Reduced Graphene Oxide Based Transparent Electrodes for Organic Electronic Devices

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Abstract
This thesis explores the utility of reduced graphene oxide and hybrid reduced graphene oxide/single walled carbon nanotubes as a transparent electrode. Graphene oxide was fabricated using the modified Hummers method, transferred to arbitrary substrates by a vacuum filtration method, and reduced chemically and thermally thus creating thin, large area reduced graphene oxide films. Films were characterized electrically, optically, spectroscopically, and topographically. Raman and X-ray photoelectron spectroscopy techniques were utilized to ensure successful fabrication of reduced graphene oxide. The reduced graphene oxide electrodes exhibit sheet resistances on the order of $10^{-1} \text{ to } 100 \text{ k}\Omega/\text{sq}$ with transparencies between 60 – 90 %. To ameliorate these electronic properties, single walled nanotubes were introduced during the filtration process to separate the graphene oxide nanoplatelets and prevent structural deformation during reduction. This nanotube doping yielded a two-fold decrease in sheet resistance for low nanotube to graphene oxide ratios, but increased sheet resistance for higher nanotube to graphene oxide ratios. Reduced graphene oxide electrodes and nanotube/reduced graphene oxide hybrid electrodes were used in organic light emitting diode and organic solar cell applications. Organic light emitting diodes exhibited current efficiencies of about 1 cd/A and organic solar cells exhibited power conversion efficiencies less than 1 % for both reduced graphene oxide and hybrid electrodes.
Résumé

Cette thèse examine l’utilité de l’oxyde de graphène réduit et de l’hybride oxyde de graphène réduit et nanotubes carbone en fonction d’une utilisation comme électrode transparente. L’oxyde de graphène a été fabriqué par la méthode de Hummers modifié puis a été transféré sur un substrat arbitraire par la méthode de filtration avec succion à vide, et a été réduit chimiquement et thermiquement pour créer des feuilles d’oxyde de graphène réduit qui sont minces et qui couvrent une grande surface. Les feuilles ont été caractérisées par des mesures électriques, optiques, spectroscopiques, et topographiques. Les spectroscopies Raman et par photoélectron induits par rayons-X ont été utilisées pour s’assurer que la fabrication de l’oxyde de graphène réduit a été obtenue. Les électrodes d’oxyde de graphène réduit montrent des résistances de feuille de 10–100 kΩ/sq avec des transparences entre 60–90 %. Pour améliorer ces propriétés, des nanotube de carbone monoparois ont été introduits pendant le processus de filtration pour séparer les nanoplatelets d’oxyde de graphène et pour éviter la déformation structurelle pendant la processus de réduction. Ce dopage de nanotubes a diminué la résistance de feuille par un facteur deux pour des proportion faibles de nanotubes avec l’oxyde de graphène, mais a augmenté la resistance pour les hautes proportions. Les électrodes d’oxyde de graphène réduit et les électrodes hybrides nanotubes/oxyde de graphène réduit ont été utilisées dans des dispositifs optoélectroniques organiques; spécialement des diodes électroluminescentes et des cellules solaires. Les diodes électroluminescentes organiques ont des rendements de courant inférieurs à 1 cd/A et les cellules solaire ont des rendements de puissance inférieurs à 1 % pour les deux types d’électrodes: oxyde de graphène réduit et hybrides.
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Chapter 1 Introduction

Transparent electrodes have such an enormous breadth of applications and have infiltrated society so pervasively, that one can scarcely spend a day without interacting with or using a transparent electrode in some capacity. They are used in liquid crystal displays, touch screens, flat panel and plasma displays; virtually any flat large area, light emitting application. Two crucially important metrics of a transparent electrode are sheet resistance and optical transparency. The perfect transparent electrode has as low sheet resistance as possible and as high optical transparency, for all wavelengths, as possible; consequently, the most dominant and widely used transparent electrode is indium-tin oxide (ITO) due to its high optical transparency and low sheet resistance. However, it suffers from weak mechanical properties and high costs, among other drawbacks. An alternative to ITO is a thin film of carbon nanotubes (CNTs). CNTs are mechanically robust and flexible, excelling in the properties where ITO is inferior; yet they have a comparatively lower optical transparency and higher sheet resistance. And where the limitations of CNTs and ITO have been realized, another material, graphene, could succeed.

Graphene is a single layer of carbon atoms densely packed into a honeycomb lattice, benzene ring structure, which has two atoms in its unit cell (see Figure 1). Three of carbon's four valence electrons bond in a plane with other carbon electrons to form \( sp^2 \) hybridized sigma bonds. The fourth electron remains unbounded and delocalizes with other such electrons in the crystal. Graphene is the basis for many other carbon based crystals and molecules: rolled into a ball it forms fullerenes, rolled into cylinders if forms carbon nanotubes, and stacks of graphene form graphite. It has been previously theorized to be physically unstable, however Novoselov et al. isolated mono- and few-layer graphene (among other 2D crystals) in 2004; work which earned them the 2010 Nobel prize in physics [1]. They fabricated graphene by repeatedly exfoliating highly order pyrolytic graphite using adhesive cellophane tape. Each successive peeling stripped the mesas of graphite down to much thinner dimensions leaving behind thin graphite, as well as few-layer graphene. In this seminal paper, it was shown that few-layer graphene has exceptionally high mobility (10,000 cm\(^2\)/Vs) while being arbitrarily n or p type depending on carrier concentration and electric field.
Later studies by Stormer *et al.* also confirmed high carrier mobilities, seen by Geim, demonstrating mobilities greater than 10,000 cm$^2$/Vs. However both Geim and Stormer's mobility values were measure with graphene on silicon thus inducing deleterious carrier scattering at the interface [2, 3]. Suspended graphene mobility measurements revealed carrier mobilities on the order of 200,000 cm$^2$/Vs [4].

Graphene is commonly referred to as a zero-gap semi-metal because the conduction and valence bands touch at only two wavevectors (the K and K' points). Furthermore, dispersion around the K points is approximately linear, not parabolic. In a typical metal, the chemical potential (or Fermi energy) lies deep within the valence band, such that only small amounts of energy are required to excite electrons to electrically conductive energy states while having a relatively infinite number of allowed energy states for these excited electrons to exist. In intrinsic graphene however, the chemical potential lies at the interface of the valence and conduction band. While small amounts of energy will excite carriers to electrically conductive states, there are comparatively very few allowable energy for the electrons to excite to states (due to the linear band structure), thus giving graphene both semi-conducting and metallic properties. Adjusting the chemical potential can be achieved by a gate voltage bias in graphene transistors.

Given these exceptional electrical properties large area graphene films could make excellent transparent electrodes as the atomically thin nature of the materials renders it optically transparent. As graphene is flatter than nanotubes, a smoother surface can be constructed at the active layer/electrode interface of a practical device. However, poor fabrication techniques for graphene currently limit its wide spread application since challenges exist in the fabrication of *large area* graphene films. Current large area graphene production techniques yield either an ensemble...
of non-uniform or disjoined graphene crystals (by solution processable techniques) or polymer contaminated graphene (by chemical vapor deposition). While the ideal graphene electrode is currently unavailable, exploiting the electronic properties of graphene could be achieved by doping what isolated, pristine graphene exists with CNTs. Such a mélange can be fabricated in two, hybrid forms; a uniform mixture of the two materials in a bulk heterojunction structure or a typical, separated heterojunction structure.

This thesis explores the utility of graphene and graphene-carbon nanotube hybrid structures as a transparent electrode for two organic electronic devices (OEDs); organic light emitting diodes (OLEDs) and organic solar cells. A solution processable approach to graphene fabrication is selected since it is easily fabricated and cleanly transferred to transparent substrates (such as glass, quartz, polyethylene terephthalate (PET), etc.). To ensure successful graphene fabrication, the graphene based electrodes are characterized by Raman and x-ray photoelectron spectroscopy and compared to other such spectroscopic analysis found in the literature. After, graphene transparent electrodes are characterized by atomic force microscopy, electrical sheet resistance, and optical transparency. Compared to other studies, the graphene electrodes presented here yield similar characteristics. Once the graphene electrodes are fully characterized, hybrid electrodes can be fabricated and characterized; to date no one has created hybrid nanotube-graphene transparent electrodes, thus there is no comparison to the literature presented. Finally, OEDs were fabricated using graphene and hybrid structures as the transparent electrodes.
Chapter 2 Current State of Transparent Electrodes

Indium-tin-oxide Electrodes

ITO has been used for over a decade as the transparent electrode in various flat panel, light emission (and absorption) electronic applications. ITO excels in sheet resistance and optical transparency achieving <10 Ω/sq and >90%, respectively [5]. ITO's work function, ranging between 4.3 – 4.75 eV, is well suited for use as the hole injecting electrode in organic light emitting devices. The inconsistency in the work function stems from the methodology for cleaning the surface. According to Sugiyama et al., the work function depends on carbon contaminants, the oxygen:indium ratio, and the indium:tin ratio at the surface [6, 7].

While ITO has great benefits, its serious drawbacks cannot be overlooked. Firstly, a U.S. Geological survey estimates there is a global indium reserve of approximately 6000 tonnes. Given the annual rate of consumption, there should be a global indium shortage by 2020 [8]. These diminishing indium sources will lead to increases in prices thus making ITO impractically expensive. Secondly, ITO is a brittle material which cracks under strain and thus increases its sheet resistance [9]; therefore, ITO cannot be used in flexible electronics. Finally, the stability of organic devices with an ITO electrode is severely compromised over a relatively short period of time [10]. This rapid degradation is due to small pin-hole defects in ITO which allow oxygen and water molecules to enter the device and react with the organic active layer [11-13]. These drawbacks demand a suitable substitute be found. Other non-carbon based electrodes have been explored, such as silver nanowire meshes [14] and other metal oxides (like zinc oxide) [15, 16]. In this work, the focus is exclusively on the carbon based transparent electrodes of CNTs and graphene in which the deleterious properties of ITO are all but benefits.

Carbon Nanotube Electrodes

Carbon nanotubes electrodes which are flexible, abundant, and devoid of migratory impurities are well suited for transparent electrodes applications. The method employed to fabricate CNT electrodes was first demonstrated by Wu et al. in 2004 and involves vacuum filtering arc discharged single-walled CNTs (SWNTs) then transferring the filtered SWNTs by dissolving the filter in a solvent [17]. However, before outlining the characteristics of vacuum filtered SWNTs, a brief review of CNTs is presented.
Nanotube Background Information

A CNT is cylindrical graphitic structure. One can imagine a SWNT to be a flat, two dimensional sheet of graphene which is rolled into a tube. Given this construction, there are two parameters which uniquely identify such a tube, the diameter of the tube and its chirality. Chirality is the direction which the nanotube has been rolled. Two nanotubes rolled in two different directions (such as Armchair and Zigzag as shown in Figure 2 below [18, 19]) will exhibit different electronic properties. One direction will make the nanotube metallic and a different direction will make it semiconducting. Controlling nanotube diameter during fabrication can be done by using different metallic catalysts however there is no known fabrication procedure for chiral specificity. Yet techniques exist for separating metallic and semiconducting nanotubes after fabrication and even growing higher ratios of metallic to semiconducting nanotubes [20, 21]. Using these techniques all metallic CNT transparent electrodes have been fabricated and exhibit electronic and optical characteristics near ITO (10 – 100 Ω/sq with > 80% transparency at 550 nm) [22-24].

Figure 2 – Left: Graphene crystal structure and its relation to chirality in CNTs, Right: a) Armchair and b) Zig-zag nanotube configurations [19]

In a CNT electrode, electrons must pass from one nanotube to another several times before exiting the electrode and the resistance at this junction leads to higher sheet resistance than ITO [25]. Also, CNTs may pose serious health risks. While current research into the toxicity of CNTs is preliminary and inconclusive as a whole, it has been shown that “under certain conditions CNTs cause inflammatory and fibrotic reactions” [26]. Despite these drawbacks, CNTs possess interesting mechanical and electronic properties. They are among the strongest materials, in terms of tensile strength (13-53 GPa) and exhibit high charge carrier mobility, 10,000 cm²/Vs, with a high electrical current density, 4x10⁹ A/cm² [27-30]. Furthermore, CNTs have a work function (4.5 – 4.1 eV) similar to ITO (4.4 – 4.9 eV), thus making it an appropriate material for hole injection in organic
electronic devices [31, 32]. This unique blend of attributes makes CNTs a candidate for flexible electronics, such as thin film transistors, organic light emitting diodes, and solar cell devices.

Characterization of Common CNT Electrode Fabrication Techniques

Since Wu et al. first employed the filtration method to fabricate macroscale CNT sheets much progress has been made in this area. Various optimization techniques, such as nitric acid doping, and printing methods, such as PDMS stamping, have been employed creating a plethora of CNT fabrication techniques. A brief outline of the characterization and properties of common fabrication techniques follows.

Filtration: Among the first research groups to employ Wu et al.'s method was Pasquier et al. who used filtered SWNTs to fabricate organic solar cells [33]. Pasquier fabricated SWNT electrodes with optical transparencies (at 550nm) between ~35-85% with corresponding sheet resistances of 100-10,000 Ω/Sq. More specifically, electrodes with high optical transparency also exhibited a high sheet resistance. Compared with ITO which has optical transparency (550nm) ~80% with sheet resistances <20 Ω/sq, CNTs seem inadequate. However, the actual solar cell with CNT electrodes ameliorated the efficiency by over 40% with a relatively consistent fill factor.

Another group to use Wu’s CNT filtration method was Aguirre et al. who fabricated an organic light emitting diode (OLED) [34]. The CNT electrodes fabricated were a vast improvement over Pasquier’s electrodes boasting optical transparencies (at 520 nm) between 10-90% with corresponding sheet resistances of 25-450 Ω/sq. A detailed comparison of turn on voltage, luminance, and current efficiency between OLEDs fabricated with CNT or ITO electrodes is summarized in Table 1. Comparatively, CNT-OLEDs fair similarly to ITO-OLEDs except in luminance where CNT-OLEDs emit half the luminance as ITO-OLEDs.

<table>
<thead>
<tr>
<th>Type</th>
<th>Turn on Voltage (V)</th>
<th>Maximum Luminance (cd/m²)</th>
<th>Current Efficiency (cd/A)</th>
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<tr>
<td>ITO-OLED</td>
<td>6.6</td>
<td>6000</td>
<td>1.9</td>
</tr>
<tr>
<td>CNT-OLED</td>
<td>6.2</td>
<td>2800</td>
<td>1.4</td>
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PDMS Stamp Transfer: This method couples the vacuum filtration technique of Wu with a PDMS lift-off and transfer procedure. Rather than using solvents, such as acetone, to dissolve the cellulose acetate filter, the CNTs are physically lifted off from the surface of the filter by a pre-patterned PDMS stamp [35]. CNTs are loosely bound to the filter and therefore even a low surface energy
material such as PDMS (19 mJ/m²) can lift off the CNTs which in turn can be deposited onto higher surface energy substrates like glass (47 mJ/m²), PET (44 mJ/m²) or PMMA (41 mJ/m²). This transfer process is easier than the solvent dissolving process as it is less likely to damage the nanotubes. However, one must fabricate a pre-patterned PDMS stamp. The utility of this method relative to the solvent dissolving method fairs comparably with optical transparencies and sheet resistances one the order of 85% and 200 Ω/sq [36, 37].

Since electrode quality is somewhat independent of fabrication technique, other methods have been explored to improve the quality of the CNT electrodes. Primarily, the use of doping agents has been shown to substantially reduce the sheet resistance [38]. With respect to acid doping (nitric and sulphuric) it is theorized that the improvement is due to the removal of highly strained CNT caps as well as the complete removal of surfactants used to disperse the CNTs prior to filtration [38, 39].

**Graphene Electrodes**

The utility for graphene as a transparent electrode is hindered by its non-uniform fabrication. The method of graphene deposition described by Novoselov et al. has been the fabrication technique used to probe and observe the electrical properties of graphene. However, the mechanically exfoliating, “Scotch tape” method produces a random, sparse distribution of graphene flakes among large, bulk graphite material. For use as a transparent electrode, uniform large area graphene films must be used. To this end, two promised fabrication techniques are explored; solution processable fabrication and chemical vapor deposition (CVD).

**Solution Processable Fabrication**

The basic idea in the solution processable fabrication procedure is to make a dispersed graphene oxide (GO) solution which can be deposited on arbitrary substrates. The GO is then reduced to form mono- to few-layer graphene. The oxidation step, developed by Hummers et al. in 1958, involves a mixture of bulk powder/flake graphite, sodium nitrate, sulphuric acid, and potassium permanganate [40]. The method was further improved by drastically increasing the oxidation reaction time by several days and including highly purifying steps. These added improvements are referred at as the modified Hummers method for GO fabrication [41]. While there are other routes to oxidize graphite (such as the Brodie method), the modified Hummer method is the most widely used [42]. Current recent research in solution processable graphene fabrication is largely focused on improving reduction schemes and developing new applications.
Reduction treatments include a hydrazine vapor, high temperature heating, and optical reduction methods [43-45]. For use as a transparent electrode, hydrazine vapor reduced electrodes had sheet resistances on the order of 1 MΩ, much too large to be used in practical devices [46, 47]. However, Becerril et al., using a post hydrazine thermal annealing step, found sheet resistances on the order of 10 kΩ/sq [44]. Currently, the most effective reduction is a high temperature thermal reduction at 1100 °C. Electrodes reduced thermally achieved sheet resistances on the order of 10^2-10^3 Ω/sq [44]. Another promising reduction technique is exposure to UV light [45, 48, 49]. This method improved the sheet resistance by an order of magnitude. The drawback of high temperature thermal reduction is that it limits reduced graphene oxide from flexible applications since there are few transparent, flexible substrates which remain stable at high temperatures.

**Chemical Vapor Deposition**

One of the drawbacks to reduced GO is its small grain sizes and its incomplete reduction. Both these problems drastically impair further reduction of the sheet resistance to that of pristine graphene, conversely recent CVD experiments have fabricated large area and grain size graphene films [50-52]. Graphene has been grown on many metals such as platinum [53], iridium [54], nickel [55], and copper [50]. However, due to difficulty in graphene film transferring from platinum and iridium, copper and nickel are used for transparent electrode application. A comparison between graphene grown on nickel (by Riena et al.) and copper (by Li et al.), shown in Figure 3, reveals that copper yields a more uniform graphene film.

![Figure 3 - Optical Comparison of graphene on Si/SO2 grown by nickel (h) [55] and copper (B) [50]](image-url)
Sheet resistance and optical transparency measurements of graphene grown on copper then transferred to a quartz substrate shows a high optical transparency and low sheet resistances [56]. Using the result from Li et al., Samsung has recently reported a roll-to-roll, 30-inch graphene fabrication technique. Their large area graphene exhibit room temperature quantum hall effect and sharp Raman peaks at 2700 and 1600 cm\textsuperscript{-1}, confirming the graphene nature of the films. Furthermore, they report 50 Ω/sq sheet resistance for a 90% optical transparency. Also, upon transference to flexible substrates, the electrical properties remain unchanged when strained (either tensile or compressive) [57]. While this breakthrough may lead to the commercialization of graphene wafers, it is an expensive fabrication technique, requiring high temperatures and high vacuums (90 mTorr at 1000°C); thus incompatible with flexible, polymer substrates. Furthermore, CVD grown graphene yields impurities when transferred to an arbitrary substrate due to the use of a polymer handle in the transfer process.
Chapter 3 Organic Optoelectronic Devices

One of the most important transparent electrode applications is found in organic optoelectronic devices (OEDs); specifically, organic light emitting diodes (OLEDs) and organic solar cells. In any light related device, photons must be able to enter/exit the structure which is accomplished via the transparent electrode. In an OLED, free charge carriers recombine at the organic material junction interface (like a p-n junction interface) creating a photon which exits the device through the transparent electrode. Conversely, in an organic solar cell light enters through the transparent electrode and interacts with electrons to excite them to liberated energy states, thus creating free charge carriers. In both applications, the transparent electrode plays a crucial role in the utility of the device.

Organic optoelectronic devices have found rapid development and interest over the last two decades since the first modern organic light emitting diode was developed by Tang et al. in the late 1980s. The function and utility of these devices hinges upon the semiconducting characteristic of the organic materials used thus conjugated systems are primarily used. A conjugated system has the characteristic of several, repeating carbon-carbon double bonds within the material structure which consists of a tightly bound σ-bond and a weaker π-bond. These repeated π-bonds, electronically, are delocalized and thus may participate in electrical conduction; thus conjugated system tend to be metallic (e.g. some nanotubes, polyacetylene, PEDOT:PSS), semimetals (e.g. graphene), or semiconducting (e.g. P3HT).

The structure of a typical OED has a transparent substrate on which is deposited a transparent electrode. Usually a material (such as PEDOT:PSS) is deposited on top of the transparent electrode to facilitate and optimize hole transport across the transparent electrode. This layer is often referred to as the hole transport layer; however, some OED constructions employ several materials and layers for this purpose. Following the hole transport layer (HTL), the active layer is deposited. The active layer is the area wherein incident photons are converted into free charge carriers (in the case of solar cells) or electron-hole pairs recombine to form photons (in the case of OLEDs). Following the active layers comes the electron transport layer (ETL) whose function is similar to the hole transport layer. Finally, a metal electrode is deposited, capping the OED.

The operation of an OLED is similar and yet opposite to an organic solar cell. In OLEDs free carriers are injected into the device through the electrodes; holes from the transparent electrode and electrons from the metal electrode. After travelling across the respective carrier transport layers,
they will recombine at the active layer/HTL or ETL/HTL junction and emit a photon which exits from the transparent substrate. Important metrics of an OLED are the current density (mA/cm²), luminance (cd/m²), current efficiency (cd/A), and turn on voltage (V).

An organic solar cell operates by exciting low energy state (highest occupied electron orbital) electrons to higher energy states (lowest unoccupied electron orbital). This excited electron is initially known as an exciton since it is a Coulombically (and locally) bound electron-hole pair. Typical organic materials have an exciton disassociation length of ~10 nm, meaning the Coulombically bound electron-hole pair has ~10 nm within which to disassociate and become free carriers lest it recombine. After successful exciton dissociation, the free carriers travel to their respective electrodes; holes to the transparent electrode and electrons to the metal electrode. Due to the exciton disassociation length, organic solar cells are constructed with a high electron affinity material (such as a fullerene) within 10 nm of the active material. Consequently, the high electron affinity material is uniformly blended with the active material and deposited together in a structure known as a bulk heterojunction (compared to a conventional heterojunction). This is schematically depicted in Figure 4.

![Figure 4 - Left: standard heterojunction structure Right: Bulk heterojunction system with fullerene](image)

The important characteristics of a solar cell device include the short circuit current ($I_{sc}$), the open circuit voltage ($V_{oc}$), the fill factor (FF), and the power conversion efficiency (PCE). Typical, non-power generating diode behavior reveals a current-voltage characteristic existing in the first and third quadrants (i.e. power consuming quadrants). Practical current-voltage characteristics of diodes exhibit an exponential dependence of current to voltage given by Equation 1.

$$I = I_0(e^{qV/k_BT} - 1)$$  \hspace{1cm} \text{Equation 1}

Solar cell diodes also exhibit a similar current-voltage characteristic yet because they are power generating, their characteristic will exist in the fourth quadrant as well. Effectively, the characteristic of Equation 1 will be shifted negatively, into the fourth quadrant due to photon
induced carrier generation, while maintaining the extant exponential behavior. Furthermore, $I_{sc}$ and $V_{oc}$ effectively represent the boundaries or axis intercepts within which the current-voltage characteristic exists in the fourth quadrant. A near ideal diode will permit infinite current for voltages greater than some threshold voltage and severely limit any current for voltages less than the threshold voltage. Thus, a near ideal solar cell diode will pass $I_{sc}$ current for voltages less than $V_{oc}$ and infinite current for voltages greater than $V_{oc}$. Consequently, the maximum power generation for a near ideal solar cell diode is the product of short circuit current and the open circuit voltage. However, a practical device will have a maximum power generation less than in the ideal case; thus the fill factor is the ratio of the practical and ideal power generation (Equation 2). It is a measure of ideality of the device. Finally, the power conversion efficiency is a measure of how efficiently the solar cell can convert the input energy to electrical energy and hence is the ratio of maximum output power to input power (Equation 3).

$$FF = \frac{P_{max}}{I_{sc}V_{oc}}$$  \hspace{1cm} Equation 2

$$PCE = \frac{P_{max}}{P_{in}} = \frac{FFI_{sc}V_{oc}}{P_{in}}$$  \hspace{1cm} Equation 3

Common organic solar cells are fabricated using poly(3-hexylthiophene) (P3HT) as the organic semiconductor with the fullerene, phenyl-C61-buryric acid methyl ester (PCBM) in a bulk heterojunction structure. Since both OLED and solar cell applications require light to either enter or exit the device, the utility of transparent electrodes is most elucidated in these organic optoelectronic applications.
Chapter 4 Experimental Methods

The experimental procedure used in this thesis to fabricate graphene is the solution processable, reduced GO method. This method was selected over CVD because of the high initial cost of fabricating graphene by CVD. The transfer methods examined include; spin-coating, vacuum filtration, and a novel aquatic method. The vacuum filtration has the benefit of thickness controllability and uniform deposition and can be transferred to any substrate that does not react with acetone. However, the transfer process is not clean and many impurities (such as dust) are deposited on the surface of the film during the transfer process. The aquatic method has the same benefits as vacuum filtration and is a clean transfer process. Unfortunately, the transfer process is not precise and has a low success rate.

Reduction methods explored include hydrazine vapor, thermal annealing, and both together. We then investigate the utility of various CNT and RGO hybrid structures as transparent electrodes. Two structures are fabricated, a bulk heterojunction and a typical heterojunction structure. Finally, OLED and organic solar cell devices are made to test the practical ability of the fabricated transparent electrodes.

Graphene Oxide Isolation

Graphene oxide is fabricated by the modified Hummers method [41]. There are two steps in the modified Hummers method, purified graphite oxide fabrication and graphene oxide isolation. These steps are outlined, in detail, below.

Purified Graphite Oxide

1. 1 g of powdered graphite (synthetic powdered graphite from Sigma-Aldrich) and 0.75 g of sodium nitrate are placed in an Erlenmeyer flask. 75 mL of 95% sulphuric acid is added to the flask with moderate stirring.
2. Slowly, 4.5 g of potassium permanganate is added over the course of several minutes. Parafilm is placed over top the flask and the solution is left to stir vigorously for 5 days.
3. 140 mL of 5% wt. sulphuric acid solution is slowly added to the flask and left to stir for about 20 minutes.
4. Finally, 3 mL of 30% wt. hydrogen peroxide is slowly added to the flask and the solution is left to stir for about 20 minutes.
5. The graphite oxide solution is placed in 50 mL centrifuge tubes and centrifuged at 3,000 RPM for 1 hour. The supernatant is removed, the solid precipitate is redispersed through
vigorous mixing in a 3% wt. sulphuric acid and 0.5% wt. hydrogen peroxide solution, and the solution is centrifuged again at 3,000 RPM for 1 hour. This process is repeated 15 times.

6. Step 5 is repeated using deionized water instead of sulphuric acid and hydrogen peroxide two times.

7. The purified graphite oxide is dried in a vacuum desiccator, producing a loose brown powder, which can be stored indefinitely.

**Graphene Oxide**

1. 0.01 g of powdered graphite oxide is added to 10 mL of deionized water and sonicated for 24 hours.

2. The sonicated solution is centrifuged at 15,000 RPM for 1 hour. A precipitate free, light brown supernatant forms which is gently removed using a pipette. The compressed solid at the bottom is discarded.

![Figure 5 - Modified Hummers method results](image)

*Figure 5 - Modified Hummers method results (left: graphene oxide dispersion in water, right: powdered graphite oxide)*

**Transfer Techniques**

**Spin-Coating GO**

Spin-coating suspended GO on substrates was first demonstrated by Gomez-Navarro et al. in 2007, revealing promising electrical characteristics [47]. This work was furthered by Becerril et al. who used this method to pattern electrodes for organic electronic devices [44]. In this method, GO solution is spin-coated according to the recipe developed by Becerril et al.; GO is deposited and left to wet the surface for 1 minute followed by spinning at 600, 800, and 1600 RPM for 1 minute at each speed. Films were left to dry in an oven for several hours before reducing. Some substrates, such as glass and quartz, require surface functionalization to enhance surface-GO adhesion while other substrates, such as PET, do not require such functionalization. In a dry glovebox, substrates...
were functionalized with 3-aminopropyltriethoxysilane (APTES) by soaking the substrates in a 3% solution of APTES in anhydrous toluene for 1 hour.

**Vacuum Filtration**

Using small sized cellulose acetate filters (0.05 µm from Millipore Inc.), GO is filtered via vacuum filtration. Firstly, ~50-100 mL of deionized water is filtered to fully wet the cellulose filter. Then the desired volume of GO dispersed in solution is filtered. Increasing the volume of filtered GO will only contribute to the overall film thickness. This is because the cellulose acetate filters used to fabricate the GO films are the same size and shape, thus the filtered area is the same for all GO films. Due to this correlation, the relative thickness of a film can be discussed without quantifying its thickness. After all the solution has been filtered, the vacuum pump is left on for ~5-10 minutes in order to ensure no solution on the surface of the filter remains and to partially dry the filter. Finally, filters are stored in a plastic, covered Petri and left to dry overnight or dried in a desiccator under vacuum for a few hours. Figure 6 depicts the vacuum filtration process (A) and the subsequent cellulose acetate filters (B) left to dry in plastic Petri dishes.

![Figure 6 - A) Vacuum filtration process B) Several dried cellulose acetate filters](image)

Once the filters are dry, they can be cut into arbitrary shapes. This is a powerful benefit to the vacuum filtration method since the electrodes can be pre-patterned, thus photolithography is unnecessary. Target substrates (glass, PET, quartz, SiO₂ on Si, copper films, etc.) are then cleaned using a Piranha solution (if permissible) followed by successive sonication in acetone, isopropyl alcohol, and water. The cut filters are then soaked in ortho-dichlorobenzene for 1 minute and then
placed on the substrate with the GO in contact with the substrate. Mild pressure is applied to ameliorate film adhesion to the substrate. This step is shown in Figure 7 A and B. This method was first demonstrated for CNTs by Wu et al. in 2004 and then for GO by Eda et al. in 2008 [17, 58].

Transferred films are placed in an acetone vapour system for at least six hours to enhance the adhesion of the films to the substrate. Figure 8 shows a photograph of the acetone vapour system. Afterwards, the films are immersed in an acetone bath to fully dissolve the cellulose acetate filter leaving the GO film adhered to the substrate. The films are left in acetone overnight to ensure the complete removal of the filter. The successfully transferred films are then soaked in IPA and deionized water to remove the acetone, then dried under a nitrogen stream, and stored in an oven.

Figure 7 - Vacuum filtration film transfer process: A) filtered GO films are immersed in ortho-dichlorobenzene for 1 minute. B) Filtered GO films are then placed (GO side down) directly on the target substrate. C) Samples are placed in an acetone vapour system to initialize the removal of the cellulose acetate filter.

Figure 8 - Acetone vapour system with various samples being transferred to arbitrary substrates. PET, glass, and Si target substrates are shown in this photograph.
Aquatic Method

The aquatic transfer method is similar to the vacuum filtration transfer method. GO is filtered, dried, and cut in the same fashion but instead of transferring the films to another substrate, they are reduced in a hydrazine vapour system for 3.5 hours. Afterwards, they are gently placed in a basin of water. Initially, the films float on the surface of the water and after a few seconds the cellulose filter separates from the reduced graphene oxide film. The cellulose filter sinks to the bottom of the basin while the reduced GO films floats on the surface of the water as shown in Figure 9. The reduced GO film can then be lifted out of the water using the target substrate.

Figure 9 - Aquatic transfer method. Left: graphene is attached to the filter. Right: graphene has separated from the filter

Reduction Methods

In this work, two reduction schemes were investigated. These reduction schemes, which can be used individually or in tandem, are adapted from the work done by Becerril et al. [44].

Hydrazine Reduction: Transferred GO films are placed in a Parafilm sealed desiccator system with 1 mL of hydrazine monohydrate. The system is heated to 40 °C to vaporize the hydrazine and the films are exposed to the hydrazine vapour for 18 hours. Afterwards, the samples are rinsed with de-ionized water, dried with nitrogen, and further dried in an oven for several hours. Figure 10 shows a GO sample on glass reducing by hydrazine vapor.
Thermal annealing: Transferred films are loaded into a quartz tube furnace and Argon is passed through the system for several minutes. After which, the Argon is cut off and a vacuum of $10^{-5}$ is made. Once the vacuum is made, the temperature is increased to at least 400 °C. More robust substrates, like silicon and quartz, can endure higher temperatures (1000 °C) permitting a more thorough reduction of the system; however substrates such as glass cannot withstand such high temperatures and are annealed no higher than 500 °C. The vacuum and argon are used to minimize deleterious atmospheric molecules (such as oxygen) which, at high temperatures, would damage the films.

**Nanotube Electrodes**

The method used to fabricate SWNT electrodes is very similar to the vacuum filtration method for reduced GO electrodes. With nanotubes, SWNTs are dispersed in a surfactant solution by sonication and subsequently isolated by ultracentrifugation. In this case, a solution of 0.1 g of sodium dodecyl sulfate (SDS) is mixed with 0.01 g of SWNTs (P2 from Carbon Solutions Inc.) and 10 mL of de-ionized water is sonicated for 24 hours. The sonicated solution is then ultracentrifuged for 1 hour at 30,000 RPM and the resulting supernatant is removed and stored. This solution can then be vacuum filtered similarly to GO however it is imperative to wash the surfactant from the filter by continuously filtering water after filtering the nanotube until the surfactant induced bubbles are no longer present. After filtration, the films are transferred in a manner identical to GO.


**Hybrid Structures**

There are two methods employed to fabricate hybrid electrodes. The first is the bulk heterojunction approach wherein the GO and SWNT solution are uniformly mixed prior to filtration. Thus the resulting film is a uniform blend of both GO and SWNT. This type of electrode is referred to as a blended electrode. The second method is to create a typical heterojunction structure by completely filtering one solution and then filtering the other solution. This type of electrode is referred to as a composite electrode. In order for the GO to be fully reduced, it must be exposed to atmosphere when the film is transferred to an arbitrary substrate. If the GO layer is sandwiched between the SWNT layer and the substrate, the hydrazine vapour reduction method will be impeded. Therefore, when fabricated composite electrodes, GO must be filtered first.

**Intermediate Substrate Transfer Method**

Flexible electronic device fabrication is a critically important application for carbon based transparent electrodes. Given that typical flexible substrates (such as PET) cannot withstand the high temperatures experienced during the thermal reduction of GO an intermediate substrate must be used. To accomplish this task, a method adapted from Kim et al. is used [52]. Figure 11 is a schematic flow diagram of the transfer process and the following steps describe in detail the procedure.

1. Cut and dried filters are soaked in ortho-chlorobenzene for 1 minute and placed on top of the cleaned, sacrificial aluminum substrate.
2. Sample is first placed in an acetone vapour system, then an acetone bath for several hours to remove cellulose filter.
3. GO is reduced in tube furnace at 500 °C for 3 hours as per the aforementioned reduction steps.
4. PMMA is drop cast unto the reduced GO/Al sample and hard baked at 100 °C until PMMA solidifies.
5. Sample is floated on a ferric chloride bath which etches the aluminum leaving the PMMA supported reduced GO film.
6. Sample is gently removed from the ferric chloride bath left to soak in a deionized water bath to remove residual ferric chloride. PET is then used to lift the sample out of the water bath, contacting the PET and the reduced GO film.
7. Finally, hot acetone gently deposited onto the sample using an eye dropper to remove the PMMA.
Organic Optoelectronics Device Fabrication

Organic Light Emitting Diodes
Green emission organic material was used to fabricate OLEDs on the transparent electrodes. The organic material consists of a blend of poly(vinylcarbazole) (PVK), 2-(4-biphenylyl)-5-(4-tert-butylphenyl)-1,3,4 oxadiazole (PBD), tris(2-phenyl-pyridinato) iridium (Ir(ppy)3), and N,N'-diphenyl-N,N'-bis(3-methylphenyl)-1, 1'-biphenyl-4,4'-diamine (TPD) into mixed solvent of 1,2-dichloroethane and chloroform. This solution of green emitting organic material was prepared as per Park et al. and processed in air [59]. A Poly(3,4-ethylenedioxythiophene):poly(4-Styrenesulphonate) (PEDOT:PSS) layer was deposited as a hole transport layer between the active layer and the transparent, hole injection electrode while LiF was deposited as an electron transport layer between the active layer and the electron injection electrode (aluminum in this case). To fabricate the device, the organic materials are spin-coated; first PEDOT:PSS and then the active layer. Finally, LiF and Al are thermally evaporated (in that order) to form the electron transport layer and metal electrode, respectively.

Organic Solar Cells
After successful fabrication, characterization, and cleaning of the transparent electrode, a 30 nm layer of PEDOT:PSS (from Clevios™) was spin-coated and baked at 120 °C for one hour and then transferred to a dry, nitrogen glove box where the active layer is deposited. The P3HT (from Rieke) and phenyl-C61-butyric acid methyl ester (PCBM) (from Sigma-Aldrich) were separately dissolved in ortho-chlorobenzene in ratios of 10 mg/ml and 8 mg/ml for P3HT and PCBM, respectively.
Individual solutions were stirred at 40 °C for one hour and then subsequently mixed (a weight ratio of P3HT:PCBM of 1:0.8) and stirred for 16 hours at 40 °C; thus completing the active layer preparation. The active layer blend was spin-coated at 1000 RPM for 60 s, transferred to a Petri dish, left to dry for one hour, and then baked at 140 °C for one hour. Samples were taken from the glove box, briefly exposed to atmosphere, and placed in a thermal evaporator. Under a 10⁻⁶ mbar vacuum, a 1 nm lithium fluoride (LiF from Sigma-Aldrich) layer and a 100 nm aluminum electrode were evaporated completing the 0.2 cm² device structure. Finally, solar cell characterization was carried out using a 150 W Oriel Xenon lamp solar simulator with an AM 1.5G filter; thus exhibiting an input power of 100 mW/cm².

**Experimental Characterization**

**UV-visible Spectrometer**

A UV-visible spectrometer is used to characterize materials optically. A known quantity of light of a specific wavelength is emitted from a light source, passes through the material, and the resulting light is collected. The difference between the quantity of light emitted with the quantity of light collected is the amount of light absorbed by the material at each specified wavelength of light. This data can be used to calculate the absorption (in arbitrary units) and optical transparency (as a percentage) spectrum of the material. Optical transparency is an import metric for gauging the quality of a transparent electrode. Typically the optical transparency of a transparent electrode is given as a percentage at 550 nm. Figure 12 shows a schematic depiction of the device operation. All measurements are made with respect to a reference or baseline measurement.
For this work, only the absorption optical transparency spectra are measured. When measuring the absorption spectrum, GO solution is put in a quartz container (1 x 1 x 4 cm$^3$) and the beam of light passes through the width of the container (i.e. it traverses a 1 cm distance of the solution). The absorption spectrum baseline measurement is taken using deionized water since the GO is suspended in deionized water. Thus all absorption spectra of GO are in solution and referenced to deionized water.

Transparency measurements are taken after the GO or reduced GO film has been produced on a transparent substrate (i.e. glass, quartz, or PET). In this case, the film-on-substrate is fixed to a support and placed in the pathway of the beam of light such that the light passes through the film. Furthermore, the transparency is referenced to the substrate; thus a baseline measurement is taken for a pristine substrate. For all measurements a Cary 300 UV-visible spectrophotometer was used. Measurements were taken from 900 nm to 300 nm for both absorption and transparency spectra.

**Four Point Probe**

The four point probe is a technique used to measure resistivity per unit thickness (or sheet resistance) of a thin film material. A typical four point probe system (schematically represented in Figure 13) has four evenly spaced probes where the outer two probes drive current into the material and the inner two probes measure the voltage. From the measured voltage, the sheet resistance can be calculated from Equation 4 whose derivation can be found in the appendix.

$$R_s = \frac{\pi V}{\ln 2 I}$$  \hspace{1cm} \text{Equation 4}

This equation is valid for film whose lateral boundaries are 3.25 probe spacing units away from the inter-probe spacing distance away from any probe and whose thickness is less than half the inter-probe spacing distance.
The specific four point probe used is from Lucas Labs (model S-304) with 1.016 mm probe spacing (denoted by the variable $s$ in Figure 13) and 40.64 $\mu$m probe radius. Thus to satisfy the boundary conditions sample sizes must be on the order of $cm^2$. The precise geometry of the minimum measurable area (based on 3.25 probe spacing units) is shown to scale in Figure 14, gives rise to a minimum area of 0.55 $cm^2$.

![Figure 14](image_url) – To scale minimum sample size for accurate four point probe measurements using Lucas Labs probe head

**Atomic Force Microscopy**

Atomic force microscopy (AFM) is a topographical measurement of a surface with nanometer resolution. Whereas conventional microscopes rely on resolving and focusing photons or electrons to view a surface, AFM quantifiably *feels* the surface. A typical AFM design uses a pointed cantilever with tip dimensions on the order of microns, as shown in Figure 15. The tip is brought into such proximity (by piezoelectric material) of the surface that the inter-atomic forces (Van der Waals, electrostatic, etc.) of the surface interact with the tip causing it to deflect ($dF$). A laser, pointed on the cantilever, is used to detect this deflection. When the inter-atomic forces cause the cantilever to deflect, the angle of reflection of the laser changes accordingly ($d\theta$) and these angular changes of the laser are detected by a photodetector.
AFM has the advantage of measuring in three dimensions whereas optical and electronic microscopies yield two dimensional figurations. Thus, surface roughness and other topographical analysis are permissible. Whereas scanning electron microscopy (SEM) requires a conductive surface, AFM has no such requirement. Furthermore, AFM can be done in ambient conditions and does not require the vacuum conditions of SEM. Conversely, AFM has the disadvantage of longer scan times (several minutes at least) and smaller scan areas (100 x 100 µm²). Under some conditions, AFM can achieve atomic resolution; however, in general and in this work the AFM resolution is of several nanometers.

For this work the NSCRIPTOR DPN from Nanolnk was used in close contact (tapping) mode to take the AFM measurements. ACL silicon tips were used from APPNano (shown in Figure 16). Finally, all AFM images were taken with maximum resolution, 1024 x 1024 pixels.
Raman Spectroscopy
Raman spectroscopy is a measurement of the Raman scattering of photons or equivalently the vibrational modes of a system. It can be used to identify molecules since vibrational modes are specific to chemical bonds. The scattering of photons can occur elastically or inelastically. In elastic scattering, or Rayleigh scattering, incident photons and scattered photons have the same energy, frequency, and wavelength and thus the change in energy is zero. Two forms of inelastic photon scattering include fluorescence and Raman scattering. Fluorescence completely absorbs the photon and over a specific decay life time the photon will be re-radiated. In Raman scattering, the electron becomes excited to a virtual energy state and is immediately re-radiated. Furthermore, Raman scattering occurs for all frequencies whereas fluorescence has specific resonant frequencies.

Figure 17 - Energy diagram comparing Rayleigh and Raman scattering mechanisms

To exploit Raman scattering as a spectroscopic tool, a monochromatic laser is used to excite electrons which will re-radiate elastically and inelastically. Elastically re-radiated photons can be filtered and a photodetector is used to measure the wavelength of the Raman scattered photons. Typical Raman spectrographs are plotted in counts (i.e. number of photons) against the difference in wavelength of the monochromatic laser and the scatter photons (in units of cm\(^{-1}\)). For this work, a confocal Raman microscope was used (Renishaw inVia) with a 514.5 nm pumping laser. For each sample, several measurements were taken, at various points on the surface of the film, and averaged. Using various software programs (OMNIC, MatLab, and Excel) the data was smoothed and the background (i.e. substrate signature) was removed.
X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) can be used to measure the elemental composition and chemical bonding of a system. In XPS, a material is irradiated with x-rays in an effort to liberate bound electrons from their material and the quantity of liberated electrons and their kinetic energy are measured. Since different elements and bonding configuration give rise to electrons with differing binding energies, one can quantifiably determine the element and bonding configuration based on the kinetic energy of a free electron by calculating the difference in kinetic energy and input energy. Finally, XPS is a surface measurement, yielding information regarding 1 – 10 nm of the material.

The binding energy of a system can be calculated from XPS measurements given a known material work function. This is because incident x-ray photons excite core shell (such as the s orbital) electrons to vacuum and measures the resulting kinetic energy. The photon energy less the kinetic energy of the photoelectron and the work function of the XPS photoelectron detector material is the binding energy of the material Equation 5. In XPS measurements, photon energy and detector work function are known and the kinetic energy is measured. This equation is depicted as an energy diagram in Figure 18.

\[ E_{binding} = h\nu - (E_{k measured} + \varphi_{spect}) \]  

Equation 5

In a focused, narrow band scan one is able to determine the elemental composition and bonding structure and this is achieved by fitting known responses or peaks (such as the response of a C-O bond or C-C bond) to reconstruct the signal. These fitted peaks represent the contribution of specific bonding structures to the overall signal; thus the peak location (in eV) identifies the specific bonding structure and the relative intensity identifies percent contribution to the composition of the material. For this work, an ESCALAB MKII from VG Scientific was used. An Mg Ka (1253.6 eV) X-ray source at 300 W (15 kV, 20 mA) power was used to take the measurements. The measured surface area was 2 mm x 3 mm with a surface penetration depth of 50 – 100 Å.
Figure 18 - XPS Diagram: Since the sample and the spectrometer share the same Fermi level, the relative vacuum levels of the sample and the spectrometer differ. Thus, the measured kinetic energy of the photoelectron is the photon energy minus the sum of the spectrometer work function and the binding energy. Since photon energy and the spectrometer work function are controllable and the electron’s kinetic energy is measurable, the binding energy can be calculated.

\[ E_{\text{kinetic}} = h\nu - \phi_{\text{sample}} - E_{\text{binding}} \]
\[ E_{\text{k measured}} = E_{\text{kinetic}} - (\phi_{\text{spect}} - \phi_{\text{sample}}) \]
\[ E_{\text{k measured}} = h\nu - \phi_{\text{spect}} - E_{\text{binding}} \]

\( E_{\text{k measured}} = \text{Kinetic Energy measured by the spectrometer} \)

\( \phi = \text{Work function} \)

\( E_v = \text{Vacuum level} \)

\( E_0 = \text{Ground state energy} \)
Chapter 5 Spectroscopic Characterization of GO and reduced GO films

In the process of fabricating hybrid CNT/reduced GO transparent electrodes, reduced graphene oxide must first be made. Thus, it is imperative to validate and verify the quality of the produced reduced GO material. Graphene is most conclusively identified by its room temperature quantum hall effect [60], however this identification technique limits its post-identification applications due to the required Hall bar contact geometry. Also, this technique has been verified only for pristine graphene and not for reduced GO. Other, noninvasive techniques to verify the quality and fabrication of GO and reduced GO are to measure the Raman spectrum and the x-ray photoelectron spectrum (XPS). Thus, the Raman spectra and XPS of the GO and reduced GO films are measured and compared to other work to verify the quality of the films. Upon comparison it is found that these spectra compare favorably with other work thus indicating the successful fabrication of GO and reduced GO.

Raman Spectroscopy

Given the topography and elemental structure of GO and reduced GO it is plausible to expect a Raman spectra similar to graphene, but not identical. The Raman spectra of pristine graphene was measured by Andrea Ferrari in which he did a comparative study of the Raman shift in single to few layer graphene, graphite, and nanotubes. It was shown that graphene exhibits strong peaks at 1600 cm\(^{-1}\) (G peak) and 2700 cm\(^{-1}\) (2D peak) with the 2700 cm\(^{-1}\) peak being several times larger than the 1600 cm\(^{-1}\) peak. Graphite also exhibits these same peaks except the 1600 cm\(^{-1}\) peak is larger than the 2700 cm\(^{-1}\) peak. Furthermore, measuring the Raman spectrum at the edge of a graphene flake revealed a third peak at 1350 cm\(^{-1}\) (D peak) [61].

Since a reduced graphene oxide film is a randomly distributed cluster of stacked graphene, the expected Raman spectrum should show a large 1600 cm\(^{-1}\) to 2700 cm\(^{-1}\) peak ratio like in graphite, however, it should also have a strong 1350 cm\(^{-1}\) peak like in graphene. This is because reduced graphene oxide is like graphite in that it is stacks of graphene however, it is unlike graphite since it is not a crystal structure; it is a disordered graphitic stack with numerous, discontinuous edges. While the work done by Andrea Ferrari does not include graphene oxide or other oxygenated carbon structures, a response from the oxygen groups is expected which can be identified by the relative change in peak intensity between the oxygen response and the other peaks. Thus the expected result is to have large 1600 cm\(^{-1}\) and 1350 cm\(^{-1}\) peaks relative to the 2700 cm\(^{-1}\) peak which are unchanging with respect to reduction and to have an response due to oxygenation which reduces in relative magnitude after reduction.
Figure 19 shows the Raman spectra of GO and reduced GO. The raw data was smoothed and the baseline (i.e. the response from the substrate) was subtracted. Table 2 – Table 4 summarize the key findings of the Raman spectra. Both samples indicate peaks at ~1360 and ~1600 cm$^{-1}$ (D and G peaks, respectively) as well as a broad response between 2500 and 3300 cm$^{-1}$ centered around 2950 cm$^{-1}$ (Ox band). The absolute Raman shift of the D and G peaks remains relatively constant between GO and reduced GO samples: 0.3% change for G and -0.1% change for D. Furthermore, the relative peak intensity between the G and D peak exhibits little change between GO and reduced GO: 4.6% change. However, the Ox band exhibits an increase in relative peak intensity by 50% (relative to the G peak) which implies that the Ox band is due to the oxygenation of graphene.

<table>
<thead>
<tr>
<th></th>
<th>G (cm$^{-1}$)</th>
<th>D (cm$^{-1}$)</th>
<th>Plateau (L) (cm$^{-1}$)</th>
<th>Ox (cm$^{-1}$)</th>
<th>Plateau (R) (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GO</td>
<td>1602</td>
<td>1358</td>
<td>2701</td>
<td>2941</td>
<td>3178</td>
</tr>
<tr>
<td>Reduced GO</td>
<td>1597</td>
<td>1360</td>
<td>2707</td>
<td>2953</td>
<td>3201</td>
</tr>
</tbody>
</table>
Table 3 – Left and right width half maximum (LWFM and RWHM, respectively) of D, G, and Ox peaks in reduced GO and GO Raman spectra

<table>
<thead>
<tr>
<th></th>
<th>Reduced GO (cm(^{-1}))</th>
<th>GO (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>D</td>
<td>G</td>
</tr>
<tr>
<td>LWHM</td>
<td>58</td>
<td>54</td>
</tr>
<tr>
<td>RWHM</td>
<td>62</td>
<td>46</td>
</tr>
</tbody>
</table>

Table 4 - Peak to peak ratios of Raman peaks in reduced GO and GO

<table>
<thead>
<tr>
<th></th>
<th>G:D</th>
<th>G:Ox</th>
</tr>
</thead>
<tbody>
<tr>
<td>GO</td>
<td>1.29</td>
<td>2.91</td>
</tr>
<tr>
<td>Reduced GO</td>
<td>1.23</td>
<td>4.39</td>
</tr>
</tbody>
</table>

In pristine graphene, there are relatively fewer unique electron transitions which can occur compared to graphene oxide. Consequently, the Raman spectrum of pristine graphene reveals only three intense peaks. However, the increased chemical complexity of graphene oxide gives rise to many more Raman responses. As expected, there is little change in the D and G peaks before and after reduction since these peaks are due to the honeycomb, carbon lattice structure of graphene and the edge states in disordered graphene; two characteristics which are unchanged by reduction. However, the Ox band is not found in graphite or graphene and changes after reduction. From this data, it is not unreasonable to suppose the Ox band is due to the various oxide groups in GO. The 2700 cm\(^{-1}\) peak found in graphene is still present here (as the left plateau) and does not shift after reduction.

The constancy of the D and G peaks between GO and reduced GO is consistent with other work [62-65]. However, the Ox band surrounding 2950 cm\(^{-1}\) peak is inconsistent with the two studies showing the Raman spectrum of GO above 2000 cm\(^{-1}\). Cuong et al. shows a 2D peak at 2655 cm\(^{-1}\) and a 3S peak at 2906 cm\(^{-1}\). These peaks are a 55 cm\(^{-1}\) shift from the Ox band and the left plateau in the presented Raman data. Furthermore, Cuong et al. does not show any data above 3000 cm\(^{-1}\) and thus it cannot be concluded whether a peak corresponding to the right plateau is present. Yang et al. also show a 2D peak at 2700 cm\(^{-1}\), but the 3S peak found by Cuong et al. is not present nor is there data above 3000 cm\(^{-1}\). While the data surrounding the Ox band may not correlate well with other studies, there is a general inconsistency among the literature in the Raman spectra of GO around the 2700 cm\(^{-1}\) peak. Furthermore, other Raman studies indicate that the Ox band signature is a result of aromatic and aliphatic C-H stretching (i.e. C-H contamination) [66, 67]. Thus, the regime labeled Ox band may not, in fact, be a result of oxidation. With limited data and a lack of
consensus among other studies it is difficult to draw any conclusions regarding the nature of the Ox band, other than the reduced peak-to-peak ratios observed in this report. Despite the inconclusive data surrounding the Ox band, the D and G peaks correspond well with literature and with the expected result, thus indicating successful GO and reduced GO fabrication.

**XPS**

In this XPS study, GO was spin-coated on adhesion treated glass substrates and subsequently reduced as per the methods described in Chapter 4 Experimental Methods. Since this chemical reduction removes oxygen from the GO film, we expect a decrease in the oxygen content of the overall system. Furthermore, the majority of the oxide groups in GO involve oxygen atoms bonded to carbon atoms. Therefore, we focus our XPS spectrum to the C1S regime. Figure 20 and Figure 21 are the figuration of the XPS measurements. The XPS of the GO film reveals peaks at 284.9, 286.0, 287.5, and 288.9 eV which correspond with C-C, C-O, C=O, and O-C=O, respectively. C=O is the most dominant peak with C-C and C-O peaks exhibiting similar magnitudes. This implies that C=O bonding is the most common bond in GO followed by C-C and C-O (and to a lesser extent O-C=O). The XPS of the reduced GO films reveals a drastic change in the relative dominance of the peaks. Here, C-C is much more dominant while the other oxygenated carbon bonds exhibit smaller magnitudes. The decrease in the oxygen content from GO to reduced GO can be quantified; 26.6% to 14.7% for C-O bonds and 26.2% to 11.0% for C=O. The addition of a fifth peak, 285.6 eV is due to C-N bonding which forms during hydrazine reduction.
By and large, the XPS data presented here correlated well with other work. While all other works have varying peak amplitudes, the C-C peak presented here is much less pronounced in comparison indicating the graphene is heavily oxidized. Conversely, the reduced GO spectrum correlates extremely well with other work [43, 44, 58, 68-70]. Deoxygenated carbon rings (284.9 eV), C-O bonds (286.0 eV), carboxyl groups (C=O, 287.5 eV), and carboxylate groups (O-C=O, 288.9 eV) are all
present in the reduced graphene oxide spectra shown in Figure 21. The comparison between this work and other work is summarized in Table 5. Given the comparable XPS spectra to other XPS studies, it is reasonable to claim that reduced graphene oxide has been successfully fabricated.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Eda et al. [58]</th>
<th>Becerril et al. [44]</th>
<th>Stankovich et al. [43]</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Graphene Oxide Peaks</strong> (eV)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>284.9</td>
<td>284.6</td>
<td>284.8</td>
<td>284.8</td>
</tr>
<tr>
<td>286.0</td>
<td>286.3</td>
<td>286.2</td>
<td>286.2</td>
</tr>
<tr>
<td>287.5</td>
<td>287.2</td>
<td>287.8</td>
<td>287.8</td>
</tr>
<tr>
<td>288.9</td>
<td>288.7</td>
<td>NR</td>
<td>289.0</td>
</tr>
<tr>
<td><strong>Reduced GO Peaks</strong> (eV)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>284.6</td>
<td>NR</td>
<td>284.8</td>
<td>284.5</td>
</tr>
<tr>
<td>285.6</td>
<td>285.6</td>
<td>285.7</td>
<td>285.9</td>
</tr>
<tr>
<td>286.3</td>
<td>NR</td>
<td>286.2</td>
<td>286.5</td>
</tr>
<tr>
<td>288.0</td>
<td>NR</td>
<td>287.8</td>
<td>287.8</td>
</tr>
<tr>
<td>289.4</td>
<td>NR</td>
<td>NR</td>
<td>289.1</td>
</tr>
</tbody>
</table>

**Conclusion of Spectroscopic Characterization**

The purpose of examining the Raman and XPS spectra of graphene oxide and reduced graphene oxide was to ensure that the modified Hummers method used to fabricate these materials would indeed produce the desired result. From the XPS spectra we see an observable decrease in the response (and therefore overall contribution) of oxide groups after reduction. Furthermore, there is an increase in the response due to de-oxygenated carbon rings; a relatively damped response in graphene oxide. From the Raman spectra we not only see similar responses to pristine graphene (G and D peaks) but we also see a decreased response in the 2500-3500 cm⁻¹ (Ox) band. This observation, coupled with the XPS spectra imply that the diminished Raman response is due to the diminished presence of the various oxide groups in reduced graphene oxide. Thus, with confidence we can claim that both graphene oxide and reduced graphene oxide have been successful fabricated.
Chapter 6 Electrode Fabrication and Characterization

Graphene Oxide in Solution

As previously described, graphene oxide films are fabricated in several different ways; by spin-coating, the aquatic method, and vacuum filtration, details of which are found in Chapter 4 Experimental Methods.

In order to make controllable GO films the concentration of the GO in solution must be constant. During the final step of the modified Hummers method the sonicated graphite oxide solution is ultracentrifuged. This results in a uniformly dispersed graphene oxide supernatant; however, the quantity of separated graphite oxide may not be constant from sample to sample and therefore the concentration of GO in solution may not be identical from sample to sample. Therefore, it is imperative to calibrate the GO in solution by measuring the concentration.

To this end the absorption spectrum of the GO in solution was measured. The simple idea being greater the GO in solution the greater the absorption and vice versa. Thus GO solution, fabricated by the modified Hummers method, was diluted in a 4:1 ratio of deionized water to GO and then the optical absorption spectra was measured using a UV-visible spectrometer. Figure 22 shows the optical absorption spectra of a GO solution (i.e. the effective concentration of GO), by which all other successive GO solutions are compared. Deviations from this absorption spectrum must be rectified prior to film fabrication to ensure consistency in film thickness, conductivity, transparency, etc. Once the GO solution has been successfully produced, it can be used to make GO films by the methods outline in Chapter 4 Experimental Methods.

![Absorption spectrum of GO in solution](image)

Figure 22 - Absorption spectrum of GO in solution
**Reduced Graphene Oxide Films**

Once the GO solution has been prepared it is first used to fabricate GO films by spin-coating, vacuum filtration, and the aquatic method. Fabrication of reduced GO films from GO films utilize a consistent reduction scheme for all reduction experiments, save for the aquatic method. It involves first reducing graphene oxide in a hydrazine vapour system followed by further reduction by thermal annealing. This GO film fabrication and the reduction scheme are described in greater detail in Chapter 4 Experimental Methods.

**Reduced GO made by Vacuum Filtration**

Using vacuum filtration, several reduced GO films were fabricated. The optical transparency spectrum for each film was measured before and after reduction. Figure 23 shows the change in optical transparency (at 550 nm) between GO and reduced GO for various amounts of GO filtered (in µl).

![Graph showing change in optical transparency](image)

Figure 23 – A comparison of optical transparency between GO and reduced GO films

Figure 23 reveals that the change in transparency for thicker films (23.4% for 80 µl) is greater than thinner films (8.8% for 30 µl). This is an obvious result in light of the fact that transparency per unit thickness multiplies with each successive unit of thickness. Since the transparency per unit volume (or thickness) of GO is greater than that of reduced GO, the difference in transparency between GO and reduced GO will increase with thicker films. This hypothesis is further supported by the fact that the average change in transparency, from GO to reduced GO, per unit volume, across all samples, is 0.3±0.02%/µl. This is a measure of the constant rate of change in optical transparency between GO and reduced GO films. The low standard deviation indicates that this is a fairly
consistent measure of change in transparency. During the measurements of the GO samples, films produced with 10 and 20 µl volumes were undetectable (by eyes) in the visible spectrum and thus it was assumed the films were lost during the successive acetone bath transfer process. Despite this assumption, the samples were fully reduced anyways and it was discovered that the films were not lost in the transfer; they were merely invisible. Therefore, transparency data for 10 and 20 µl reduced GO exists but not for unreduced GO. The dotted line is extrapolated from the existing data using the average change in transparency per unit volume and reveals that the films, at 550 nm, are ~100% transparent; an approximation consistent with observation.

An AFM image of a reduced GO sample made by vacuum filtration and transferred to a 300 nm SiO$_2$ on Si substrate is shown in Figure 24. The surface roughness for this image is 5.54 nm and 9.52 nm for average roughness and RMS roughness, respectively with an average height of 32.19 nm. This surface roughness is possibly due to the topography of the cellulose acetate filter. Since the filter itself is not smooth, the GO nanoplatelets will conform to the shape of the filter. However, the defects present in the AFM image are not uniformly distributed as might be expected. Thus, the surface defects are likely caused by a deformation of the GO nanoplatelets upon reduction. Since zero and one dimensional structures are thermodynamically more stable than two dimensional structures, the GO nanoplatelets crumple into lower dimensional structures upon reduction [71, 72]. Further evidence supporting this hypothesis is presented in subsequent sections of this chapter.
The set of reduced GO films from Figure 23 were electrically characterized by sheet resistance measurements. The relationship between sheet resistance and optical transparency at 550 nm is shown in Figure 25. Fabricated reduced GO films compare favorably in optical transparency and sheet resistance (10 kΩ/sq, ~50 kΩ/sq, and ~100 kΩ/sq for 60%, 70%, and 90%, respectively) with data presented in other work [44, 58, 73].

![Figure 25- Relationship between optical transparency and sheet resistance for reduced GO films [44, 58, 73]](image)

While the reduced GO results presented in this thesis compare well with other work on reduced GO electrodes, it is unfavorable when compared to other transparent electrodes, such as carbon nanotubes ($10^2 - 10^3$ Ω/sq) (Figure 27) and indium tin oxide (~10 Ω/sq) (commercially available from Sigma-Aldrich, SPI, NanoCS, and others). Thus in an effort to ameliorate the overall sheet resistance of the transparent electrode, hybrid nanotube-reduced GO electrodes are explored.

**Hybrid Nanotube and Reduced GO Electrodes**

The highlight of this thesis is the exploration and experimentation of combining nanotubes with reduced GO to fabricate hybrid nanotube-reduced GO electrodes. There are two basic hybrid structures one could construct to form an electrode: a heterojunction-like structures and a blended structure. The heterojunction structures have the materials stacked on top of each other and an interface between the GO and the nanotubes is formed whereas the composite structure is a uniform mixture. However, to completely understand the utility of hybrid electrodes, they must be benchmarked against both reduced GO only and nanotube only electrodes. Whereas reduced GO
electrodes have already been fully characterized, the full nanotube electrode characterization follows.

**Nanotube Electrodes**

After the dispersed nanotube solution was produced by the method described in Chapter 4 Experimental Methods, the absorption spectrum of the solution was measured as a comparative metric for future nanotube solutions, like with the GO solution shown in Figure 22. The absorption spectrum of the nanotube solution is shown in Figure 26.

![Absorption Spectrum of dispersed SWNTs in solution](image)

Comparatively, the absorption spectrum of nanotubes follows a similar trend to that of GO with one important distinction; the van Hove singularities of the nanotubes are present the spectrum. By filtering 1000, 500, 250, 125, and 60 µl of this nanotube solution several electrodes were fabricated. The relationship between optical transparency and sheet resistance relationship is shown in Figure 27.
Using the benchmarks established by the nanotube electrodes and the reduced GO electrodes (Figure 25 and Figure 27, specifically) the utility of the hybrid structures can be appropriately measured.

**Characterization of Hybrid Electrodes**

The hybrid electrodes were fabricated, using the information garnered from the GO and CNT studies, by mixing controlled quantities of SWNT solution and GO solution and employing the vacuum filtration technique described in Chapter 4 Experimental Methods. Firstly, two blended and two composite electrodes were compared; one with a relatively high SWNT to GO ratio and one with a relatively low SWNT to GO ratio. More precisely, the high ratio solution used 1000 µl of SWNT and 30 µl of GO and the low ratio solution used 80 µl of SWNT and 60 µl. These specific values were chosen as they were the relatively extreme cases in the GO and CNT studies. That is, 1000 and 80 µl of SWNT were relatively large and small volumes of solution for which SWNT electrodes were fabricated, likewise for GO solution (see Figure 23 and Figure 27 for details on reduced GO and SWNT electrodes, respectively).

Since the nanotubes do not require a reduction step, the electrodes are conductive even with unreduced GO. Thus, the electrical impact of reduction on GO can be somewhat quantified. Figure 28 shows the effects on the electrical properties of reduction on hybrid electrodes.
Figure 28 - Comparison of sheet resistance between reduced and unreduced hybrid structures for blended and composite structures. A) nanotube:GO ratio of 1000:30 µl B) nanotube:GO ratio of 60:80 µl

Figure 28 shows for relatively low CNT:GO ratio electrodes, the sheet resistance expectedly decreases after reduction. Conversely, relatively high CNT:GO ratio electrodes exhibited increased sheet resistance after reduction. The reason for this increased sheet resistance is explored later in this section.

Next, the sheet resistance is compared between the fully reduced hybrid structure and its constituent parts; reduced GO and carbon nanotubes. In order to quantify the electrical improvement, there should be a benchmark for comparison. To this end, the simplistic model of parallel resistors is used for two reasons. First, the construction of the hybrid structures is in a parallel, as opposed to a series, configuration. Secondly, the parallel resistor model is the simplest analytic model for such a construction. The analytical formulation is shown in Equation 6. Figure 29 shows the sheet resistance for the constituent reduced GO and carbon nanotubes (CNT) parts, the composite and heterojunction hybrid structures, and the theoretical hybrid structure sheet resistance, calculated from Equation 6. Note that in Figure 29, the sheet resistance for reduced GO is given by the right, secondary axis in both figures.

\[
\frac{1}{R_{Hybrid}} = \frac{1}{R_{CNT}} + \frac{1}{R_{RGO}} \quad \text{Equation 6}
\]
Irrespective of the hybrid structure, the high nanotube:GO electrode exhibits an *increase* in sheet resistance after reduction, whereas there is a substantial decrease (~70%) in post-reduction sheet resistance for the low nanotube:GO ratio. Furthermore, in the high nanotube:GO ratio the blended structure yields lower sheet resistances than its composite structure counterpart. However, the opposite is true for the low nanotube:GO ratio case. Analysis of Figure 29 reveals that for the high nanotube to GO ratio, both hybrid structures have higher sheet resistances than both the theoretically calculated and the CNT sheet resistances, whereas the converse is true for the lower nanotube to GO ratio. The inconsistencies revealed by Figure 28 and Figure 29, in light of the topographical defects found in Figure 24, imply the odd electrical characteristics of the hybrid electrodes are due to the film’s topography. To investigate this inconsistent nature the topography of high, even, and low nanotube to GO ratio films were measured. These films were fabricated by vacuum filtration and then transferred to 300 nm SiO$_2$ on Si substrates. These measurements were done using an optical microscope, AFM, and SEM.

Figure 30 shows the optical micrographs for low (top row), even (middle row), and high (bottom row) nanotube to GO ratio blended films. Across each row (i.e. the columns), from left to right, show the increasing magnification of the same region using 10X, 20X, 50X, and 100X lens’. These optical micrographs show that low ratios of nanotube to GO are uniform whereas the higher ratios are not uniform. Evident by the even nanotube to GO ratio film, the nanotubes (white) clump together and
thus there are dense and sparse regions of nanotubes. This clumping is less evident in the high nanotube to GO ratio film not because it is free from clumping, rather because the nanotubes have saturated the film and the quantity of nanotubes demands the filling of the sparse areas.

The higher than expected sheet resistance in the high CNT:GO ratio film is because blended nanotube and reduced GO films do not uniformly mix. Consequently, the electrical properties of graphene cannot be fully exploited. Conversely, the low nanotube, high GO film is uniform and optically, there is no discernable segregation of nanotubes from reduced GO. Hence, low nanotube and high GO systems yield a uniform mélange which can exploit the electrical characteristics of the reduced GO nanoplatelets.

Figure 31 shows SEM and AFM images of blended hybrid structures of the varying CNT:GO ratio. The top row shows SEM images of (from left to right) low (A), even (B), and high (C) CNT to GO ratio films. The bottom row shows AFM images of the same films in the same order (D-F). These films were prepared by vacuum filtration and transferred to SiO\textsubscript{2} on Si substrates. The white scale bars represent 1 μm for SEM images (A-C) and 4.2 μm for AFM images (D-F).
Figure 31 – SEM and AFM images of various blended hybrid films. Top row (A – C) are SEM images, bottom row (D – F) are AFM images. The left, middle, and right columns show low, even, and high CNT:GO ratio films, respectively. SEM scale bars represent 1 µm, AFM scale bars represent 4.2 µm.

The increase in CNT:GO ratio is evident in both the SEM and AFM images as evinced by the increased quantity of nanotubes. Also, the bulking effect apparent in the optical micrographs of Figure 30 is also seen in the AFM of the middle CNT:GO ratio film. Nanotubes are clearly seen on the extremity of the image and decrease in density closer to the center. Also, nanotubes are clearly resolved in the SEM and AFM images of the low CNT:GO ratio film but become increasingly blurred at higher concentrations. For example, though the same solution of nanotubes is used, SEM imaging of the higher CNT:GO ratio show thicker nanotubes than the lower CNT:GO ratio. Finally, in comparing the AFM of the blended hybrid structures with the AFM of pure reduced GO, shown in Figure 24, there is an overall decrease in topographical defects.

Since nanotube doped reduced GO electrodes (i.e. low CNT to GO ratio electrodes) yields ameliorated sheet resistance, several such blended electrodes were fabricated, using a constant volume of nanotubes. In this case, the constituent nanotube electrode, individually, yielded 13.6 kΩ/sq and 97% optical transparency at 550 nm. Specifically, 100 µl of SWNT solution is mixed with 100, 200, 400, and 600 µl of the GO solution. Here, the resulting blended solutions are vacuum filtered and reduced hybrid electrodes are produced. The blended and fully reduced electrode is then characterized by sheet resistance and optical transparency the results of which are plotted in Figure 32. A theoretical calculation of the sheet resistance (calculated using Equation 6) is also shown in Figure 32. The theoretical optical transparency is calculated by multiplying the optical
transparencies of the nanotube and reduced GO components. Compared to the theoretical
calculation, the blended hybrid sheet resistance is superior by a factor of at least two for each
electrode.

![Graph showing sheet resistance vs. optical transparency comparison]

Figure 32 – Blended hybrid electrode sheet resistance vs. optical transparency comparison; reduced GO (triangles) correspond to the right y-axis while hybrid (diamond) and theoretical (square) curves correspond to the left axis.

Figure 32 shows that reduced GO films lightly doped with SWNTs uniformly improve the sheet resistance of the blended hybrid device whereas films heavily doped with SWNTs hinder the sheet resistance as a result of the non-uniformity of nanotube distribution. In this non-uniform nanotube distribution, areas of fewer nanotubes yield a higher resistance, while areas of more nanotubes are favored for electron transport. However, the bulking effect reduces the effective area of favored electron transport thus increasing the overall resistance. While this bulking effect provides insight into the reasons for increased sheet resistance compared to the parallel resistance model, it does not explain why low CNT:GO ratios yield consistently improved sheet resistances. This result can be explained by the AFM and SEM imaging. Comparing Figure 24 and Figure 31 it is evident that there are fewer defects in a low nanotube:GO blended structure than in a purely reduced GO structure. This is because GO becomes increasingly thermodynamically unstable upon reduction and will crumple, wrinkle, and restack with other reduced GO nanoplatelets to produce thermodynamically more stable zero, one, and three dimensional graphitic structures. Thus the defects apparent in Figure 24 are due to this crumpling of GO upon reduction [74, 75]. Lightly doping GO with SWNTs creates separation of the GO nanoplatelets, thus upon reduction there is less crumpling and the crystallinity of the reduced GO is preserved. Consequently, there is an improvement in the electrical properties of the hybrid films.
Intermediate Substrate Transfer Method

Using the Intermediate Substrate Transfer Method outlined in Chapter 4 Experimental Methods, nine different transfers were attempted; three to PET, three to SiO$_2$/Si, and three to glass substrates. Of the nine attempts, only one transfer (to glass) was successful. The critical step is the PMMA removal wherein unsuccessful transfers met with difficulty. Typically, films did not adhere well to the target substrate and, upon PMMA removal, would become displaced and slip off the substrate. One problem is that drop casting deposits a large quantity of PMMA thus more acetone is required to remove the PMMA which increases the possibility of film loss. An alternative would be to spin coat PMMA, thus only a thin film of PMMA is deposited and can easily be removed.

The successfully transferred film yielded a sheet resistance of 121 Ω/sq with a 31% optical transparency at 550 nm. The same filter transferred and reduced on a glass substrate directly resulted in a comparable optical transparency and a sheet resistance of 276 Ω/sq. This ameliorated electrical characteristic is likely due to a doping effect from the Al intermediate substrate. A solar cell device was fabricated using this film and the results are presented in Chapter 7 Fabrication of OEDs using graphene based electrodes.

Conclusion of Electrode Fabrication and Characterization

Reduced GO and hybrid electrodes were successfully fabricated and characterized. Reduced GO electrodes yielded sheet resistances on the order of 10 kΩ/sq for optical transparencies between 50 and 90%. Hybrid electrodes yielded sheet resistances of $10^3$ Ω/sq for comparable optical transparencies. The improvement in sheet resistances is due to the separation of the GO nanoplatelets created by the introduction of SWNTs; thus upon reduction the GO nanoplatelets preserved their crystallinity instead of distorting and crumpling to more thermodynamically stable states. Support of this hypothesis is most evinced by comparing AFM images of hybrid films with homogenous reduced GO films. This improvement was only seen in films with a relatively low SWNT:GO ratio. In films with a large SWNT:GO ratio, the nanotubes tended to bundle creating areas of dense nanotubes and areas virtually devoid of them. Furthermore, reduced GO and hybrid films were successfully transferred the intermediate substrate transfer method in order to produce fully reduced films on flexible substrates. These aforementioned reduced GO and hybrid electrodes were subsequently used to fabricate organic optoelectronic devices which is the subject of the following chapter.
Chapter 7 Fabrication of OEDs using graphene based electrodes

Organic Solar Cells

Two organic solar cells were compared; one using reduced GO as the transparent electrode and the other using a blended hybrid electrode. In both cases, the same organic device structure was used, as described in Chapter 3 Organic Optoelectronic Devices. For this work, the reduced GO electrode was reduced by hydrazine only and deposited on a PET substrate. The hybrid electrode was fabricated by the intermediate substrate transfer process described in Chapter 6 Electrode Fabrication and Characterization. The measured current density is plotted in Figure 33 and a summary of their key characteristics is presented in Table 6.

In comparing the two fabricated solar cell devices, we see that hybrid electrode device yielded a power conversion efficiency (PCE) three times that of the reduced GO device. The $V_{oc}$ of both devices were similar whereas the hybrid device $J_{sc}$ was twice that of the reduced GO device. The hybrid electrode had more than a 10,000 fold decrease in sheet resistance with a 61% decrease in optical transparency compared to the reduced GO electrode. This translated to a 200% increase in PCE suggesting that optical transparency has a greater impact on device efficiency than electrode sheet resistance.

While successful solar cell devices were fabricated using reduced GO and hybrid transparent electrodes, they exhibited poor filling factors and PCEs. The poor filling factor is most likely due to the non-diode like behavior after the open circuit voltage. The current-voltage characteristic is approximately linear after the open circuit voltage implying resistor impedance as opposed to semiconductor impedance (given by an exponential dependence); thus implicating the sheet resistance of the transparent electrode as the limiting factor. For highly transparent electrodes more photons pass through the device and engaged in electron excitation. However, for graphene based electrodes, increases in transparency generally correspond to increases in sheet resistance thus limiting the number of free carriers exiting the device and the short circuit current.

Table 6 - Device characteristics for P3HT:PCBM solar cells using graphene based transparent electrodes

<table>
<thead>
<tr>
<th>Solar Cell</th>
<th>$T$ (%)</th>
<th>$R_s$ (kΩ/sq)</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>$V_{oc}$ (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reduced GO</td>
<td>80</td>
<td>&gt; 2000</td>
<td>-1.44</td>
<td>0.43</td>
<td>36.48</td>
<td>0.23</td>
</tr>
<tr>
<td>Hybrid</td>
<td>31</td>
<td>0.12</td>
<td>-3.25</td>
<td>0.42</td>
<td>48.53</td>
<td>0.67</td>
</tr>
</tbody>
</table>
It has previously been shown that the open circuit voltage has been shown to depend on the work function difference between the electrodes and the LUMO/HOMO difference between the electron donor and electron acceptor materials [76-78]. Since both solar cells are made with similar material the open circuit voltages should be similar and in fact differ by only 0.01 V. The transparent electrode sheet resistance of the hybrid solar cell is substantially lower than the sheet resistance of the first solar cell (~100 Ω/sq compared to > 2 MΩ/sq) thus the hybrid current density higher. Despite the lower optical transparency of the hybrid solar cell, the power conversion efficiency percent increase is comparable to the percent increase in the current density (125% increase in current density vs. 200% increase in power conversion efficiency). Since the open circuit voltage is primarily material dependant, improving the PCE of these devices amounts to improving the current density which, for the hybrid electrode, amounts to increasing the optical transparency of the device.

**Reduced GO OLEDs**

Three reduced GO electrodes, fabricated by vacuum filtration on glass substrates, were used to construct the OLEDs described in Chapter 4 Experimental Methods. Figure 34 shows the current density vs. voltage curves for each electrode. Expectedly, the lower sheet resistance electrode yielded the higher the current density. Furthermore, the current density here is mostly linear (i.e. resistive) as opposed to exhibiting an exponential, diode-like behavior. This indicates that the sheet resistance of the transparent electrode is the limiting factor of the current density.
Finally device luminance, as seen in Figure 35, shows little luminance before 15 V after which it increases. Interestingly, the low transparency electrode yielded the highest luminance. This is because the loss of photons due to the high opacity is smaller than the increase in generated photons due to the low sheet resistance (low sheet resistance permits a greater number of charge carriers and therefore more electron-hole recombination events).

Maximum current density, maximum luminance, and current efficiency as well as sheet resistance and optical transparency are summarized in Table 7. Here, the high sheet resistance, high
transparency electrode yielded the highest efficiency (the ratio of luminance and current density). This is evident by the fact that this device yielded only three times less the maximum luminance for over five times less the current density. In other words, the highly resistive electrode requires three times less power to output the same luminance as the least resistive electrode.

Table 7 - Summary of OLED characteristics for reduced GO devices

<table>
<thead>
<tr>
<th>Optical Transparency (% @ 550 nm)</th>
<th>Sheet Resistance (kΩ/sq)</th>
<th>Maximum Current Density (A/m²)</th>
<th>Maximum Luminance (cd/m²)</th>
<th>Current Efficiency (cd/A)</th>
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<tr>
<td>88</td>
<td>53.4</td>
<td>197</td>
<td>48.1</td>
<td>0.24</td>
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<td>80</td>
<td>24.2</td>
<td>450</td>
<td>44.7</td>
<td>0.10</td>
</tr>
<tr>
<td>76</td>
<td>18.8</td>
<td>1059</td>
<td>139.5</td>
<td>0.13</td>
</tr>
</tbody>
</table>

Reference OLEDs

Park et al. fabricated OLEDs using indium tin oxide (ITO) electrodes as opposed to a carbon based material. ITO exhibits optical transparencies of > 80% at 550 nm with sheet resistances on the order of 10 Ω/sq. Using the fabrication method outlined by Park et al., ITO based OLEDs were fabricated as reference OLEDs. Three reference OLEDs (device 1, 2, and 3 in Figure 36) were fabricated each exhibiting current density and luminance values on the order of 10³ cd/m² and 100 mA/cm², respectively, for bias voltages less than 20 V. These reference OLEDs yielded efficiencies of nearly 30 cd/A, depending on the operating voltage. This data is summarized in Figure 36. Using this information, the reduced GO and hybrid electrodes can be appropriately compared.

Comparatively, the reference OLEDs are substantially superior to the work presented in this thesis. Current densities, luminance measurements, and device efficiencies are all order of magnitudes
higher than reduced GO electrodes. Furthermore, the current density vs. bias voltage shows an exponential relationship which is a diode-like trend as well as exhibiting a lower turn on voltage. Given the low sheet resistance of ITO, this corroborates the hypothesis that the linearity of the reduced GO current density curves is due to the relatively high resistance of the material. Thus improving the sheet resistance is of critical importance; hence hybrid electrodes are explored.

**Hybrid electrodes for OLEDs**

Three OLEDs were fabricated using three different hybrid transparent electrodes. The hybrid electrodes used were the same hybrid films shown in Figure 30 and Figure 31; high, even and low CNT:GO ratio electrodes with sheet resistances of 276 Ω/sq, 1.05 kΩ/sq, and 2.33 kΩ/sq, respectively. Figure 37 and Figure 38 show the current density and luminance of the OLEDs. Like the reduced GO electrodes, the current density vs. voltage reveals a linear relationship. However, the current densities are substantially higher for these devices than for the reduced GO and ITO counterparts. Maximum current densities achieved for reduced GO and ITO OLEDs were approximately 100 and 500 mA/cm², respectively, whereas the least resistive hybrid electrode devices yielded a maximum current density of nearly 2000 mA/cm². Despite the increase in current density, the luminance of the hybrid devices is orders of magnitude lower than that of the reference ITO and reduced GO electrodes. Before device breakdown (due to high input power), the maximum luminance achieved (by the 1.05 kΩ/sq hybrid electrode) was less than 4 cd/m². Consequently, the current efficiency of these devices is on the order of $10^{-6}$ cd/A which is $10^{7}$ lower than that of the reference ITO based devices and $10^{5}$ lower than the reduced GO based devices. Another set of OLEDs were fabricated using hybrid and reduced GO transparent electrodes, however during OLED fabrication the electrodes were damaged yielding unreliable results. For completeness, the results of these OLEDs are presented in the Appendix.

The relatively poor luminance is most likely due to the lower optical transparency. Even though the current density is higher, which in turn increases the number of recombination events, the low optical transparency of the electrodes limits the photons from exiting the device; thus reducing the luminance and current efficiency. However, when comparing the 1.05 and 2.33 kΩ/sq devices (which have the same optical transparency), we see that the maximum current density of the 1.05 kΩ/sq device is three times higher than the 2.33 kΩ/sq, whereas the luminance is 19 times higher.
There are two reasons for the poor performance of reduced GO relative to ITO. The first is the higher sheet resistance and the second is the lower work function; both limit the charge carrier injection. With respect to reduced GO, the high sheet resistance limits the number of charge carriers traversing across the electrode from the device to the external voltage source. Thus, a higher voltage is required to inject the same number of carriers; in other words, to achieve comparable current densities and therefore instances of electron-hole recombination events, one must apply a relatively higher voltage. Furthermore, the nearly linear characteristic of the current-voltage density figures (Figure 34, Figure 37, and Figure 42 in the appendix) indicate that the high sheet resistance is the limiting factor of the carrier injection. In fact, calculating the resistance from the
current-voltage density measurements reveals resistances on the same order as resistance calculations derived from the sheet resistance measurements.

The poor luminance performance of hybrid electrodes relative to ITO is a result of the low optical transparency. The lower sheet resistance and higher current density comes at a cost of lower optical transparency. Thus, generated photons are unable to contribute to the overall luminance of the device which leads to poorer device efficiency and luminance.

Another limiting factor in device operation is the lower work function of reduced GO. Work function studies of graphene indicate a work function (4.6 eV [79]) similar to ITO (4.7 eV [80-82]) whereas reduced GO has been shown to have a work function substantially lower at 4.2 eV [83]. Given that PEDOT:PSS has a work function around 5.0 eV [81, 84], there is a significant work function mismatch thus producing a non-Ohmic contact. Contrasting the reduced GO with hybrid electrodes, where the global work function includes the higher SWNT work function (~4.6 eV [33, 85-87]), the effective work function (4.2 – 4.6 eV depending on SWNT:GO ratio) is higher and thus able to drive a higher current density. Yet in both hybrid and reduced GO systems, there will be charge trapping due to band bending at the electrode/PEDOT interface. This will lead to a charge carrier imbalance within the active layer of the OLED and reduce the overall efficiency since maximum device efficiency occurs when the electron and hole densities are equal.

**Conclusion of OEDs**

In summary, graphene based OEDs were fabricated. The fabricated organic solar cells revealed that improving the optical transparency of the hybrid electrode would lead to an increase in the current density and power conversion efficiency. Successfully fabricated reduced GO based OLEDs yielded poorer luminance and current density values than its ITO counterpart. The relatively high sheet resistance of the reduced GO electrodes is primarily responsible for the device performance; a fact most elucidated by the linearity of the current density vs. voltage curves shown in Figure 34. Hybrid electrodes, which yield improved sheet resistances, were also used in OLEDs. However, they exhibited low optical transparencies and thus yielded low luminance and current efficiencies. Despite their improved electrical characteristics, hybrid electrodes yield marginal improvements in organic solar cells and poorer characteristics in OLEDs than reduced GO and ITO based devices. Thus in its current state, hybrid electrodes are not suitable for OEDs. However, given its flexibility and potential applications, should not be abandoned without thoroughly investigating improvements to the electrode and the corresponding OED device.
Chapter 8 Discussion and Conclusion

The purpose of this work was to investigate the utility of reduced GO films as transparent electrodes and to improve these films by SWNT doping. To measure the effectiveness of the reduced GO/SWNT hybrid electrode, first reduced GO films were fabricated. Subsequently, the transparent electrode properties of reduced GO and SWNT films were measured as a benchmark. Finally, the hybrid electrodes were fabricated, measured, and compared against its constituent parts. For completeness of the comparison, organic optoelectronic devices were built using reduced GO and hybrid transparent electrodes.

Firstly, reduced GO was fabricated by vacuum filtration of graphene oxide (produced by the modified Hummers method) and subsequent thermal and chemical reduction schemes. In order to ensure that reduced graphene oxide had been successfully produced, the Raman and x-ray photoelectron spectra were measured. The Raman spectra indicated prominent D and G peaks with a suppressed 2D peak. While the D and G peaks were present, the 2D was buried within the Raman response from the oxide groups. Evidence supporting the oxide characteristic of the Raman response is seen by diminishing of the response after reduction. However, other published work indicates that there is a lack of consensus regarding the Raman spectrum of the oxide response. Furthermore, x-ray photoelectron spectra indicated revealed strong C=C, C=O, C=O, and C=C aromaticity for graphene oxide films. Reduced graphene oxide films presented diminished oxide bonds with strong C=C bonds as well as a new C-N bond peak induced by hydrazine reduction. These results and the results from the Raman spectroscopic analysis are consistent with other, published spectra. Ultimately, the purpose of the spectroscopic analysis was to ensure accurate fabrication of reduced graphene oxide. Given the results of this analysis and its comparison with other studies, it is plausible to conclude that reduced graphene oxide was successfully fabricated.

Next reduced graphene oxide transparent electrodes were fully characterized topographically, electrically, and optically. Typical sheet resistance measurements were on the order of $10 - 100 \, \text{k}\Omega/\text{sq}$ (depending on film thickness) with optical transparencies greater than 60%; data which correlates very well with literature. However, compared to ITO which achieves a sheet resistance of $10 \, \Omega/\text{sq}$ at 80% transparency these results are still inferior. Published work and experimental evidence has shown that upon reduction, graphene oxide nanoplatelets crumple into more one or three dimensional structures (i.e. physically stable structures). However, this crumpling will have adverse effects on the electronic properties of the electrode thus (in part) accounting for the high sheet resistance. Thus, preventing the structural deformation of graphene oxide upon reduction
will lead to improved electrical characteristics of the individual reduced graphene oxide nanoplatelets.

To ameliorate the electrical characteristics, single-walled carbon nanotubes were mixed with the graphene oxide nanoplatelets during the vacuum filtration process. The idea was that separating the nanoplatelets would limit the crumpling effect upon reduction thus improving the sheet resistance. This hypothesis was partially supported. When a relatively low ratio of nanotubes to graphene was employed sheet resistances consistently improved by a factor of two (relative to the parallel resistive calculation). However, when larger nanotube to graphene ratios were used an unforeseen bulking of the nanotubes occurred wherein large quantities of nanotubes existed next to areas relatively devoid of them. The nature of this bulking is unknown; however, the impact on the electrical characteristic is evident. This bulking reduces the effective pathways of electrical conduction; instead of electrons experiencing the same resistance in all directions, they experience a lower resistance within the bulked nanotubes and thus non-uniform electrical conduction occurs. This is evident by the increase in the sheet resistance (relative to the parallel resistance calculation) as opposed to the decrease seen with the lower ratio electrode.

In an effort to realize flexible organic electronics, a technique to deposit fully reduced hybrid electrodes onto a flexible substrate (PET) was used. After filtration, the hybrid film was transferred to an aluminum substrate and then chemically and thermally reduced. PMMA was then drop cast on the reduced hybrid film and the aluminum was etched leaving behind the hybrid film on PMMA. The hybrid film can then be transferred to PET and the PMMA dissolved in acetone leaving behind a fully reduced hybrid electrode on a flexible substrate. Attempts to accomplish this feat were unsuccessful primarily because the hybrid film would not adhere well to the PET substrate and would lift off during the PMMA removal. However, using this technique, one sample was successfully transferred to a glass substrate and shows sheet resistances two fold lower than identical films transferred and reduced to glass conventionally. This sheet resistance improvement is likely due to doping from aluminum atoms and it was from this sample that the hybrid organic solar cell was made.

Organic solar cells fabricated with hybrid electrodes showed resistive characteristics for voltages greater than the open circuit voltage yet yielded typical an exponential trend for lower voltages. Unfortunately, whether produced with only reduced graphene oxide or with hybrid electrodes, power conversion efficiencies were less than 1%. OLEDs based on blended hybrid electrodes were also fabricated with mixed results. Current density measurements were much improved over
reduced GO and ITO based devices, however device luminance was orders of magnitudes smaller. This result is likely due to the relatively low optical transparency of the hybrid electrodes. Consequently, device efficiencies were substantially reduced. Apart from the transparent electrodes themselves, material choices in the organic solar cell and OLED could be improved. For example, the work function mismatch between reduced GO and PEDOT:PSS impairs device performance, this and other materials in the devices could be tailored to improve device efficiencies. Furthermore, the OED fabrication procedure requires the organic material to be briefly exposed to air thus degrading the organic layer and further limiting the device efficiency. Fully encapsulated devices would also lead to improved device efficiencies.

In conclusion, a significant volume of work was done to develop and fabricate reduced graphene oxide based transparent electrodes. Despite the relatively modest performance of the electrodes, it was found that doping reduced graphene oxide with nanotubes leads to ameliorated results. Yet, to fully exploit this fact, it is necessary to understand the nature of this improvement. How do the nanotubes separate the nanoplatelets and preserve their crystallinity? How can this process be engineered and controlled? Can other materials, such as nanoparticles, be used instead of nanotubes? Answering these questions will lead to further improvement in reduced graphene oxide based transparent electrodes. Ultimately, the full benefit of reduced graphene oxide electrodes is found in flexible electronics. Using the unique transfer process initially developed in this thesis, one can produce fully reduced graphene oxide based transparent electrodes on flexible substrates by improving the procedure for PMMA removal.

While reduced graphene oxide is unlikely to become a dominant material for transparent electrodes, it is an interesting material which demands further investigation. Because graphene oxide is a solution processable nanostructure it lends itself to interesting electrochemical applications. For example, graphene oxide nanoplatelets could be used in the active layer of an organic electronic device. The fabrication procedure used in this process disperses graphene oxide in water which is unsuitable for organic materials, but graphene oxide could be dispersed (to varying degrees) in other solvents more suitable for organic materials. Thus, it is possible that reduced graphene oxide could be used as a high electron affinity material in the active layer of an organic solar cell instead of fullerenes. Furthermore, graphene oxide could be used as a semi conducting material. Physical confinement and free electron occupation in graphene has been shown to split the graphene band gap and graphene oxide possesses both physical confinement by nanoplatelet structure and free electron occupation with the various bonded oxide groups.
Furthermore, graphene oxide absorption measurements presented herein indicate that graphene oxide does not absorb in the high wavelength, visible spectrum but absorbs (at exponentially increasing rates) in the low wavelength, visible spectrum to UV spectrum. However, development of these applications requires a deeper study of the material itself. Yet the study of graphene oxide is still very much in its infancy as is the field of graphene in general. Undoubtedly further, profound discoveries are coming which will open new and interesting avenues for both graphene and graphene oxide.
Appendix

Sheet Resistance of a four point probe

Resistance, $R$, can be defined as the resistivity, $\rho$, multiplied by the length of a material, $x$, and divided by the material's surface area, $A$. In sheet resistance measurements, $x$ is the spacing between the probes. Therefore, changes in $x$ will lead to changes in $R$.

\[ dR = \rho \frac{dx}{A} \]

Assuming the probes make contact with the material at a singular finite point, the area, $A$, is a function of $x$. In bulk materials, this dependence is proportional to distance squared (assuming spherical emanation of current from the probes). However, in thin film materials, this dependence is linear with distance. Thus, the effective area seen by the current in a bulk material is the surface area of a hemisphere of radius $x$ while in a thin film it is the surface area of a cylinder of radius $x$ and thickness $t$.

\[ A_{\text{bulk}} = \frac{1}{2} 4\pi x^2 \]

\[ A_{\text{thin}} = 2\pi x t \]

Therefore, the thin film resistance is given by the following integral.

\[ R = \int_s^{2s} \rho \frac{dx}{2\pi xt} = \frac{\rho}{2\pi t} \ln x \bigg|_s^{2s} = \frac{\rho}{2\pi t} \ln 2 \]

From the topography of the measured voltage and the resulting superposition of the currents, the resistance can be expressed by the following:

\[ R = \frac{V}{2I} = \frac{\rho}{2\pi t} \ln 2 \]

Consequently, resistivity per unit thickness or sheet resistance is given by the following:

\[ \frac{\rho}{t} = R_s = \frac{\pi}{\ln 2} \frac{V}{I} \]
In the case of non-infinite surfaces, boundary conditions must be taken into account. Valdes calculated several boundary conditions for four point probe measurements [88]. Two such conditions apply to this work, where the probe tips are perpendicular to the boundary where they are parallel to the boundary as shown in Figure 39 and Figure 40. The error induced by a boundary was analytically solved by Valdes and the functions are plotted in Figure 41. The plots reveal that even when measurements are taken at distances on the order of two probe spacing’s away from a boundary, the error is less than 5%. In order to ensure a less than 1% error in any measurement the measurement should be taken at least 3.25 probe spacing’s away from any boundary.

Figure 39 – Perpendicular (⊥) Four Point Probe Boundary Condition

Figure 40 - Parallel (ǁ) Four Point Probe Boundary Condition

Figure 41 - Percent Error induced by the boundaries of surface on four point probe measurements
Organic Light-Emitting Diodes

For comparison, four OLEDs were fabricated, two using blended hybrid electrodes and two using reduced GO electrodes. The hybrid electrodes were fabricated by filtering the same volume of GO used to create the reduced GO electrodes with an additional 100 µl of the nanotube solution, as was done in Figure 32. All electrodes were fabricated by vacuum filtration and deposited on glass substrates. Current density and luminance curves for these OLEDs are shown in Figure 42 and Figure 43, respectively. In both figures, like color indicates the same volume of GO was filtered. The current density curves reveal the expected trend where the lower sheet resistance yielded the higher current density. Conversely, the luminance was very low for all devices and followed the opposite trend.

![Graph showing current density vs. voltage for various reduced GO and blended hybrid electrode based OLEDs.](image)

Figure 42 - Current Density vs. Voltage for various reduced GO and blended hybrid electrode based OLEDs
From comparing Figure 35 with Figure 43, it is evident that the luminance is substantially lower in Figure 43, irrespective of the type of transparent electrode. This is likely due to damage incurred during fabrication. During the photolithographic process, the electrodes began to flake off the substrate resulting in physically non-uniform electrodes. Consequently, device luminance decreased. The expected trend seen in the current density (despite the damage) is maintained because the degree of electrode damage is constant with respect to all electrodes.
Bibliography


