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Covalent Surface Modifications of Carbon Nanotubes

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Covalent Surface Modifications of Carbon Nanotubes

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Abstract

A report meant to document the chemistries investigated by the author for covalent surface modification of CNTs. Oxidation, cycloaddition, and radical reactions were explored to determine their success at covalently altering the CNT surface. Characterization through infrared spectroscopy, Raman spectroscopy, and thermo gravimetric analysis was performed in order to determine the success of the chemistries employed. This report is not exhaustive and was performed for CNT surface modification exploration as it pertains to the "Next Gen" project.

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NOMENCLATURE

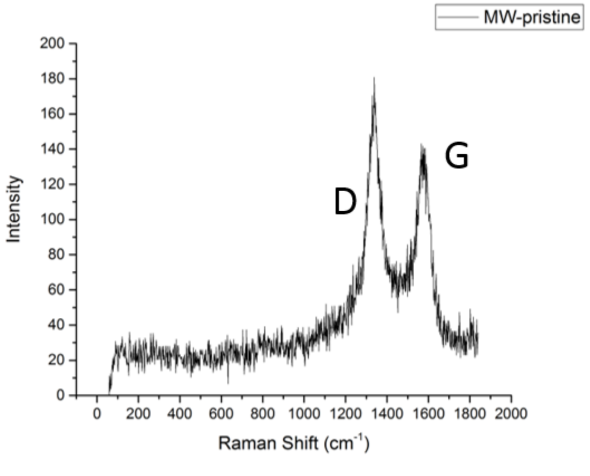
Abbreviation	Definition
CNTs	Carbon nanotubes
DWCNT	Double-walled carbon nanotube
MWCNT	Multi-walled carbon nanotube
SWCNT	Single-walled carbon nanotube
IR	Infrared
PI(OH)-BDA	Hydroxyl polyimide-grafted bisphenol A diglyceryl acrylate
***m*-CPBA**	3-Chloroperbenzoic acid
DCM	Dichloromethane
$AlCl_3$	Aluminum chloride
TGA	Thermo gravimetric analysis
NMP	*N*-methyl-2-pyrrolidone
AIBN	2,2'-azobis(2-methylpropionitrile)

1. INTRODUCTION

Since their elusive discovery, carbon nanotubes (CNTs) have attracted the attention of researchers due to their unique properties; notably their light weight, high aspect ratio, mechanical properties, and thermal and electrical conductivity. Carbon nanotubes come in three varieties, single-walled (SWCNT), double-walled (DWCNT), and multi-walled (MWCNT). In order to achieve an electrically conductive system, percolation of CNTs throughout the structure is needed. To achieve high levels of percolation, a highly dispersed system is required. Chemical functionality added to the CNT backbone structure provides a two-fold benefit to the incorporation of carbon nanotubes into a matrix. The first is a decrease in the agglomeration of tubes into bound structures that prevent high network connectivity. Secondly, chemical functionality can act as a handle to covalently impart crosslinks throughout the percolated network, thereby increasing mechanical performance as well as reducing the gap between nanoparticles under appropriate conditions.

Commonly, infrared (IR) and/or Raman spectroscopy of modified systems are reported as evidence of covalent changes. For the purpose of this report, the experiments outlined herein were performed on SWCNTs since their "ordered" structure allows for a more facile characterization regime. The nature of IR spectroscopy makes it difficult to discern between a material blend and a reacted CNT sample, however, through Raman spectroscopy, a clearer picture may be observed, and thus although both analytical data are presented, we focus strongly on Raman data for conclusive evidence of a successful covalent surface modification.

CNTs have unique optical and spectroscopical properties due to the 1D confinement of electronic and phonon states. Typically, we focus on three Raman signal bands when reporting on CNT materials: G-band, D-band, and G'-band at *ca*. 1582, 1350, and 2700 cm^{-1}, respectively. Radial breathing mode features in Raman are unique to CNT materials and appear between 100-500 cm^{-1}. The G-band, referred to as the order band, corresponds to planar vibrational modes and the D-band (disorder band) comes about from imperfections in the CNT structure. As seen on figure 1, SWCNTs have a very small disorder band when compared to MWCNTs.



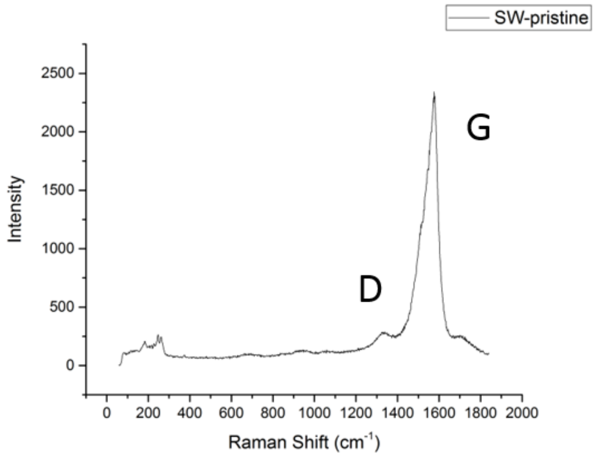


Figure 1. Raman spectroscopy of MWCNTs (left) and SWCNTs (right).

Covalent chemical attachment onto the surface increases imperfections on the CNT material and increases the intensity of the disorder band. In order to better visualize the efficiency of the chemistries tested here, SWCNTs were used.

2. REACTIONS ON CNTS

The most common method for CNT modification is by treatment with nitric acid which haphazardly oxidizes the CNT surface resulting in the formation of carboxylic acid groups that can then be used to impart other desired groups.[1-4] It is important to note that any and all covalent bonds extending from the CNT surface disrupts the conjugated system and therefore may affect the conductivity of the material (Table 1). Figure 2 shows the effects of this reaction in both SWCNTs and MWCNTs.

Sample	CNT (mg)	Thickness (cm)	Resistivity (Ω cm)
MW-P	15.4	0.00302	0.0573
MW-N	16.6	0.00221	0.0801
SW-P	17.3	0.00518	0.184
SW-N	17.7	0.00549	0.941

* Thickness measurement was very rough. Average was based on SW-P.

Table 1. CNT systems were suspended in *N*-methyl-2-pyrrolidone (NMP) and filtered through 0.2 µm omnifilter. The resulting "Bucky paper" was analyzed using a four-point probe to determine conductivity. Thickness was determine using profilometry.

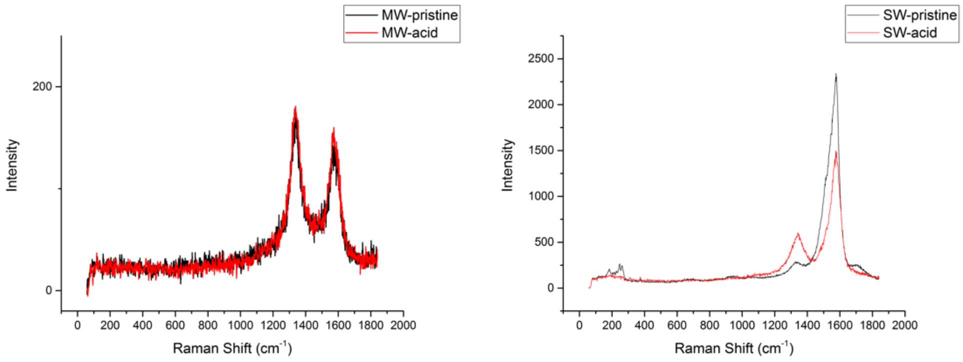


Figure 2. Raman spectroscopy of MWCNTs (left) and SWCNTs (right) showing pristine (black) and nitric acid treated (red) material.

Using the oxidation by nitric acid as a base line, we explored alternative chemistries for surface modification. This report is meant to be a documentation of the reactions attempted by the author base on previous literature research.

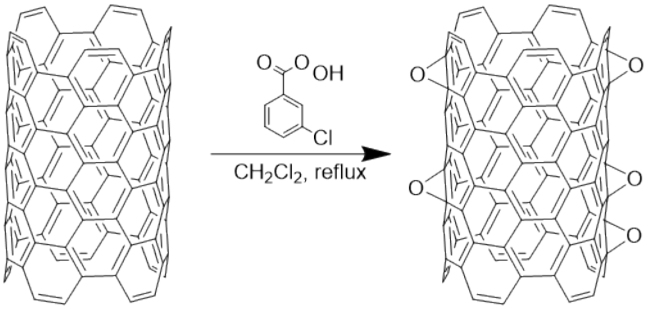
2.1. Oxidation

Oxidation through nitric acid treatment is so prevalent and effective, a natural continuation was to explore other oxidation chemistries. The two techniques described here are epoxidation, to impart an epoxide ring on the surface of the CNTs, and Friedel-Crafts reaction to install a halide that was later modified with a hydroxide salt.

2.1.1. *Epoxidation*

A hybrid covalent and non-covalent interaction approach was implemented in order to generate SWCNTs with enhanced solubility in organic solvents.[5] Yuan *et al*. designed and applied a novel dispersant, hydroxyl polyimide-grafted bisphenol A diglyceryl acrylate (PI(OH)-BDA), onto the surface of SWCNTs following a surface modification using 3-chloroperbenzoic acid (*m*-CPBA).

Surface epoxidation of SWCNTs (scheme 1) was performed using similar conditions as published by Yuan and coworkers. Briefly, SWCNTs (204.3 mg) were suspended in dichloromethane (DCM) (100 mL) with the aid of sonication. The *m*-CPBA was added to the suspension and the reaction vessel was heated to reflux, *ca*. 40 °C for 18 h. The reaction mixture was filtered through a 0.2 μm omnifilter and washed with excess DCM followed by thorough washing with methanol. The brown filtrate was discarded and the black solid was dried *in vacuo*. The IR and Raman characterization of the resulting material can be viewed in figure 3.



Scheme 1. Epoxide formation onto CNT system using *m*-CPBA.

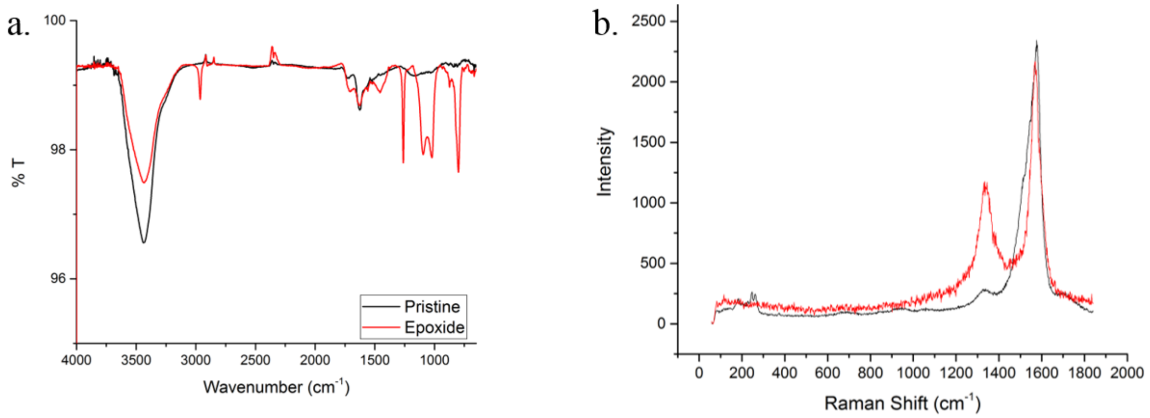
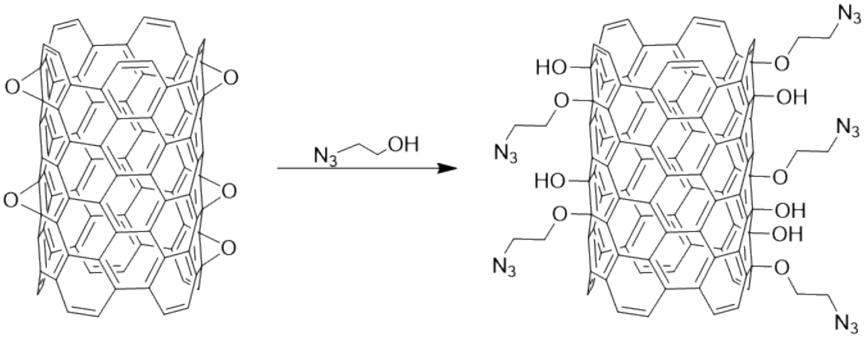


Figure 3. IR (a) and Raman (b) characterization of CNT epoxidation

2.1.1.1. Ring opening to afford other functionalities

Utilizing the epoxy-CNTs, ring opening was attempted as a facile means to obtain additional functionalities (scheme 2). Previously synthesized 2-azidoethanol was used as a test molecule since the azide functionality has a distinct IR band isolated from common organic bands, notably the stretching azide band *ca*. 2100 cm^{-1}. Briefly, enough of the liquid 2-azidoethanol (941 mg) was added to completely cover the epoxy-CNT (47.6 mg). The neat reaction mixture was heated to 75 °C and allowed to react for 16h. A control reaction with non-reacted CNTs was also conducted in order to determine if the presence of azide in IR characterization was due to a physical mixture after washing of the CNT material with excess water and tetrahydrofuran (THF). In figure 3, the appearance of a small stretching band at 2100 cm^{-1} can be observed for the reaction and not on the control material.



Scheme 2. Epoxide ring opening using 2-azidoethanol.

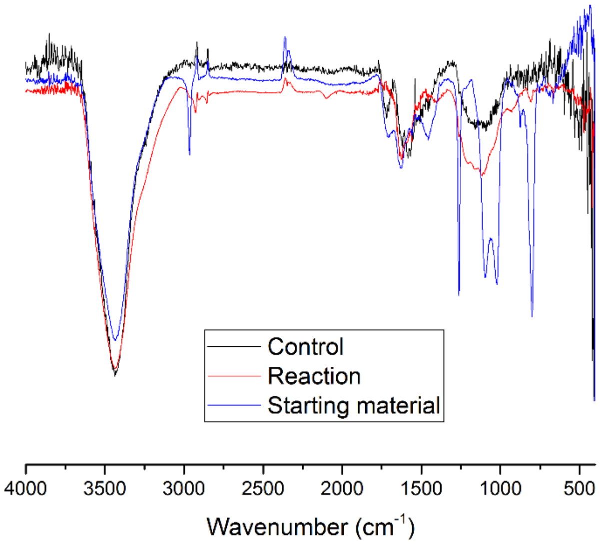
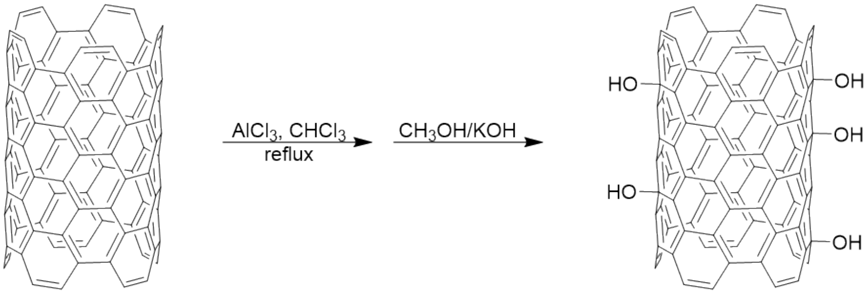


Figure 4. IR characterization showing the non-reacted control CNTS (black), reacted CNTs showing an azide stretching mode (red) and the starting epoxy-CNTs (blue).

2.1.2. *Friedel-Crafts*

Halogenated solvent molecules were grafted onto the surface of SWCNTs through a Friedel-Crafts reaction using aluminum chloride ($AlCl_3$) and chloroform subsequently treated with a potassium hydroxide solution (scheme 3).[6] In a glove bag purged with a nitrogen atmosphere, CNTs (104.59 mg) and $AlCl_3$ (621.95 mg)were ground together using a mortar and pestle. The black powder was added to a flask equipped with a condenser followed by addition of chloroform (125 mL). The reaction mixture was exposed to three cycles of brief vacuum and refilled with an inert atmosphere. Reflux was maintained for 60 h. A saturated potassium hydroxyl solution in methanol (5 mL) was added to the cooled reaction. Reflux was maintained for an additional 24 h. Although Choi *et al*. claim addition of desired functional groups, Raman and IR spectroscopy did not corroborate their results (figure 5). Additionally, thermo gravimetric analysis (TGA) was conducted but a minimal change was observed (less than 5% of mass loss change) (figure 6).



Scheme 3. Friedel-Crafts reaction for imparting –OH functionality onto CNT surface.

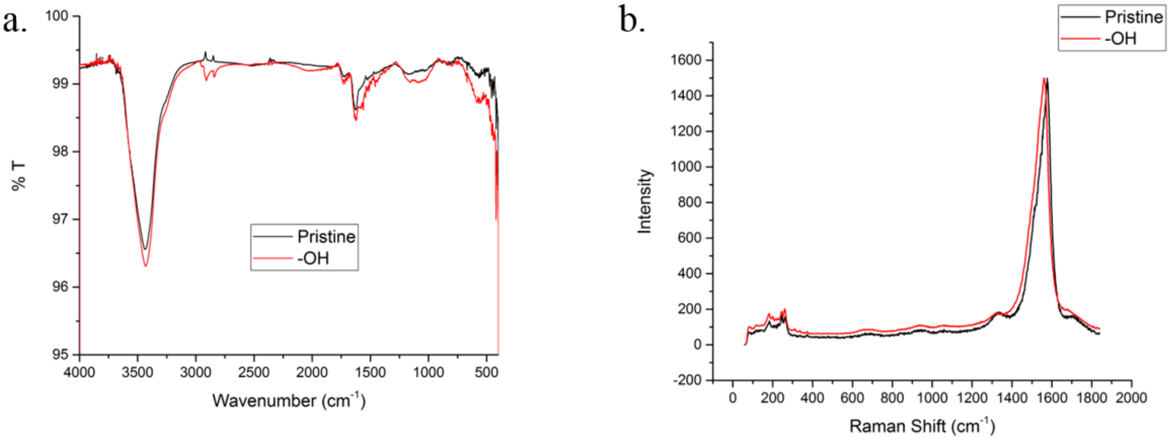


Figure 5. IR (a) and Raman (b) characterization of –OH modified CNTs

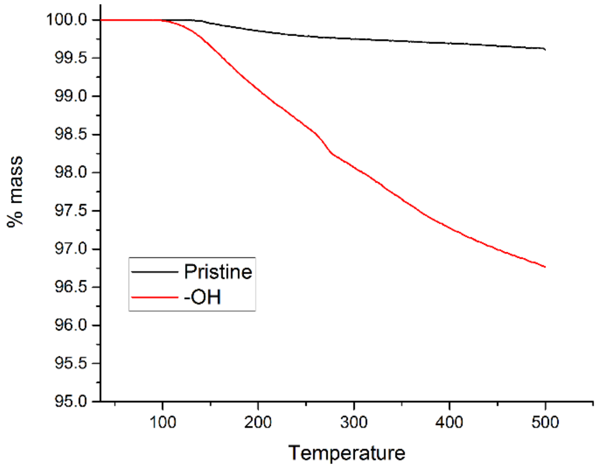


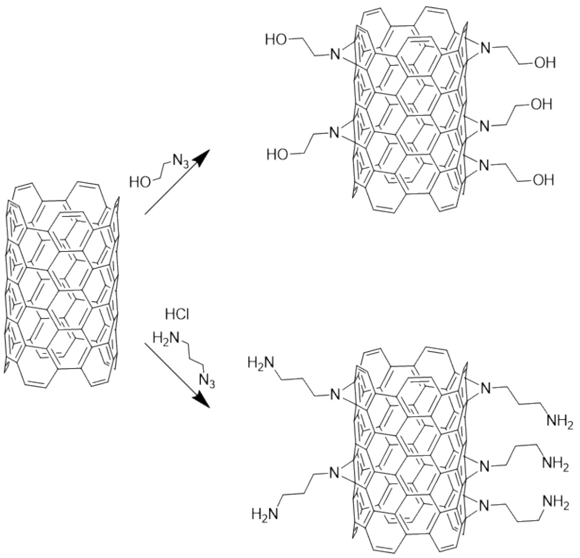
Figure 6. TGA showing difference in thermal decomposition of pristine CNTs (black) and –OH modified CNTs (red)

2.2. Cycloadditions

Utilizing the inherent conjugation of CNTs, cycloaddition is a “softer” way for surface modification when compared to the harsh environment experienced with traditional oxidation in nitric acid. The two cycloadditions explored in this section are nitrene cycloaddition and Diels-Alder [4+2] cycloaddition.

2.2.1. Nitrene cycloaddition

Azides ($-N_3$) can undergo thermolysis which results in the formation of nitrene species (containing unshared valence electrons) that can then partake in cycloadditions with CNTs. Several examples can be found in the literature. Kar *et al*. reported the immobilization of polystyrene onto the surface of MWCNTs through nitrene addition. As evidence, they reported IR characterization and the disappearance of the $-N_3$ stretching band from the polymeric material.[7] Similarly, Holzinger and coworkers reported the attachment of several small molecules onto SWCNTs using nitrene cycloadditions. Extensive characterization of the resulting material is presented including Raman, UV-Vis, and XPS.[8] Another literature examples of nitrene cycloaddition is the work of Gao *et al*. where they showed the attachment of several small molecules onto MWCNTs.[9] Based on this literature research, nitrene cycloaddition of 2-azidoethanol or 3-azisopropylamine hydrochloride (20 wt. eq.) onto CNTs (1 wt. eq.) was attempted (scheme 4). Initial attempts of thermolysis assisted nitrene cycloaddition were not successful. However, based on work from Kong *et al*., microwave assisted reactions were also attempted.[10] Table 2 shows the microwave reaction conditions for the reactions performed.



Scheme 4. Nitrene cycloaddition of 2-azidoethanol and 3-azisopropylamine hydrochloride

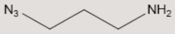
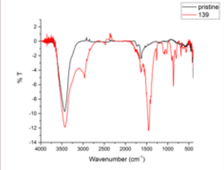
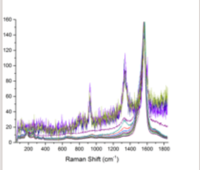
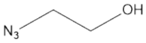
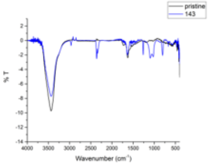
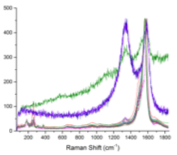
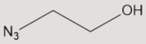
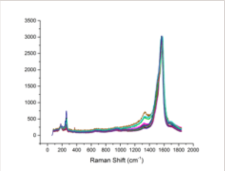
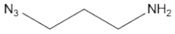
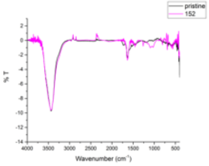
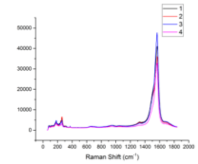
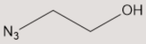
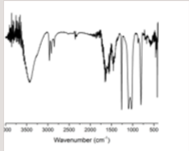
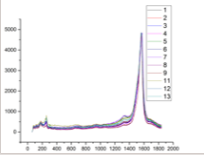
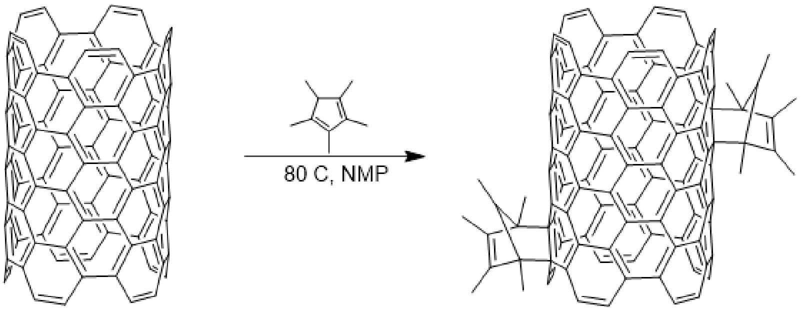
RXN	Substrate	Conditions	IR	Raman
139*		P=100 T= 150 t= 1h		
143		P=100 T= 150 t= 2h		
148		P=100 T= 180 t= 5h	NA	
152		P=100 T= 150 t= 8h		
162		P=100 T= 200 t= 1h		

Table 2. Microwave assisted reaction conditions.

The reaction entry labeled 139 suffered from an instrument malfunction which resulted in a lack of feedback of the heating component. The resulting material showed successful cycloaddition under the malfunctioning conditions and not under the conditions documented. The proceeding microwave assisted reactions were performed in an attempt to replicate the results, but this was unsuccessful.

2.2.2. *Diels-Alder cycloaddition*

Another cycloaddition that has been reported to work on CNT surfaces is a traditional Diels-Alder cycloaddition with the CNT serving as the dienophile. Several articles have reported successful surface modification of CNTs through Diels-Alder. [11-13] A test reaction was performed using excess pentamethylcyclopentadiene onto CNTs in NMP (scheme 5). The initial reaction was successful despite the use of a sterically hindered diene, as see in figure 7, and thus another reaction with excess furfuryl glycidyl ether (scheme 6) which had similar spectroscopic results (figure 8).



Scheme 5. Diels-Alder cycloaddition using pentamethylcyclopentadiene.

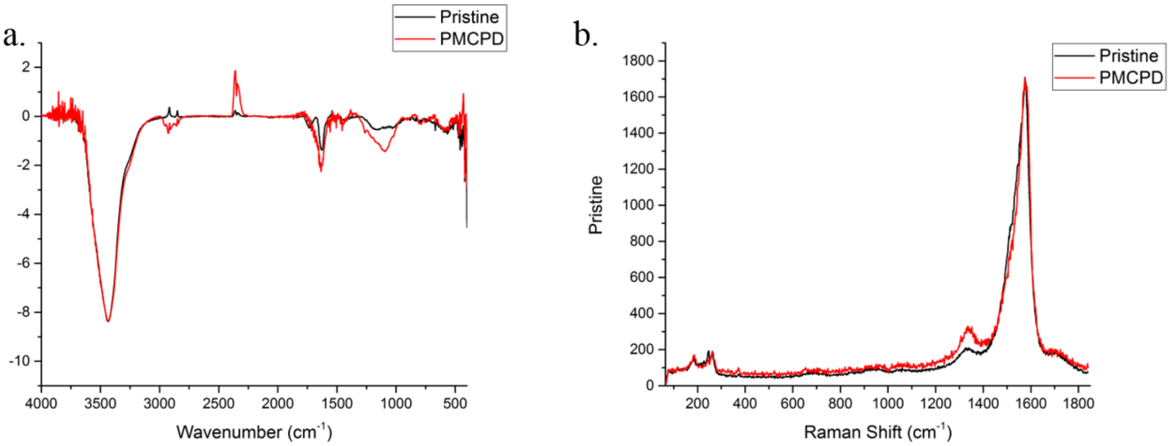
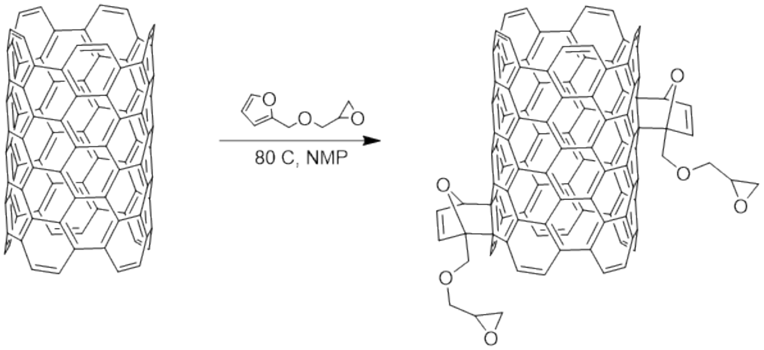


Figure 7. IR (a) and Raman (b) characterization of cycloaddition with pentamethylcyclopentadiene.



Scheme 6. Diels-Alder cycloaddition using furfuryl glycidyl ether.

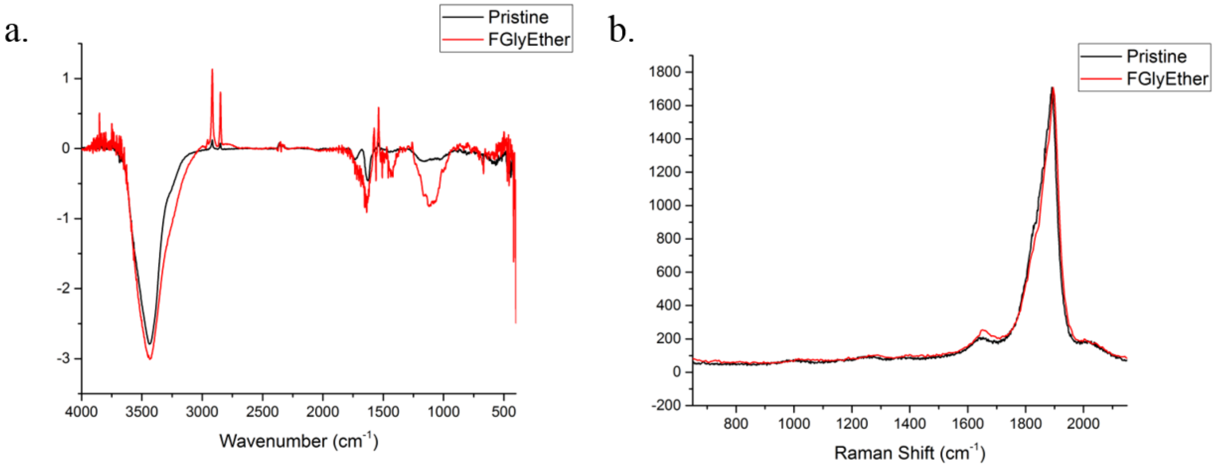


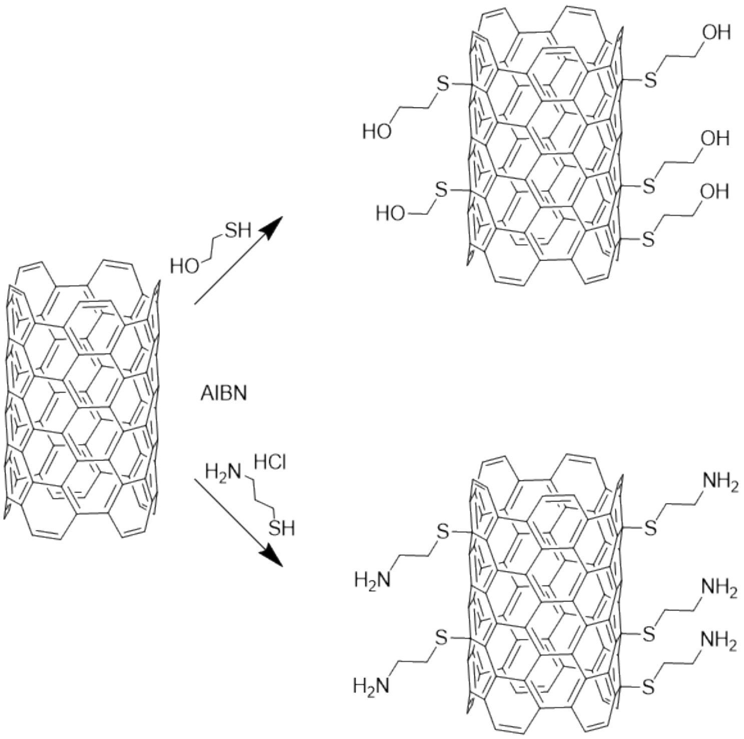
Figure 8. IR (a) and Raman (b) characterization of cycloaddition with furfuryl glycidyl ether.

2.3. Radical

Radical reactions are another "softer" alternative for CNT surface modification. Thiol-ene reactions are explored.

2.3.1. Thiol-ene

Zabihi *et al*. successfully imparted amine functionalities onto SWCNTs through a one-pot reaction using dicumyl peroxide in the presence of 2-aminoethanethiol.[14] Similarly, polymeric materials have also been "clicked" onto CNT surfaces by thiol-ene chemistry as demonstrated by Temel and coworkers.[15] Thiol-ene attachment was tested with both an amine containing and a hydroxyl containing thiol with 2,2'-azobis(2-methylpropionitrile) (AIBN) at 70 °C (scheme 7).



Scheme 7. Thiol-ene reactions with AIBN radical initiator.

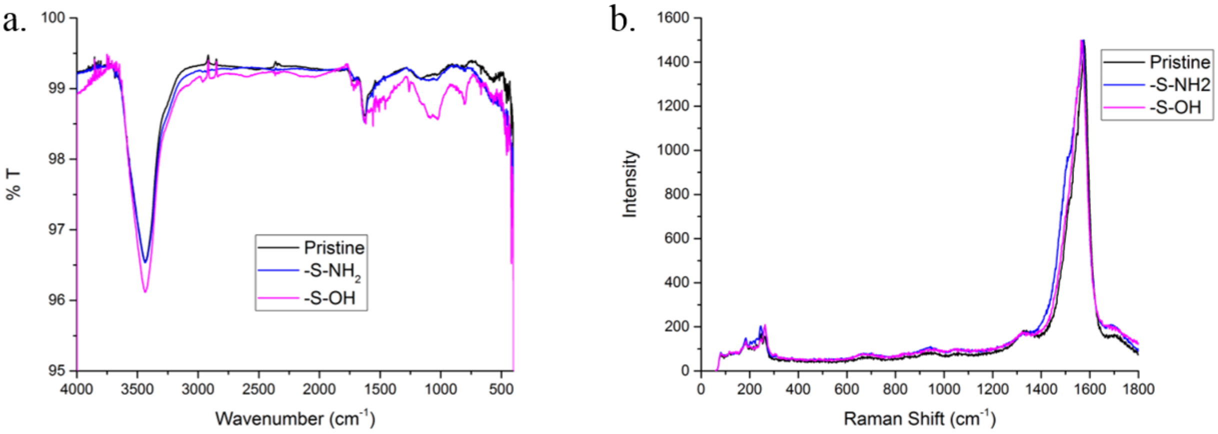


Figure 9. IR (a) and Raman (b) characterization of amine (blue) and hydroxy substituted thiol-ene reactions (pink).

This reaction is believed to not have been successful based on the lack of change in the disorder band in the Raman spectrum and the little to no change observed in IR characterization.

3. SUMMARY AND CONCLUSIONS

This report has been prepared to document the chemistries investigated by the author in order to obtain surface modified CNTs. Oxidation, cycloaddition, and radical reactions were explored to determine their success at covalently altering the CNT surface. Of these chemistries, epoxidation and Diels-Alder cycloaddition showed a superb ability to impart new chemical functionalities onto CNTs as evidenced by IR and Raman characterization. Friedel-Crafts and thiol-ene addition showed little to no evidence of successfully altering the CNT surface. Nitrene cycloaddition shows promise of success but further exploration into the reaction conditions is necessary.

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