalent linking, with the remaining carboxylic acid moieties available for bioconjugation. FET sensors based on this scheme were developed for proteins.\textsuperscript{232} The nitrogen position of PPy was functionalized with biomolecules, and the materials were used to detect cancer antigens (CA125),\textsuperscript{233} bacteriophages,\textsuperscript{234} bacterial spores,\textsuperscript{235} or human serum albumin.\textsuperscript{236}

1.8 Roadmap for future developments

The last two decades have produced many innovations in nanofabrication, and we are in an opportunity-rich environment for the creation of functional NW sensors. The sensor designer must continue expanding the toolbox of options in order to tackle problems of selectivity, drift, sensitivity, and stability. Improved understanding of the basis of analyte detection in NW sensors is needed to guide this development. We suggest areas of need and opportunities for the inspired sensor researcher.

1.8.1 Improving selectivity
To many critics, a fundamental limitation is that chemical/biological sensors often lack the ability to identify unambiguously an analyte. It is true that high-resolution mass spectrometry can give near-perfect identification of small, readily volatilized molecules. Even so, front-end separation by gas or liquid chromatography is often necessary. There has been massive investment in creating portable spectrometers, but these systems generally sacrifice precision for portability and only offer incremental advances. In most cases, NW sensors will not provide superior identification. However, they provide useful information at a fraction of the cost by eliminating the need for expensive electronics, power supplies, and physical structures.

Broad adoption of NW chemical/biological sensors will require improvements in selectivity. Solutions will involve a combination of innovations in integration of molecular recognition as well as in increasing computational innovations and the dimensionality of sensing data.

1.8.2 Mitigating sensor drift

The effects of drift can be mitigated through data manipulation such as baseline correction or reference device normalization but remains a fundamental limitation that hinders adoption in applications, especially for continuous monitoring and for ultra-low-cost devices without the power or computational budget to execute these techniques.

The key to minimizing thermally induced drift is developing new techniques that limit nanoscopic rearrangements of thin film sensor components. Covalent chemistries such as cross-linking that bind NWs to themselves or the substrate should continue to be developed, and matrices may also decrease drift and improve device lifetimes.
When the NW transducer and selector are distinct, drift can be minimized by strengthening the selector binding to the NW to mitigate phase segregation. Tethering can be accomplished by covalent attachment\textsuperscript{96,211} or by increasing the number or strength of non-covalent binding moieties.\textsuperscript{238}

Drift is also induced electrically and is dependent upon the strength of the applied field. This contribution to drift can be minimized by decreasing the voltage bias, performing a medium-to-high voltage AC pretreatment to accelerate equilibration processes, or using thermal or UV treatments to release trapped charges. Devices that operate under instantaneous applied voltage instead of a static electric field should drift less per unit time; passive RF devices are a promising platform. Less drift should lead to longer device lifetimes. It may also be possible to mitigate drift by creating dynamic fluid environments that maintain equilibrium. Indeed, mucus protects the mammalian olfactory epithelium\textsuperscript{239}, and designer fluids could selectively partition and transport analytes to sensors.

1.8.3 Improving Sensitivity

Strategies for enhanced sensitivity include the following: (1) The design of molecular recognition elements where analyte interactions are intimately coupled to carrier transport/generation/depletion. Innovations here can be made by bottom-up chemical designs employing molecular recognition, designer NWs with engineered work functions, coupling of biological recognition/catalysis, and nanostructures. (2) Developing sensors that leverage junctions between NWs and electrodes. Schottky barriers\textsuperscript{36,103,149} and swelling-induced expansion of tunnelling barriers\textsuperscript{113,122,216,240} have been introduced as important mechanisms. A major opportunity lies in placing responsive materials/molecules in the tunnel junction that can be chemically triggered to have resonant electronic states with the NWs. Rectifying
interfaces between p- and n-NWs can also provide opportunities for amplification in analogy to gain produced by avalanche photodiodes. (3) Complex signals can be used to minimize noise, and combinations of resistive and capacitive responses need to be understood. Advances in capacitive sensing are possible by utilizing charge polarization along the length of NWs isolated by resistive junctions. Space charge contributions to a material’s dielectric constant are much larger than simple dipolar effects. Effectively harnessing space charge changes in chemical/biological sensors will involve careful positioning (orienting) of NWs, controlling the electrical transport and dielectric coupling between NWs, and choice of optimal fields and frequencies.

1.8.4 Mechanistic Analysis of Responses

Ideal designs exploiting the aforementioned mechanisms require comprehensive understanding of their contributions to NW sensor responses, which remains elusive. Deconvolution of sensor response contributors is a challenge that holds great promise for the field. In addition to informing rational design of molecular recognition and their implementation in NW sensors, the ability to extract multi-dimensional information out of a single NW sensor device is an attractive prospect. NW FETs and resonant circuits hold promise as device architectures capable of accomplishing this task, but advances in multi-dimensional experimental design will be required.

1.8.5 Current and emerging applications

The first consideration when designing a NW sensor should be its environment. Common environmental problems include temperature, humidity, interferents, EM effects, and biofouling. One must also consider how data will be retrieved and how often, which leads us to consider power requirements and sensor stability. If the sensor operates for a long period
and operates passively, then a coin-cell battery and a pre-determined data logging time interval may be optimal. Conversely, if data is required on demand, a larger on-board power source may be required. Novel approaches to powering sensors include triboelectric methods, remote photo- or thermal power harvesting, and resonant inductive coupling. The concept of coupling NWs into devices capable of wireless power transfer is relatively new, but early reports are promising. One must also consider whether the sensor will be in a durable or expendable form factor.

Next, one must consider how the analytes are likely to encounter the sensing element. Point surveillance is often sufficient for object-level monitoring, while area surveillance may be necessary for situational awareness in a large 3-D space. Area surveillance requires more than one sensor, and therefore, the total cost of goods should be considered.

Selectively recognizing an analyte is perhaps the heart of sensor design. Analytes are categorized as VOCs, oxidizers and reducers, particulates, biological macromolecules, and viruses and bacteria. The ability to detect VOCs continues to improve as molecular design principles are introduced and coupled to NWs. Oxidizers and reducers are often detected by exploiting their influence on carrier concentrations and the Schottky barrier. Greater efforts are needed to detect particulates due to their vast size, shape, and charge dispersity. Biological macromolecules can be targeted by leveraging nature’s biomolecular machinery, but this is not a general design approach. Viruses and bacteria interact by multivalent processes, and translating these collective processes into robust signals that are discernable from other events are needed. Robust inexpensive trace virus and bacterial detection has far-reaching implications for human health and safety.

The fidelity of information is of critical importance in chemical/biological sensing. The vast majority of chemical sensors have low specificity, and practitioners often assume that
more data from, for example, a large sensor array is better. However, Occam’s razor is generally the best approach with inspired designs that produce high specificity in individual sensors. Such sensors can serve their purpose without an unnecessarily expensive or cumbersome design.

Reversible sensing is generally specified for most applications. However, for many situations where crossing a threshold is relevant, an irreversible dosimeter can be employed that conveys information about the history of the device.

New approaches to extracting more information out of a single sensor or device are beginning to emerge.\(^\text{251}\) By combining multivariate extraction of orthogonal parameters with statistical techniques such as PCA, discrimination among analytes with an array is possible.

There is a new sensor paradigm on the horizon. The trend is moving from discrete comprehensive data collection to continuous, parsimonious data collection. Such a move will require the deployment of wireless distributed sensor networks that are linked directly to cloud storage. Chemists, material scientists, physicists, and practitioners will need to work together to develop new modalities that minimize cost per sensor and cost per sensed event. Additionally, opportunities will unfold for fusing chemical information with other inputs to derive new insights about our environment and behavior.

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2.1 Abstract

Chemical warfare agents (CWA) continue to present a threat to civilian populations and military personnel in operational areas all over the world. Reliable measurements of CWAs are critical to contamination detection, avoidance, and remediation. The current deployed systems in United States and foreign militaries, as well as those in the private sector offer accurate detection of CWAs, but are still limited by size, portability and fabrication cost. In this chapter, we report a chemiresistive CWA sensor using single-walled carbon nanotubes (SWCNTs) wrapped with poly(3,4-ethylenedioxythiophene) (PEDOT) derivatives. We demonstrate that a pendant hexafluoroisopropanol group on the polymer that enhances sensitivity to a nerve agent mimic, dimethyl methylphosphonate, in both nitrogen and air environments to concentrations as low as 5 ppm and 11 ppm, respectively. Additionally, these PEDOT/SWCNT derivative sensor systems experience negligible device performance over the course of two weeks under ambient conditions.

2.2 Introduction

Intelligence surveillance and reconnaissance efforts in the military arena benefit from increasing the number of sensors on the battlefield. Placing networked chemical sensors on individual soldiers without increasing an already onerous soldier-load would exponentially surge the information density to reduce uncertainty and the “fog of war”.¹ Responsive, selective, low-energy and low-cost are essential characteristics of such systems. Current military chemical warfare agent (CWA) sensors are sensitive to CWAs to the low ppb level, selective and networkable; but they are cumbersome, expensive, energy and training intensive.² These unfavorable characteristics may be mitigated in the future by using employing chemiresistive devices that can be deployed in large numbers, inexpensively and networked together.³
Chemiresistive devices utilizing single-walled carbon nanotubes (SWCNTs), with their unique mechanical and electrical properties, offer a promising platform to meet these requirements and are excellent substrates on which to build CWA sensors for use on the modern battlefield.4–7

There are many established ways to functionalize SWCNTs to impart selectivity for different analytes. Previous reports have used covalent-sidewall functionalization,8–14 defect group functionalization,15 non-covalent exohedral functionalization16–20 (with polymer, surfactants, or composite mixtures) and endohedral functionalization.21,22 Non-covalent exohedral functionalization with conjugated polymers was chosen for this study because the native conductivity of SWCNTs is preserved without disruption of the π-electronic states in the nanotube sidewalls. We chose to develop polymer-wrapped composites for this sensing application in lieu of a simple, physical mixture because physical mixtures containing SWCNTs phase segregate as a result of strong interactions between the nanotubes that allow them to aggregate. Favorable π-π stacking interactions between the SWCNTs and polymers disrupt this aggregation and allow for processing and the inclusion of polymer originated molecular recognition groups.23,24

Our group has previously demonstrated that composites of SWCNTs and polythiophenes (PTs) modified with a hexafluoroisopropanol group (HFIP) make effective chemiresistive material for a CWA simulant, dimethyl methylphosphonate (DMMP) sensing.14 Shown in Figure 2.1a, the HFIP group exhibits a strong hydrogen bonding interaction with phosphate esters,25 which are a common structural component of nerve agents, including sarin, soman, tabun and VX (Figure 2.1b).26
Building upon our experience, we report here a sequel to our previous method by using a derivatized poly(3,4-ethylenedioxythiophene) (PEDOT) polymer to produce a more robust CWA sensor. Though the fabricated PT/SWCNT devices proved to be selective and sensitive (sub ppm detection limit), they experienced significant performance degradation within days of fabrication, likely due to SWCNT aggregation. PEDOT, in comparison to PT, is much more polarizable and an electron-rich material, which generates stronger interactions to form a polymer-SWCNT composite with improved stability.\textsuperscript{27,28} HFIP groups are introduced to impart selectivity for binding of DMMP and are introduced through the functionalization of terminal alkene-containing sidechain attached to the PEDOT backbone. Alkene cross metathesis reactions facilitate the attachment of molecular recognition elements to the side chains to create derivatized PEDOT polymers with desired selectivity.\textsuperscript{29} In this chapter, we detail three PEDOT analogs, \( P_1 \), \( P_2 \) and \( P_3 \), to wrap SWCNTs to create CWA sensitive chemiresistive sensors (Figure 2.2a). The designed PEDOT derivatives also impart the necessary solubility to effectively de-bundle and disperse SWCNTs as shown in Figure 2.2b. In contrast to our previous work, where thin films were spin-casted upon a glass substrate, these chemiresistor devices are fabricated by drop casting of a polymer/SWCNT dispersion between two metal electrodes on a glass substrate to form random networks of polymer-wrapped SWCNTs (Figure 2.2c, top). Using

Figure 2.1 (a) Hydrogen bonding interaction between HFIP and DMMP; (b) Structures of CWAs and a CWA simulant, DMMP.
this drop-casting methodology, a very small amount of polymer/SWCNT is used to make a large number of devices.

**P2** is functionalized with a pendant HFIP group on the side chain that is known to form strong hydrogen bonds with phosphonates. This interaction concentrates the selected analytes proximate to the SWCNT. The conductance is then modulated through a combination of mechanisms including directly affecting transport along a given SWCNT by charge transfer to change the doping level\textsuperscript{30,31} or electrostatic interactions with the positive charge characters through dipolar induced pinning or scattering.\textsuperscript{32} Inter-SWCNT transport can also be modulated by the binding of analytes to the HFIP group on the polymer sidechains and an associated swelling increases the inter-SWCNT distance to create wider tunnel junctions between SWCNTs that lower the conductivity.\textsuperscript{4} A cartoon demonstrating the latter mechanism is drawn in Figure 2.2c. In this report we demonstrate CWA selective chemiresistors based upon a P2/SWCNT composition and reveal strong responses upon exposure to low concentrations (5 ppm) of the nerve agent simulant DMMP. We also demonstrate a fairly reliable performance of the \textbf{P2}/SWCNT sensor in the presence of air containing 24% relative humidity (RH). Furthermore, we explore the effects of device aging under ambient conditions. In addition, our experiments confirm that EDOT derivatives create a versatile platform polymer for the development of polymer wrapped SWCNT chemiresistors.
2.3 Results and Discussion

2.3.1 Dispersion of SWCNTs with functionalized PEDOTs

Our goal was to create polymer/SWCNT dispersions that are resistant to re-bundling to be able to reproducibly create durable devices. Dispersed and de-bundled nanotubes have increased surface area for interaction with analytes and can create conductive pathways that can be more readily disrupted by analyte binding as is preferred for sensing applications. We generated our derivatized polymer/SWCNT dispersions after experimentally determining the ratios of polymer to SWCNTs in the dispersions that produced the highest chemiresistive responses to DMMP. We identified the optimal ratio by weight of polymer/SWCNT/solvent was 2/1/1 (see Figure A.2.13).

Figure 2.3 (a-c) presents UV-vis-NIR absorbance spectra of P1-P3 overlayed with the spectra of their respective diluted SWCNT dispersions. The absorption spectrum suggests the presence of both semiconducting and metallic nanotubes. Absorption bands in the 800 to 1600
nm as well as the 550 to 900 nm region are indicative of the E_{11} and E_{22} van Hove singularity transitions of semiconducting carbon nanotube, while the transitions of metallic nanotubes can be found in the region of 400-600 nm.\textsuperscript{33,34} The clarity and resolution in these bands in Figure 2.3 indicate the presence of de-bundled SWCNTs in the polymer/SWCNT dispersions. All compositions have some broad absorptions in the 400-600 nm region, indicating the presence of metallic SWCNTs. The resolved absorption bands located at 880, 990, and 1120 nm are evidence of the presence of (6,5) SWCNTs.\textsuperscript{35} It may be inferred that P3 (Figure 3c) is more effective at dispersing SWCNTs than P1 and P2 from inspection of the intensity ratios of the SWCNT-based absorbances at 990 nm relative to that associated with P3 (\lambda_{\text{max}} = 553 nm). The features at 1550 nm are attributed to a vibrational overtone from hydrazine,\textsuperscript{36} which is used to prevent oxidation of the dispersions and stabilize de-bundled state.
Figure 2.3 UV-vis/NIR spectra of polymer/SWCNT dispersions. (a) P1/SWCNT, (b) P2/SWCNT, (c) P3/SWCNT.

Resonance Raman spectroscopy is a useful tool in confirming the presence of SWCNTs in polymer dispersions. The full resonance Raman spectra of the composites and pure polymer are given in Figures A.2.14 and A.2.15. Thin film samples were prepared for analysis by drop casting dispersions from THF (P1 and P3) or DMF (P2) onto a silicon wafer. A pristine SWCNT thin film was prepared by drop casting (6,5) enriched SWCNTs from a fresh dispersion in ortho-dichlorobenzene on to a silicon wafer. The spectra were taken using a 633 nm excitation wavelength and are normalized to the intensity of the G-band, at 1590 cm$^{-1}$ and offset for clarity.

In Figure 2.4a, Raman spectrum for the D-G band region is displayed. The D-band, located at 1290 cm$^{-1}$, is indicative of the disruption of the sp$^2$ network in conjugated nanocarbon systems. The ratio of intensities of the D band (1290 cm$^{-1}$), to the G band ($I_D/I_G$) can give relative measure of disruption of the graphene $\pi$-system. After dispersion, there is a large increase in $I_D/I_G$ from
the pristine SWCNTs to the polymer-dispersed SWCNTs. Specifically, the $I_D/I_G$ is 0.06 in pristine SWCNTs and 0.9, 0.8, and 0.7 for the P1/SWCNT, P2/SWCNT and P3/SWCNT composites, respectively. This indicates an increase in the number of defects in the SWCNT sidewalls within the dispersion. The source of the disruption in this case is hypothesized to be breaking of the conjugation of the SWCNT sp$^2$ network during the sonication step in the dispersion preparation or the result of strong associations between the graphene walls and the dispersing polymers or other molecules/molecular fragments. The broad Raman peak located at 1422 cm$^{-1}$ in the polymer dispersions is attributed entirely to the polymer and can be seen distinctly in Figure A.2.15. The radial breathing modes (RBM), shown in Figure 2.4b, are the signature for the presence of carbon nanotubes and are located between 100-300 cm$^{-1}$. The peak frequencies are inversely proportional to tube diameter. The as received pristine SWCNTs gave a peak at 252 cm$^{-1}$ and overlapping peaks at 277 cm$^{-1}$ and 290 cm$^{-1}$, whereas the polymer/SWCNT dispersions are slightly narrowed maxima and positioned at 283 cm$^{-1}$ and 297 cm$^{-1}$.
Figure 2.4 Resonance Raman spectra (truncated) of polymer/SWCNT dispersions with focus on the (a) D&G band region (1200-1700 cm\(^{-1}\)) and the (b) RBM region (100-300 cm\(^{-1}\)).
2.3.2 Polymer/SWCNT composites for DMMP detection in dry N$_2$ and air (24% RH)

Figure 2.5 (a) Conductance traces of four P2/SWCNT-based chemiresistors to five concentrations of DMMP in dry N$_2$ at room temperature. (b) Conductance traces of four P2/SWCNT-based chemiresistors to four concentrations of DMMP in air (24% RH) at room temperature. c) Saturated chemiresitive responses averaged across quadruplicate trials for P2/SWCNT devices for varying amounts of DMMP in dry N$_2$ (blue triangles) and air (24% RH) (red diamonds) at room temperature.

With stable composites in hand, we sought to investigate the efficacy of our polymer/SWCNT composite system in detecting the nerve agent simulant, DMMP. The sensory response was investigated by measuring the change in current between two electrodes at a constant bias voltage of 0.10 V. The change in current was converted to a negative change in
conductance \([-\Delta G/G_o (\%) = ((I_o-I)/I_o) \times 100\%]\), where \(I_o\) is the initial current. This normalized response allows for small differences in the resistivity that can complicate device to device comparisons. Figure 2.5a shows baseline-corrected responses of four chemiresistive devices that were tested in parallel incorporating our HFIP-PEDOT/SWCNT system (P2/SWCNT) that is designed to selectively detect DMMP. Figure 2.5a shows the response in dry N\(_2\), while Figure 2.5b shows the response in air with 24\% RH. Exposure times were varied to reach full saturation of the devices. In both carrier gases, the sensors show a reversible response across this concentration range. We do observe increased baseline drift in the N\(_2\) conductance trace in contrast to the more stable baseline in the air trace. We suggest that the stability is due to the steady presence of water and oxygen at the device interface that acts to maintain consistent electronic environment in the sensor material. In Figure A.2.16, the device response becomes saturated in a shorter time period at all concentrations in air than in N\(_2\). In Figure 2.5c, we observed a linear responses range for DMMP from 5-48 ppm in dry N\(_2\) and air. The dynamic range extends to 98 ppm, but the response curve suggests saturation behavior of the detector at or near 48 ppm. We noted a 0.30\% response to DMMP at a concentration of 5 ppm with a linear response up to 48 ppm for the P2/SWCNT response in dry N\(_2\). We calculated a 2.7 ppm detection limit in dry N\(_2\) using a signal to noise ratio method\(^{40}\) for P2/SWCNT. While we could not detect DMMP at a concentration of 5 ppm in air with 24\% RH, we observed a 0.60\% response to DMMP at a concentration of 11 ppm with a linear response up to 48 ppm for the P2/SWCNT. The calculated detection limit for P2/SWCNT in air is 6.5 ppm. Figure A.2.51 demonstrates the linear response curve for experiments in N\(_2\) and air. The P2/SWCNT composite device covers an operationally relevant range for the detection of nerve agents such as sarin (GB), for which DMMP is a simulant.\(^{41}\) The chemiresistive detection of DMMP by a decrease in
conductance is consistent with the notion of a transduction mechanism that relies upon a swelling of the SWCNT network or direct modulation of the SWCNT conductance by charge transfer of dipolar mechanisms. These effects are all consistent with the DMMP being concentrated in the polymer HFIP-terminated side chain as a result of hydrogen-bonding interactions with the P2/SWCNT composite (Figure 2.1a). Uptake of the analyte DMMP into the SWCNT network increases the resistance (reduces the current) as a result.

**Figure 2.6** (a) Chemiresistive responses averaged across four P1-P3/SWCNT devices to 60 s exposures of VOCs at a flow rate of 200 ml/min in dry N₂. (b) Chemiresistive responses averaged across four P1-P3/SWCNT devices to 60 s exposures of VOCs at a flow rate of 200 ml/min in air (24% RH).
Detecting CWAs in a real-world environmental sample demands a strategy for detecting trace quantities in a complex background containing other vapors that may be present in higher concentrations. Figure 2.6a shows chemiresistive responses for devices P1-P3/SWCNTs exposed to various volatile organic chemicals (VOCs) for 60 s followed by a 140 s recovery time at a constant flow rate of 200 mL/min at room temperature in dry N₂. Figure 2.6b shows results for a similar experiment obtained by using air (24% RH). The concentrations of vapors selected to confound the sensors for this experiment were chosen to be sufficiently high to obtain a measureable response from pristine SWCNTs (Figures A.2.17, A.219 and A.2.20). In both dry N₂ and air, it is clear that the P2/SWCNT composite responds to polar and hydrogen bonding analytes to a much greater degree than the HFIP free reference composites (P1/SWCNT and P3/SWCNT). The enhanced response is therefore attributed to presence of the polar and proton donating HFIP group of P2.

The P2/SWCNT composite responds to all analytes in N₂ and air tested but exhibits exceptional selectivity for DMMP above all others in dry N₂. Vapor challenges of 1297 ppm THF, 4000 ppm acetone and 6600 ppm MeOH all have similar magnitude responses (around 1.0 %) to what is observed for 16 ppm DMMP in N₂. In air, the responses of all P1-3/SWCNT are slightly lower than in dry N₂. We hypothesize that the introduction of water at lower concentrations into the gas mixture offers competition as a hydrogen bond donor to DMMP. Therefore, the presence of water decreases the amount of DMMP that may be bound to the P2/SWCNT composite, thus lowering the chemiresistive response.
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Figure 2.7 (a) Chemiresistive response ratio ($-\Delta G/G_0$ (\%/ppm)) for P2/SWCNT to VOCs in N2. (b) Chemiresistive response ratio for P2/SWCNT to VOCs in air (24 % RH).

It is clear that the P2/SWCNT is selective as designed in N2 and air. To put this selectivity for DMMP in perspective, we have provided a response ratio by dividing the negative change in conductance by the concentration in ppm [($-\Delta G/G_0$)/ppm] at the given flow rate (200 ml/min). Figure 2.7b shows that the P2/SWCNT response ratio for DMMP in N2 is an order of magnitude larger than that for the P1/SWCNT and P3/SWCNT composites. A similar, though smaller response ratio is shown for P2/SWCNT in air. The P2/SWCNT composite garners a nearly a two orders of magnitude larger response ratio to DMMP over the other VOCs. An interesting result
in Figures 2.6a and 2.6b show an increase in conductance for the P1/SWCNT and P3/SWCNT composites upon exposure to acetonitrile, chloroform, hexanes, methanol and water. This may be explained by a secondary doping effect\cite{42}. Considering that the SWCNTs are naturally p-doped by molecular oxygen\cite{43} and that the polymers are strong electron donors, the carrier levels in the SWCNTs will be reduced by strong charge transfer interactions or electron donation from the polymers to nanotubes. Some of the solvents may reduce these interactions and thereby affect an increase in carrier density. If the organic vapor molecules do not have strong interactions with the SWCNTs that pin or scatter the carriers, increased carrier levels will give rise to an increased conduction as we observe.

To establish the stability of the P2/SWCNT composites, we conducted a device aging study in which we measured the chemiresistive response to exposure to 11 ppm DMMP in N\textsubscript{2} over the course of two weeks (Figure A.1.21). These devices were stored under ambient lab conditions on the benchtop. We found no significant change in the response over that time period. However, though not recorded, we did observe that devices stored under ambient conditions over the course of a more than a month experienced significant degradation in performance. We also tested the stability of the devices in humid air (50\% RH). The results in Figure A.2.22 show a slightly enhanced and reliable response at 11 ppm to this level of humidity with a response of 0.95 \%. As mentioned before, the response in air (24\% RH) was 0.60\%. While the presence of water at lower RH served to compete with the P2/SWCNT composite for hydrogen bonding with DMMP, at higher RH, there likely is water available in the gas mixture to compensate hole carriers in the p-type SWCNTs, thus reducing conductance. This observation of decreasing conductance of SWCNTs with increasing humidity has been reported
previously\textsuperscript{44,45} and is linear until high RH (> 65 % are reached). It will continue be important in future SWCNT-based device design to take into account the effect of humidity.

2.4 Conclusions

In summary, we developed a chemiresistive sensor for the detection of nerve agent simulant DMMP. This sensor was fabricated using a derivatized PEDOT/SWCNT composite and with strong responses to 5 ppm DMMP and a calculated detection limit of 2.7 ppm in N\textsubscript{2}. The same devices in a “real world” environment (air with 24% RH), experienced a strong response at 11 ppm and a detection limit of 6.5 ppm. We explored the effects on the devices of aging in an ambient environment and higher humidity (50% RH). Additionally, we propose that the transduction mechanism responsible for the decrease in conductance in the device upon the introduction of DMMP is a hydrogen bonding interaction between the DMMP and an HFIP moiety incorporated in the derivatized PEDOT sidechain. Finally, we demonstrated that our polymer/SWCNT composites maintain stable, debundled dispersions in solution via resonance Raman and UV–vis–NIR spectroscopy.

2.5 Experimental

2.5.1 Materials

All chemicals and reagents were purchased from Sigma-Aldrich and used without additional purification, except that tetrahydrofuran was distilled from sodium metal and benzophenone. SWCNTs (6,5 chirality, carbon (95%), with 93% as SWCNTs) were acquired from Sigma Aldrich, Inc. (Saint Louis, MO, USA). 3,4-dimethoxythiophene (95%) and 2-(allyl)hexafluoroisopropanol (99%) were purchased from Matrix Scientific (Columbia, SC, USA). 1,3-bis(diphenylphosphino)propane nickel (II) (99%) was purchased from Strem
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Chemicals (Newburyport, MA, USA). Deuterated solvents for NMR were obtained from Cambridge Isotope Laboratories (Tewksbury, MA, USA).

2.5.2 Instrumentation

$^1$H, $^{13}$C and $^{19}$F NMR spectra were recorded at 400 MHz (100 MHz) or 500 MHz (125 MHz) using either Bruker AVANCE-400 or JEOL JNM-ECZR-500 NMR spectrometers, respectively. Chemical shifts are reported in ppm and referenced to residual NMR solvent peaks ($^1$H NMR: δ 3.62 ppm for THF, δ 7.26 ppm for CDCl$_3$; $^{13}$C NMR: δ 77.2 ppm for CDCl$_3$). High-resolution mass spectra were determined with a Bruker Daltonics APEXIV 4.7 Tesla FT–ICR–MS using ESI or DART ionization. The MALDI-MS spectra were acquired in linear and reflection modes in the Koch Institute at MIT using a Bruker Microflex MALDI-MS spectrometer. UV–Vis absorption spectra were measured using an Agilent Cary 4000 Series UV–Vis spectrophotometer. Gel permeation chromatography (GPC) measurements were performed in tetrahydrofuran using an Agilent 1260 Infinity system and calibrated with a polystyrene standard. ATR–FTIR spectra were acquired using a Thermo Scientific Nicolet 6700 FT–IR with either a Ge or ZnSE crystal for ATR and subjected to the ‘atmospheric suppression’ correction in OMNIC™ Spectra software. Raman spectra were collected with excitation at 633 nm laser using a Horiba LabRAM HR800 Raman spectrometer.

2.5.3 Synthesis of monomers and polymers

Detailed procedures for the synthesis of all compounds can be found in the supplementary information. Briefly, brominated EDOT monomers can be polymerized using Kumada catalyst transfer polycondensation (KCTP) [33–38]. The monomer synthesis begins by O-alkylation of the inexpensive reagent solketal (1) to yield compounds 3a and 3b in moderate yields (Scheme 2.1). Intermediates 4a and 4b were next obtained by acid-catalyzed deprotection in a
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mixture of 1.0 M HCl (aq) and THF. Monomer precursors 6a and 6b were formed by an acid-catalyzed substitution of the methoxy groups of compound 5 by diols 4a and 4b. Products 6a and 6b were then brominated with N-bromosuccinimide (NBS) in THF to provide KCTP monomers 7a and 7b.

Scheme 2.1 (a) Synthesis of derivatized EDOT monomers for (b) Kumada catalyst transfer polycondensation (c) Post-polymerization modification via alkene cross-metathesis of P1 and allyl-HFIP to form P2.

KCTP was chosen as the polymerization method to generate our derivatized PEDOT derivatives over electrochemical polymerization$^{52,53}$ and FeCl₃-catalyzed oxidative polymerization.$^{54}$ Though oxidative polymerizations do not often yield cross-linked polymer products in the preparation of polythiophenes, in this case, both of these methods yielded insoluble products that appeared to be highly cross-linked. We hypothesize that the terminal
alkene on the side chain of P1 reacts with the radical cation intermediates generated under oxidizing conditions to give cross-linked products.

P1 is, in principle, a platform polymer upon which we can incorporate a number of desired recognition elements. P2 contains a HFIP moiety that was attached via a cross metathesis reaction. As a result of its unique hydrogen bonding characteristics, HFIP is a known selector for DMMP (Figure 2.1). P3 was studied as a control polymer. P1 and P3 were synthesized using KCTP, which were then solvent fractionated to isolate the highly soluble material. Such soluble fractions were produced in acceptable yields (15–40%) (Scheme 2.1b), with $M_n$ values of 2700 to 2900 g/mol and polydispersities of 1.2–1.3 (Figure A.2.1). Although higher molecular weight fractions with masses up to 6100 g/mol were identified using MALDI-MS for P1 (Figure A.2.2), higher molecular weight samples were found to be only slightly soluble in organic solvents and unable to form composites with SWCNTs. For P1–P3, we observed that molecular weights determined by MALDI MS were smaller than that of GPC. Additionally, molecular weights determined by end group analysis with $^1$H NMR are higher than GPC or MALDI MS results (Table A.2.3 and Figures A.2.2, A.2.4-A.2.6). The lower molecular weights obtained by MALDI MS analysis as compared to GPC is consistent with previous work that demonstrated GPC tends to overestimate molecular weights of rod-like conjugated systems [44]. It is possible that MALDI-MS analysis provides smaller molecular weights than $^1$H NMR end group analysis because the higher laser power required to volatize higher molecular weight fractions leads to chain fragmentation.

P2 was synthesized via a post-polymerization modification of P1 using an alkene cross metathesis reaction (Scheme 2.1c). This transformation was successful, as evidenced by an increase in molecular weight from 2900 to 3900 g/mol. The conversion of a terminal alkene in
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**P1** to an internal alkene in **P2** was confirmed by analysis of the $^1$H NMR spectrum. The disappearance of a doublet at $\delta$ 5.78 ppm and multiplet centered at $\delta$ 4.96 ppm in **P1** (Figure A.2.7) to yield a doublet at $\delta$ 5.40 ppm in **P2** indicates full conversion of the terminal alkene to an internal olefin (Figure A.2.8). The intensity of both peaks in this doublet suggests an approximately equal proportion of both *cis* and *trans* stereoisomers are present in **P2**. In Figure A.2.9, $^{19}$F NMR confirms the presence of a HFIP group in **P2** with a resonance at $\delta$ 76.7 ppm.

**2.5.4 Preparation of polymer/SWCNT dispersions**

To a solution of **P1(P3)** ($M_n = 2900$ g/mol, 10 mg) in dry tetrahydrofuran (THF, 5 mL) or **P2** in dry dimethyl formamide (DMF, 5 mL), 5 mg of SWCNT was added and followed by 10 $\mu$L hydrazine (a reducing/de-doping agent). Then the resulting mixture was sonicated for 1 h in an ultrasonic bath (Branson, 3510) chilled with ice and then allowed to reach room temperature. Subsequently, the suspension was centrifuged for 30 min at 9500 g. The supernatant was decanted and centrifuged again for an additional 30 min at 9500 g and allowed to stand overnight undisturbed. The isolated supernatant was directly used for the device fabrication via dropcasting unless otherwise indicated. For UV–vis–NIR absorption spectroscopy, the isolated supernatant was diluted to 1:2 in THF or DMF, further sonicated for 5 min, and recorded in a 1 cm optical path quartz cuvette.

**2.5.5 Preparation of gold electrodes on glass microscope slides**

Glass substrates deposited with chromium adhesion layers (10 nm) and gold electrodes (100 nm) were prepared according to a literature procedure. Briefly, glass slides (VWR Microscope Slides) were cleaned by sonication in acetone for 5 min followed by UV-ozone treatment using a UVO cleaner (Jelight Company Inc., Model 42, Irvine, CA, USA, for 20 min. A 15 nm layer of
chromium (99.99%, R.D. Mathis) and a subsequent 150 nm layer of gold (99.99%, R.D. Mathis) were deposited through a custom stainless steel mask using a thermal evaporator (Angstrom Engineering, Kitchener, Ontario, Canada), which resulted in three sets of four channel electrode patterns on a single glass slide, which was cut into three individual devices. Each device contains a gold pattern of four isolated working electrodes with one shared reference-counter electrode on the glass substrate. The gap between one pair of gold electrodes is 1 mm.

2.5.6 Fabrication of a polymer-SWCNT chemiresistor platform

The desired amount of polymer-SWCNT dispersion in THF or DMF was dropcasted with a 20 µL syringe between four gold electrode pairs on the glass substrate. Typically, between 4–20 µL of the dispersion was required to reach the target electrode resistance of 10–50 kΩ.

2.5.7 Volatile organic compound (VOC) gas detection measurement

For VOC gas detection measurement, the fabricated array device was placed into a custom-built PTFE enclosure with a small gas inlet and outlet, the gold electrodes of the device were connected to a PalmSens EmStat potentiostat with a MUX16 multiplexer. A KIN-TEK gas generator system calibrated for each VOC was used to deliver to the device’s enclosure a known concentration of a given VOC analyte diluted in N₂ gas at a fixed gas flow rate (200 mL/min) to minimize drift in the baseline resistance. For calibration, emission rate of each VOC by monitoring the decrease in mass of each liquid for an hour at a 200 mL/min flow rate and a designated temperature (40 °C–70 °C). Three trials for each VOC were performed. The potentiostat applied a constant potential of 0.1 V across the electrodes, and the current for each channel of the device was recorded using PS Trace software (v. 4.7) during 60 s of VOC vapor exposures. After a linear baseline correction, the change in current resulting from exposure to the
analyte was converted to the negative change in conductance \((-\Delta G/G_0\%) = (I_0 - I/I_0) \times 100\), where \(I_0\) is initial current), which was taken as the device’s response. Schematics and photographs of the experimental setup can be found in the Chapter 2.7 Appendix, Figure A.2.11 (Schematic/cartoon for sensing experimental set up), Figure A.2.12 (Photograph of sensing experimental set up) and Figure A.2.13 (Schematic/cartoon for sensing experimental set up in humid air).

2.6 References
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2.7 Appendix

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<table>
<thead>
<tr>
<th>Analytical Technique</th>
<th>P1 MW (repeat units)</th>
<th>P2 MW (repeat units)</th>
<th>P3 MW (repeat units)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>3,900 g/mol D=1.2 (8)</td>
<td>2,700 g/mol D=1.2 (9)</td>
</tr>
<tr>
<td>$^1$H NMR (end group analysis)</td>
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<td>9,300 g/mol (33)</td>
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<tr>
<td>MALDI-TOF MS</td>
<td>2,245 g/mol (8)</td>
<td>1322 g/mol (3)</td>
<td>3,395 g/mol (12)</td>
</tr>
</tbody>
</table>

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![13C NMR, CDCl₃, 125 MHz](image)

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![FTIR-ATR](image)
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CHAPTER 3

Chemiresistive Detection of Ethylene Oxide and Mustard Gas:

Poly(vinylpyridine)/Single Walled Carbon Nanotube Composites

This work was supported in part by the U. S. Army Research Laboratory and the U. S. Army Research Office through the Institute for Soldier Nanotechnologies, under contract number W911NF-13-D-0001.
3.1 Abstract

The selective robust detection of alkylating agents using carbon nanotube chemiresistive devices has confounded researchers in the sensor field for quite some time. In this work, we address this quandary by fabricating a chemiresistive device consisting of poly(4-vinylpyridine)/single walled carbon nanotube/lithium bromide composites that is able to detect gaseous ethylene oxide (EO) and a mustard agent simulant, 2-chloroethyl ethylsulfide (CEES). Our devices were sensitive to EO and CEES down to 1048 ppm and 33 ppm, respectively. We achieve calculated theoretical detection limits of 212 ppm for EO and 10 ppm for CEES. These results should encourage researchers in the field to tackle analytes once thought to be undetectable via carbon nanotube chemiresistive devices, as they offer a low cost and low power alternative to current options.

3.2 Introduction

Carbon nanotubes continue to offer promise as the active sensor material in both chemiresistive\(^1\) and field effect transistor devices.\(^2,3\) To date, the unique electrical, thermal and mechanical properties of carbon nanotubes\(^4\) have been used to detect industrial and agriculturally important gases,\(^5,6\) explosive compound precursors,\(^7\) biological molecules and chemical warfare agents (CWAs), amongst others.\(^8\)\(^-\)\(^11\) Although they are promising materials for sensing, single walled carbon nanotubes (SWCNTs) often lack selectivity for target analytes that do not have a high affinity for the hydrophobic graphitic surface of nanotubes. To address this limitation, researchers have developed three main approaches to impart selectivity to their carbon nanotube-based systems: physical mixtures and covalent and non-covalent functionalization of SWCNTs.\(^12\) Each method has its inherent advantages and disadvantages. Physical mixtures allow for rapid prototyping of SWCNT composites for sensing materials, but they often lack stability.
and phase segregate over a short time frame. Covalent modifications disrupt the π-electron system and generate defects on the nanotube surface, but produces soluble nanotubes that can be solution processed. Non-covalent functionalization does not disrupt the π-electron system, but favorable van der Waals and π-interactions between the SWCNTs and the polymer are necessary for durable composites to be produced.

A common tactic for non-covalent functionalization is polymer wrapping. With this approach, interactions between the polymer, SWCNTs, and the target analyte(s) can be tuned by rational selection of the polymer backbone and side chains. Recently, our group has developed a surface-anchored, poly(4-vinylpyridine)/SWCNT system. This method involved the surface immobilization of a P4VP/SWCNT composite via a quaternization reaction between surface-bound bromopropylsilane and the pyridyl units of P4VP. Unreacted pyridyl units in this quaternization reaction are free to coordinate metal nanoparticles or ions chosen to grant selectivity and sensitivity to target gas analytes.

We sought to extend the use of this P4VP/SWCNT platform by focusing on the nucleophilic nature of the pyridine moiety in P4VP. We hypothesized that the pyridyl nitrogens can react or strongly interact with electrophilic analytes and result in a chemiresistive response. To increase this response, we proposed that the addition of a metal salt (MX) could act to stabilize a forming intermediate or have favorable activating associations with the selected electrophilic analyte. We selected ethylene oxide (EO) and 2-chloroethyl ethylsulfide (CEES), a CWA simulant for sulfur mustard (SM), because of their high reactivity as electrophilic analytes to detect chemiresistively with a P4VP/SWCNT composite. After some initial assays with a variety of metal salts and additives (Figure A.3.7) for CEES detection, we selected LiBr due to its chemiresistive response when incorporated into a P4VP/SWCNT
EO is a highly reactive gas, the simplest cyclic ether. It is used as a raw material in the production of ethylene glycols, surfactants and ethanolamines.\textsuperscript{21} Interestingly, EO is also used as a fumigant\textsuperscript{22,23} and a sterilizing agent for medical equipment.\textsuperscript{24} Despite its broad utility, EO is known to be mutagenic\textsuperscript{25} and carcinogenic\textsuperscript{26} in addition to being extremely flammable and explosive. EO is very reactive because its highly strained three membered ring can be opened easily by a variety of nucleophiles (Figure 3.1a).

CEES, SM, and nitrogen mustard derivative (HN-2) share the common characteristic of forming cyclic, three membered ring intermediates \textit{in situ} (Figure 3.1b,c).\textsuperscript{27} These cyclic cationic
sulfonium intermediates are formed via an intramolecular nucleophilic attack of sulfur (nitrogen for HN-2) on a primary carbon attached to a halogen, such as chlorine. The formation of the cyclic intermediate in CEES is the origin of its high instability, reactivity and toxic health effects. Sulfur mustard is a strong vesicant which causes severe skin/eye blistering and lung lesions upon exposure and may lead to death. Furthermore, mustard agents have been demonstrated to be carcinogenic and mutagenic. SM differentiates itself from the other classes of CWAs by persistence in the environment, latency of biological activity, and debilitating effects that incapacitate its victims and cause a burdensome response on evacuation medical care systems. In effect, both EO and CEES are electrophilic alkylating agents susceptible to nucleophilic attack and subsequent ring opening by a variety of nucleophiles to include water, alcohols, amines and biomolecules under the favorable conditions.

Herein, we fabricate and characterize chemiresistive devices consisting of P4VP/SWCNT and P4VP/SWCNT/LiBr as the active sensing material. We demonstrate that the P4VP/SWCNT/LiBr composite gives a chemiresistive response to EO and CEES. Additionally, the response to CEES is selective in comparison to other volatile organic compounds (VOC). We show that the presence of LiBr in the P4VP/SWCNT composite increases the chemiresistive response over P4VP/SWCNT composites.
Figure 3.2 (a) Schematic of fabrication of a P4VP/SWCNT-based chemiresistive sensor dropcasted on an interdigitated electrode and photograph of the P4VP/SWCNT dispersion in DMF. (b) Proposed interaction between the P4VP/SWCNT/LiBr composite and target analytes EO (top) and CEES (bottom).

3.3 Results and Discussion
3.3.1 Dispersion of SWCNTs with P4VP

To quickly assay our hypothesis of using the P4VP-SWCNT dispersion in the presence of LiBr for the chemiresistive detection of EO and CEES, we fabricated devices as shown in Figure 3.2a. After the synthesis of P4VP via free radical polymerization (yield = 20%, \( M_n = 57.8 \) kDa, \( D = 3.1 \)), dispersions with P4VP/SWCNT in \( N,N \)-dimethylformamide (DMF) were generated using established procedures. \(^9\) \(^{17}\) LiBr (4 mg/mL in DMF) was incorporated into the dispersion at a concentration of 10\% (v/v). Next, the dispersions were dropcasted via micropipette onto interdigitated electrodes (CC1.W1, BVT Technologies) on a hot plated heated to 130 °C to rapidly remove solvent. Next, the IDEs were placed under vacuum at 50 °C until for a minimum of two hours.

3.3.2 Spectroscopic characterization of P4VP-SWCNT composites

A necessary characteristic of durable polymer/SWCNT dispersions for chemiresistive devices is to ensure that the dispersions are resistant to re-bundling and phase segregation. Sensing applications demand percolative pathways that can be easily disrupted by analyte binding. These pathways are achieved by dispersing and de-bundling the nanotubes by polymer wrapping, which leads to higher surface area for interaction amongst the analyte and polymer/nanotube composite.

We determined the ratio of P4VP/SWCNT/DMF to be 10 mg/1 mg/2 mL based our previous work with P4VP/SWCNT system. Figure 3.3 presents UV–Vis–NIR absorbance spectra of P4VP, P4VP/SWCNT, and P4VP/SWCNT/LiBr dispersions in DMF. It is clear that P4VP has no significant absorption in this region of the spectrum and we can attribute all absorptions to the presence of SWCNTs and the LiBr additive. The absorption spectra of P4VP/SWCNT suggests the presence of both semiconducting and metallic nanotubes.
Figure 3.3 UV–vis/NIR spectra of polymer/SWCNT dispersions in DMF. P4VP only (blue); P4VP/SWCNT (purple); P4VP/SWCNT/LiBr (green).

Absorption bands in the 800 to 1600 nm region as well as the 550 to 900 nm region are indicative of the E11 and E22 van Hove singularity transitions of semiconducting carbon nanotubes, respectively, while the transitions of metallic nanotubes can be found in the region of 400–600 nm. The clarity and resolution in these bands in Figure 3.3 indicate the presence of de-bundled SWCNTs in the P4VP/SWCNT dispersions. All compositions have some broad absorptions in the 400–600 nm region, indicating the presence of metallic SWCNTs. The P4VP/SWCNT/LiBr spectra is differentiated from the P4VP/SWCNT spectra by the relatively large absorbance at 1400 nm. We attribute the feature to vibrational overtones from water absorbed by LiBr, which is known to be extremely hygroscopic and is often used as a dessicant. The resolved absorption bands located at 650 and 1159 nm are evidence of the presence of (7,6) SWCNTs.
Figure 3.4 (a) Resonance Raman spectra of p-SWCNT only (black); P4VP/SWCNT (purple); P4VP/SWCNT/LiBr (green), and (b) those in the RBM region.
Resonance Raman spectroscopy can confirm the presence of SWCNTs in polymer dispersions. The full resonance Raman spectra of the composites and pure polymer are shown in Figure A3.5. Thin film samples were prepared for analysis by drop casting dispersions from DMF onto a silicon wafer. A pristine SWCNT thin film was prepared by drop casting enriched SWCNTs from a fresh dispersion in ortho-dichlorobenzene onto a silicon wafer. The spectra were taken using a 633 nm excitation wavelength and are normalized to the intensity of the G-band, at 1590 cm$^{-1}$ and offset for clarity. In Figure 3.4a, Raman spectrum for the D-G band region is displayed. The D-band, located at 1290 cm$^{-1}$ is diagnostic of the disruption of the sp$^2$ network in conjugated nanocarbon systems. The ratio of intensities of the D band (1290 cm$^{-1}$) to the G band (I_D/I_G) can give relative measure of disruption of the graphene system. After dispersion, there is an increase in I_D/I_G from the pristine SWCNTs to the P4VP-dispersed SWCNTs. Specifically, the I_D/I_G is 0.09 in pristine SWCNTs and 0.59 and 0.65 for the P4VP/SWCNT and P4VP/SWCNT/LiBr composites, respectively. An increase in the I_D/I_G indicates an growth in the number of defects or strong chemisorption to the carbon atoms in the SWCNT sidewalls within the dispersion. The source of the disruption in this case is posited to be due to interruptions of the conjugation of the SWCNT sp$^2$ network during the sonication step in the dispersion preparation or the outcome of strong interactions between the nanotube graphitic walls and the dispersing polymers or other molecules/molecular fragments. The radial breathing modes (RBMs) are located between 100–300 cm$^{-1}$ and are shown in Figure 3.4b. They are the signature for the presence of single walled carbon nanotubes. At the 633 nm excitation wavelength, peaks below 250 cm$^{-1}$ represent larger diameter metallic SWCNTs, while peaks above 250 cm$^{-1}$ represent smaller diameter semi-conducting SWCNTs. We observe that
all SWCNTs used in this work are slightly enriched in semi-conducting SWCNTs based upon the relative intensity of the peaks above and below 250 cm⁻¹.

FTIR-ATR was used to confirm the incorporation of LiBr into the P4VP-SWCNT composite (Figure 3.5). The shift of the absorbance of the pyridine ring stretches (C-N str) to higher wavenumbers in the P4VP/SWCNT/LiBr dispersion from 1595 cm⁻¹ to 1640 cm⁻¹ can be attributed to increased coordination of pyridine to Li⁺. The lack of any residual absorbance at 1595 cm⁻¹ suggest that all pyridines have been coordinated to Li⁺. Additionally, the full FTIR-ATR spectra (Figure A.3.9) of P4VP/SWCNT/LiBr shows a broad, strong absorption at 3450 cm⁻¹ that is not observed in the other dispersions: this is further evidence that the P4VP/SWCNT/LiBr contains water.

**Figure 3.5** Offset FITR-ATR spectra of polymer/SWCNT dispersions focused on the pyridine ring stretch region (1550-1670 cm⁻¹). P4VP only (blue); P4VP/SWCNT (purple); P4VP/SWCNT/LiBr (purple).
3.3.3 P4VP/SWCNT/LiBr composite for the detection of ethylene oxide (EO) and 2-chloroethyl ethylsulfide (CEES)

Having developed stable composites and successfully characterizing them, we set out to study the efficacy of our P4VP/SWCNT composite system in detecting ethylene oxide (EO). Chemiresistive sensors were prepared by drop casting 2-3 μL of the P4VP/SWCNT dispersions onto interdigitated Au electrodes (0.2 mm gaps) until a resistance of 20-50 kΩ was reached. The variation in the conductivity upon exposure to various types of analyte vapors, including EO and CEES, was measured by detecting the current with an applied bias voltage of 0.1 V. The change in current was converted to a negative change in conductance \[-\Delta G/G_o (\%) = ((I_o-I)/I_o) \times 100\%\], where \(I_o\) is the initial current. This normalized response allows for small differences in the resistivity that can complicate device to device comparisons. Figure 3.6a shows representative baseline-corrected response of a chemiresistive
device incorporating a P4VP/SWCNT/LiBr that was designed to detect EO and CEES. Exposure times were limited to 300 seconds followed by a 900 second recovery time. The sensors show a reversible response across this concentration range under N\textsubscript{2} atmosphere, from 1048-2048 ppm. In Figure 3.6b, we observed a 0.40% response to EO at a concentration of 1048 ppm with an increasing, slightly exponential response up to 2048 ppm. We calculated a theoretical detection limit of 212 ppm.\textsuperscript{41} This is an operationally relevant range for the detection of EO, since the concentration of EO which is of immediate danger to life and health (IDLH) is 800 ppm.\textsuperscript{42} The chemiresistive detection of EO by a decrease in conductance is consistent with the notion of a transduction mechanism that relies upon a swelling of the SWCNT network or direct modulation of the SWCNT conductance by charge transfer or dipolar mechanisms. These effects are all consistent with oxygen of the EO being coordinated to the lithium ions or H-bond with water molecules associated with the polymer salt wrapper (Figure 3.2b). In the case of a reaction with the EO, these same interactions can stabilize the oxyanion produced. As mentioned above, water is present in the P4VP/SWCNT/LiBr composite. Water may act as a concentrator for EO at the device surface and increase the effective concentration of EO through hydrogen bonding. These effects all contribute to the swelling of the polymer/SWCNT network which acts to increase the resistance (reduces the current) as a result.\textsuperscript{9} It is important to note that the sensing traces in Figure 3.6a appear to be reversible. This provides evidence for interaction of the pyridine:LiBr complex to the EO rather than covalent bond formation between pyridine and EO via quaternization.

Having successfully detected EO, we turned our attention to CEES sensing. The signal transduction mechanism is likely similar to that of EO, as the most stable conformation of CEES is that of a cyclic sulfonium ion (Figure 3.1c) and also may be attacked by a nucleophilic
pyridine group. Figure 3.7a shows representative baseline-corrected response of a chemiresistive device incorporating P4VP/SWCNT/LiBr that was designed to detect CEES (and EO). Exposure and recovery times were identical as those used with EO. The sensors show a reversible response across a 33-72 ppm concentration range under N₂. In Figure 3.7b, we observed a 0.30% response to CEES at a concentration of 33 ppm with an exponential response up to 72 ppm. We calculated a theoretical detection limit of 10 ppm. Though this is not an operationally relevant range for the detection of CEES (IDLH of sulfur mustard is 140 ppb), it is a step toward a sulfur mustard detector using chemiresistive, carbon nanotube based device. Since there is a decrease in conductance upon CEES exposure, and structural similarities between EO and CEES, we propose a swelling mechanism to explain the chemiresistive response of P4VP/SWCNT/LiBr towards CEES. Moreover, we propose the greater strength of the chemiresistive response to CEES (0.40% at 33 ppm) over EO (0.40% at 1048 ppm) is ascribed to the more reactive nature of the sulfonium ion towards coordination with pyridine. Interestingly, we would expect the
increased reactivity of CEES would lead to an alkylation reaction with pendant pyridines. Evidence for this case would be an irreversible or dosimetric sensing response. In contrast, we observed a dominantly reversible response which indicates that the alkylation of the pyridyl groups is not occurring with CEES. We have hypothesized that equipping our polymer wrapping system with a group more nucleophilic than pyridine would lead to alkylation of CEES and a dosimetric chemiresistive response. To this end, our group has made efforts into include vinyl imidazole in a copolymer with vinylpyridine for this purpose. However, the polymer failed to provide high stability dispersions with SWCNTs.

To assess the relative degree of selectivity of the P4VP/SWCNT/LiBr composite, Figure 3.8a demonstrates the device’s chemiresistive response to various volatile chemicals for 60 seconds exposure followed by a 140 second recovery time at a constant flow rate of 200 mL/min at room temperature in N₂. The concentrations of these vapors were chosen to be sufficiently high enough to obtain a measurable response to the P4VP/SWCNT composite, a control device. The P4VP/SWCNT and P4VP/SWCNT/LiBr devices respond to all of these VOCs in addition to EO and CEES. However, it is clear that the presence of LiBr in the P4VP/SWCNT composite amplifies the response across the panel. Furthermore, when we utilize
Chemiresistive Detection of Ethylene Oxide and Mustard Gas

Figure 3.8 (a) Chemiresistive responses for P4VP/SWCNT (purple) and P4VP/SWCNT/LiBr (green) averaged across three devices to 60 s exposures of VOCs at a flow rate of 200 mL/min in N₂; (b) Chemiresistive response ratio (ΔG/G₀ (%)/ppm) for P4VP/SWCNT (purple) and P4VP/SWCNT/LiBr (green) to VOCs in N₂.

a response ratio,⁹ as shown in Figure 3.8 (b), we see that CEES provides the greatest response per ppm of analyte by a factor of more than four. In contrast, EO barely registers a response for this metric (see Table 3.A.1). This analysis reinforces the lower reactivity of EO in comparison to CEES toward our P4VP/SWCNT-based chemiresistor.

3.3.4 Related work: Poly(4-vinylpyridine) copolymers with vinyl ferrocene (P4VP-co-VFc) and ferrocenylmethacrylate (P4VP-co-FcMMA)

The ability to surface anchor the P4VP/SWCNT composite system (not performed in this work) to glass and other surfaces brings to mind a myriad of applications outside of gas sensing. We propose that we can use this method to anchor P4VP/SWCNT composites to an electrode surface for electrochemical detection of anions in aqueous environments.⁴⁴-⁴⁶ To this end, we developed two copolymers that include electroactive ferrocene-based repeat units into the P4VP main chain. We accomplished this via free radical polymerization and set the loading of the
ferrocene-containing units at 9-10% to retain enough pyridine units to quaternize to a surface and coordinate to metal centers for sensing applications\textsuperscript{47–50}. The resulting random copolymers, vinyl pyridine with vinyl ferrocene (P4VP-co-VFc) and with ferrocenylmethylymethacrylate (P4VP-co-FcMMA) were synthesized in good yields and their composites with SWCNTs were characterized via $^1$H NMR (Figures A.3.2-3), FTIR-ATR (Figures A.3.8-10), gel permeation chromatography (GPC) (Figure A.3.4) and thermogravimetric analysis (TGA) (Figures A.3.11-13).

### 3.3.4.1 Spectroscopic characterization of P4VP, P4VP-co-VFc and P4VP-co-FcMMA composites with SWCNTs

A key requirement for any application in which either P4VP-co-VFc and P4VP-co-FcMMA are to be used in a composite with SWCNT is that they must form stable dispersions that resist aggregation and re-bundling in solution with SWCNTs. We used UV-vis/NIR (Figure 3.9a) and Resonance Raman spectroscopy (Figure 3.9b) to confirm that the dispersions with

![Figure 3.9](image-url)

**Figure 3.9** (a) UV–vis/NIR spectra of polymer/SWCNT dispersions in DMF. P4VP/SWCNT only (purple); P4VP-co-VFc/SWCNT (orange); P4VP-co-FcMMA /SWCNT/ (pink). (b) Resonance Raman spectra of pristine-SWCNT (black); a P4VP-SWCNT composite (purple); P4VP-co-VFC/composite (orange); a P4VP-co-FcMMA/SWCNT composite (pink).
vinyl pyridine based copolymers were stable. The UV-vis/NIR and Raman spectra very closely resemble the P4VP/SWCNT spectra that were discussed in Figures 3.3 and 3.4, respectively.

3.3.4.2 Electrochemical characterization of P4VP, P4VP-co-VFc and P4VP-co-FcMMA composites with SWCNTs via cyclic voltammetry.

With stable composites in hand, we set out to conduct cyclic voltammetry (CV) to determine baseline behavior of these composites in aqueous environments in preparation for aqueous anion sensing. We deposited 20 µL of each polymer/SWCNT dispersion in DMF on a glassy carbon electrode (GCE) and evaporated residual solvent to form films on the GCE. The reference electrode was Ag/AgCl and the counter electrode was platinum. We conducted the CV experiments in a 0.10 M KCl(aq) electrolyte solution and scanned from -1.0 to 1.0 V. Voltammograms in which we varied the scan rate were informative with respect to reversibility of the electron transfer in the copolymer films. The CVs at scan rates of 50, 100, and 500 mV/s for the P4VP/SWCNT film (Figure A.3.15) were featureless because it lacks an electroactive center. An Fc/Fc+ wave couple appears in the ferrocene-containing copolymer/SWCNT films, P4VP-co-VFc/SWCNT (Figure A.3.16) and P4VP-co-FcMMA (Figure A.3.17) films. We observed different electron transfer rates and peak potentials for each scan rate for the Fc/Fc+ wave couple. These observations are characteristic of electrochemically irreversible (slow electron transfer) processes likely are due to the limited amount of the electroactive ferrocene repeat units (recall the copolymers contain only 9-10% ferrocene repeat units). Moreover, the copolymer/SWCNT composite film likely changes conformation in the aqueous media as it swells in solution and adjusts to a changing electronic environment.
3.3.4.3 Electrochemical detection of $\text{HSO}_4^-$ and $\text{H}_2\text{PO}_4^-$ with a P4VP-co-VFc film

![Graph](image)

**Figure 3.10** (a) Electrochemical detection via CV of $\text{HSO}_4^-$ anion with P4VP-co-VFc film under aqueous conditions. Bottom (black), P4VP-co-VFc film on a GCE. Top (red), P4VP-co-VFc film exposed to 100 $\mu$L of 0.10 M NaHSO$_4$ and a scan rate of 100 mV/s in 0.10 M KCl. (b) Electrochemical detection of $\text{H}_2\text{PO}_4^-$ anion with P4VP-co-VFc film under aqueous conditions. The black trace represents the film prior to exposure to NaH$_2$PO$_4$ at a scan rate of 100 mV/s in 0.10 M KCl. The red, blue and green traces represent the CV after delivering successive 100 $\mu$L aliquots of 0.10 M NaH$_2$PO$_4$ to the electrochemical cell.

A first step towards aqueous anion sensing using polymer/SWCNT sensing was ensuring that our copolymers alone could indeed give a detectable electrical response to anions. To analyze this response, we observed the changes to the CV trace as we added sodium salts of the analytes $\text{HSO}_4^-$ and $\text{H}_2\text{PO}_4^-$ to an electrochemical cell equipped as above with a P4VP-co-VFc film on a GCE. In Figure 3.10a, the Fe/Fe$^+$ wave couple experiences an anodic peak shift of -125 mV and cathodic peak shift of -20 mV upon delivery of 100 $\mu$L of 0.10 M HSO$_4^-$. In Figure 3.10b, we added successive aliquots of 100 $\mu$L of 0.10 M H$_2$PO$_4^-$ and the Fe/Fe$^+$ wave couple undergoes an anodic peak shift of -93 mV and cathodic peak shift of -5 mV. The larger shift in anodic potential for HSO$_4^-$ indicates an affinity of the Fe$^+$ moiety for that anion. These initial experiments with P4VP-co-VFc were promising and warrant further exploration in compositions with SWCNTs.
3.4 Conclusions

We demonstrated an extended utility of the P4VP/SWCNT composite chemiresistive system with the introduction of the metal salt, LiBr. The infusion of LiBr into the P4VP/SWCNT composite produced a sensor material that enabled our devices to detect the industrial gas EO and the CWA stimulant CEES. The calculated detection limits for EO and CEES were 10 ppm and 212 ppm, respectively. Moreover, we demonstrated that P4VP/SWCNT/LiBr composite based device is four times as selective for CEES as it is for other VOCs tested. The device is not selective for EO, and we attribute this low selectivity to the significantly lower reactivity of EO to nucleophiles when compared to CEES. Additionally, we identified that water was present in our P4VP/SWCNT/LiBr composite and posit that it could play a role in device performance by increasing adsorption of analytes in/on the composite. Though at present, the chemiresistive detection of EO and CEES is not competitive with commercial or military sensors, this does represent a step towards chemiresistive devices that may be a low cost, low power, simple alternative to complicated, expensive and energy intensive sensors that are currently in field use. Finally, we synthesized two new copolymers, P4VP-co-VFc and P4VP-co-FcMMA with the intent of utilizing them for anionic sensing in aqueous media. We conducted initial electrochemical experiments and successfully detected $\text{HSO}_4^-$ and $\text{H}_2\text{PO}_4^-$ in 0.10 M KCl.

3.5 Experimental

3.5.1 Materials

All chemicals and reagents were purchased from Sigma-Aldrich and used without additional purification, except that tetrahydrofuran was distilled from sodium metal and
benzophenone. Purified SWCNTs (UPT 200, Batch 1167-24) were acquired from Nano-C, (Westwood, MA) or Sigma Aldrich, Inc. (Saint Louis, MO, USA) (6,5 chirality, carbon (95%), with 93% as SWCNTs). 3-Bromopropyltrichlorosilane was purchased from Gelest (Morrisville, PA, USA). 2-(2-hydroxy-1,1,3,3,3-hexfluoroisoproyl)-1-napthol was purchased from Synquest Laboratories (Alachua, FL, USA). 1,3-bis[3,5-bis(trifluoromethyl)-phenyl]thiourea was purchased from TCI America (Portland, OR, USA).

3.5.2 Instrumentation

$^1$H NMR spectra were recorded 500 MHz using a JEOL JNM-ECZR-500 NMR spectrometer. Chemical shifts are reported in ppm and referenced to residual NMR solvent peaks ($^1$H NMR: δ 7.26 ppm for CDCl$_3$). UV–vis/NIR absorption spectra were measured using an Agilent Cary 4000 Series UV–Vis spectrophotometer. ATR–FTIR spectra were acquired using a Thermo Scientific Nicolet 6700 FT–IR with either a Ge or ZnSE crystal for ATR and subjected to the ‘atmospheric suppression’ correction in OMNIC™ Spectra software. Raman spectra were collected with excitation at 633 nm laser using a Horiba LabRAM HR800 Raman spectrometer. Gel Permeation Chromatography (GPC) was performed on an Agilent 1260 LC stack equipped with an Agilent multiwavelength UV/vis detector, Wyatt TrEX refractive index detector, Wyatt DAWN EOS 18-angle light scattering detector, and two Shodex KD-806M GPC columns. The GPC system was set to 60 °C with a 1 mL/min flow rate with 0.025M LiBr in DMF. 8W SANKYO DENKI Black light lamps emitting near ultraviolet rays (315 nm – 400 nm) with peak emission at 352 nm, were used as the UV radiation source. Interdigitated microelectrode (CC1 .W1) with electrode gap of 200 μm was purchased from BVT Technologies for some sensing experiments. Cyclic voltammetry experiments were performed on a BioLogic VSP work station.
3.5.3 Synthesis

3.5.3.1 Synthesis of poly(4-vinylpyridine) (P4VP).

\[
\text{Yield}=49\% \\
M_n=57.8 \text{ kDa} \\
M_n/M_w=3.1
\]

To a flame dried 25 mL round-bottomed Schlenck flask, 15.23 mg of azobisisobutyronitrile (AIBN) was added then evacuated and refilled three times with argon. Then, 10 mL of dry benzene and 975 mg 4-vinylpyridine was added via syringe. The reaction mixture was subjected to three freeze-pump-though cycles. After eight hours of stirring at 70 °C, the reaction mixture was precipitated into cold diethyl ether and filtered. The resulting white solid powder was precipitated and filtered again and then placed in a vacuum oven overnight at 60 °C. The reaction yielded 611 mg (49%) of a white, fluffy powder.

3.5.3.2 Synthesis of poly(4-vinylpyridine-co-vinylferrocene) (P4VP-co-VFc).

\[
\text{Yield}=20\% \\
M_n=60.5 \text{ kDa} \\
M_n/M_w=3.84
\]

To a flame dried 25 mL round-bottomed Schlenck flask, 15.23 mg of azobisisobutyronitrile (AIBN) and 196 mg of vinylferrocene was added then evacuated and refilled three times with argon. Then, 10 mL of dry benzene and 975 mg 4-vinylpyridine was added via syringe. The reaction mixture was subjected to three freeze-pump-though cycles. After eight hours of stirring at 70 °C, the reaction mixture was precipitated into cold diethyl ether and filtered. The resulting yellowish white solid powder was precipitated and filtered again and then placed in a vacuum oven overnight at 70 °C. The reaction yielded 634 mg (20%) of a white, fluffy powder.
3.5.3.3 Synthesis of poly(4-vinylpyridine-co-ferrocenylmethacrylate) (P4VP-co-FcMMA)

To a flame dried 25 mL round-bottomed Schlenck flask, 15.62 mg of azobisisobutyronitrile (AIBN) and 270.22 mg of ferrocenylmethacrylate (FcMMA) was added then evacuated and refilled three times with argon. Then, 10 mL of dry benzene and 1.00 mg 4-vinylpyridine was added via syringe. The reaction mixture was subjected to three freeze-pump-though cycles. After eight hours of stirring at 70 °C, the reaction mixture was precipitated into cold diethyl ether and filtered. The resulting yellowish white solid powder was precipitated and filtered again and then placed in a vacuum oven overnight at 70 °C. The reaction yielded 523 mg (41%) of an off white, fluffy powder.

3.5.4 Chemiresistor and gas sensing experiments

3.5.4.1 Dispersion of SWCNT and device fabrication

To a solution of 50 mg P4VP in DMF, 5 mg of SWCNT was added. The resulting mixture was sonicated for 1 h in an ultrasonic bath (Branson, 3510) chilled with ice and then allowed to reach room temperature. Subsequently, the suspension was centrifuged for 30 min at 9500 g. The supernatant was decanted and centrifuged again for an additional 30 min at 9500 g and allowed to stand overnight undisturbed. The isolated supernatant was directly used for the device fabrication via dropcasting unless otherwise indicated. To fabricate chemiresistive
devices, 2-3 µL of the P4VP/SWCNT or P4VP/SWCNT/LiBr dispersions were dropcasted onto an interdigitated microelectrode (CC1.W1 from BVT Technologies, Czechoslovakia) to reach the target electrode resistance of 20-40 kΩ. For UV–vis/NIR absorption spectroscopy, the isolated supernatant was diluted to 1:2 in DMF and further sonicated for 5 min, and recorded in a 1 cm optical path quartz cuvette.

3.5.4.2 Ethylene oxide (EO) Gas Detection Measurement

For EO detection measurement, the fabricated array device was placed into a custom-built PTFE enclosure with a small gas inlet and outlet, the gold electrodes of the device were connected to a PalmSens EmStat potentiostat with a MUX16 multiplexer. The inlet port was connected to a gas delivery system (Sierra’s Smart-Trak Series 100). Delivery of controlled concentration of gases to devices. To obtain concentrations of EO between 834 ppm – 2000 ppm, a 4% mixture of EO in N₂ was supplied from a gas cylinder (Airgas) was diluted further N₂ using the gas mixing system at total flow rate supplied to devices ranging between 200 – 700 mL/min. Controlled delivery of gas to devices was accomplished by encasing a device within a custom-built teflon chamber equipped with an inlet and an outlet for gas flow. The potentiostat applied a constant potential of 0.1 V across the electrodes, and the current for each channel of the device was recorded using PS Trace software (v. 4.8) during 60 s or 300 s of EO vapor exposures. After a linear baseline correction, the change in current resulting from exposure to the analyte was converted to the negative change in conductance \((-\Delta G/G_0 \%) = (I_o - I)/I_o \times 100\), where \(I_o\) is initial current), which was taken as the device’s response.
3.5.4.3 VOC gas detection measurement

The fabricated array device was placed into a custom-built PTFE enclosure with a small gas inlet and outlet, the interdigitated microelectrodes of the devices were connected to a PalmSens EmStat potentiostat with a MUX16 multiplexer. A KIN-TEK gas generator system calibrated for each VOC was used to deliver to the device’s enclosure a known concentration of a given VOC analyte diluted in N₂ gas at a fixed gas flow rate (200 mL/min) to minimize drift in the baseline resistance. For calibration, emission rate of each VOC by monitoring the decrease in mass of each liquid for an hour at a 500 mL/min flow rate and a designated temperature (40 °C–70 °C). Three trials for each VOC were performed. The potentiostat applied a constant potential of 0.1 V across the electrodes, and the current for each channel of the device was recorded using PS Trace software (v. 4.8) during 60 s of VOC vapor exposures. After a linear baseline correction, the change in current resulting from exposure to the analyte was converted to the negative change in conductance \((-\Delta G/G_0 (\%) = (I_0 - I)/I_0 \times 100)\), where \(I_0\) is initial current), which was taken as the device’s response.

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Chapter 3: Chemiresistive Detection of Ethylene Oxide and Mustard Gas: Poly(vinylpyridine)/Single Walled Carbon Nanotube Composites

3.7 Appendix

Chapter 3: Chemiresistive Detection of Ethylene Oxide and Mustard Gas: Poly(vinylpyridine)/Single Walled Carbon Nanotube Composites

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Figure A.3.2 1H-NMR of poly(4-vinylpyridine-co-vinylferrocene) taken in CDCl₃ on a JEOL 502MHz NMR. 9% mole percent loading of vinyl ferrocene into the free radical polymerization.
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Figure A.3.4 Gel permeation chromatogram of P4VP ($M_n = 57.8$ kDa; $M_D = 3.1$); P4VP-$\text{co-}$VFC ($M_n = 60.5$ kDa; $M_D = 3.84$); P4VP-$\text{co-}$FcMMA ($M_n = 11.8$ kDa; $M_D = 1.75$).
Figure A.3.5 Resonance Raman spectra of pristine-SWCNT (black); a P4VP-SWCNT composite (purple); a P4VP/SWCNT/LiBr composite (green). Measurements were taken at a 633 nm excitation wavelength. Samples were drop casted on a Si wafer with a 120 nm SiO$_2$. 

![Resonance Raman spectra graph](image-url)
Figure A.3.6 Chemiresistive traces of the responses of various additives (10 v/v % additive) in P4VP/SWCNT dispersion in DMF. Concentration of additives was 4 mg/mL in DMF.

2-(2-Hydroxy-1,1,1,3,3,3-hexafluoroisopropyl)-1-naphthol was also assayed as an additive, but with no measurable response.
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Figure A.3.8 FTIR-ATR spectra of P4VP.
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Figure A.3.10 FTIR-ATR spectra of P4VP-co-FcMMMA.
Figure A.3.11 Thermogravimetric analysis of P4VP.
Figure A.3.12 Thermogravimetric analysis of P4VP-co-VFC.
Figure A.3.13 Thermogravimetric analysis of P4VP-co-FcMMA
Table A.3.1 Table listing the average chemiresistive responses, their standard deviations and response ratio. This data is charted in Figure 3.8 (a, b).

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<td>P4VP/SWCNT/LiBr</td>
<td>0.25</td>
<td>0.28</td>
<td>0.42</td>
<td>0.26</td>
<td>0.20</td>
<td>0.52</td>
<td>0.10</td>
<td>0.006000006</td>
<td>0.007324219</td>
</tr>
<tr>
<td></td>
<td>0.85</td>
<td>1.04</td>
<td>1.18</td>
<td>0.95</td>
<td>0.52</td>
<td>0.46</td>
<td>0.18</td>
<td>4.15</td>
<td>0.114196875</td>
</tr>
</tbody>
</table>
Figure A.3.14 Cyclic voltammogram of SWCNT deposited on a glassy carbon working electrode from o-dichlorobenzene (o-DCB). Residual o-DCB was removed under reduced pressure. The film was subjected to various scan rates in a 0.10 M solution of KCl. The counter and reference electrodes were platinum Ag/AgCl, respectively.
Figure A.3.15 Cyclic voltammogram of P4VP/SWCNT dispersion dropcasted from DMF on a glassy carbon working electrode. Residual DMF was removed via reduced pressure. The film was subjected to various scan rates in a 0.10 M solution of KCl. The counter and reference electrodes were platinum Ag/AgCl, respectively.
Figure A.3.16 Cyclic voltammogram of P4VP-co-VFc/SWCNT dispersion dropcasted from DMF on a glassy carbon working electrode. Residual DMF was removed via reduced pressure. The film was subjected to various scan rates in a 0.10 M solution of KCl. The counter and reference electrodes were platinum Ag/AgCl, respectively.
Figure A.3.17 Cyclic voltammogram of P4VP-co-FeMMA/SWCNT dispersion dropcasted from DMF on a glassy carbon working electrode. Residual DMF was removed via reduced pressure. The film was subjected to various scan rates in a 0.10 M solution of KCl. The counter and reference electrodes were platinum Ag/AgCl, respectively.
Figure A.3.18 Cyclic voltammogram of P4VP dropcasted from chloroform on a glassy carbon working electrode. Residual chloroform was removed via reduced pressure. The film was subjected to a 100mV/s scan rate in a 0.10 M solution of KCl. The counter and reference electrodes were platinum Ag/AgCl, respectively.
Figure A.3.19 Cyclic voltammogram of P4VP-co-VFc dropcasted from chloroform on a glassy carbon working electrode. Residual chloroform was removed via reduced pressure. The film was subjected to a 100mV/s scan rate in a 0.10 M solution of KCl. The counter and reference electrodes were platinum Ag/AgCl, respectively.
Figure A.3.20 Cyclic voltammogram of P4VP-co-FcMMA dropcasted from chloroform on a glassy carbon working electrode. Residual chloroform was removed via reduced pressure. The film was subjected to a 100mV/s scan rate in a 0.10 M solution of KCl. The counter and reference electrodes were platinum Ag/AgCl, respectively.
Figure A.3.21 Cyclic voltammogram of P4VP-co-VFc dropcasted from chloroform on a glassy carbon working electrode. Residual chloroform was removed via reduced pressure. The film was subjected to a 50 and 100mV/s scan rate in a 0.10 M solution of KCl. The counter and reference electrodes were platinum Ag/AgCl, respectively.
Figure A.3.22 Cyclic voltammogram of P4VP-co-FeMMA dropcasted from chloroform on a glassy carbon working electrode. Residual chloroform was removed via reduced pressure. The film was subjected to a 50 and 100 mV/s scan rate in a 0.10 M solution of KCl. The counter and reference electrodes were platinum Ag/AgCl, respectively.
Covalent Functionalization of Single Walled Carbon Nanotubes

via [2+1] Cycloaddition and Trifluoromethylation Reactions

This work was supported in part by the U. S. Army Research Laboratory and the U. S. Army Research Office through the Institute for Soldier Nanotechnologies, under contract number W911NF-13-D-0001.
4.1 Abstract

The covalent functionalization and characterization of single walled carbon nanotubes (SWCNTs) by dihalocarbenes and the trifluoromethylating Togni’s reagent is explored in this chapter. Covalent functionalization reactions were performed to increase the SWCNT solubility, imparting n-type semiconducting behavior while maintaining the native conductivity of the conjugated sp$^2$ network. Previous computational studies predicted the conservation of the electrical conductivity of SWCNTS after carbene additions, but experimental work to verify the electrical properties has not been performed. In the studies presented herein, we utilized five different covalent functionalization methods to modify SWCNTs and utilized X-ray photoelectron spectroscopy (XPS) in tandem with Resonance Raman spectroscopy to characterize our products. Though electrical characterization was not performed, we improved upon literature methods concerning the dichlorocarbene addition of –CCl$_2$ groups to pristine SWCNTs.

4.2 Introduction

Carbon nanotubes continue to offer significant promise as a material that will be useful in a variety of technological areas.$^{1,2}$ The inimitable electrical, thermal, optical and mechanical properties of semiconducting single walled carbon nanotubes (SWCNTs) have found utility as key materials in sensors, capacitors, catalysis filters, and membranes.$^{3-6}$ However, SWCNTs have a major drawback in the form of limited solubility in both aqueous and organic solvents because of the strong π-π interactions between SWCNTs that leads to aggregation. Covalent functionalization of the SWCNTs offer a way to increase the solubility and the environmental stability of these materials.
In recent years, a manifold of methodologies has been developed in the carbon nanotube covalent functionalization arena which has been documented in a variety of reviews. The research objective or commercial application determines the target properties, and it follows that the desired characteristics are governed by the type of covalent modification. In this work, we wish to increase the solubility of SWCNTs and impart n-type semiconducting behavior by targeting the preparation of SWCNT-CCl$_2$, SWCNT-CF$_2$ and SWCNT-CF$_3$ adducts.

To generate SWCNT-CCl$_2$ and SWCNT-CF$_2$ adducts, we chose to employ dihalocarbenes as a reactive intermediate. Carbene [2+1] cycloadditions with other moieties have been demonstrated to increase the solubility of SWCNTs in organic solvents. Furthermore, it was expected that halocarbenes would convey increased electron affinity to their SWCNT adducts, making them electron-accepting materials and conducive to the reduction by adding electrons; the key characteristic of n-type semi-conductors. Additionally, computational experiments have shown that the SWCNT-CX$_n$ adducts maintain a significant portion of their conductivity after covalent functionalization.

To produce SWCNT-CF$_3$ adduct, we employed a trifluoromethylation tactic using a hypervalent iodine compound, Togni’s reagent. In principle, a pendant -CF$_3$ group covalently bound to the surface of a SWCNT would create an electron-acceptor material with very high electron affinity as well as with increased solubility and thereby be classified as an acceptor material. An n-type SWCNT and a p-type polymer (such as polythiophene or PEDOT) could be excellent partners in a charge transfer type interaction that may be an advantageous characteristic for the polymer wrapping of SWCNTs for sensor applications.

Dihalocarbenes can be formed in a variety of ways. One of which involves the deprotonation of a haloform such as chloroform or bromoform and subsequent $\alpha$-elimination of
the halogen (Scheme 4.1a). Another way to access the dihalocarbene species is the
decarboxylation and α-elimination of a halogen from the sodium salts of trichloroacetate and
difluorochloroacetate (Scheme 4.1b-c). In reactions using trichloroacetate, we chose to
mechanically mill (MM) the reaction rather than using a solvent. Both of these methods produce
dihalocarbenes that are known to generate singlet carbenes,\(^{10,18,19}\) which can undergo a \([2+1]\)
cycloaddition with a double bond on the SWCNT (Scheme 4.1d). In keeping with our goal on
creating n-type SWNTs, we were inspired by the work of Buchwald and co-workers concerning
the copper-catalyzed trifluoromethylation of unactivated alkenes.\(^{20,21}\) A reaction between
SWCNTs and the Togni’s reagent is demonstrated in Scheme 4.1e. This electrophilic
trifluoromethylating reagent is employed in concert with a copper catalyst to generate SWNT–
CF\(_3\).

We examined the efficacy of the chemical transformations to SWCNT adducts using two
analytical techniques. First, we used X-ray photoelectron spectroscopy (XPS) to verify the
atomic composition of SWCNT adducts. Using XPS atomic composition data, we estimated the
degree of SWNT functionalization according to a calculation reported by Hu and co-workers:\(^{11}\)

\[
C_{\text{wall}}\% = (C\% - C_{\text{adduct}}\%) \approx (C\% - 0.5\% \text{Cl})
\]

The degree of functionalization is given by \((C_{\text{wall}}/CCX_n)\)

Next, we used Resonance Raman spectroscopy to corroborate the XPS results.\(^{22}\)
Specifically, the ratio of intensities of the Raman D (1290 cm\(^{-1}\)) and G bands (1590 cm\(^{-1}\)) \((I_D/I_G)\)
is used to evaluate the disruption of the \(sp^2\) network in conjugated nanocarbon systems\(^{22}\). An
increase in \(I_D/I_G\) from the pristine SWCNTs (p-SWCNT) to the SWCNT adducts has been used
as an indicator of the increase in the number of defects in the SWCNT sidewalls within the
dispersion \(^{22}\) or the disruption of the \(sp^2\) network of p-SWCNTs, likely due to the chemical
functionalization. The radial breathing modes (RBM) are also a signature for the presence of
carbon nanotubes and are located between 100-300 cm\(^{-1}\).

Herein we survey five methodologies to covalently modify the sidewalls of
SWCNTs with \(-\text{CCl}_2\), \(-\text{CBr}_2\), \(-\text{CF}_2\), and \(-\text{CF}_3\) groups. We used dihalocarbenes to create the first
four SWCNT adducts and electrophilic trifluoromethylations employing Togni’s reagent to
construct SWCNT-\text{CF}_3. We characterize the SWCNT adducts using XPS and Resonance Raman
spectroscopy.
Covalent Functionalization of Single Walled Carbon Nanotubes

Scheme 4.1 Formation of dihalocarbenes and synthesis of SWCNT-CX$_2$ and SWCNT-CF$_3$ adducts. (a-c) Formation of dihalocarbenes, (d) Synthesis of SWCNT-CX$_2$ adducts, (e) Synthesis of SWCNT-CF$_3$ from Togni’s reagent
4.3 Results and Discussion

<table>
<thead>
<tr>
<th>Entry</th>
<th>Reactants/ carbene source</th>
<th>Conditions</th>
<th>% Cl (Br)</th>
<th>C_{wall}/CCl₂ (CBr₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CHCl₃</td>
<td>THF, tert-BuOK, DOWEX (1x2), 22 °C, 10 min</td>
<td>0.64±0.18</td>
<td>143±38</td>
</tr>
<tr>
<td>2</td>
<td>CHCl₃</td>
<td>THF, tert-BuOK, DOWEX (1x2), 22 °C, 10 min</td>
<td>2.27±0.41</td>
<td>35±8</td>
</tr>
<tr>
<td>3</td>
<td>CHCl₃</td>
<td>THF, tert-BuOK, DOWEX (1x2), -78 °C, 10 min</td>
<td>0.77±0.06</td>
<td>122±10</td>
</tr>
<tr>
<td>4</td>
<td>CHCl₃</td>
<td>THF, tert-BuOK, DOWEX (1x2), 40 °C, 10 min</td>
<td>0.79±0.16</td>
<td>113±12</td>
</tr>
<tr>
<td>5</td>
<td>CHCl₃</td>
<td>THF, tert-BuOK, DOWEX (1x2), 60 °C, 10 min</td>
<td>0.84±0.02</td>
<td>109±12</td>
</tr>
<tr>
<td>6</td>
<td>CHCl₃</td>
<td>THF, tert-BuOK, 22 °C, DOWEX (1x2), 10 min</td>
<td>0.47±0.03</td>
<td>200±13</td>
</tr>
<tr>
<td>7</td>
<td>CHCl₃</td>
<td>THF, 22 °C, DOWEX (1x2), 10 min</td>
<td>0.22±0.05</td>
<td>444±23</td>
</tr>
<tr>
<td>8</td>
<td>CHCl₃</td>
<td>o-DCB, tert-BuOK, DOWEX (1x2), 60 °C, 600 min</td>
<td>2.98±0.08</td>
<td>30±1</td>
</tr>
<tr>
<td>9</td>
<td>CHCl₃</td>
<td>o-DCB, tert-BuOK, DOWEX (1x2), 22 °C, 600 min</td>
<td>2.01±0.42</td>
<td>48±11</td>
</tr>
<tr>
<td>10</td>
<td>CHCl₃</td>
<td>o-DCB, tert-BuOK, DOWEX (1x2), 22 °C, 10 min</td>
<td>0.75±0.08</td>
<td>127±11</td>
</tr>
<tr>
<td>11*</td>
<td>CHCl₃</td>
<td>o-DCB, tert-BuOK, DOWEX (1x2), 75 °C, 10 min</td>
<td>1.86±0.22</td>
<td>48±7</td>
</tr>
<tr>
<td>12*</td>
<td>CHBr₃</td>
<td>o-DCB, tert-BuOK, DOWEX (1x2), 60 °C, 600 min</td>
<td>8.33±1.90</td>
<td>7±3</td>
</tr>
</tbody>
</table>

Table 4.1 Reaction conditions for the formation of SWCNT-CCl₂ (1-11) and SWCNT-CBr₂ (12*). (*) indicates the use of Sigma-Aldrich (6,5) enriched SWCNTs. % Cl (Br) and C_{wall}/CCl₂ (CBr₂) determined using XPS analysis.

4.3.1 Functionalization of SWCNT via [2+1] cycloaddition using chloroform with potassium tert-butoxide or sodium trichloroacetate to form SWCNT-CCl₂

With an established literature procedure in hand for the dichlorocarbene [2+1] cycloaddition to p-SWCNTs,¹⁰ we set out to produce the SWCNT-CCl₂ adduct. Unfortunately, we were not able to achieve reproducible results with acceptable chlorine incorporation into the
SWCNTs as determined by XPS (Table 4.1, entries 1-6). However, we did note that a control experiment showed that running the reaction without a base markedly decreased the % Cl by XPS analysis (Table 4.1, entry 7). The presence of residual chlorine in the control reaction not subjected to potassium tert-butoxide treatment may indicate incomplete removal of chloroform during washing of the SWCNT-CCl₂.

After attempting four different temperature regimes using THF as the reaction solvent, we changed the solvent to ortho-dichlorobenzene, (o-DCB)²³ to increase the sparing solubility of SWCNTs. We observed better than a two-fold increase in the degree of functionalization of the SWCNTs using o-DCB with higher temperatures and longer reaction times (Table 4.1, entries 8,9,11). Our results with this dichlorocarbene addition method are on the same order of magnitude of those using similar carbene additions with CHCl₃.²⁴

Figure 4.1a-c shows two reactions to form SWCNT-CCl₂. The reaction on the left shows optimized conditions for the chloroform-derived dichlorocarbene. XPS and Raman results are tabulated in Figure 4.1b, while XPS and Raman spectra are shown in Figure 4.1c-d, respectively. XPS results show clearly the presence of chlorine at 200 eV (2.98±0.08 %) in the SWCNT that is not present in the p-SWCNT. A calculated \( \frac{C_{\text{wall}}}{Cl_{\text{atoms}}} \) of 48 indicates that there is one dichlorocarbene group per five hexagonal units on the SWCNT sidewall surface. The \( \frac{I_D}{I_G} \) from the Raman spectra shows an increase from 0.076 in the p-SWCNT to 0.56 in the SWCNT-Cl₂ adduct indicating disruption of the sp² network and successful functionalization via dichlorocarbene.
Figure 4.1 (a) Reactions of SWCNT to form SWCNT-CCl₂ adduct via chloroform and organic base (left) and MM with sodium trichloroacetate (right). (b) Table showing Raman I_D/I_G ratio, atomic composition (%), and calculated carbon atoms per chlorine atom. (c) XPS survey spectrum of chloroform-derived SWCNT-CCl₂ and p-SWCNT. (d) Resonance Raman spectrum of chloroform-derived SWCNT-CCl₂ and p-SWCNT. (e) XPS survey spectrum of sodium trichloroacetate-derived SWCNT-CCl₂ and p-SWCNT. f) Resonance Raman spectrum of sodium trichloroacetate-derived SWCNT-CCl₂ and p-SWCNT.
Entries 1-3 in Table 4.2 show our attempts at the solvent-free preparation of SWCNT-
CCl₂ via MM with sodium trichloroacetate. The extrusion of CO₂ and the formation of NaCl(s)
drives the formation of the dichlorocarbene species. Using this method, we earned much less
degree of functionalization. XPS analysis gave only 0.77±0.08 % Cl and a Cwall/CCl₂ of 121. The
Raman ID/G gave a ratio of 0.053, which shows no significant difference with that of p-SWCNT.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Reactants/carbene source</th>
<th>Conditions</th>
<th>% Cl</th>
<th>Cwall/CCl₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>30 eq NaCO₂CCl₃, 1 eq SWCNT</td>
<td>MM, 15 min, 30 Hz</td>
<td>0.77±0.08</td>
<td>121±13</td>
</tr>
<tr>
<td>2</td>
<td>60 eq NaCO₂CCl₃, 1 eq SWCNT</td>
<td>MM, 15 min, 30 Hz</td>
<td>0.65±0.14</td>
<td>147±34</td>
</tr>
<tr>
<td>3</td>
<td>15 eq NaCO₂CCl₃, 1 eq SWCNT</td>
<td>MM, 15 min, 30 Hz</td>
<td>0.70±0.03</td>
<td>130±9</td>
</tr>
</tbody>
</table>

Table 4.2 Reaction conditions for the formation of SWCNT-Cl₂ from the MM of NaCO₂Cl₃.

4.3.2 Functionalization of SWCNT via [2+1] cycloaddition using bromoform with
potassium tert-butoxide to form SWCNT-CBr₂

We applied similar conditions for the sidewall functionalization of SWCNTs with
bromoform as we did with chloroform (Table 4.1, entry 12). XPS and Raman data are reported
in Figure are reported in Figure 4.2 (a-c). XPS analysis shows the presence of bromine
(8.33±1.90 %) that indicates the successful cycloaddition of –CBr₂. This gives a calculated one
–CBr₂ groups per 7 sidewall carbon atoms. However, the occurrence of chlorine (3.95±0.59 %)
implies the presence of residual o-DCB that was not removed during washing procedures. The
Raman analyses substantiates the XPS evidence and shows a and ID/G of 0.61 in the bromoform-
derived SWCNT-CBr₂, an increase from 0.076 in the p-SWCNTs.
Figure 4.2 (a) Reaction of SWCNT to form SWCNT-CBr₂ adduct via bromoform and organic base. (b) Table showing Raman I_D/I_G ratio, atomic composition (%), and calculated carbon atoms per -CBr₂ group. (c) XPS survey spectrum of SWCNT-CBr₂ and p-SWCNT. (d) Resonance Raman spectrum of SWCNT-CBr₂ and p-SWCNT.

4.3.3 Functionalization of SWCNT via [2+1] cycloaddition using sodium difluorochloroacetate to form SWCNT-CF₂.
Given our limited success with the solvent-free preparation of SWCNT-Cl$_2$ with sodium trichloroacetate, we attempted to perform the difluorocarbene addition to SWCNTs under solvent conditions using difluorochloroacetate. Under the conditions in entry 1, Table 4.3, we achieved similar results for the –CF$_2$ cycloaddition to SWCNTs as we did for the solvent free preparation of the SWCNT-Cl$_2$. As reported in Figure 4.3, we observed a modest amount of fluorine functionalization of the SWCNTs (0.96±0.16 %) with a calculated one –CF$_2$ groups per 110 sidewall carbon atoms.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Reactants/carbene source</th>
<th>Conditions</th>
<th>% F</th>
<th>C$_{wall}$/CF$_2$(CF$_2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NaCO$_2$ClF$_2$, DMF, diglyme, 90 °C, 720 min</td>
<td>0.96±0.16</td>
<td>110±2</td>
<td></td>
</tr>
<tr>
<td>2*</td>
<td>Togni’s Reagent, SWCNT/Tognis/Cu(I)=1/5/0.1</td>
<td>0.69±0.01</td>
<td>138±1</td>
<td></td>
</tr>
<tr>
<td>3*</td>
<td>Togni’s Reagent, SWCNT/Tognis/Cu(I)=1/15/0.3</td>
<td>0.91±0.17</td>
<td>106±19</td>
<td></td>
</tr>
<tr>
<td>4*</td>
<td>Togni’s Reagent, SWCNT/Tognis/Cu(I)=1/6.7/0.15</td>
<td>1.21±0.11</td>
<td>78±8</td>
<td></td>
</tr>
<tr>
<td>5*</td>
<td>Togni’s Reagent, SWCNT/Tognis/Cu(I)=1/15/0.3</td>
<td>1.00±0.37</td>
<td>102±42</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.3 Reaction conditions for the formation of SWCNT-CF$_2$ from NaCO$_2$ClF$_3$ (1) and the formation of SWCNT-CF$_3$ from Togni’s reagent (2-5)
**Chapter 4**

*Covalent Functionalization of Single Walled Carbon Nanotubes*

**Figure 4.3** (a) Reaction of SWCNT to form SWCNT-CF₂ adduct via MM of SWCNT and sodium difluorochloroacetate. (b) Table showing atomic composition (%), and calculated carbon atoms per fluorine atom. (c) XPS survey spectrum of SWCNT-CF₂ and p-SWCNT
4.3.4 Functionalization of SWCNT via trifluoromethylation using Togni’s reagent to form SWCNT-CF₃

After experimenting with different ratios of SWCNT/Togni’s reagent/Cu (I) catalyst, we settled on the conditions in entry 4 of Table 4.3. Our best result, reported in Figure 4.4, afforded 1.21±0.11 % fluorine via XPS. This gave a calculated on –CF₃ group per 78 sidewall carbon atoms. The I_D/I_G from Raman analysis is 0.11. This result is very modest in comparison to our Raman analysis of SWCNT-CCl₂ functionalization efforts. This low level of functionalization may be attributed to a wide variety of sources: dimerization of the trifluoromethyl radical, recombination of the radical with its parent molecule (Togni’s reagent), or just an insufficient amount of –CF₃ radical formation under the conditions selected. Regardless of the reason, more experiments could be performed to improve upon this preliminary data set.
a) Togni’s reagent, [(MeCN)₄Cu₁PF₆], DMF, 60 °C, 4 hr

b) Table of atomic composition (%), and calculated carbon atoms per fluorine atom.

<table>
<thead>
<tr>
<th>Material</th>
<th>Raman I_p/I_G</th>
<th>XPS % C1s</th>
<th>XPS % O1s</th>
<th>XPS % F1s</th>
<th>#C atoms per F atom</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-SWCNT</td>
<td>0.066</td>
<td>92.84±0.55</td>
<td>7.01±0.56</td>
<td>0.00±0.00</td>
<td>N/A</td>
</tr>
<tr>
<td>SWCNT-CF₃</td>
<td>0.11</td>
<td>95.24±1.17</td>
<td>3.43±0.88</td>
<td>1.21±0.11</td>
<td>78±8</td>
</tr>
</tbody>
</table>

c) Raman spectra of SWCNT-CF₃ and p-SWCNT.

Figure 4.4 (a) Reaction of SWCNT to form SWCNT-CF₃ adduct via Togni’s reagent. (b) Table of atomic composition (%), and calculated carbon atoms per fluorine atom. (c) XPS survey spectrum of SWCNT-CF₃ and p-SWCNT.

4.3.5 SWCNT-CF₂ and SWCNT-CF₃ for chemiresistive ammonia sensing

We sought to investigate the efficacy of our fluorinated SWCNT adducts in detecting NH₃. NH₃, a well-known electron donor, is known to initiate a charge transfer type response to the SWCNTs. The sensory response was investigated by measuring the change in current between two electrodes at a constant bias voltage of 0.10 V. The change in current was converted to a negative change in conductance [-ΔG/G₀ (%) = ((I₀-I)/I₀) x 100%], where I₀ is the initial
current. This normalized response allows for small differences in the resistivity that can complicate device to device comparisons. **Figure 4.5** shows baseline-corrected responses of three chemiresistive devices that were tested in parallel incorporating p-SWCNT, SWCNT-CF$_2$ and SWCNT–CF$_3$ adducts. Interestingly, the response towards NH$_3$ for this particular batch of Nano-C brand p-SWCNTs was 40 times lower than previously reported under similar conditions by our group.$^{26}$ The trifluoromethylated SWCNTs show virtually the same response to NH$_3$ as the p-SWCNTs. The SWCNT-CF$_2$ give a reduced sensitivity to NH$_3$. There is not enough information to determine what the cause of the reduced response could be.

![Graph showing chemiresistive responses](image)

**Figure 4.5** Chemiresistive responses averaged across three p-SWCNT/SWCNT-CF$_2$/SWCNT-CF$_3$ devices to 60 s exposures of NH$_3$ at a flow rate of 200 mL/min in dry N$_2$.

**4.4 Conclusions.** In summary, five different approaches to the covalent functionalization of SWCNTs have been conducted and characterized via XPS and Resonance Raman spectroscopy. [2+1] cycloadditions of dichlorocarbenes to SWCNTs to form the SWCNT-CCl$_2$ adduct under
elevated temperatures and extended reaction times gave the best functionalization rates: 2.98% chlorine from XPS and a calculated one –CCl₂ group per 48 sidewall carbon atoms. Furthermore, Raman analysis shows an increase in the intensity of the D band relative to the G band to give a I_D/I_G of 0.56, indicating an increase in the number of sidewall defects and the breaking of the conjugation of the SWCNT sp² network. Though more work is required to confirm, SWCNT-CBr₂ generated from bromoform, gave promising initial results (3.95 % Br; Cwall/CBr₂; I_D/I_G=0.61). Solvent-free preparation using mechanical milling, MM, to synthesize SWCNT-CCl₂ was attempted and modest results were achieved (0.77% Cl; Cwall/CCl₂=121; I_D/I_G=0.53). Fluorination of SWCNTs to form both SWCNT-CF₂ and SWCNT-CF₃ adducts were also performed. Both preparations afforded modest results, with the trifluormethylation (1.21% F; Cwall/CF₃=78; I_D/I_G=0.11) generating slightly better results than dichlorocarbene cycloaddition (0.96% F; Cwall/CF₂=121; I_D/I_G=0.53). For the SWCNT-CF₂ and SWCNT-CF₃ adducts, we tested their response to NH₃ and found the response to be the same or lower than the native p-SWCNT response.

From the above results, it is clear that the solvent-based approach using o-DCB as a solvent at elevated temperatures is the most viable path forward to attaining SWCNT-CCl₂ and SWCNT-CBr₂ n-type SWCNTs. The mechanical milling approach is operationally simpler, but suffers from poor functionalization rates. To advance this project, additional methods confirming the functionalization were necessary. UV-vis/NIR spectroscopy and thermogravimetric analysis of the SWCNT adducts can help verify the efficacy of the functionalization. The objective of this work was to synthesize n-type SWCNTs. Electrical characterization of these SWCNT adduct materials in a FET system is required to confirm whether or not n-type characteristics have been achieved as anticipated and designed.¹³,²⁷
4.5 Experimental

4.5.1 Materials

All chemicals and reagents were purchased from Sigma-Aldrich and used without additional purification, except that tetrahydrofuran was distilled from sodium metal and benzophenone. Purified SWCNTs (UPT 200, Batch 1167-24) were acquired from Nano-C, (Westwood, MA) or Sigma Aldrich, Inc. (Saint Louis, MO, USA) (6,5 chirality, carbon (95%), with 93% as SWCNTs).

4.5.2 Instrumentation

**Mechanical Milling.** Sensing materials were generated by solvent-free ball milling of carbon (e.g., SWCNTs) with commercial small molecule “selectors” using an oscillating mixer mill 3 (MM400, Retsch GmbH, Haan, Germany) within a stainless-steel milling vial (5 mL) equipped with a single stainless steel ball (7 mm diameter). Unless otherwise indicated, a typical experiment involved filling the milling vial with carbon powder (e.g., SWCNTs) and reactant (total mass of powder = 620 mg) and ball milling the mixture for 30 min at 30 Hz.

**X-Ray photoelectron spectroscopy (XPS).** XPS measurements were performed on a Phi Versaprobe II instrument at the MIT Center for Materials Science and Engineering.

**Raman spectroscopy.** Raman spectra were collected with excitation at 532 nm (or 633, where noted) laser using a Horiba LabRAM HR800 Raman spectrometer at the MIT Institute of Soldier Nanotechnology.

4.5.3 Synthesis

**Synthesis of SWCNT-CCl₂ functionalized via dichlorocarbene generated from chloroform.** A typical 10-hour reaction involved immersing 25 mg SWCNT into a well-stirred, highly basic solution of potassium tert-butoxide dissolved in 10 mL o-DCB at 60 °C in the
presence of phase transfer catalyst, DOWEX (1, 2). Dry chloroform was then added drop-wise to the mixture in an inert gas environment. The reaction was quenched with 10 mL of water after the designated reaction time period. The reaction mixture was filtered through a 2.0 μm Millipore membrane filter. The solid filtrate was then scraped off of the membrane and placed in a centrifuge tube with 4.0 mL water, sonicated for 30 seconds and centrifuged for 10 minutes at 8000 rpm. The water was decanted and refilled with an additional 4.0 mL, sonicated and centrifuged. This same sonication/centrifugation procedure was repeated with ethanol and hexanes. Finally, the modified SWCNTs were heated at 100 °C for 5 min on a hot plate to remove chemical residuals before Resonance Raman spectroscopy and X-ray Photoelectron (XPS) measurements. SWCNT-CBr$_2$ adducts were prepared in the same manner as above.

**Synthesis of SWCNT-CCl$_2$ functionalized via dichlorocarbene generated from NaCO$_2$CCl$_3$.** 600 mg of NaCO$_2$CCl$_3$ and 20 mg of SWCNT were added to a stainless steel milling vial and mechanically mixed for 30 minutes at 30 Hz. The product powder was placed in 15 mL centrifuge tubes and diluted with 4.0 mL water. The solid filtrate was then scraped off of the membrane and placed in a centrifuge tube with 4.0 mL water, sonicated for 30 seconds and centrifuged for 10 minutes at 8000 rpm. The water was decanted and refilled with an additional 4.0 mL, sonicated and centrifuged. This same sonication/centrifugation procedure was repeated with ethanol and hexanes. Finally, the modified SWCNTs were placed in a vacuum oven at 80 °C for ten minutes.

**Synthesis of SWCNT-CCF$_2$ functionalized via dichlorocarbene generated NaCO$_2$CCIF$_2$.** To 40 mL DMF and 10 mg of SWCNT in a round bottom flask fitted with a magnetic stir bar under an Ar atmosphere, a mixture of 50 mg of NaCO$_2$CCIF$_2$ in 5 mL of diglyme were delivered. The mixture was refluxed overnight. The reaction was quenched with 10 mL water. The crude
reaction mixture was filtered through a 2 μm Millipore membrane filter and then washed three times with diethyl ether. Finally, the modified SWCNTs were placed in a vacuum oven at 80 °C for ten minutes.

_Synthesis of SWCNT-CF₃ functionalized via generated Togni’s Reagent._

To 40 mL DMF and 10 mg of SWCNT in a round bottom flask fitted with a magnetic stir bar under an Ar atmosphere, 15.3 mL of a 1 mg/mL of [(MeCN)_₄Cu]PF₆ was delivered. Subsequently, 70 mg of SWCNT were added. After a designated reaction period, the reaction mixture was filtered through a 0.2 μm Millipore membrane filter and washed with DMF. The functionalized SWCNT were then sonicated in DMF, then filtered. Sonication and filtration were repeated in diethyl ether. Finally, the modified SWCNTs were placed in a vacuum oven at 100 °C for 30 minutes.

**4.5.4 Chemiresistor fabrication and gas sensing experiments**

_Preparation of gold electrodes on glass microscope slides._ Glass substrates deposited with chromium adhesion layers (10 nm) and gold electrodes (100 nm) were prepared according to a literature procedure.²⁸ Briefly, glass slides (VWR Microscope Slides) were cleaned by sonication in acetone for 5 min followed by UV-ozone treatment using a UVO cleaner (Jelight Company Inc., Model 42) for 20 min. A 10 nm layer of chromium (99.99%, R.D. Mathis) and a subsequent 100 nm layer of gold (99.99%, R.D. Mathis) were deposited through a custom stainless steel mask using a thermal evaporator (Angstrom Engineering), which resulted in three sets of four channel electrode patterns on a single glass slide, which was cut into three individual devices. Each device contains a gold pattern of four isolated working electrodes with one shared reference-counter electrode on the glass substrate. The gap between one pair of gold electrodes is 1 mm.
Fabrication of SWCNT-adduct chemiresistor platform. p-SWCNT and SWCNT adduct dispersions were prepared with a concentration of 0.25 mg/mL in o-DCB. The desired amount of SWCNT adduct dispersion was dropcasted with a 20 µL syringe between four gold electrode pairs on the glass substrate. Typically, between 4-20 µL of the dispersion was required to reach the target electrode resistance of 10-50 kΩ.

Ammonia Gas Detection Measurement. For NH₃ detection measurement, the fabricated array device was placed into a custom-built PTFE enclosure with a small gas inlet and outlet, the gold electrodes of the device were connected to a PalmSens EmStat potentiostat with a MUX16 multiplexer. The inlet port was connected to a gas delivery system (Sierra’s Smart-Trak Series 100). Delivery of controlled concentration of gases to devices. To obtain concentrations of NH₃ between 250 ppm – 5000 ppm, pure NH₃ supplied from a gas cylinder (Airgas) was diluted with N₂ using the gas mixing system at total flow rate supplied to devices ranging between 400 – 1000 mL/min. To obtain concentrations of NH₃ between 0.5 ppm – 80 ppm, 1% NH₃ in N₂ supplied from a gas cylinder (Airgas) was diluted with N₂ using the gas mixing system at a total flow rate supplied to devices ranging between 500 – 10000 mL/min. Controlled delivery of gas to devices was accomplished by encasing a device within a custom-built teflon chamber equipped with an inlet and an outlet for gas flow. The potentiostat applied a constant potential of 0.1 V across the electrodes, and the current for each channel of the device was recorded using PS Trace software (v. 4.7) during 60 s of NH₃ vapor exposures. After a linear baseline correction, the change in current resulting from exposure to the analyte was converted to the negative change in conductance (\(-\Delta G/G_0\) (%) = \((I_0 - I)/I_0\) x 100), where \(I_0\) is initial current), which was taken as the device’s response.
4.6 References

(19) Gao, X.; Ishimura, K.; Nagase, S.; Chen, Z. Dichlorocarbene Addition to C$_{60}$ from the


Work Experience

Graduate Research Assistant (June 2013 – June 2017)
MIT, Department of Chemistry
Advisor: Professor Timothy M. Swager

Operations and Plans Officer (June 2011 – May 2013)
10th Special Forces Group Support Battalion (Airborne)
United States Army, Fort Carson, CO

Assistant Professor of Chemistry (June 2008 – June 2010)
United States Military Academy (USMA)
United States Army, West Point, NY

Graduate Researcher (June 2006 – May 2008)
National Renewable Energy Lab, Golden, CO
Colorado School of Mines, Department of Chemistry, Golden, CO
M.S. Thesis: “The Preparation of Aminosilane Surfaces for DNA Microarray Applications”
Advisor: Professor Scott M. Cowley

Iraqi Security Forces Liaison Officer (January 2006-May 2006)
Headquarters Troop, 3D Armored Cavalry Regiment
United States Army, Iraq

Company Commander (June 2004 - December 2005)
89th Chemical Company, 3D Armored Cavalry Regiment
United States Army, Fort Carson, CO and Iraq

Training and Operations Officer (January 2003 - May 2004)
43rd Area Support Group
United States Army, Fort Carson, CO and Iraq

Operations and Chemical Officer (January 2002 - December 2002)
Engineer Brigade, 2d Infantry Division
United States Army, Republic of Korea

Support Command Chemical Officer (January 2001 - April 2001)
Division Support Command, 3rd Infantry Division
United States Army, Fort Stewart, GA

Executive Officer (January 2000 - December 2000)
92d Chemical Company, 3rd Infantry Division
United States Army, Fort Stewart, GA
Platoon Leader (August 1999 - December 2000)
92d Chemical Company, 3rd Infantry Division
United States Army, Fort Stewart, GA

Operations and Chemical Officer (October 1997 - August 1999)
3rd Battalion, 7th Infantry Regiment, 3rd Infantry Division
United States Army, Fort Stewart, GA and Kuwait

Education

Massachusetts Institute of Technology (June 2013 – June 2017)
Ph.D., Organic Chemistry
Thesis: “Polymer and Covalent Functionalization Of Single Walled Carbon Nanotubes For Electronic Sensor Applications”
Research Advisor: Professor Timothy M. Swager

Graduate, U.S. Army Command and General Staff College (July 2010-May 2011)
Fort Leavenworth, KS, 2011

Colorado School of Mines (June 2006 to May 2008)
M.S., Chemistry
Thesis: “The Preparation of Aminosilane Surfaces for DNA Microarray Applications”
Research Advisor: Professor Scott M. Cowley

Graduate, Chemical Officer Advanced Course (April 2001 – September 2001)
Fort Leonard Wood, MO

Graduate, Chemical Officer Basic Course (May 1997 – October 1997)
Fort McClellan AL

Providence College (September 1993 – May 1997)
B.S., Chemistry

Teaching Experience

Kansas City Kansas Community College
Instructor, College Chemistry (Fall 2010)

United States Military Academy
Instructor, Quantitative Chemical Analysis (Fall 2009 - Spring 2010)
Instructor, General Chemistry I-II (Fall 2008 – Summer 2009)

Awards

2015 Best Poster, ACS Polymer Division, 2015 ACS Fall Meeting, Boston MA
2013 Army Commendation Medal (also 2004)
2013 United States Army Advanced Civil Schooling Doctoral Fellowship
2011 Meritorious Service Medal (also 2002 and 2005, 2010)
2009 Defense Threat Reduction Agency Grant Award
2006 United States Army Advanced Civil Schooling Masters Fellowship
1993  United States Army ROTC Scholarship

Publications


Presentations


Leadership and Service

May 2016 – present
January 2016 - June 2016
September 2015 – June 2016
January 2015 – June 2015
June 2008 – May 2010
May 1997 – January 2015

MIT Veterans Club Representative
Contributor, Synfacts
Math Coach, Hanscom Primary School
Contributor, Synfacts
American Chemical Society Representative, USMA
Commissioned Officer, United States Army

Memberships

American Chemical Society, Polymer Chemistry Division
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