Synthesis of Cross-Linked Carbon Nanotube Mats and Their Applications

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“SYNTHESIS OF CROSS-LINKED CARBON NANOTUBE MATS AND THEIR APPLICATIONS”

By

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For anyone that has overcome insurmountable odds
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$2^{nd}$ generation DSSC I-V plot

$2^{nd}$ generation DSSC I-V plot, without N719
LIST OF ABBREVIATIONS

Au NP   gold nanoparticle
BQ   benzoquinone
CCVD   catalytic chemical vapor deposition
CNT   carbon nanotube
DMA   dimethylacetamide
DMF   dimethylformamide
DSSC   dye-sensitized solar cell
FFS   filtration from suspension
FCMV   force-current and measure-voltage
HiPco   High pressure carbon monoxide conversion
ITO   indium tin oxide
MWCNT   multi-walled carbon nanotube
MWCNT-NH$_2$   amine functionalized multi-walled carbon nanotube
MWCNT-SH   thiol functionalized multi-walled carbon nanotube
MWCNT-COOH   carboxylic acid functionalized multi-walled carbon nanotube
Pd NP   palladium nanoparticle
RBM   radial breathing mode
SEM   scanning electron microscope
SWCNT   single-walled carbon nanotube
TEM   transmission electron microscope
XPS   x-ray photoelectron spectroscopy
ABSTRACT

Carbon nanotubes (CNTs) possess excellent tensile strength and electron transport properties that make them a promising component in future materials and technologies. The covalent cross-linking of carbon nanotubes is one avenue of producing thin, flexible mats that can be used in a variety of applications. Here we describe the cross-linking of functionalized CNTs through the Michael addition and imine formation reaction schemes. Our method of cross-linking is an improvement over traditional techniques such as laser irradiation because it is not detrimental to the nanotube structure. Our method also does not rely on weak van der Waals interactions that are sometimes used in the synthesis of nanotube mats. Furthermore, our filtration-from-suspension procedure can be readily scaled up for industrial use and does not require high pressure or high temperature reaction chambers. Such CNT-based composites can be used in a wide variety of applications. We demonstrate their use in a hydrogen sensor and a dye-sensitized solar cell.
CHAPTER 1:
CARBON NANOTUBES: SYNTHESIS, PROPERTIES, AND APPLICATIONS

Carbon nanotubes (CNTs) are sheets of graphene that are rolled into cylinders with diameters in the nanometer range. In 1976, Moribu Endo first reported the existence of these graphene tubes during the decomposition of benzene [1]. However, there wasn’t much interest in CNTs until 1991 when Sumio Iijima rediscovered these intriguing structures [2]. Iijima’s rediscovery led to much interest as he and many researchers began to realize the superior properties of nanotubes. Nanotubes have excellent electrical, mechanical, and thermal properties. Nanotubes also have a low mass density and can be easily functionalized. Because of these properties, CNTs have potential applications in a wide array of fields including construction materials, electronics, batteries, photovoltaics, sensors, flat panel displays, and drug delivery systems. However, further research is necessary as very few viable applications currently exist.

This dissertation illustrates the design of CNT-based materials for various applications, specifically hydrogen sensing and photovoltaics. Chapter 1 outlines the background information of carbon nanotubes including its properties, functionalization, and current applications. Chapter 2 describes the synthesis and characterization of covalently cross-linked thiol functionalized multi-walled carbon nanotube (MWCNT-SH) mats with a benzoquinone linker. Chapter 3 describes an alternate method of covalently linking amine functionalized multi-walled carbon nanotubes (MWCNT-NH$_2$). Chapter 4 demonstrates how the MWCNT-NH$_2$ mats can be utilized as light-weight and flexible hydrogen sensors with the integration of palladium nanoparticles (Pd NPs). Finally, Chapter 5 discusses the synthesis of CNT/cellulose based composites for applications in dye-sensitized solar cells.

1.1 Structure
Carbon nanotubes can be best described as tubes of graphene with nanometer-sized diameters. As shown in Figure 1, they can exist as either single-walled carbon nanotubes (SWCNTs) or multi-walled carbon nanotubes (MWCNTs). Nanotubes can also be either be capped or uncapped at their ends depending on the synthetic methods. Synthetic methods include arc discharge, laser ablation, chemical vapor depositions, and HiPco [2-5]. The chirality of CNTs,
or the angle which the graphene sheet is rolled, can be described through the equation below where \( a_1 \) and \( a_2 \) are unit vectors on the graphene sheet and \( n, m \) are integers \((0 \leq |m| \leq n)\).

\[
C_h = na_1 + ma_2
\]

The chiral vector, \( C_h \), is the axis at which the graphene sheet is rolled and the chiral angle, \( \theta \), is the angle between \( C_h \) and the vector \( a_1 \). The indices \((n, m)\) can be used to describe the chirality of the nanotube. The nanotubes are called “zigzag” when \( m = 0 \) and called “armchair” when \( n = m \). For all other values for \((n, m)\), the nanotubes are known as “chiral”. Like the indices \((n, m)\), the chiral angle describes the type nanotube and its subsequent structure. For instance, when \( \theta = 0^\circ \) or \( 30^\circ \), the nanotubes are described as zigzag or armchair, respectively. Or if \( 0^\circ < \theta < 30^\circ \), the nanotubes are described as chiral (Fig. 2).

![Carbon nanotube structure](image)

Figure 1: Carbon nanotube structure
Figure 2: Graphene lattice with vectors
1.2 Synthesis

Over the last couple decades, several methods for CNT synthesis have been developed. The main synthetic methodologies are catalytic chemical vapor deposition (CCVD), arc discharge, laser ablation, and high pressure carbon monoxide conversion (HiPco). In conjunction with different reaction conditions, each methodology can influence the type of nanotube produced. For instance, there are specific synthetic procedures that favor the production of MWCNTs and other procedures that favor the growth of SWCNTs. SWCNTs are predominately grown through catalytic chemical vapor deposition or laser ablation and MWCNTs are produced through arc discharge. However, all the synthetic methods come with limitations. Nanotubes are often produced with structural defects that can negatively affect their properties [6]. The growth of completely defect-free or pristine CNTs is a desired goal as presently there are no synthetic methods that completely inhibit these defects. Another challenge facing researchers is the length in which nanotubes can be grown as it is currently limited to the centimeter range [7]. Although nanotube lengths have steadily increased since they were first discovered, the ability to make them much longer would greatly aid in the development of new materials.

Developed by Sumio Iijima, the arc discharge technique is the original method for synthesizing carbon nanotubes (Fig. 3a). His technique is similar to the procedure for producing C$_{60}$ [2]. This method, however, produced only marginal amounts of nanotubes. The procedure was further modified by Ebbesen and Ajayan who improved the nanotube yield [8]. Their procedure placed the ends of two carbon rods a short distance apart (one cathode, one anode) in a pressurized reaction chamber within a 500 torr helium atmosphere. It was determined that 500 torr was the optimum reaction pressure as any other pressure decreased the overall yield. In a typical arc discharge set up, the anode is longer than the cathode but has a smaller diameter (6 mm vs. 9 mm). Also, a voltage of 20 V and current of 50 - 100 A is applied while the anode is slowly positioned closer to the cathode until arcing occurs. Using too high of a current results in a burned, carbonaceous material with very few nanotubes. Arcing occurs at a distance of 1 mm and results in the growth of MWCNTs on the cathode. Because arcing consumes the graphite, it is necessary to maintain the 1 mm gap between the two rods throughout the duration of the synthesis. It has also been reported by Iijima et al. [9] and Bethune et al. [10] that SWCNTs can be grown by incorporating metal particles such as iron, cobalt or nickel into the cathode. A post-
Figure 3: a) Arc discharge [2] and b) laser ablation schematics [5].
Figure 4: a) CCVD [4] and b) HiPco schematics [3].
An alternate method for synthesizing carbon nanotubes is through laser ablation, a method developed by Smalley et al. in 1995 (Fig. 3b). This method consists of the vaporization of a carbon source within a heated reaction chamber under vacuum (1200 ºC, < 10 mTorr). 1200 ºC is the optimum reaction temperature for this synthetic methodology as low-quality, defect-ridden nanotubes were observed at alternate temperatures. To create MWCNTs, graphite is used as the carbon source. Like arc discharge, SWCNTs can be formed instead of MWCNTs by uniformly dispersing metal particles within the carbon source. A 532 nm Nd:YAG laser providing 10 ns, 250 mJ pulses at 10 Hz is utilized to vaporize the carbon source into C\textsubscript{2}. This vapor is then carried through the reaction chamber via an inert carrier gas where it is cooled and deposited on a copper collector. The residue deposited on the copper collector consists of carbon nanotubes and other carbonaceous materials [5].

One of the more common methods of producing nanotubes is through catalytic chemical vapor deposition (CCVD). Growth by CCVD (Fig. 4a) is one of the more popular methods due to its large scale production capabilities [11]. This method was developed by Jose-Yacaman et al. and was further refined by others over the years. It consists of flowing a carbon source gas, such as methane or acetylene, over metal nanoparticles in a reaction chamber at temperatures ranging from 750 - 1200 ºC. Most often these metal catalysts are iron, cobalt, or nickel nanoparticles but can also consist of other transition metals. Interactions between the carbon vapors and the metal nanoparticles results in the formation of carbon nanotubes [4]. Other benefits of synthesizing nanotubes via CCVD include the ability to tune nanotube diameter, high purity, and cost efficiency. However, CCVD grown nanotubes tend to have more defects than CNTs synthesized via arc discharge and are subsequently more curved in structure. Although mostly utilized to produce SWCNTs, the CCVD method can also produce MWCNTs at a lower temperature range of 500 - 900 ºC [12].

Another method of synthesizing SWCNTs is through a process known as high pressure carbon monoxide conversion (HiPco). Developed by Smalley et al., the HiPco method utilizes carbon monoxide as the carbon source and Fe(CO)\textsubscript{5} as the metal catalyst (Fig. 4b). A gas containing a mixture of CO and Fe(CO)\textsubscript{5} is flowed through a quartz reaction vessel at 850 ºC which leaves a black deposit containing mostly SWCNTs on the chamber walls. Smalley et al.
determined that the reaction would proceed at a significant rate only if the temperature within the reactor was greater than 500 °C and that the yield was highest when the temperature was raised to 1200 °C. Smalley et al. also varied the CO pressure from 1 to 10 atm and concluded that the higher pressures yielded more nanotubes [3].

1.3 Growth Mechanism

In 2007, Rodriguez-Manzo et al. successfully grew a MWCNT within a host nanotube using electron beam irradiation and examined its growth in real time. It was observed through TEM that after a short period of irradiation and at temperatures exceeding 600 °C, a graphitic sheet formed within the core of the nanotube and eventually migrated to the metal catalyst where nanotube growth is initiated. It was also observed that the metal catalyst remained crystalline throughout the process and its surface turned from flat to curved as the nanotube grew. In addition, the curvature of the metal catalyst increased proportionally with nanotube length and the capping of the nanotube end seemed to coincide with the formation of a near spherical metal catalyst [13]. Nanotube growth can also terminate when optimal reaction conditions, such as temperature or pressure, are altered. Despite extensive research, the mechanism behind CNT growth is not completely understood. There are, however, widely accepted theories. One such theory involves the solvation of the carbon vapor into the metal catalysts. Then at some point, perhaps when the metal particle is saturated with carbon, sp² bonded carbon is then pushed outwards from the metal-carbide intermediate in the form of a tube. Because the surface energy of graphite is much lower than that of the transition metal catalysts, the aggregation of carbon to the metal surface is favored [14]. This results in two possible scenarios: the wrapping of multiple graphene layers around the particle or the growth of carbon nanotubes (Fig. 5).
Figure 5: Carbon nanotube growth mechanism [15].
1.4 Impurities and Defects

Structural defects consist of two categories: atomic vacancies and Stone Wales defects. In atomic vacancy defects, carbon atoms are missing from the graphene lattice. A carbon or a whole section of carbons may be absent from the nanotube in this type of defect. In the second type, Stone Wales defects, carbon atoms are arranged in a pentagonal or heptagonal manner instead of the normal hexagonal arrangement. These defects prevent the linear growth of CNTs and subsequently results in curved nanotubes [16-18].

1.5 Purification and Separation

The purification of carbon nanotubes is necessary as the synthesis also produces unwanted byproducts such as amorphous carbon and metal catalysts. Such impurities are often removed via an acid treatment method. However, this may introduce additional and potentially unwanted structural defects in the nanotube. Additionally, metallic and semiconducting nanotubes are often produced concurrently. This may pose a problem for applications that require a specific nanotube chirality. In result, several separation methods have been investigated. To separate out the semiconducting nanotubes, the metallic nanotubes can be destroyed through electrical heating. This method, however, is not completely effective as not all metallic nanotubes are destroyed. Furthermore, this method is only feasible on the small-scale [19]. Solvent-based methods of separating nanotubes have also been developed in recent years with some success. This success, however, is limited as it will depend on the solubility of the nanotubes in the solvent. CNTs are inherently insoluble in most solvents and thus some modification to the nanotubes is needed, such as functionalization, for them to go into solution. Another technique, developed by An et al. [20], separates armchair and zigzag nanotubes through a series of chemical reactions involving the use of diazonium reagents. One promising separation technique available, the methane plasma method, was developed by Zhang et al. This method separates out the semiconducting SWCNTs while minimizing modification to the sp² structure of the nanotubes. This technique involves the removal of the metallic nanotubes through a hydrocarbon anion reaction scheme using methane plasma at 400 °C. This process destroys all smaller diameter nanotubes (< 1.4 nm) due to the greater structural strain and subsequent higher reactivity. However, for nanotubes with diameters in the 1.4 – 2 nm range, only the metallic SWCNTs are destroyed due to the higher chemical reactivity while leaving the semiconducting nanotubes intact. Their experiments also separated out the semiconducting SWCNTs at very
high yields. Most of the defects caused by the methane plasma were minimized through an annealing step at 600 °C [21]. Although this methane plasma method of separating nanotubes is promising due to its industrial viability, it is only feasible with SWCNTs of a specific diameter range. Subsequently, further research and development is needed to improve such separation techniques.

### 1.6 Electron Transport Properties

Since their discovery, it has been determined that CNTs possess remarkable electron transport properties. Nanotubes are one of the better conductors known. They have a current density of $4 \times 10^9$ A/cm$^2$ which makes them about a thousand times more conductive than copper [22]. Carbon nanotubes can also exhibit semiconductive or metallic behavior depending on their chiral angle and tube diameter. This ability to tune electron transport properties gives nanotubes a unique property and makes them a promising material for future electronics.

Since nanotubes consist of rolled graphene sheets, the electronic properties of CNTs are similar to graphene. The dispersion relation for graphene can be plotted (Fig. 6b) where the upper section of the plot is the conduction band and the lower section is the valence band. The hexagon outlined in white is the Brillouin zone and the points where the conduction and valence band meet are the K points where energy is zero at the Fermi level. Therefore, if the cross section of a nanotube ($n$, $m$) crosses any of these K points on the Brillouin zone (Fig. 6a), then the band gap is zero and the nanotube is metallic. If the cross-section of the nanotube crosses anywhere except at the K points, then the nanotube is semiconductive. Using the tight-binding model, it can also be predicted that roughly 1/3 of all the nanotube structures are metallic while the remaining 2/3 are semiconductive. Predicted by band theory, the semiconductive nanotubes’ band gap can be approximated by the equation below where $d_t$ is the nanotube diameter (nm):

$$E_g = \frac{0.7 \text{ eV}}{d_t}$$

The metallic nanotubes fall under two categories: true metallic nanotubes and small bandgap metallic nanotubes. The true metallic nanotubes have a bandgap, $E_g = 0$, and are extremely rare as most nanotubes have at least a nominal bandgap due to strain and curvature. The small bandgap nanotubes are more common and have a very small bandgap that is typically less than 100 mV.
Figure 6: a) Brillouin zone and b) energy dispersion relation plot for graphene [23].

Because CNT lengths are much longer than their diameter, nanotubes can be regarded as a 1D system where electron transport is axial through the π orbital system that sits parallel to the length of the nanotube. However, it has been reported that electrons can also travel radially through each layer in a MWCNT [24]. As mentioned earlier, structural defects can affect the electronic properties of nanotubes. Impurities, structural vacancies, Stone-Wales defects, and mechanical deformations such as strains and twists can all cause electron scattering and subsequently reduce conductivity.

1.7 Mechanical Properties

In addition to their intriguing electronic characteristics, carbon nanotubes also exhibit remarkable mechanical properties. CNTs are reported to be several hundred times stronger than steel despite having a low mass density. Such properties make them an ideal component in construction or reinforcement applications. Due to the nanotubes’ sp² character, it is theorized that CNTs can have tensile strengths higher than any other material known. According to molecular dynamic simulations and modeling, CNTs are calculated to have a tensile strength of about 300 GPa [25, 26]. Table 1 compares the CNT theoretical tensile strength to other common materials.
Table 1: Theoretical Tensile Strength of Carbon Nanotubes and Other Common Materials [27, 28]

<table>
<thead>
<tr>
<th>Material</th>
<th>Tensile Strength (GPa)</th>
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<tbody>
<tr>
<td>Carbon Nanotubes</td>
<td>300</td>
</tr>
<tr>
<td>Kevlar™</td>
<td>3.5</td>
</tr>
<tr>
<td>Tungsten Carbide</td>
<td>0.3448</td>
</tr>
<tr>
<td>Titanium</td>
<td>0.24 – 0.37</td>
</tr>
<tr>
<td>Iron</td>
<td>0.350</td>
</tr>
<tr>
<td>Copper</td>
<td>0.22</td>
</tr>
<tr>
<td>Aluminum</td>
<td>0.04 – 0.05</td>
</tr>
<tr>
<td>Lead</td>
<td>0.012</td>
</tr>
</tbody>
</table>

However when determined experimentally, the tensile strength values for nanotubes were lower than the theorized values. Yu et al. were able to measure the tensile strength of CNTs by attaching a CNT to two AFM tips and pulling on the nanotube until structural failure was observed. They experimentally measured the tensile strength of SWCNT bundles to range from 13 - 52 GPa and MWCNT bundles to range from 11 - 63 GPa [25, 29]. These lower than expected values can be attributed to the inherent defects that are produced during the synthesis of CNTs. It was also observed that CNTs exhibit ductile properties at higher temperatures. At temperatures greater than 2000 ºC, it was observed that SWCNT could be stretched up to 280% [30]. Similar ductile properties in MWCNTs have also been reported.

1.8 Thermal Properties

In addition to the CNT properties already discussed, they also have extraordinary thermal properties. For example, nanotubes are stable at a wide range of temperatures as their thermal stability is comparable to that of graphite. They are also excellent thermal conductors in that they can transfer heat along their structure very efficiently and have a high thermal conductivity that exceeds diamond ( > 3000 W/m-K) [31]. These properties make them potentially useful as heat sinks or as components in high temperature electronics.

It has been shown through theoretical studies that there is a direct correlation between the nanotube diameter, and thus strain/curvature, and its stability. Therefore, it is believed that SWCNTs have a lower thermal stability than MWCNTs as they have a smaller diameter and
more structural strain. Furthermore, SWCNTs would be more likely to fuse together at high temperatures to form a wider nanotube or MWCNTs because reductions in strain of a larger diameter tube are more energetically favorable [32].

1.9 CNT Phonons and Raman Spectroscopy

There are three characteristic phonon modes of carbon nanotubes: 1) the D-band, 2) the G-band, and 3) the radial breathing mode or RBM. These three phonon modes are useful in the Raman spectroscopy of carbon nanotubes. The D-band appears in 1300 - 1400 cm$^{-1}$ range and describes the “disorder” of the nanotube. This disorder refers to the defects that may be present in the carbon nanotube such as dangling or sp$^3$ bonds. The D-band intensity is also correlated to the amount of impurities present such as amorphous carbon. The D-band intensity tends to be much more prevalent in MWCNTs than in SWCNTs as synthetic methods for the former tend to produce a greater amount of defects. The G-band which appears in the 1500 - 1600 cm$^{-1}$ range is also found in graphene. The shape of the G-band correlates to the electron transport properties of the nanotube. The G-band tends to be much broader in metallic nanotubes than in semiconducting nanotubes. Lastly, the RBM mode is related to the radial vibrations of the nanotube structure. The position and intensity of the RBM band can be used to describe the CNT diameter. The RBM peak intensity is inversely proportional to the nanotube’s diameter. Shifts in the D- and G-band are also useful in the characterizations of carbon nanotubes as a shift in either of these bands indicate structural stress and strain in the carbon nanotube structure. [33-35].

1.10 Functionalization

Generally, pristine carbon nanotubes are chemically inert due to the stability of the sp$^2$ bonding. However, current synthetic methodologies also produce defects. At these defect sites and at areas of sp$^2$ destabilization, such as nanotube ends or sidewalls, the attachment of functional groups is possible. There are three types of carbon nanotube functionalization: covalent, non-covalent, and endohedral. The first type involves a bond linkage between the nanotube and functional group. The second type, non-covalent functionalization, utilizes π-π stacking or van der Waals interactions. Lastly, endohedral functionalization involves the placement of materials within the hollow nanotube structure.
Figure 7: Carbon nanotube functionalization [36].
Functionalization via covalent bonding and electrostatic interactions are the more common methods. Both types have their advantages and disadvantages. Covalent functionalization is more advantageous than noncovalent functionalization if a strong bond between the nanotube and functional group is needed. However, the drawback is that the covalent functionalization diminishes CNT properties as the sp² character is altered, especially in SWCNTs where there is only one graphene layer. One possible way to preserve the nanotube properties is to covalently functionalize the outer walls of a MWCNT, which leaves the inner walls intact. One of the more customary methods of covalently functionalizing CNTs is through carboxylation, or the chemical attachment of a carboxylic acid group. Carboxylation can be achieved through the acid treatment of the CNTs with a 3:1 mixture of sulfuric and nitric acid. Afterwards, it is then possible to react the carboxylic acid with thionyl chloride to produce acyl chloride functionalized carbon nanotubes. Further reacting the acyl chloride groups with amines produces R-NH functional groups. The acid treatment of CNTs demonstrates how this initial carboxylic acid functionalization can lead to an array of further chemical modifications (Fig. 7).

The second type of functionalization, noncovalent functionalization, maintains CNT properties more effectively than covalent methods since it is not destructive to the sp² bonding as it relies on van der Waals interactions and π-π stacking. Such interactions allow nanotubes to be embedded into polymers where they can act as reinforcement agents. However, since these forces are relatively weak, the nanotubes are more prone to slide within the host material and subsequently results in only minor improvements in the mechanical strength properties of nanotube-reinforced materials.

1.11 CNT Mats / Thin Films

Despite all the intriguing properties of CNTs, very few viable applications currently exist. The development of CNT-based materials is necessary if nanotubes are to play a paradigm-shifting role in future applications. CNT-based thin films, also known as “mats” and “Buckypaper”, have the potential to form strong and lightweight materials [37]. These mats have been studied extensively and were the first attempts to convert CNT properties from the nanoscale to the macroscale. However, further optimizations are needed as many of the current mats do not have the same exceptional properties exhibited by individual tubes. Several MWCNT-based mats have been produced and tailored to a range of possible applications such as field effect
transistors [38] and diodes [39]. CNT mats can be made through a variety of ways including high compression, filtration-from-suspension (FFS), and high energy irradiation techniques.

High compression techniques are often used to help facilitate van der Waals interactions to hold the nanotubes together. Because these forces are relatively weak, the mechanical properties of such materials are significantly lower than the predicted properties of individual nanotubes. In addition, since the conductivity of such nanotube films is mainly governed by intertube junctions, poor interfacial binding can diminish the electron transport properties in such thin films.

Nanotube mats can also be produced via a FFS procedure. Like the high compression technique, FFS also relies on electrostatic interactions. Although the results are promising, CNT mats produced this way also do not exhibit the same properties seen in individual nanotubes. The Young’s Modulus of such sheets produced through FFS is comparable (1 - 4 GPa) to that of ordinary organic polymers. By removing impurities, the Young’s Modulus can be improved by 0.3 – 6 GPa [40].

Another development in the fabrication of these materials has been the use of ion-beam technology to fuse the nanotubes together [41, 42]. While this method can be achieved on both SWCNTs and MWCNTs, this technique of cross-linking has both its advantages and disadvantages. One advantage is that the setup is simple and there are no chemical reactions that need to be performed. Another advantage is that the bonds formed between the tubes are much stronger than the van der Waals interactions that are sometimes used to link nanotubes. According to simulations, ion irradiation will affect SWCNTs and MWCNTs differently. The incident energy from irradiation will scatter carbon fragments from a SWCNT, and a percentage of these fragments will be redistributed along the nanotube surface. In the end, these fragments will form the cross-links between the nanotubes. It was predicted that a much higher percentage (~50%) of the fragments will be redistributed between the inner walls of MWCNTs. Therefore, cross-linking via irradiation is more suitable for SWCNTs but it can still be used to reinforce the inner walls of MWCNTs. These theoretical predictions for cross-linking nanotubes have been confirmed experimentally by researchers. An improvement in electron transport properties in SWCNT bundles due to increased intertube coupling, after exposure to an Ar⁺ beam, has also been demonstrated [43]. In addition, improved mechanical properties have also been demonstrated in MWCNTs. It has been shown that electron irradiation of MWCNTs can
reinforce the inner walls and stiffen the tubes by up to five times [44]. Studies have also looked into the possible mechanisms involved in the radiation induced modification of CNTs [45]. Similar results have been reported and have demonstrated improvements in fracture strength [46]. Despite all these advantages and promising results for irradiation cross-linking, there are a few drawbacks. One disadvantage is that it destroys the sp² bonding of the nanotube which could be detrimental to the tubes’ intrinsic properties. Another disadvantage of this technique is that the cross-linking capabilities are dependent on where the nanotube can be exposed to the electron or ion beam. If you wanted to produce a cross-linked nanotube mat, only the surface layers of the CNT mat would be cross-linked as the interior tubes would not be exposed to the incident beam.

All in all, it is apparent that SWCNTs cannot be chemically functionalized to any significant extent without destroying their unique structural and electronic properties, the two basic characteristics on which their paradigm-shifting advanced applications depend. However, it should be possible, at least in part, to chemically functionalize the outer walls of MWCNTs and still leave the inner cylinders intact. Therefore, it may be advantageous to use MWCNTs in such materials.

1.12 Carbon Nanotube Applications

A wide variety of applications are being developed for carbon nanotubes. Due to their excellent electron transport properties, CNTs may be used in various applications such as electronics, sensors, or photovoltaics. In addition, nanotubes may be used as reinforcement in construction materials or vehicles because of their high tensile strength properties.

1.12.1 CNT Electronics

Since their discovery, it has been theorized that carbon nanotubes could eventually replace silicon based electronics due to their excellent conductive properties as well as their convenient nanometer size. It is said the silicon transistors can be no smaller than 10 nm. However, CNTs are a viable substitute since they can be as small as 1 nm. In addition, modern electronics also utilize copper components which have inferior properties to carbon nanotubes. Compared to CNTs, copper has a lower current density and is more susceptible to electron scattering. Because transistors are one of the basic pieces of integrated circuits, the exploration of such nanotube-based components is necessary. In the early stages of nanotube electronics development, this idea came into fruition when IBM successfully created a CNT field effect transistor (FET) [47].
1.12.2 CNT Polymer Composites
Carbon nanotubes have also been integrated within polymers to act as conductive or reinforcement components in advanced composites. Such CNT-polymer composites can be used in a variety of applications including automotive paint, construction materials, and charge dissipaters. In these composites, a thorough dispersion of the nanotubes is important as an even distribution is necessary for the nanotube properties to be translated from the nanoscale to the macroscale. It has been demonstrated that aligned nanotubes can improve a polymer composite’s conductivity [48]. Additionally, CNTs can be used as reinforcement components in a polymer matrix. Nanotubes are an ideal material for this purpose because they are lightweight, stiff, and have a high-aspect ratio. Nanotubes can be incorporated into such polymer matrices through either noncovalent or covalent bonding. Some well-studied polymers that have been used noncovalently with nanotubes are polyvinyl pyrrolidone (PVP) and polystyrene sulfonate (PSS) [49]. An assortment of methods has been investigated to improve the solubility of CNTs into the polymer matrix including sonication and functionalization. Furthermore, the covalent bonding of nanotubes into polymers has also been investigated. As expected, the covalent attachment of nanotubes to the surrounding polymer matrix can improve the mechanical properties [50].

1.12.3 CNT Gas Sensors
Nanotube-based gas sensing is one technology that has exhibited much potential. Gas sensors are needed for a wide variety of applications including environmental analysis and medical diagnostics. Some issues reported with current sensors include lack of flexibility, poor sensitivity, and the inability to operate at high temperatures. Carbon nanotubes may be the solution to these obstacles. It has been shown that CNTs can provide quick response times and trace detection capabilities. Due to their conductive properties, nanotubes can be used as simple resistance-measuring sensors. Furthermore, nanotubes are lightweight and can be used at high temperatures. CNT-based sensors have already been fabricated for detecting a wide variety of gases such as CH$_4$, O$_2$, and CO$_2$.

Single-walled, multi-walled, pristine, aligned, chemically modified, and metal NP-functionalized CNTs have all been used in the development of sensors. Many sensors have been based on SWCNTs as they have better conductive properties than MWCNTs [51]. Kong et al. reported that pristine SWCNTs were sensitive to NO$_2$ and NH$_3$. They developed a sensor that
had a response time of a couple seconds and had a recovery time of about 12 hours. This recovery time was reduced to approximately 1 hour when the nanotubes were heated. Three models have been proposed to explain this sensing phenomenon. The first is that there is a charge transfer between the gas molecules and the CNTs. The second model proposed is that there is a molecular gating effect with polar molecules such as NO₂. The last model is that there is a Schottky barrier change between the CNTs and the electrodes. Although many sensors utilize SWCNTs, MWCNT-based sensors are still a promising material as they are cheaper to produce. However, like their single-walled counterpart, they also have a slow recovery time. It could take heating at 100 °C for several days for the sensor to revert to normal functioning. Gas sensors based on aligned nanotubes exhibited improved sensitivity and response time to gases such as NO₂, NH₃, and H₂. Modifying the CNTs with functional groups or nanoparticles can change the electron transport properties of the nanotubes and subsequently alter its sensitivity to specific gases. For instance, carboxyl functionalized SWCNTs and MWCNTs both exhibited NO sensing abilities. Nanotubes have also been functionalized with a variety of conducting polymers. Qi et al. functionalized SWCNTs with polyethyleneimine (PEI) which resulted in improved sensing capabilities for NO₂ in which the device was able to detect the gas at < 1 ppb. The device was also able to detect a variety of other gases such as CO, CO₂, CH₄, H₂, and O₂ [52]. Additionally, it has also been demonstrated that CNTs can be covalently functionalized with poly-(m-aminobenzene sulfonic acid) (PABS) for sensing NH₃ at 5 ppm.

For specifically sensing H₂, the recruitment of palladium nanoparticles (Pd NPs) onto nanotubes has also been investigated. Pd NPs have been thought to be useful in hydrogen sensing applications as they are H₂ selective and have a high sensitivity. Over the years, there has been some success in synthesizing CNT/Pd based hydrogen sensors. In 2007, Sun et al. were the first researchers to create flexible hydrogen sensors. They utilized Pd NP decorated carbon nanotubes whose sensing capabilities were comparable to traditional rigid substrate sensors. Sun et al. were able to achieve this by transfer printing a network of SWCNTs onto a poly(ethylene terephthalate) with a thin layer of epoxy resin. They also used Ti/Pd layers as electrodes and grew Pd NPs onto the CNTs. The resulting flexible, thin film was able to detect H₂ gas by measuring the resistance between the two electrodes. It was observed that there was an increase in resistance in the presence of hydrogen and a decrease in resistance in the absence of it [53].
CHAPTER 2: 
ASSEMBLY OF MWCNT-SH MATS

Here we report the successful covalent cross-linking of multi-walled carbon nanotubes via a Michael addition reaction mechanism to form thin, flexible mats (Fig. 8). In this reaction, we utilized thiol functionalized carbon nanotubes (MWCNT-SH) and benzoquinone (BQ) as the cross-linker. A filtration-from-suspension method was used to produce these mats (Fig. 9). It was determined that the optimal cross-linker to nanotube ratio was 5:1 by weight. This ratio produced mats with the highest tensile strength properties while still maintaining flexibility. MWCNT:BQ ratios less than 5:1 produced mats with weaker tensile strengths. A 1:1 ratio did not sufficiently cross-bond the nanotubes together resulting in “platelets”. Ratios greater than 5:1 produced stronger mats. However, this increase in tensile strength is accompanied by a loss of flexibility.

2.1 Experimental

The MWCNT-SHs were purchased from Nanocyl SA and according to their specifications, the average diameter of the tubes is 9.5 nm, lengths are < 1 μm, and the thiol group coverage over the nanotube surface is between 0.5 - 1%. Benzoquinone and dimethylformamide were purchased from Sigma-Aldrich.

2.1.1 MWCNT-SH Mat Formation

MWCNT-SHs (20 mg) were dispersed in DMF (15 mL) by sonication. In a separate reaction vessel, benzoquinone (100 mg, Sigma-Aldrich) was dissolved in DMF (10 mL). While stirring the nanotube suspension, the benzoquinone solution was injected at a rate of about 0.1 mL per minute. After the addition of benzoquinone, the reaction mixture was allowed to stir for 12 h at 75 ºC. The solution was vacuum filtered at 75 ºC onto filter paper and dried. The temperature during filtration was maintained at 75 ºC by the use of a heat gun.

2.1.2 Synthesis of BSPP Capped Au Nanocrystal (5.7 ± 0.3 nm)

Au nanocrystals were synthesized using the sodium citrate (Sigma-Aldrich) and tannic acid (Fisher Chemicals) reduction of auric acid (Sigma-Aldrich) [54]. A solution was prepared containing sodium citrate (2 mL solution of 1% w/v solution) and tannic acid (0.45 mL of 1% w/v solution) and rapidly added to a solution of tetrachloroaauric acid (100 mL of 0.001% w/v,
The solution was stirred under reflux for an additional 5 minutes followed by cooling to room temperature. This reaction produced a colloidal gold solution (pH 4.5). The gold nanoparticles exhibited a mean diameter of 5.7 ± 0.3 nm. 4-bis-sulfonatophenylphenylphosphine (25 - 30 mg) was added to a solution of freshly prepared tannic acid/citrate stabilized gold nanocrystals and stirred under inert atmosphere for 72 hours. Upon completion of the phosphine capping of the gold nanocrystal, a saturated solution of NaCl was added slowly to a stirred solution until the solution turned blue. The reaction was then centrifuged and the solids collected. A second purification was carried out by precipitating the phosphine-stabilized nanocrystals with ethanol from aqueous solution, centrifuging off the precipitate, and drying it under vacuum.

2.1.3 Au Nanocrystal Recruitment to MWCNT Mats

In an argon atmosphere, rectangular sections of the nanotube mats (approximately 5 mm x 15 mm) were cut out using a razor blade. A solution of Au nanocrystals (5.7 ± 0.3 nm diameter) was made by suspending the nanocrystals in deionized water. Using a pipette, 2 - 3 drops of this Au nanocrystal solution were dropped onto the surface of the nanotube mat. Unattached Au nanocrystals were removed by washing the mat several times with deionized water. After washing, the mat was left to dry in a desiccator.

![Figure 8: Michael addition reaction mechanism.](image-url)
Figure 9: CNT mat synthesis setup.
Figure 10: MWCNT-SH mat
2.1.2 Tensile Measurements

Tensile strengths of the CNT mats were measured using a Thümler TH 2730 instrument. A mat section of known dimensions was cut and was placed in the instrument sample holder. The sample was then stretched at a rate of 1 mm per minute while concurrently measuring elongation (mm) and the force applied (N) until a failure point was reached. Strain can be measured with the following equation where \( L_0 \) is the original length of the mat and \( L \) is the length of the CNT mat at its fracture point:

\[
\text{Strain} = \frac{L - L_0}{L_0}
\]

Stress is calculated with the following equation where \( F \) is the force applied at the fracture point and \( A \) is the area of the CNT mat:

\[
\text{Stress} = \frac{F}{A}
\]

2.1.3 I-V Measurements

Four-wire resistance measurements were performed on the MWCNT-SH mats of different cross-linker:MWCNT ratios (1:1, 5:1, and 10:1) using the force-current and measure-voltage (FCMV) testing method. Four-wire testing was used because this technique takes into account the resistance from instrument wiring and results in more accurate measurements of the sample. Mats were cut into thin strips of known dimensions and were placed perpendicularly to the axis of the 4 Pt wires. In FCMV testing, a known amount of current is applied to the mat and the voltage is measured. Our measurements consisted of applying a current in the range of -1 mA to 1 mA at increments of 0.1 mA with multiple sweeps, resulting in the collection of 43 data points. Using LabVIEW software, the current (I) is then plotted as a function of voltage (V).

2.1.6 Scanning Electron Microscopy

The mats were examined using a FEI Nova 400 Nano Scanning Electron Microscope. Low magnification images were recorded using an Everhart Thornley Secondary Electron Detector (ETD) and high magnification images were acquired using the Through Lens Detector (TLD) in the immersion mode at an accelerating voltage of 7 keV.
2.1.7 Raman Spectroscopy

The laser used for Raman characterization was a Toptica Photonics DL 100 grating-stabilized diode laser emitting 80 mW at 785 nm with a narrow linewidth (\(< 0.4\) cm\(^{-1}\)). The power at the sample is between 1.5 - 5 mW. The Raman spectrograph was a Horiba JY LabRAM HR800 UV 800 mm focal length microRaman system using a holographic notch filter to couple the laser into the microscope sample area (Olympus BX40) and reject the laser scatter from entering the spectrograph stage. The detector is a Wright 1024 x 256 pixel EEV open electrode CCD. The objective lens used was a Leica HC PL Fluotar 50X NIR sensitive objective with a working distance of 0.5 mm.

2.2 Results and Discussion

Fig. 8 shows that there are two possible points of attachment on benzoquinone resulting in the two adducts with respect to the thiolated positions on the quinone. The 2,5-dithioMWCNT 1,4-cyclohexanedione adduct may be favored due to steric interactions although if two tubes were to orient themselves parallel or end-on, then the 2,6-dithioMWCNT 1,4-cyclohexanedione adduct would be favored. The use of MWCNT’s for “Buckypaper” instead of SWCNT’s is still in its infancy with the experimental work focused on aligning the tubes to optimize intermolecular force interactions. However, nanotube alignment is not actually an advantage in covalent functionalization because the reaction depends on the random distribution of functional groups along a tube. It is well documented that there is a higher degree of functional groups at the ends of the nanotubes so a random arrangement of tubes within a mat should favor end-tube to body-type cross-linking. Through the filtration-from-suspension (FFS) method of MWCNT-SH, the fabrication of a nanotube mat is possible. Thiol functionalized nanotubes also facilitate the attachment of gold nanoparticles via sulfur–metal bonds. The resulting hybrid structures consist of paper-like, pliable mats on the surface of which chemically bonded gold particles are randomly distributed. Using various concentration ratios of MWCNT-SH to Michael reagent, the thiolated nanotubes were cross-linked with benzoquinone.

It was observed that mats produced at a concentration of 10:1 benzoquinone:MWCNT-SH were significantly more brittle than the 5:1 composite – presumably due to a higher degree of cross-linking. Studies carried out at a concentration ratio of 0.1:1 did not form nanotube mats due to too low a degree of cross-linking. Under these conditions, small nanotube containing platelets formed which fragmented easily when manipulated with tweezers. Virtually the same
Figure 11: MWCNT-SH mat flexibility.
phenomenon was observed during control experiments in which attempts to form mats without a cross-linker were carried out. Fig. 10b shows a SEM image of a typical 5:1 mat giving a qualitative representation of the surface roughness. Fig. 11 shows a few examples of the degree of flexibility in the 5:1 mat. The mat can be folded just like paper and even rolled up into a scroll. This ease at which the mat can be manipulated allows for its potential to be used for flexible electronic applications. A well-documented property of CNTs is their tendency to flocculate in solution. This behavior facilitates cross-linking as the CNTs are brought into close proximity sterically favoring cross-linking which manifests itself in increased tensile strength. Our process actually benefits from areas of inhomogeneity for two reasons. Firstly, it ensures that all the thiol groups don’t react at once which would prevent tube-tube cross-linking and it also allows any unreacted thiol groups to react with the gold nanocrystals.

The mats, produced by the FFS method, varied in thickness between 80 and 270 µm as the domain size of cross-linked regions varied across the mat. Although less variation in uniformity would have been preferable, it had the advantage of providing increased surface area for nanoparticle attachment. The FFS method provides a modest degree of control, over the diameter and thickness, via funnel dimensions. Fig. 10a shows the size of a mat in comparison to a United States 25 cent coin. The optimal ratio by weight of benzoquinone to MWCNT-SH for mat synthesis was 5:1 in terms of producing a stable and flexible cross-linked mat.

Fig. 12 presents a graph of stress vs. strain measurements on the 5:1 and 10:1 mats. The tensile strength was measured to be 1.98 ± 0.18 MPa for the 5:1 mat. This demonstrated an improvement in the technique of covalently linked FFS based high carbon nanotube component films. In the case of the mats, variation in the measured strength is related directly to the variation in nanotube packing since the mats were not pressurized during or after the filtration process. The observations documented in this chapter indicate that the present approach, involving the creation of composites containing MWCNTs, shows significant promise in the future development of advanced materials. However, the behavior that the paradigm-shifting bulk mechanical properties, that the intrinsic properties measured for individual nanotubes suggests should be achievable, is some way off. In our experiments, it is clear that the low nanotube surface coverage of thiol groups limits the degree of cross-linking in the mat infrastructure. As noted, increasing the cross-linking reagent to form a mat in the ratio of 10:1 benzoquinone:MWCNT-SH resulted in brittle mats which increased the tensile strength to 3.63 ±
Figure 12: MWCNT-SH stress vs. strain.
Figure 13: MWCNT-SH I-V plot.
0.29 MPa. This increase was due to the increase in cross-linking. The main problem in obtaining tensile strength data for the 10:1 mat was the fracturing on clamping due to brittleness. However, when successfully clamped the stress–strain curve showed a low strain/high stress profile typical of brittle materials. The modest tensile strength observed for the mats may also be attributed partly to the strength of the carbon–sulfur bonds which is approximately 255 kJ/mol in comparison to the carbon–carbon double bond or single bond at 620 and 347 kJ/mol, respectively [55]. High resolution SEM studies show the presence of some interesting < 500 nm diameter tightly bound cables with lengths in the micron range which imply relatively efficient cross-linking. Fig. 13 shows the I–V characteristics of thiolated mats vs. the concentration ratios of benzoquinone:MWCNT-SH from 1:1 to 10:1. There is a general trend of increasing resistivity with increasing concentration of benzoquinone from 4:1 to 10:1. This may be explained in the simplest case by the increase in the amount of stress on the outer walls of the tubes which change the electronic transport properties of the individual tubes decreasing the efficiency of electron hopping from tube to tube as a function of benzoquinone concentration. The increase in cross-linking provides an alternative but not necessarily beneficial pathway for the electrons. This conclusion is supported by the stability of the 5:1 mat and the increased brittleness of the 6:1 to 10:1 mats. The 1:1 to 3:1 composites show a reverse trend which may be due to the optimization of electron mobility by intertube hopping and cross-linking. The results suggest that the best mats in terms of conductivity may not be the preferred mats in terms of mechanical properties such as flexibility.

X-ray photoelectron spectroscopy (XPS) provided confirmation on the change in binding energy from the unreacted thiolated nanotubes to the cross-linked mat. A Mg anode and photon energy 1253.6 eV were used in the XPS characterization. Figure 14 shows that the S2p binding energy for the CNT-SH mat was 164.4 eV (S2p$_{1/2}$). This binding energy is consistent with the formation of thioether bonding between the sulfur on the nanotube and the carbon of the benzoquinone cross-linker. The unreacted CNT-SH had a binding energy lower than usual for unbound thiols at 163.9 eV (S2p$_{3/2}$) however this appears to be typical for samples of MWCNT-SH [56-58]. To investigate the carbon environments that occur we conducted an analogous reaction in which MWCNT-SHs were replaced with benzenethiol. The carbonyl group $^{13}$C NMR peak was downshifted to 207 ppm (Fig. 16). However, the combination of the low abundance of thiol groups on the surface of the nanotubes (0.5 – 1%) and the 1.1% of $^{13}$C nuclei downshifted
Figure 14: MWCNT-SH XPS spectra
from the carbonyl group on the 1,4-cyclohexanedione was enough to consign the carbonyl shift to noise in the presence of the abundant $^{13}$C MWCNT nuclei. Due to the randomness of cross-linking, a significant number of thiol groups remain unreacted and are available for gold nanoparticle attachment. Gold particles were chosen because of the affinity of gold to bind to sulfur and the nanocrystals are, due to strong electron scattering, easily observed by SEM. Figure 15a shows a SEM image of a section of a mat in which a roughly semicircular section, centered near the bottom right-hand corner, can clearly be seen to be lighter than the upper left-hand region due to the attachment of gold nanoparticles. This was a region where a drop of gold nanocrystal solution had been deposited and washed demonstrating that the mat could be selectively functionalized. Figure 15b shows a high magnification image of a gold-coated section of the surface giving a useful qualitative visual indication of the extent to which the surface can be covered by gold particles. The Raman data show some interesting features. Firstly, the ratio of $I_D/I_G$ exhibits a general decreasing trend on going from the raw MWCNT-SH powder to the mat and to the mat with gold attached. This trend indicates an increase in order from the tubes due to bond formation. Figure 17 indicates that cross-linking of thiolated carbon nanotubes together with subsequent attachment of gold nanoparticles results in a blue shift in the D- and G- bands at each phase of the process. The Raman spectra for the 5:1 MWCNT mat exhibited 3 and 6 cm$^{-1}$ shifts of D- and G-bands respectively, when compared with the MWCNT-SH powder. The recruitment of gold nanoparticles resulted in additional 7 and 6 cm$^{-1}$ shifts. Shifts in these two Raman features are indicative of stress and strain in the nanotube structure [35]. The covalent cross-linking of CNTs results in increased stresses and strains of the tubes as they become bound to each other. The addition of spherical gold nanoparticles adds further stress to the nanotubes as it has a large electron density giving the effect of decreasing the graphitic nature of the tubes by inducing sp$^3$ character into the system. In the examination of MWCNT-SH we find that there is a very weak C–S vibration peak, $v$(CS), at 412 cm$^{-1}$ and a stronger S–H vibration $v$(SH) at 2559 cm$^{-1}$ [59]. The mat exhibits a $v$(CS) peak at 410 cm$^{-1}$ and a reduction in the intensity of the $v$(SH) peak at 2559 cm$^{-1}$. The mats with gold attached exhibits a further reduction in the intensity $v$(SH) and a broad peak from 305 to 320 cm$^{-1}$ which relates to the Au–S vibration $v$(AuS). An additional peak at 673 cm$^{-1}$ can be attributed to the $v$(CS). The asymmetric stretch of C=O in 1,4-cyclohexadione was observed at 1788 cm$^{-1}$ which was close to the literature value [60], and the C–S–C skeletal deformations at 326 and 384 cm$^{-1}$ were shifted
Figure 15: MWCNT-SH + Au NP SEM image
from the literature values [61]. The nature of attachment of the gold to nanotubes meant that surface enhanced Raman spectroscopy would not eliminate the v(SH) completely because with 5:1 cross-linking there are still a number of free thiols left, but there is a reduction in the intensity. When gold is attached to the surface of the mat, the I–V characteristics show an increased resistance. Figure 18 shows the results for the 5:1 mat with and without gold nanocrystals attached. The effect can be attributed to the bond formation between the gold and thiol and the electron dense gold nanocrystals which are known to transfer their electron density to the n* states of the MWCNTs.

Furthermore, it was observed under SEM that there were tightly-wound CNT bundles in our mats (Fig. 19) suggesting successful cross-linking through the Michael addition reaction scheme. These cross-linked “ropes” were several hundred nanometers in width and had lengths in the micrometer range. Such bundles were not observed in unreacted MWCNT-SH.

In summary, we have developed a relatively straight-forward approach to creating carbon nanotube mats to which nanoparticles can be readily attached. The intrinsic intra-nanotube binding in thin films has been achieved by chemical cross-linking without the need for polymer grafting. Furthermore, we have produced a useful surface to which nano-structures, in this case 5.7 ± 0.3 nm gold crystals, can be chemically attached. The materials preparation approach developed here is relatively simple and ideally suited to the creation of new and novel catalytic structures as well as electrode surfaces and sensing elements. The facility with which gold nanoparticles have been integrated with the structures indicates that it is a general method for attaching other materials such as nanocrystals and functional moieties. This approach can be readily scaled up for industrially viable processes involving such carbon nanotube mats. We are currently exploring the use of other cross-linkers such as bis-maleimido based synthons to improve the electrical and mechanical properties of these types of mats which would make them useful as flexible electrodes in thin-film batteries and as components in flexible photovoltaic devices.
Figure 16: $^{13}$C NMR spectra for benzenethiol/benzoquinone reaction.
Figure 17: MWCNT-SH Raman spectra

1 - MWCNT-SH Powder
2 - 5:1 MWCNT-SH Mat
3 - 5:1 MWCNT-SH Mat, Gold Attached
Figure 18: MWCNT-SH + Au NP I-V plot.
Figure 19: Tightly-bound MWCNT-SH bundles.
CHAPTER 3: ASSEMBLY OF MWCNT-NH₂ MATS

An alternative route to synthesizing carbon nanotube mats is through amine functionalized multi-walled carbon nanotubes (MWCNT-NH₂) and the imine formation pathway. One possible benefit of cross-linking nanotubes through this method is that the conjugated bonds on the benzoquinone molecule are retained which could help the conductivity in such materials. Another benefit is that the amine functionalized CNTs can be integrated with palladium nanoparticles to create a hydrogen sensor, which will be discussed in the next chapter. The amine moieties are better suited for such applications than the thiol functionalized tubes as the thiol groups may poison the palladium nanoparticles and inhibit its reaction with H₂.

![Figure 20: Imine formation reaction scheme.](image)

3.1 Experimental

MWCNTs-NH₂ were purchased from Nanocyl SA while dimethylformamide (DMF) and benzoquinone were purchased from Sigma-Aldrich. According to Nanocyl specifications, these nanotubes have an average diameter of 9.5 nm, average length of < 1 µm, amine coverage of < 0.5%, and a carbon purity of > 95%.

3.1.1 MWCNT-NH₂ Mat Formation

MWCNT-NH₂ (20 mg) were dispersed in DMF (15 mL) by sonication. In a separate reaction vessel, benzoquinone (100 mg) was dissolved in DMF (10 mL). Acid was also added to the DMF/benzoquinone solution so that it had a pH of 5 as the reaction is acid catalyzed. Using a syringe, the benzoquinone solution was slowly injected into the nanotube suspension at 75°C for
24 hours. Mats were formed using the filtration-from-suspension (FFS) technique where the nanotube suspension is vacuum filtered onto filter paper and then allowed to dry. A heat gun was utilized to maintain the suspension temperature at 75°C during the filtration. The resulting mat was then rinsed with solvent to remove unreacted benzoquinone and dried in a desiccator.

3.1.2 Tensile Strength Measurements
Tensile strengths of the CNT mats were measured using a Thümler TH 2730 instrument. A section a mat was cut into known dimensions and was placed in the sample holder of the instrument. The sample was then stretched at a rate of 1 mm per minute while concurrently measuring elongation (mm) and the force applied (N) until a failure point was reached.

3.1.3 I-V Measurements
Four-wire resistance measurements were performed on the MWCNT-NH$_2$ mats of different cross-linker:MWCNT ratios (1:1, 5:1, and 10:1) using the force-current and measure-voltage (FCMV) testing method. Four-wire testing was used because this technique takes into account the resistance from instrument wiring and results in more accurate measurements of the sample. Mats were cut into thin strips of known dimensions and were placed perpendicularly to the axis of the 4 Pt wires. In FCMV testing, a known amount of current is applied to the mat and the voltage is measured. Our measurements consisted of applying a current in the range of -1 mA to 1 mA at increments of 0.1 mA with multiple sweeps, resulting in the collection of 43 data points. Using LabVIEW software, the current (I) is then plotted as a function of voltage (V).

3.1.4 Scanning Electron Microscopy
The mats were examined using a FEI Nova 400 Nano Scanning Electron Microscope. Low magnification images were recorded using an Everhart Thornley Secondary Electron Detector (ETD) and high magnification images were acquired using the Through Lens Detector (TLD) in the immersion mode at an accelerating voltage of 7 keV.

3.1.4 Raman Spectroscopy
For the Raman characterizations, a Renishaw inVia micro-Raman system with 785 nm excitation wavelength was used (0.5 mW) and 50x objective lens.
Figure 21: MWCNT-NH$_2$ stress vs. strain
3.2 Results and Discussion

There was a direct correlation between mat tensile strength and cross-linker amount suggesting that successful cross-linking had occurred as shown in Figure 21. A 1:1 ratio of benzoquinone to MWCNT produced a mat of the lowest tensile strength of 0.94 ± 0.17 MPa. The 10:1 ratio yielded a mat with the highest tensile strength of 6.06 ± 0.14 MPa but at the loss of flexibility. The 5:1 composite had a tensile strength of 3.21 ± 0.24 MPa while still maintaining some degree of flexibility. Despite having an amine coverage of < 0.5%, there was still an improvement in the tensile strength over MWCNT-SH mats we had produced earlier (3.21 vs. 1.98 MPa). This increase in tensile strength can be attributed to the higher bond energy of the imine in comparison to the thioether bond (418 kJ/mol vs. 255 kJ/mol) [55, 62]. It was also determined that there was an improvement in conductivity in the MWCNT-NH$_2$ mats over the MWCNT-SH counterpart. For five samples, the average conductivity of the MWCNT-NH$_2$ and MWCNT-SH mats were 14.8 ± 0.74 S/cm and 5.0 ± 0.25 S/cm, respectively.

4-wire resistance measurements were also performed on mats with concentration ratios ranging from 1:1 to 10:1 (Fig. 22). It was determined that increasing the amount of benzoquinone increased the resistivity of the mat. This trend was similar to the resistivity measurements we reported for MWCNT-SH mats. The higher resistivity demonstrates how increasing the number of covalent linkages between nanotubes does not necessarily create beneficial pathways for electrons. The data suggests that a specific range of covalent pathways is needed for optimal electron transport and that increasing the degree of cross-linking beyond this range reduces mat conductivity.

Additionally, IR spectroscopy was performed on the reaction product of 2-naphthylamine and benzoquinone. Due to the low percent functionalization on the MWCNT-NH$_2$, it was difficult to see imine peaks so IR spectroscopy was performed on an analog reaction. It was observed that there was a peak at 1679 cm$^{-1}$ corresponding to an imine bond and no ketone peak from benzoquinone, indicative of successful imine formation (Fig. 23).
Figure 22: MWCNT-NH$_2$ conductivity.
Figure 23: IR spectra for 2-naphthylamine and benzoquinone reaction.
Due to the need for a cleaner substitute to fossil fuels, many alternative sources for energy have been explored. One promising option to fossil fuels is hydrogen. Continued research and development is needed to improve current H\textsubscript{2} storage technology and transform it into a viable and efficient substitute to fossil fuels. Gas sensing is one aspect of the field that could be further improved as it is necessary for proper device management and safety precautions as hydrogen gas is flammable in air at concentrations as low as 4\% [63]. Current hydrogen sensors consist of rigid inorganic substrates such as glass, quartz, and silicon wafers. The rigidity of such substrates could prevent the use of hydrogen storage in applications that require flexible materials [53]. There has some been some success with the integration of carbon nanotubes (CNTs) into sensors but the technology is still in its infancy. It is well known that nanotubes have excellent electrical and mechanical properties that make them a very intriguing material [23, 25, 64]. Carbon nanotube mats are a promising substitute to such traditional substrates as they are light-weight, conductive, and flexible. The use of palladium nanoparticles (Pd NPs) in sensing technology is also promising as they have selective hydrogen absorption and can detect trace amounts of H\textsubscript{2} gas. There has been some success in the past in the production of nanotube/palladium based hydrogen sensors. Much of the previous work involved the use of SWCNTs and electrodeposition of Pd NPs onto the nanotubes.

In this work, we create a H\textsubscript{2} sensor using MWCNTs which are cheaper to produce than SWCNTs. Additionally, we demonstrate a method in which no Pd electrodeposition is needed. Subsequently, this alternative method makes the production of CNT-based H\textsubscript{2} sensors not only flexible and light-weight, but also industrially viable. We previously reported the successful synthesis of thiol functionalized multi-walled carbon nanotube (MWCNT-SH) mats via a Michael addition reaction mechanism [65]. To create the sensor, we use a similar reaction scheme which still uses benzoquinone (BQ) as the cross-linker. However, we utilize amine functionalized multi-walled carbon nanotubes (MWCNT-NH\textsubscript{2}) instead of MWCNT-SHs to
Figure 24: MWCNT-NH$_2$/Pd composite flexibility.
prevent thiol poisoning of the Pd NPs. Past attempts at creating a sensor using thiol functionalized nanotubes were unsuccessful, probably due to thiol poisoning of the palladium nanocrystals.

4.1 Experimental

The palladium nanoparticles were purchased from Sigma-Aldrich. According to their specifications, the Pd NPs had diameters of less than < 25 nm and had a purity of 99.9%. The MWCNT-NH$_2$ were purchased from Nanocyl SA. According to their specifications, these nanotubes have an average diameter of 9.5 nm, average length of < 1 µm, amine coverage of < 0.5%, and a carbon purity of > 95%. Pure hydrogen gas and the 95:5 N$_2$:H$_2$ gas mixture were purchased from Airgas, Inc.

4.1.1 MWCNT/Pd NP Mat Synthesis

The synthesis of the MWCNT-NH$_2$ mats (Fig. 24) was similar to the method we had used and reported earlier to produce our MWCNT-SH mats. In a reaction vessel, 20 mg MWCNT-NH$_2$ was suspended and dispersed via sonication in 20 mL of DMF. 100 mg of BQ was added to the solution so that the cross-linker to nanotube ratio was 5:1. A small amount of acid was then added to the solution until the pH was approximately 5. The acid acts as a catalyst in the imine formation reaction. It is important that the solvent have a pH of 5 as a higher or lower pH will inhibit the imine formation reaction. The resulting mat was then stored in a desiccator under an inert atmosphere.

To create the nanotube mats with integrated Pd NPs, the nanoparticles were first dispersed in a small amount of dichloromethane using a probe sonicator. This mixture was then combined with the MWCNT-NH$_2$/DMF solution and heated to 75°C which helped to facilitate the electrostatic recruitment of the Pd NPs onto the nanotubes (Fig. 25). This step is necessary as it prevents the loss of Pd NPs during the FFS step. It also allows for a greater number of Pd NPs to be integrated within the CNT mat as well as on its surface.

4.1.2 Resistance Measurements

The resistance measurements were performed using the setup shown in Figure 26. The setup consisted of cutting a known section of the MWCNT-Pd mat and securing it on a glass substrate. Four silver wires (0.25 mm diameter) were fixed to the mat using silver paint. These wires were then affixed to an HP 3457A multimeter. Next, the MWCNT-Pd mat and glass substrate were placed in a glass chamber in which hydrogen gas was flowed through at approximately 2 psi.
Figure 25: MWCNT-NH$_2$ + Pd SEM/TEM images.
Figure 26: H₂ sensing setup.
Resistance was measured as a function of time using LabVIEW software. The hydrogen gas was allowed to flow through the chamber at intervals of 10 minutes. The time interval which the hydrogen gas was turned off was also 10 minutes.

4.1.3 Scanning Electron Microscopy
The mats were examined using a FEI Nova 400 Nano Scanning Electron Microscope. Low magnification images were recorded using an Everhart Thornley Secondary Electron Detector (ETD) and high magnification images were acquired using the Through Lens Detector (TLD) in the immersion mode at an accelerating voltage of 7 keV.

4.1.4 Raman Spectroscopy
The laser used for Raman characterization was a Toptica Photonics DL 100 grating-stabilized diode laser emitting 80 mW at 785 nm with a narrow linewidth (< 0.4 cm-1). The power at the sample is between 1.5-5 mW. The Raman spectrograph was a Horiba JY LabRAM HR800 UV 800 mm focal length microRaman system using a holographic notch filter to couple the laser into the microscope sample area (Olympus BX40) and reject the laser scatter from entering the spectrograph stage. The detector is a Wright 1024 x 256 pixel EEV open electrode CCD. The objective lens used was a Leica HC PL Fluotar 50X NIR sensitive objective with a working distance of 0.5 mm.

4.2 Results and Discussion
It is well known that palladium’s crystal lattice will expand by approximately 3% in the presence of hydrogen gas to form palladium hydride [66, 67]. It is also well known that this reaction is reversible [68]. When the palladium nanoparticles are integrated within the mats and in the presence of H₂, its lattice expansion forces the nanotubes to bend and change the amount of nanotube-nanotube junctions. We have previously shown that increasing the amount of nanotube-nanotube junctions will change the conductivity of the mat [65]. Previous work done by Kong et al. [51] and Khalap et al. [69] demonstrated that palladium functionalized CNTs will exhibit a decrease in conductivity when exposed to hydrogen. This increase in resistance is due to the decrease in the work-function of the palladium as it is exposed to hydrogen and becomes palladium hydride. The lower work-function allows more electrons to travel from the palladium hydride to the nanotube which decreases the amount of hole-carriers in the CNT and subsequently decreases conductivity. Our CNT mat sensor operates using the same concept by exhibiting a change in resistance when exposed to hydrogen gas.
Figure 27: MWCNT-NH$_2$, 2x1 mm surface deposited Pd NP resistance measurements
Figure 28: MWCNT-NH$_2$, 1x1 mm surface deposited Pd NP resistance measurements.
An experiment was performed where 10 mg of Pd was suspended in a small amount of dichloromethane and deposited onto the surface of the MWCNT-NH$_2$ mat using a pipette. The Pd NPs were deposited on a selected area of the mat (2x1 mm and 1x1 mm). Areas in which the Pd NPs are deposited can be controlled by covering parts of the mat with a protective layer of paper. It was observed that the resistance in the mats increased by approximately 0.4 Ω under both 100% and 5% H$_2$ concentrations when Pd NPs were surface deposited on a 2x1 mm area (Fig. 27). When Pd NPs were deposited on a 1x1 mm area, the resistance increased by about 0.1 Ω in the 100% H$_2$ environment. In the 5% H$_2$ environment, the sensor was unable to detect the presence of H$_2$ as the resistance remained linear (Fig. 28). This observation suggests that there is a direct correlation between Pd NP loading and sensor effectiveness.

We also investigated the effect of integrating the Pd NPs within the MWCNT-NH$_2$, as opposed to just surface depositing them. To create the nanotube mats with integrated Pd NPs, the nanoparticles were first dispersed in a small amount of dichloromethane using a probe sonicator. This mixture was then combined with the MWCNT-NH$_2$/DMF solution and heated to 75 ºC which helped to facilitate the electrostatic recruitment of the Pd NPs onto the nanotubes. This step was employed to prevent the loss of Pd NPs during the filtration-from-suspension procedure. It also allowed for a greater number of Pd NPs to be integrated within the CNT mat as well as on its surface.

For the Pd NP integrated mats, it was determined there was a decrease in resistance when hydrogen gas was flowed through the reaction chamber (Fig. 29). As hydrogen is absorbed onto the Pd NPs and a palladium hydride complex is formed, the nanoparticles increase in size which adds strain to the surrounding graphitic lattice of the CNTs, but also increases the surface area of the NP available to interact with surrounding nanotubes, essentially acting as an additional cross-linking agent. This provides a path for electrons to travel increasing the conductivity of the mat. When the hydrogen is turned off, it was observed that the resistance increased, returning back to the baseline. This is attributed to the fact that the palladium and hydrogen reaction is reversible. The Pd-integrated MWCNT-NH$_2$ mat exhibited about a 3 Ω decrease in its resistance when exposed to 100% H$_2$. A control experiment was performed where the resistance was measured on a MWCNT-NH$_2$ mat without Pd NPs and there were no significant changes in the mat conductivity when the H$_2$ was turned on or off. The decrease in resistance is intriguing because the application of palladium nanoparticles to p-type materials like CNTs is known to increase the
Figure 29: MWCNT-NH₂ + Pd NP integrated resistance measurements.
Figure 30: Force-induced resistance changes
Figure 31: MWCNT-NH$_2$ + Pd integrated 5%/100% H$_2$ resistance measurements
resistance of the tubes due to electron transfer at the Pd-CNT interface. The decrease in resistance observed with our samples may be explained through the increase in CNT-Pd-CNT junctions that are created with the lattice expansion in the Pd NPs. Also, an increase in the Pd NP size would also cause an increase in CNT-CNT intertube junctions by forcing a reduction in the space between the tubes. We demonstrated the effect of increased CNT-CNT intertube junctions by performing a simple experiment where a non-conductive weight of 1.6 g was placed on a mat at intervals of 10 seconds while the resistance was measured (Fig. 30). The resistance decreased slightly ($\approx 0.3 \ \Omega$) when the weight was applied and returned to baseline when it was removed. This decrease in resistance suggests that by applying a force, additional nanotube-to-nanotube junctions are created to increase mat conductivity.

The gas sensing experiment was repeated with a 5% $H_2$ / 95% $H_2$ gas mixture on the Pd integrated MWCNT-NH$_2$ (Fig. 31). Although the change in resistance was smaller, the sensor was still able to detect the presence of hydrogen. There was a decrease in the mat’s resistance as $H_2$ gas was flowed through the testing chamber and the mat’s resistance returned to baseline when the gas was turned off. The smaller decrease in resistance (2.5 vs. 1 $\Omega$) can be attributed to a smaller lattice expansion in the Pd NPs or a smaller amount of induced CNT-CNT junctions due to a decreased amount of $H_2$ exposure.

Raman spectroscopy was also performed on unreacted MWCNT-NH$_2$, the 5:1 MWCNT-NH$_2$ mat, the Pd NP surface deposited MWCNT-NH$_2$ mat, the MWCNT-NH$_2$ integrated Pd NP mat, and MWCNT-NH$_2$ integrated Pd NP mat in an $H_2$ environment. The spectra were analyzed and the $I_D/I_G$ ratios are shown in Figure 32. It is well known that the $I_D/I_G$ ratio describes the defect density of the carbon nanotube and that there is a direct correlation between the $I_D/I_G$ ratio and the amount of defects. Our results showed that the unreacted MWCNT-NH$_2$ had an $I_D/I_G$ ratio of 1.645 but decreased to 1.547 with the cross-linked mat. This decrease in disorder can be attributed to the loss of immobilized lattice fragments on the tubes and the subsequent covalent cross-linking of the MWCNT-NH$_2$. There is a further decrease in the $I_D/I_G$ ratio to 1.517 and 1.513 when Pd NPs are either integrated throughout the mat structure or surface deposited, respectively. This decrease is due to the nanoparticles affinity to electrostatically bond to the defect sites of the nanotube. There were also shifts in the D- and G-bands going from the unreacted MWCNT-NH$_2$ to the MWCNT-NH$_2$ mat of approximately 1 and 3 cm$^{-1}$, respectively.
This is expected as shifts in the D- and G-band are indicative of stress and strain [33, 34] on the nanotubes as they become cross-linked.

In summary, we have developed a novel method of creating a light-weight and flexible MWCNT-NH$_2$/Pd nanoparticle H$_2$ sensor (Fig. 33). This method is an improvement over previous nanotube-based H$_2$ sensors as it uses a covalently cross-linked flexible MWCNT mat as both the substrate and sensor. In addition, palladium nanoparticles may be either integrated within the mat or surface deposited without additional reaction schemes. It was demonstrated that the mat’s H$_2$ sensing effectiveness is directly correlated with Pd NP loading and that the sensor could detect H$_2$ concentrations as low as 5%. It was also observed that the conductivity will increase in Pd integrated MWCNT-NH$_2$ mats.
Figure 32: MWCNT-NH$_2$ analogs Raman spectra

1) Unreacted MWCNT-NH$_2$
2) 5:1 MWCNT-NH$_2$ mat
3) Pd NP surface deposited mat
4) Pd NP integrated mat
5) Pd NP integrated mat under H$_2$
Figure 33: MWCNT-NH$_2$/Pd NP sensor
CHAPTER 5:
CARBON NANOTUBE-BASED COMPOSITES AND THEIR USE IN PHOTOVOLTAIC APPLICATIONS

In addition to synthesizing carbon nanotube mats via the covalent bonding of benzoquinone, we also investigated the cross-linking of CNTs through electrostatic interactions with nanoparticles. Additionally, we explored the integration of CNTs into a cellulose matrix and their application in photovoltaics.

5.1 Electrostatic Cross-linking of Carbon Nanotubes via Pd NPs

It is also possible to cross-link CNTs using the electrostatic interactions of nanoparticles. This alternate method of synthesizing mats is convenient as no cross-linker or chemical reaction is needed, potentially making mat synthesis even more cost-effective and industrially viable. Here we report the synthesis of mats via the electrostatic recruitment of oleylamine functionalized palladium nanoparticles (Fig. 34). All chemicals used for the Pd NP synthesis were purchased from Sigma-Aldrich. Pristine MWCNTs were purchased from Nanocyl SA. According to their specifications, the tubes had an average diameter of 9.5 nm, an average length is 1.5 μm, and a purity of > 95%.

5.1.1 Palladium Nanoparticle Synthesis

The synthesis of the oleylamine-mediated 4 nm Pd NPs was developed by Mazumder et al. All reactions were performed under an inert atmosphere. In short, 75 mg of Pd(acac)2 was dissolved in 15 mL oleylamine and the resulting mixture was heated at 60 °C for 10 min. Next, 300 mg of a borane tributylamine complex dissolved in a small amount of oleylamine, was injected into the Pd solution and heated to 90 °C for 1 hour. After cooling down to room temperature, the Pd NPs were precipitated out with 30 mL ethanol and centrifuged. The Pd NPs were then dispersed in hexane. [70]. Confirmation of successful synthesis of the particles was determined by TEM.
Figure 34: MWCNTs + oleylamine functionalized Pd NPs TEM images
Figure 35: Electrostatically cross-linked MWCNT TEM images
5.1.2 MWCNT/Pd Mat Synthesis

The Pd NP powder was added to a mixture of 20 mg MWCNT suspended in 20 mL of sparged DMF. This solution was then sonicated for approximately 15 – 20 minutes to ensure even dispersion of the Pd NPs. Using the same filtration-from-suspension technique described earlier, carbon nanotubes mats were produced and stored in a desiccator.

5.1.3 Results and Discussion

On the macroscopic level, the resulting mats were similar to the other mats in appearance. Under high magnification, successful cross-linking was apparent as very tight nanotube bundles of ≈100 nm diameters, with integrated Pd NPs, were observed under a TEM (Fig. 35). Similar tight bundles were seen in the cross-linking of MWCNT-SHs with benzoquinone. When a 5:1 ratio of BQ:MWCNT was added in addition to the Pd NPs, the resulting mat was more rigid than an analog mat without the BQ. This increase in rigidity is a characteristic of an over cross-linked material and suggests that the Pd NPs can also act as a cross-linker.

5.2 MWCNT-Cellulose Composites for Dye-Sensitized Solar Cells

We have also investigated MWCNTs embedded in a cellulose (Fig. 36) matrix as a possible useful nanotube-based composite. Cellulose is an intriguing polymer for many reasons. It is a renewable resource, environmentally friendly, and cost-effective. Using such cellulose-based composites in dye-sensitized solar cells (DSSCs) would also allow these devices to be flexible and light-weight.

![Cellulose structure](image)

Figure 36: Cellulose structure
Figure 37: Dye sensitized solar cell schematic.
Figure 38: Spin-coating instrument.
DSSCs (also known as Grätzel cells) were first developed by Michael Grätzel and Brian O’Regan in 1991 as an alternative to silicon-based photovoltaics. The device consists of a semiconductor, a photosensitized anode, and an electrolyte. Due to its low cost to manufacture, DSSCs are a promising technology. Although the conversion efficiency is lower than other photovoltaic devices, its cost effectiveness still makes it a competitive alternative. Grätzel cells (Fig. 33) consist of titanium dioxide (TiO$_2$) nanoparticles which are covered in a photosensitive dye that are then placed between a cathode and an anode in an electrolyte solution containing a redox couple (I$^-$/I$_3^-$). As sunlight penetrates the transparent anode, it excites the valence electrons of the photosensitive dye into the conduction band of the TiO$_2$ nanoparticles. Due to an electron concentration gradient, electrons travel to the conducting anode where they are transported to an external circuit. The photosensitive dye replaces its lost electron by oxidizing iodide into triiodide. In turn, the triiodide can take an electron from the counter electrode. This process is cyclical and can be repeated when sunlight promotes another electron from the photosensitive dye [71].

5.2.1 Cellulose Composites
Before any attempts at introducing nanotubes into the cellulose matrix, we first made composites consisting solely out of cellulose to test their thermal stability. It has been previously shown that inorganic compounds could contribute to cellulose degradation at high temperatures [72]. Thus, we wanted to test the thermal stability our cellulose composites as heat could be detrimental to our photovoltaic device.

Cellulose, dimethylacetamide (DMA), and LiI were purchased from Sigma-Aldrich. The spin-coating device was provided by Specialty Coating Systems (Fig. 38). The cellulose (16 g) was thoroughly dissolved in an ionic solution consisting of 12 g lithium chloride and 100 mL DMA resulting in a viscous, whitish-yellowish solution. This cellulose pulp-containing solution was then poured onto a silicon wafer with a 2-inch diameter until the substrate’s surface was covered. The wafer was then spun using the spin coater at 800 rpm with a ramp time of 25 seconds. A second spin cycle was started while concurrently spraying the cellulose film with small amounts of water to solidify the film. The cellulose composite was then removed from the silicon substrate and stored in a desiccator. In the end, the film was spun for a total of 3 minutes. This procedure produced semi-translucent, thin films with an average thickness of $\approx 11 \mu$m and a relatively smooth surface (Fig. 39).
Figure 39: SEM image of cellulose film surface.
Figure 40: Cellulose degradation.
The cellulose thin films were heated until a point of visible degradation to explore the thermal stability of the composites. To ensure even heat distribution throughout, the films were placed in Petri dishes and heated over a hot plate with digital controls. Starting at 25 ºC, the temperature of the hot plate was increased by 10 ºC every 3 minutes. It was observed that the thermal degradation of the cellulose films commenced at 125 ºC. Although there was minor “browning” on the edges of the film, the overall structure maintained its flexibility. It was not until 125 ºC that significant oxidation was prevalent and the film began to lose its flexibility (Fig. 40).

5.2.2 TiO\textsubscript{2} Recruitment to MWCNT

In order for electrons to be transported from the TiO\textsubscript{2} to the MWCNTs in a DSSC, titania nanoparticles need to be attached to the nanotubes. The simplest method of achieving this is through electrostatic interactions. In this process, a stock solution of 100 mg TiO\textsubscript{2} (< 25 nm, Sigma-Aldrich) in 100 mL DMA was prepared. 20 mg of MWCNTs were added to 20 mL of the TiO\textsubscript{2}/DMA solution and sonicated for 30 minutes. The successful electrostatic recruitment of TiO\textsubscript{2} onto the CNTs was verified under high magnification using SEM.

5.2.3 Synthesis of CNT-Cellulose Composites

16 g of cellulose, 12 g LiCl was dissolved in 100 mL of DMA. Next, 5 mg of MWCNTs/TiO\textsubscript{2} was added to the solution and sonicated for an hour. The composite was made using the same procedure used to make the cellulose thin films. In short, the resulting mixture was poured on to a silicon wafer, placed in the spin-coater, and spun for one cycle. To harden the composite, it was spun for a second cycle while concurrently being sprayed with small amounts of water. Successful embedding of the CNTs into the cellulose matrix was verified by SEM.

The resulting films were black, semi-transparent, and flexible with a uniform CNT distribution throughout the composite (Fig. 41). SEM showed a smooth surface with some rough areas, which indicated that some fibrous cellulose domains were still present (Fig. 42).

5.2.4 1st generation CNT-Cellulose Dye Sensitized Solar Cell

Our original MWCNT-based DSSC was designed to be a multilayer system. It was designed to have multiple layers in order to have sufficient separation between the top and bottom layers to create an electrode potential in the device. In the end, this first generation DSSC we developed had a total of four layers (Fig. 43).
Figure 41: MWCNT/cellulose composite flexibility and semi-transparency.
Figure 42: SEM image of cellulose, MWCNT, and TiO$_2$ composite surface.
It has been previously reported that indium tin oxide (ITO) plates had been used as the semiconducting top layer (or positive terminal). ITO is typically used because of its highly conductive properties [71]. Subsequently, we decided to incorporate ITO particles into our top layer as well. ITO was mixed with the cellulose pulp in DMA to produce a viscous mixture and was sonicated for 30 minutes. It was determined that 200 mg of ITO in 10 mL of the cellulose/ionic/DMA solution (or cellionic solution) was the optimal ratio to make the top layer conductive as cellulose, by itself, is not conductive. This was also the optimal ITO:cellulose ratio for producing a mixture viscous enough to use on the spin coater.

The second layer was composed of 200 mg TiO$_2$, 3mM N719 (Fig. 44), 10 mL cellionic solution, and a 1:1 ratio of the I/I$_3$ redox couple. N719 is a ruthenium-based photosensitive dye that was provided by Solaronix. It was imperative to allow time for the photosensitive dye to absorb onto the surface of the TiO$_2$ because this is where the redox potential of the iodide and triiodide cycled back and forth to facilitate the conversion of N719 from the excited state back to the ground state. This was achieved by making a 3 mM solution of N719 in absolute ethanol, adding it to the TiO$_2$, sonicating for 2 hours, and then allowing the ethanol to evaporate overnight. The dye-covered TiO$_2$ was then sonicated in 10 mL of cellionic solution until dispersed.

The third cellulose-based layer contained equal amounts of iodide and triiodide. This layer’s purpose was to act as a divider and maintain a charge separation between the top and lower layers and allow the generated electrons to migrate.

The fourth layer served as the negative terminal. To achieve this, MWCNTs functionalized with negatively-charged carboxyl groups (MWCNT-COOH) were integrated into the layer. 100 mg of MWCNTs was added into the iodide-cellulose solution and this mixture was sonicated in 100 mL of DMA for 30 minutes. Following the previously described spin-coating procedure, this became the bottom negative-layer plate/terminal. Conductivity measurements were performed and an I-V graph was plotted for the 1$^{st}$ generation DSSC (Fig. 45). It was determined that the device had a charging effect as the plot had hysteresis characteristics. It was also determined that the device was non-functioning as the efficiency was calculated to be essentially 0%. Several modifications were made to create a 2$^{nd}$ generation DSSC.
Figure 43: Original 4-layer DSSC prototype
Figure 44: N719 photosensitive dye
Figure 45: 1st generation DSSC I-V plot
5.3.4 2nd generation CNT-Cellulose Dye Sensitized Solar Cell

There were several potential issues in the original DSSC prototype that could have prevented the device from functioning and would have to be addressed in the 2nd generation DSSC (Fig. 46). One possible issue was that the top layer was too thick and not conductive enough. We attempted to address this by making the anode a thin layer consisting solely of ITO. In hindsight, the incorporation of non-conducting cellulose into the anode would have just inhibited electron transport. This new anode was also much thinner than the original which would allow the electrons to travel a shorter distance and hopefully improve efficiency.

Additionally, the second layer was integrated with 24 μm glass beads (refractive index of 1.95) which would allow photons to enter the beads and exit at various angles (Fig. 47). This would allow the dye-covered TiO$_2$ particles deep within the cellulose matrix to receive photons where they would not normally be able to receive it, potentially increasing the conversion efficiency and allowing for a much thicker sensitizer layer. The second layer also consisted of a 3:1 ratio of I$^-$/I$_3^-$. An intentional concentration gradient of I$^-$/$I_3^-$ was created between the second and bottom layer to help facilitate the cyclical reaction of the redox couple and hopefully improve efficiency.

Furthermore, the separation or third layer in the original design may have reduced the efficiency at which the electrons could migrate between layers especially since cellulose is not a good conductor. Therefore, the third layer consisting of cellulose, iodide, and triiodide was omitted. With the third layer removed, the new bottom layer consisted of MWCNT-COOH and a 3:1 ratio of I$_3^-$/I$^-$ in a cellulose matrix. After all these modifications, the resulting device was much thinner and flexible (Fig. 48).

Conductivity measurements were performed and an I-V graph was plotted for the 2nd generation DSSC (Fig. 49). Like the 1st generation, the device did exhibit charging characteristics as the I-V plot was non-linear. However, the modifications proved to be successful as the device’s efficiency was calculated to be 0.2%. Although this percent is low, it is still promising as this modified version was able to produce a small amount of current unlike the 1st generation DSSC. The results are also promising because DSSCs, as a whole, are still an emerging technology whose record efficiency of 11% is also relatively low compared to other types of photovoltaics [73].
Control experiments were performed on the 2\textsuperscript{nd} generation DSSC without the N719 dye under light and dark conditions to determine if the photosensitizer was the source for the small change in power when doing multiple sweeps on the I-V plot (Fig. 50). However, these characteristics still existed in both samples suggesting that other components were the cause for the change in power.

Figure 46: Second generation DSSC

**Modifications:**
- Glass beads
- I\textsuperscript{-}/I\textsubscript{3}\textsuperscript{-} conc.
- Removed separation layer
- Used thinner ITO layer

MWCNT-COOH, cellulose layer, higher conc. I\textsubscript{3}\textsuperscript{-}. Titania, dye, glass beads, higher conc. I\textsuperscript{-}. Indium Tin Oxide
Figure 47: Glass bead diagram.
Figure 48: 2nd generation DSSC flexibility.
Modified 2\textsuperscript{nd} generation DSSC

Figure 49: 2\textsuperscript{nd} generation DSSC I-V plot

efficiency = 0.2 %
current DSSC record = 11%
Figure 50: 2nd generation DSSC I-V plot, without N719
CONCLUSION

Due to their outstanding electronic and mechanical properties, CNTs have the potential to play an integral role in paradigm shifting technologies. This dissertation describes methods in which we can create carbon nanotubes composites that can be used for various applications including hydrogen sensing and dye-sensitized solar cells.

We have demonstrated the ability to synthesize covalently cross-linked MWCNT mats through two reaction schemes: 1) Michael addition and 2) imine formation in which the former utilizes MWCNT-SH while the latter uses MWCNT-NH$_2$. Both reactions utilize benzoquinone as the cross-linker. Our method of producing these nanotube mats is an improvement over traditional methods that require high energy irradiation or high compression procedures. This method is not destructive to the sp$^2$ bonding which the superior properties of CNTs depend upon nor does it rely on nanotube alignment or weak van der Waals forces for cross-linking. Furthermore, our filtration-from-suspension method is industrially viable as it can be scaled up for large-scale production.

In addition, we have also shown the use of MWCNT-NH$_2$ mats in hydrogen sensor applications. We were able to create a light-weight and flexible H$_2$ gas sensor that has the ability to detect H$_2$ gas with concentrations as low as 5%. Its low mass density and flexibility are an improvement over current hydrogen sensing technologies which typically utilize rigid and heavy substrates such as glass or silicon wafers. An interesting observation was that there was a decrease in resistance in the Pd NP integrated CNT mat when exposed to H$_2$. This phenomenon is the opposite of what typically occurs in CNT mats with surface deposited Pd NPs.

Lastly, we have also developed a CNT/cellulose composite for dye-sensitized solar cell applications. We are able to create a DSSC with an efficiency of 0.2%. Although the efficiency is low, the results are still promising as our device does lay the groundwork for a CNT/cellulose-based DSSC that is light-weight, flexible, and environmentally friendly.
REFERENCES


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(Summer 2001)
• Analyzed and entered data into Materials Management Inventory System

KRAFT FOODS, INC. – Niles, Illinois
Quality Control Chemist
(Summer 2004)
• Analyzed moisture, fat content, salt percent, and other properties of food products

AWARDS / ACHIEVEMENTS

• Dissertation Research Grant Award
(2010)
• Hoffman Merit Award
(2005)
• Ranked 6 / 177 (annualized return) in FSU investing network
(Feb. 2011)
on Updown.com. Outperformed S&P 500 (33.4% vs. 21.2%) since start.
AFFILIATIONS / VOLUNTEER EXPERIENCE

• American Chemical Society (2008 – Present)
• Global Educational Outreach for Science Engineering and Technology (2005 – Present)
• National Association for Business Economics (2009 – Present)
• Literacy Volunteers of Leon County (2010)

PUBLICATIONS

• Ventura, D.; Li, S.; Baker, C.; Breshike, C.; Strouse, G.; Kroto, H.; Acquah, S. “Flexible and Light-Weight Multi-Walled Carbon Nanotube Mats for Hydrogen Sensing Applications” To Be Published, expected 2011

PRESENTATIONS

Oral Presentations:
• “Synthesis of Cross-Linked Carbon Nanotube Mats and their Applications”, Florida State University, 2011
• “Assembly of Multi-Walled Carbon Nanotube Mats Through Covalent Cross-Linking”, Florida State University, 2009
• “Chemistry of Carbon Nanotubes”, Florida State University, 2007
• “Nanodiamonds and Potential Applications”, Florida State University, 2007

Poster Presentations:
• “Assembly of Cross-Linked Multi-Walled Carbon Nanotube Mats”, FLACS Florida Annual Meeting and Exposition, Tampa, FL, 2010
• “Assembly of Cross-Linked Multi-Walled Carbon Nanotube Mats”, Graduate Student Visiting Weekend, Florida State University, 2010