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Development of Highly Concentrated Dispersions of Chemically Functionalized Carbon Nanotubes as Thermally and Electrically Conductive Sprayable Coatings

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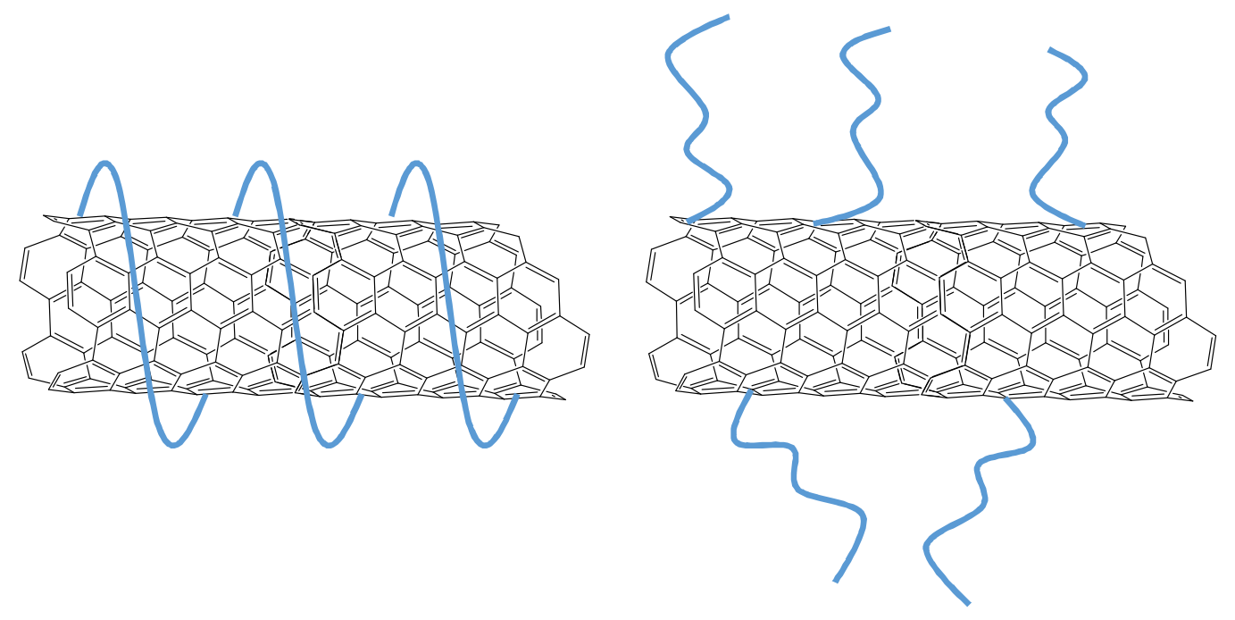
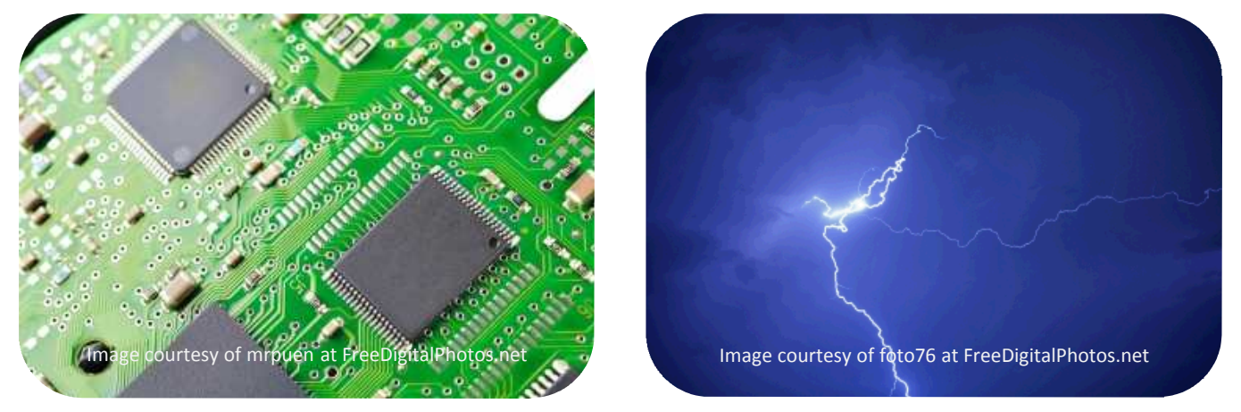
Abstract

Carbon nanotubes (CNTs) encompass many desirable properties including excellent thermal and electrical characteristics and can be used to impart beneficial characteristics to composite materials fabricated with CNT fillers. Conductive and sprayable coatings have historically been prepared through the non-covalent incorporation of CNTs in polymeric matrices and rely on π- π and other relatively weak interactions between the two system components. Additionally, these composite coatings can often yield materials with less than optimal conductive properties due to the insulating nature of the polymeric component and poor percolation of the CNT network. Herein, we propose the development of analogous systems utilizing surface-modified CNTs that would allow for covalent bonds to be established between CNTs, thereby allowing a continuous network formed wholly of CNT junctions for increased performance and hypothetically eliminating the need of a non-participating binder matrix. Several chemistries including radical, Friedel-Crafts, and epoxidation, among others, were explored for the installment of various functional groups (*i.e.* -OH, $-NH_2$, -SH, epoxides, *etc.*) onto the surface of CNTs in order to produce a library of modified CNTs to be explored for optimum desired properties.



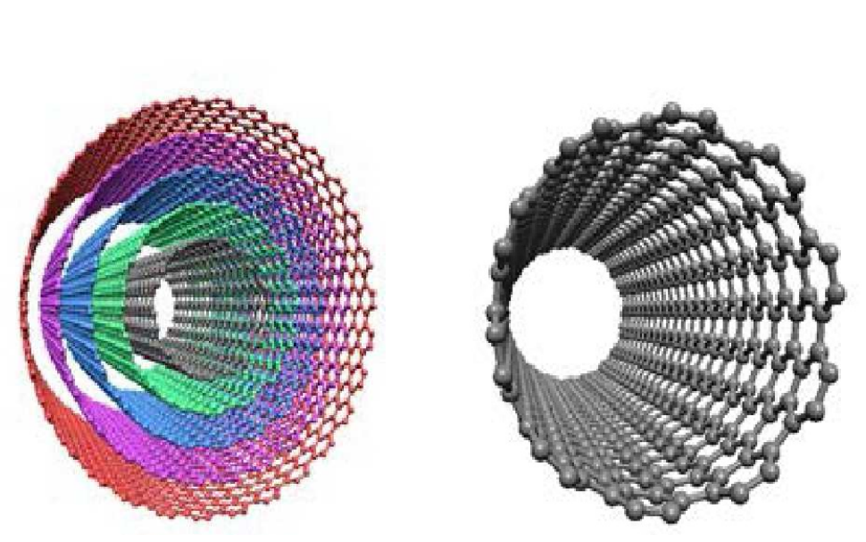
Non-covalent (left) and covalent (right) attachment onto carbon nanotubes



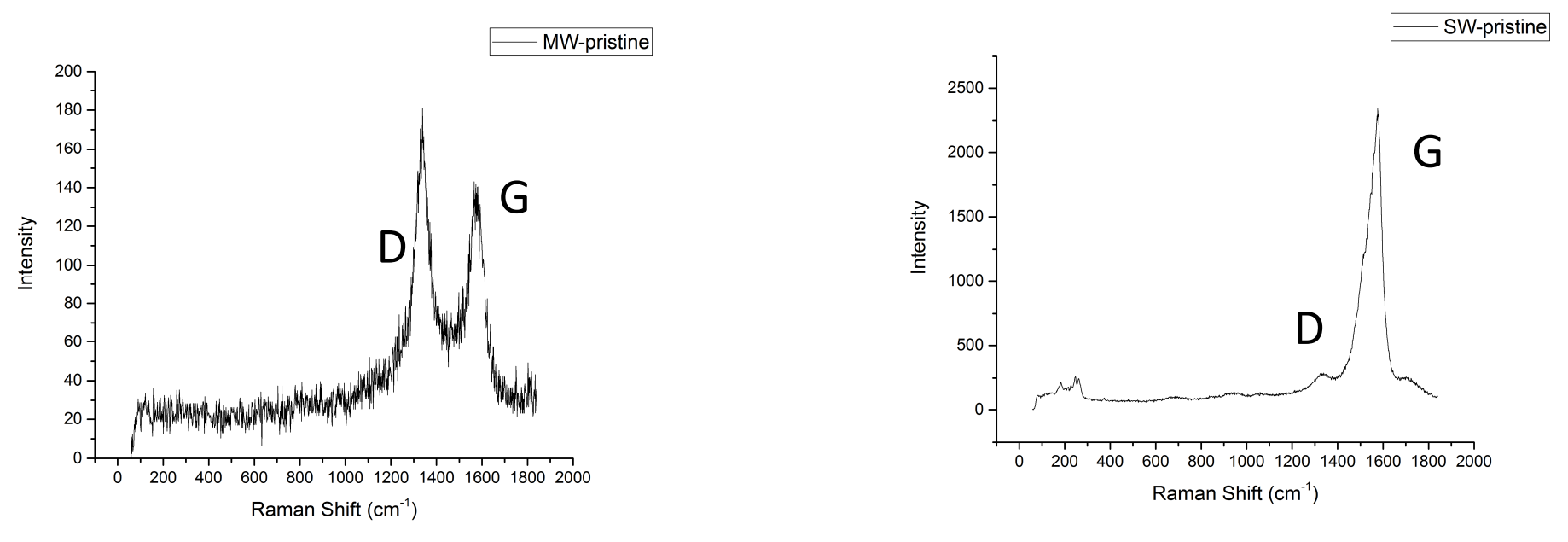
Conducting paints may be used for electromagnetic radiation/ electromagnetic interference shielding and lightning strike protection

Introduction to Project and Previous Work

Characterization is not trivial – ambiguous analytical data[1-4]
 Infrared (IR)
 Thermogravimetric analysis (TGA)
Raman most reliable to indicate *covalent* modification
 Order (G) band 1582 cm^{-1}
 Disorder (D) band 1350 cm^{-1}
Single-walled carbon nanotubes will be used for method development
 More concrete evidence of surface modification



http://lobizone.com/engineering/aeronautical-engineering/individual-carbon-nanotube-cnt



Raman characterization of pristine multi-walled (left) and single-walled (right) CNTs

Nitric acid pretreatment of CNT surface is a widely used first step for many surface modification methods.[5-7] However, this method may substantially hinder the conductive properties of this materials. Analysis of pristine and acid treated CNTs conducted in our laboratory show a significant change in the resistivity of the filmed samples.

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

Table showing electrically conductive properties of multi-walled (MW) and single-walled (SW) before (P) and after (N) nitric acid treatment

Herein, we present various methods to obtain surface modified SWCNTs without the need for nitric acid pretreatment. Several chemistries were utilized as a means to develop a library of modified CNT materials that would allow for the generation and further exploration of these materials for the production of sprayable coatings. Because of the inherent diversity, orthogonal systems may be manufactured with increasing complexities to ultimately produce elegant functional materials.

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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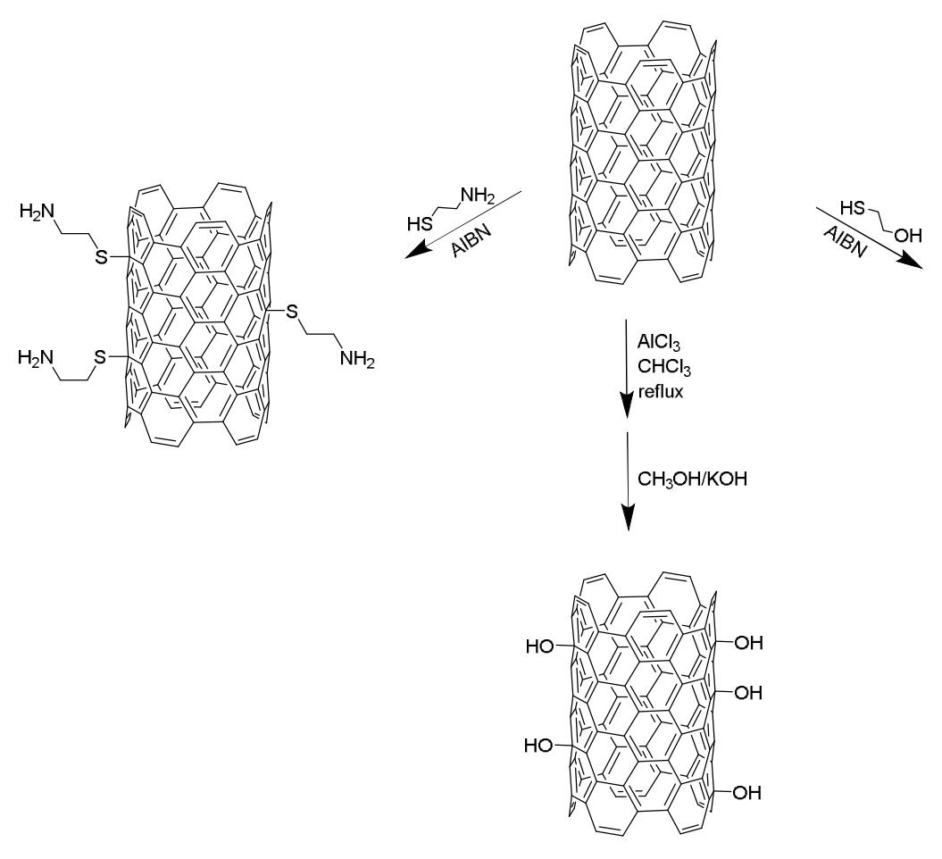
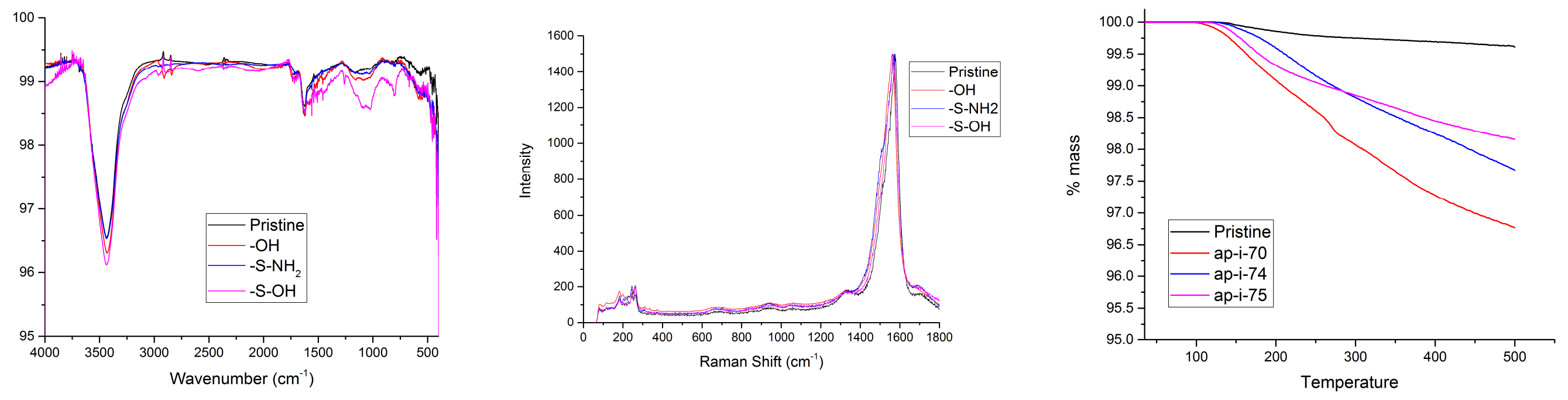
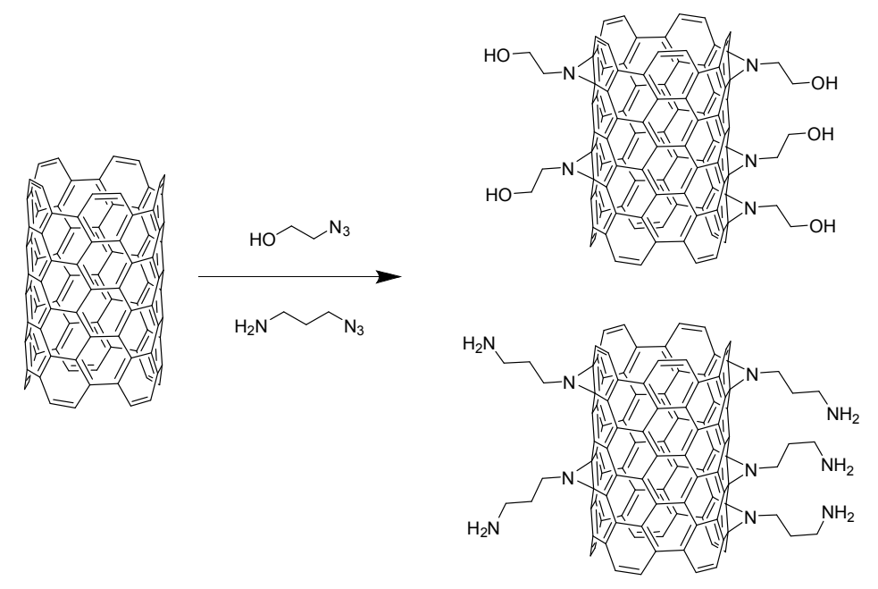
Imparting $-NH_2$ and –OH Functional Groups

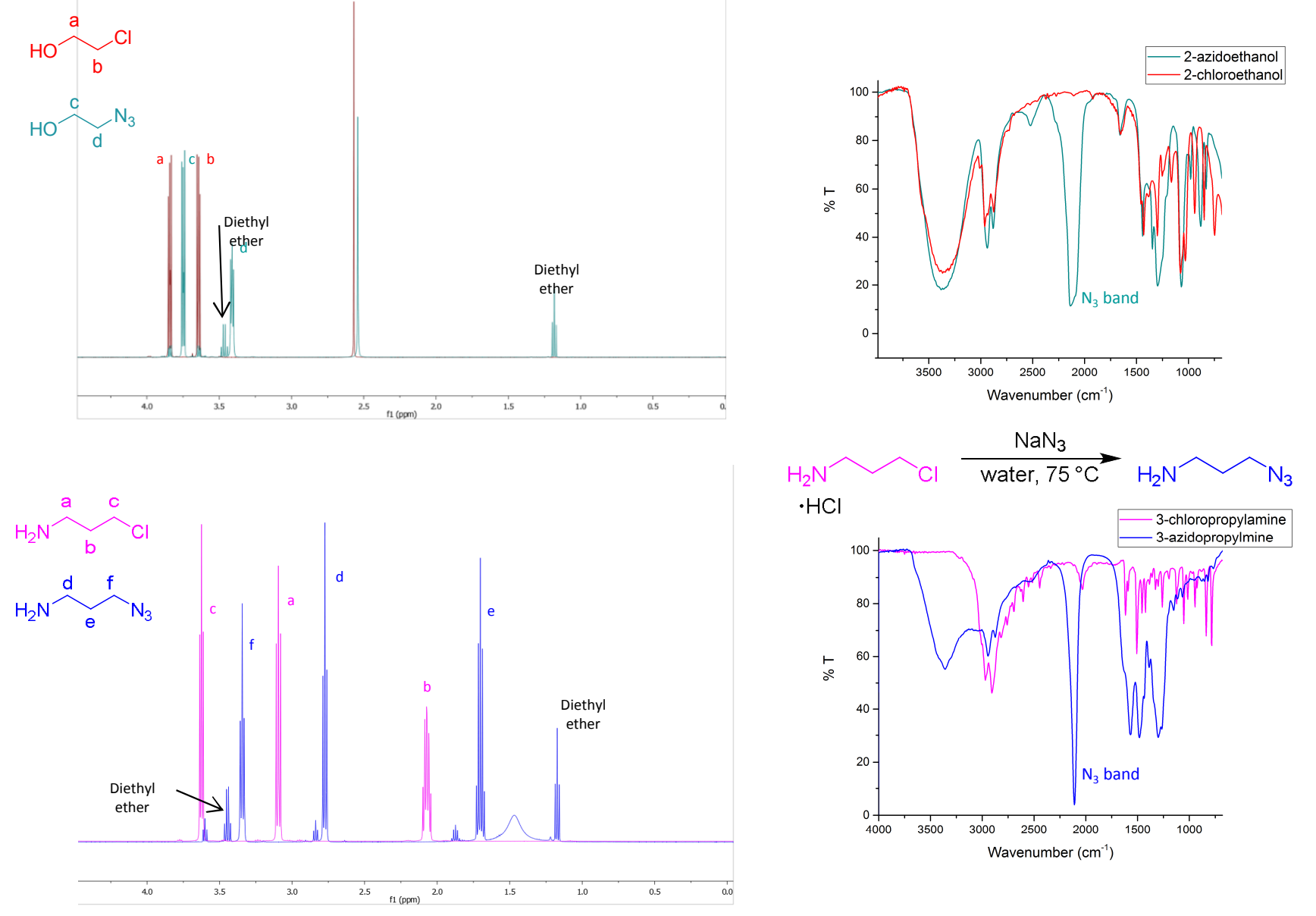




Thiol-ene click chemistry was explored as a means of obtaining both $-NH_2$ and –OH functionalized CNTS by "clicking" cystamine and 2-mercaptoethanol, respectively, onto CNTs. Additionally, a Friedel-Crafts addition of chloroform onto the CNT surface followed by a base treatment with KOH was also investigated for the incorporation of –OH groups. Although infrared (IR) spectroscopy (performed by the generation of KBr pellets) showed changes in the fingerprint region of these materials, Raman spectroscopy showed a non-detectable incorporation of these groups onto the CNT surfaces. Thermogravimetric analysis (TGA) was used to quantify the amount of incorporation and was determined to be less than 3% for the three methods explored.

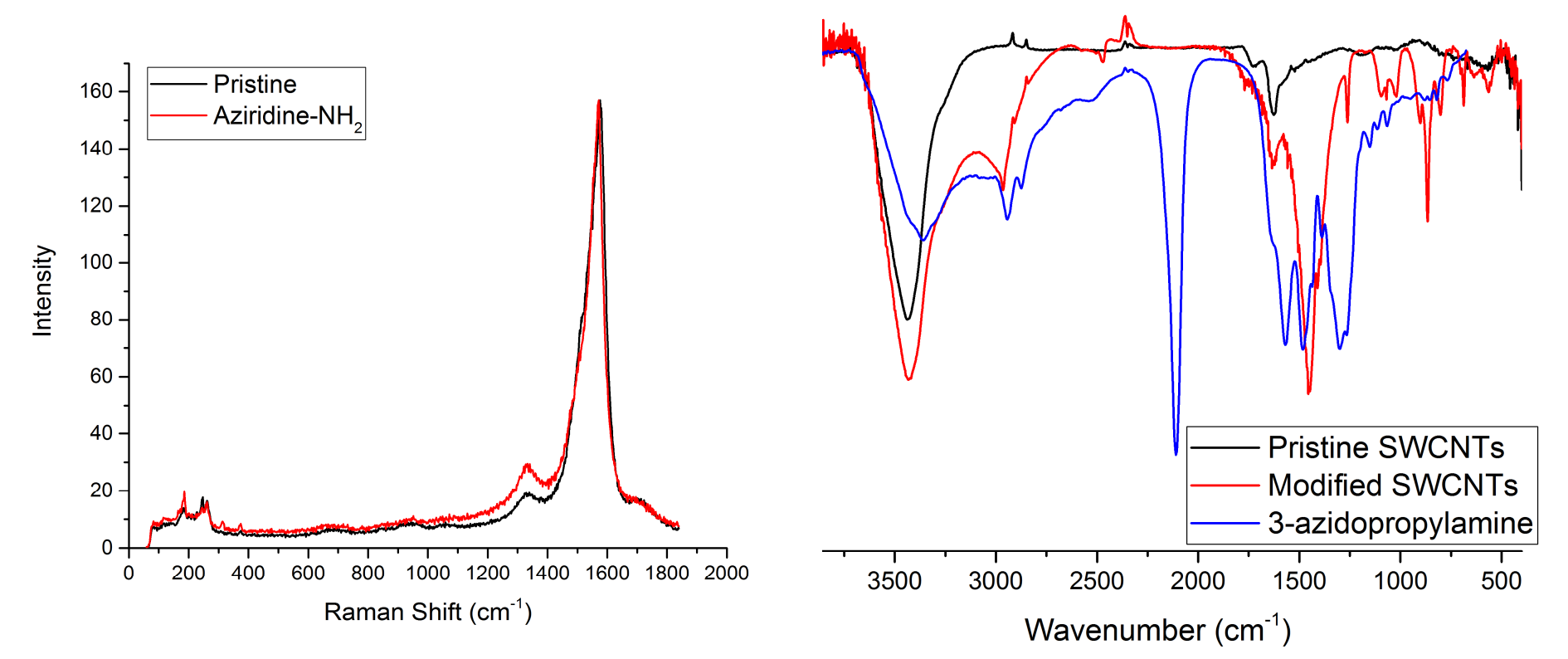


The formation of aziridine groups on the surface on CNTs has been previously reported in the literature.[3,8] Aziridine formation is obtained through the thermal decomposition of azide functionalities, which produces nitrene groups, that subsequently react with the aromatic CNT system. Two azide containing molecules were synthesized to impart $-NH_2$ and –OH functionalities. 2-Azidoethanol and 3-azidopropylamine were synthesized through nucleophilic substitution of 2-chloroethanol and 3-chloropropylamide hydrochloride, respectively. It is important to mention that both or these compounds are shock-sensitive materials and so their synthesis and manipulation must be performed in a careful and controlled environment. This work is ongoing, but with promising results and expedited reaction times through the use of microwave-assisted thermal decomposition of the azide containing compounds.



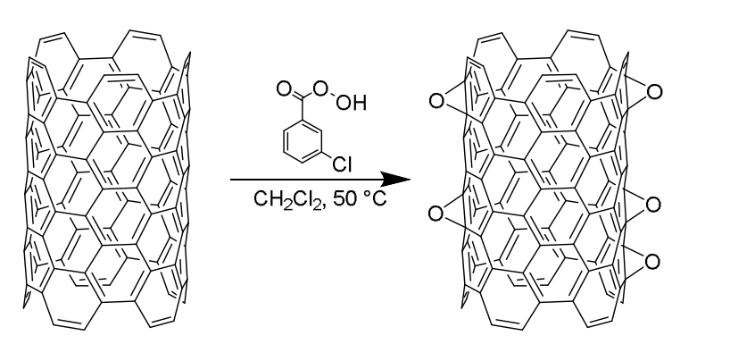
Synthetic path and ^1H NMR and IR characterization of 2-azidoethanol (top) and 3-azidopropylamine (bottom)

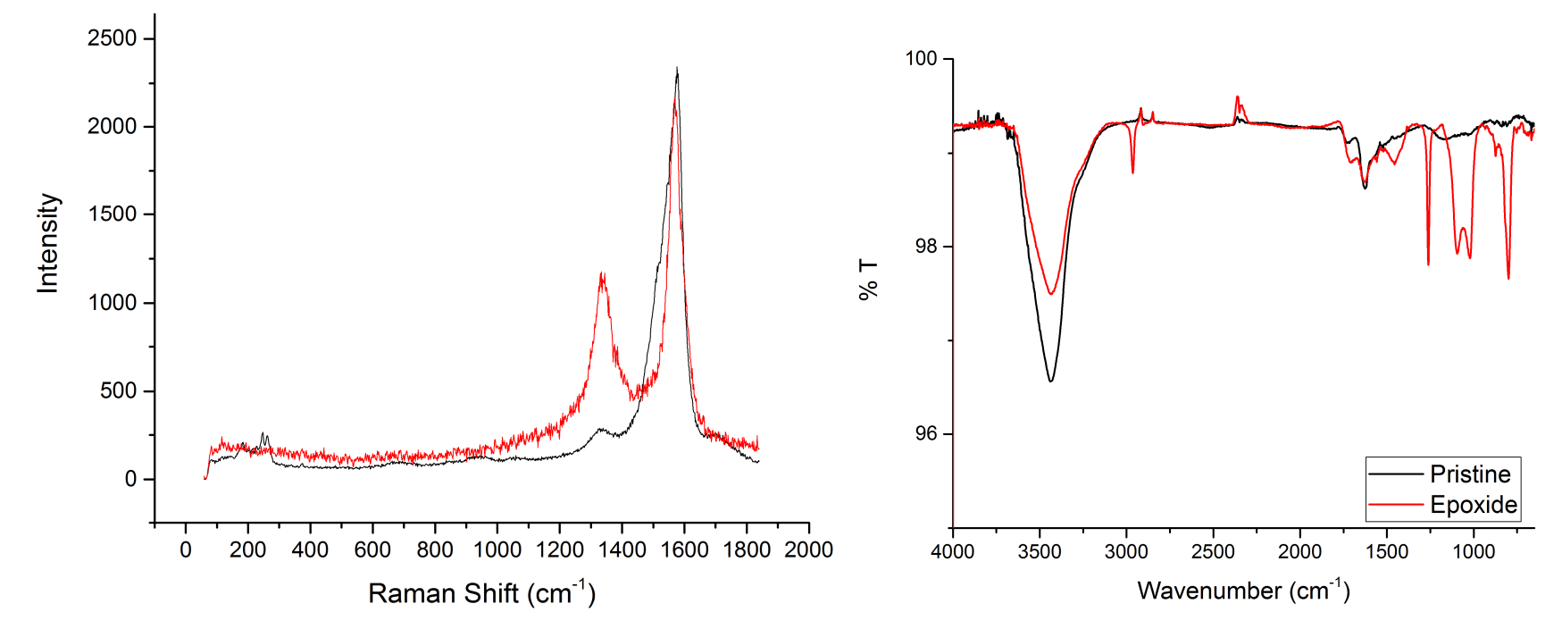
The data shown below was obtained through a microwave-assisted method and represents $-NH_2$ modified SWCNTs. These results came about following an error with the microwave instrument and ongoing work is focused on replicating these data.



Raman (left) and IR (right) characterization of surface modified SWCNTs obtained through aziridine formation using 3-azidopropylamine

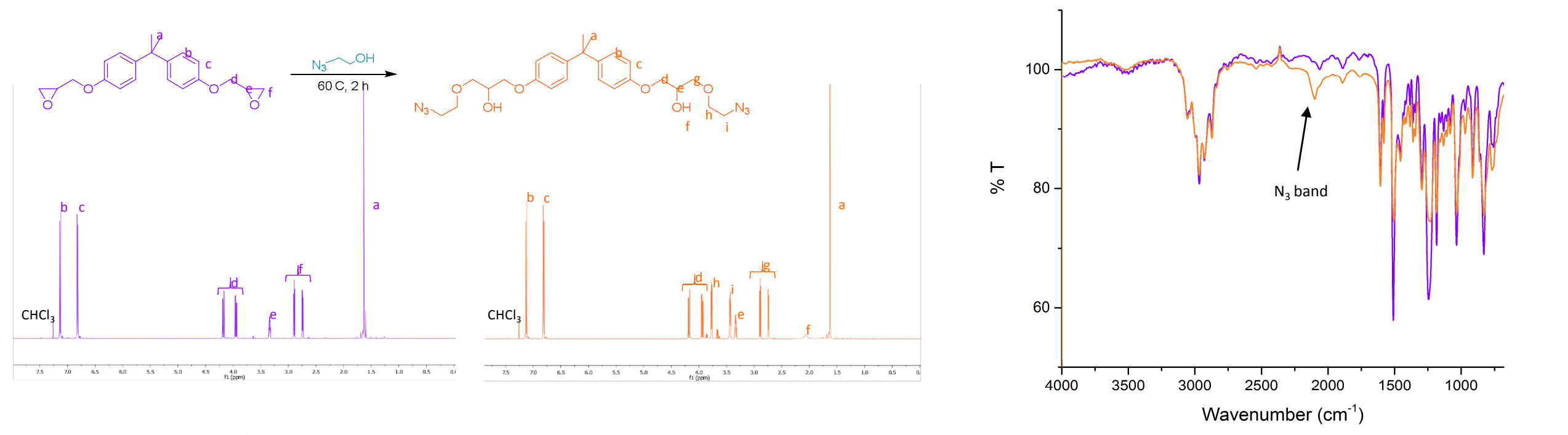
Epoxide and Azide Modified CNTs





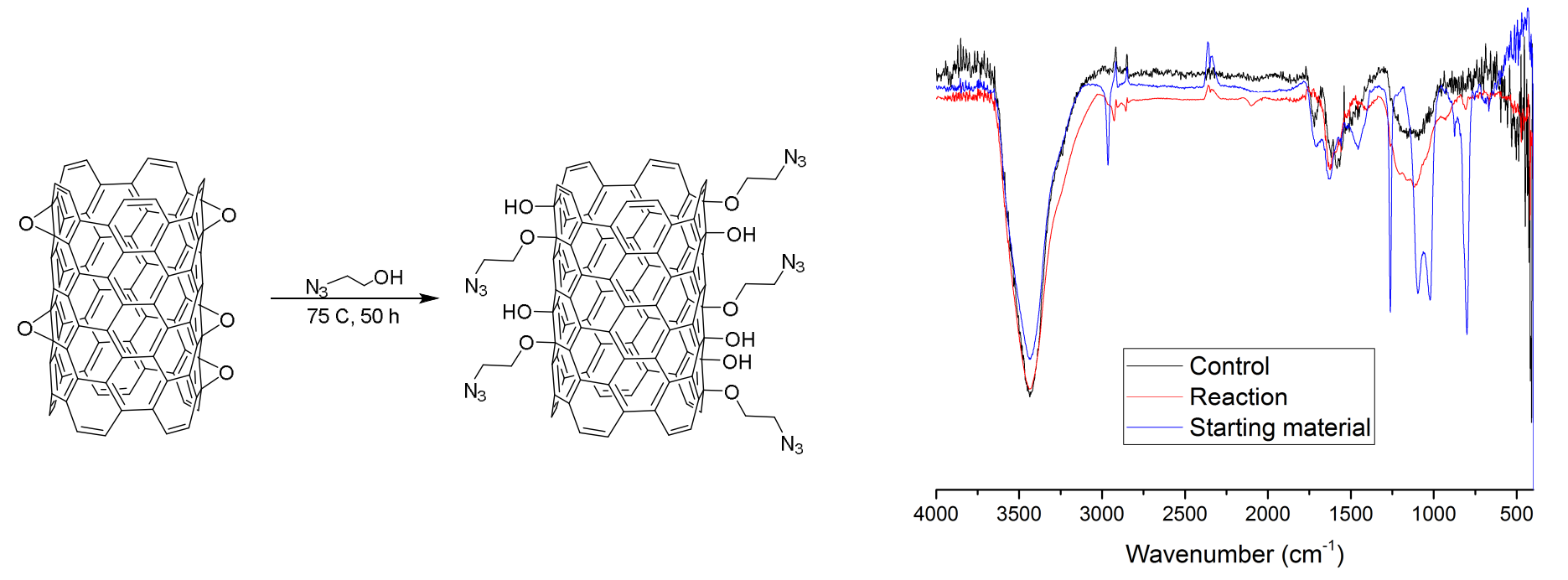
Raman (left) and IR (right) characterization of epoxide modified CNTs obtained from reacting pristine CNTs and meta-chloroperoxybenzoic acid (*m*-CPBA)

Epoxide modified CNTS were obtained through an epoxidation reaction between SWCNTs and *m*-CPBA as previously reported.[9] This simple, one-step reaction has successfully shown to impart epoxide functionality onto SWCNTs. These materials open the door for many possible approaches. Notable, an alternative route of imparting other desired functional groups onto CNTs. A model reaction was first tested in order to confirm proof of concept using bisphenol A digycidyl ether (BPAdGE) as the model compound for nucleophilic attack by 2-azidoethanol.



Synthetic path and ^1H NMR and IR characterization of the epoxide ring opening of BPAdGE by 2-azidoethanol

The model reaction showed successful ring opening on the epoxide ring by the azide containing nucleophile with very high purity. The azide group contains a distinctive and recognizable band in an otherwise quiet region in the IR spectrum (*ca.* 2100 cm^{-1}).

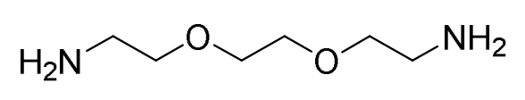


Synthetic path and IR characterization of azide modified CNTS

Longer reaction conditions were needed for the epoxide ring opening of the modified CNTs due to steric differences between the model and the CNTs reactions. IR characterization showed a loss of bands associated with epoxide groups (1260, 1100, 1023, 800 cm^{-1}) and the appearance of a new band (2100 cm^{-1}) associated with the presence of an epoxide.

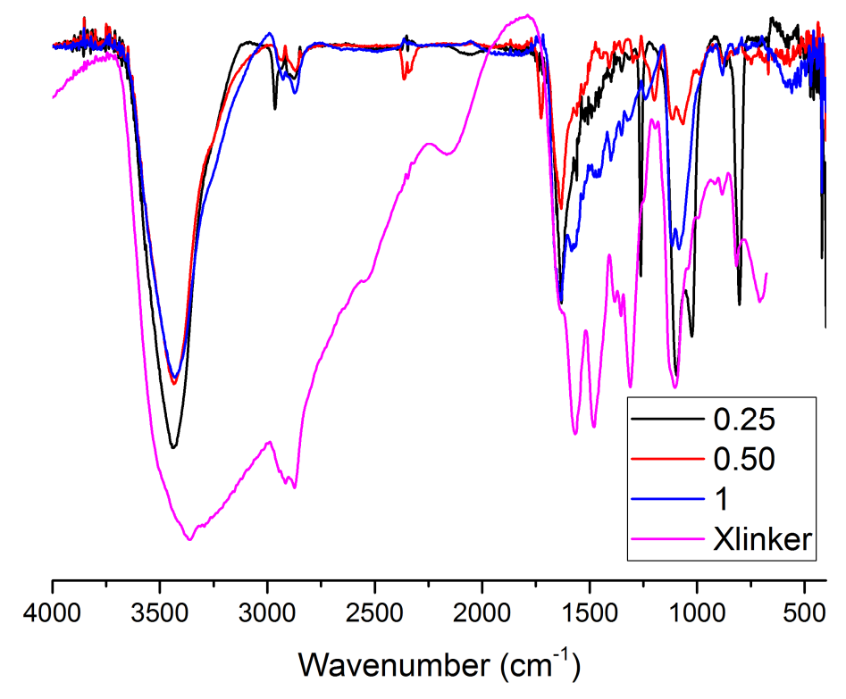
Crosslinked CNT Paints

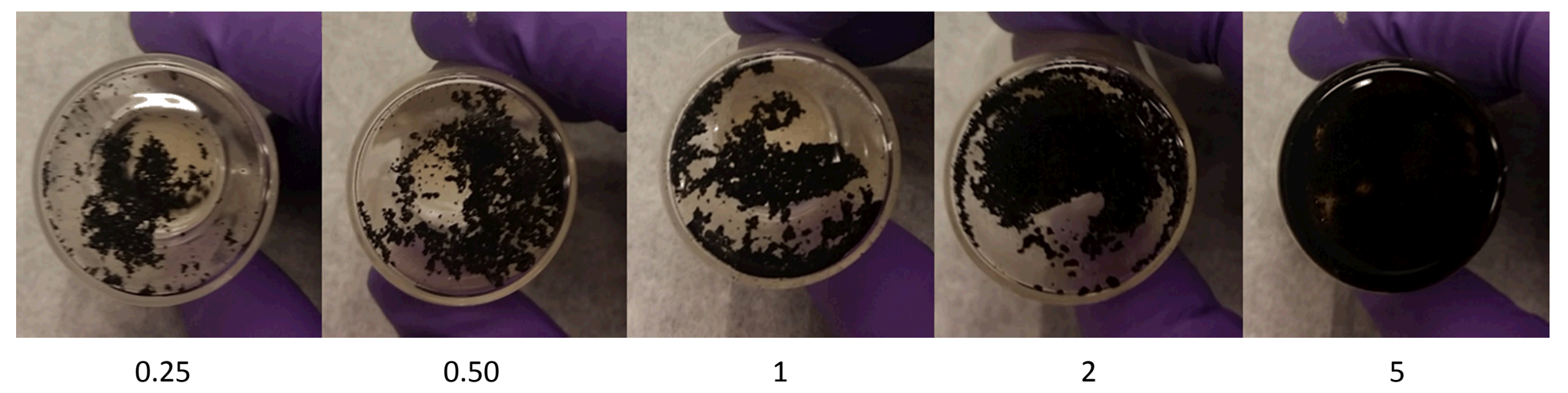
After the successful ring opening of the epoxide modified CNTs, the concept of a crosslinked CNT network was explored. Commercially available 2,2'-(Ethylenedioxy)bis(ethylamine) crosslinker was used in 0.25, 0.5, 1, 2, and 5 wt. equivalences to crosslink epoxide modified CNTs. Oven curing at 75 °C was performed in an oven for a 48 h period as a means to obtain film-like materials. Qualitative analysis of the reactions was performed. For the 0.25 sample, *ca.* 60% of the CNT starting material was not crossinked and was observed as loose black powder. The 0.5 and 1 samples showed materials with no free powder and no excess crosslinker. Samples 2 and 5 had excess crosslinker and appeared to have a wet look. IR KBr pellets were obtained by breaking down the "caked" material. IR samples of 2 and 5 were not possible due to the wetness of the material which resulted in non-transmissive brittle opaque pellets. IR characterization of the samples (right) showed a decrease in some the bands (160 sand 800 cm^{-1}) as the amount of crosslinker was increased. The apparent increase of the other bands can be attributed to the presence of excess crosslinker which also has vibrational and rotations bands in that region of the spectrum.



2,2'-(Ethylenedioxy)bis(ethylamine) crosslinker

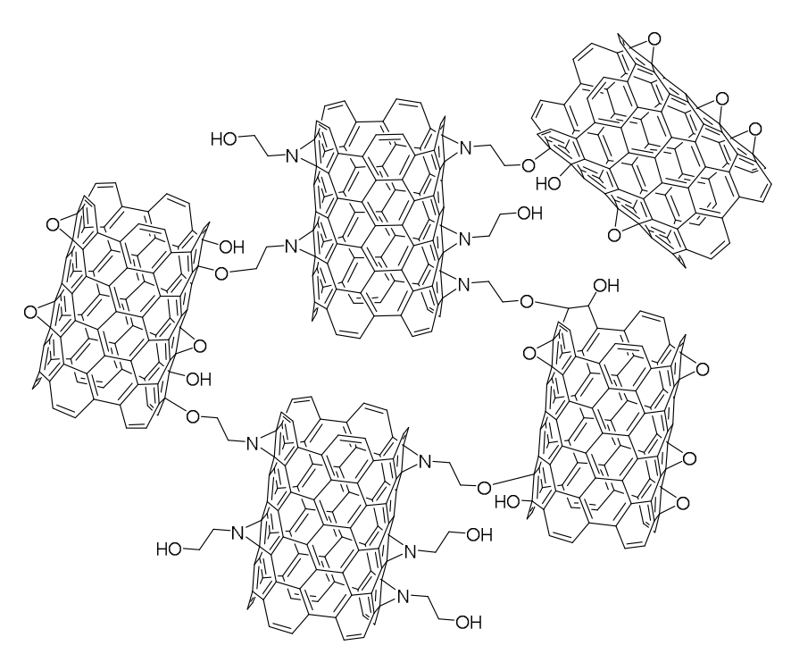
Samples	Comments
0.25	Loose CNT material present
0.5	Material "caked" at bottom of vial
1	Material "caked" at bottom of vial
2	Some excess crosslinker present
5	Excess crosslinker present



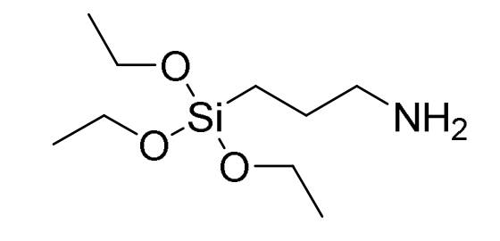


Future Work

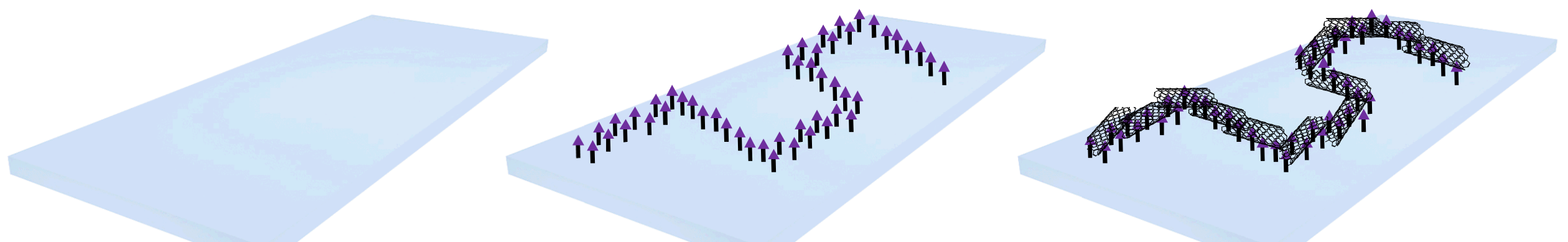
Using two modified CNTs materials produced here, a CNT-CNT crosslinked is envisioned. Epoxide modified CNTs will experience ring opening by $-NH_2$ and/or –OH modified CNTs and produce a mostly CNT crosslinked network.



Continuing to utilize the highly useful epoxide modified CNTs, CNT surface attachment onto glass slides or silicon wafers will be explored in order to produce electrically conductive materials. (3-Aminopropyl)triethoxysilane (APTES) is a commonly used substrate with a pendant amino group that may be printed onto the surface in a desired pattern. Nucleophilic ring opening of the epoxide rings on the CNT surfaces by APTES will create a covalently bonded conductive material .



APTES



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