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SIDEWALL COVALENT FUNCTIONALIZATION OF SINGLE WALL CARBON NANOTUBES THROUGH C-N BOND FORMING REACTIONS OF FLUORONANOTUBES WITH UREA, GUANIDINE AND THIOUREA (Preprint)

Merlyn X. Pulikkathara and Valery N. Khabashesku

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14. ABSTRACT

Sidewall covalent functionalization of carbon nanotubes is necessary to achieve smaller bundles, link to other functional moieties, and to aid in better dispersion in composites. In the present study, we present a one-step functionalization method which uses fluorinated single wall carbon nanotubes (F-SWNTs) as starting materials in the reactions with either urea, thiourea, or guanidine. Through these reactions, the derivatives with terminal amide and heteroamide groups on the nanotube sidewalls have been prepared. The products still contain some residual fluorine creating bifunctional nanotubes. These derivatives were characterized by Raman spectroscopy, Fourier transform infrared (FTIR), thermo gravimetric analysis (TGA), scanning electron microscopy (SEM), x-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM) and atomic force microscopy (AFM). Compared to fluorinated tubes, the urea-F-SWNTs, among the three derivatives, have shown the highest stability in water and aqueous urea solutions, thereby creating new opportunities for biomedical applications with nanotubes. These bifunctional derivatives will aid in creating an interface between the SWNTs and polymers, which will result in much stronger composites. The three derivatives are easily and rapidly synthesized, and the method can be easily scaled up for applications such as creating an integrated polymer network for stronger composites, coatings, for use in biomedical applications and nanoelectronic devices.

15. SUBJECT TERMS

Functionalization, nanotubes, urea, thiourea, guanidine, nanoelectronic

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Sidewall Covalent Functionalization of Single Wall Carbon Nanotubes Through C-N Bond Forming Reactions of Fluoronanotubes with Urea, Guanidine and Thiourea

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Abstract: Sidewall covalent functionalization of carbon nanotubes is necessary to achieve smaller bundles, link to other functional moieties, and to aid in better dispersion in composites. In the present study, we present a one-step functionalization method which uses fluorinated single wall carbon nanotubes (F-SWNTs) as starting materials in the reactions with either urea, thiourea or guanidine. Through these reactions, the derivatives with terminal amide and heteroamide groups on the nanotube sidewalls have been prepared. The products still contain some residual fluorine creating bifunctional nanotubes. These derivatives were characterized by Raman spectroscopy, Fourier Transform infrared (FTIR), thermo gravimetric analysis (TGA), scanning electron microscopy (SEM), x-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM) and atomic force microscopy (AFM). Compared to fluorinated tubes, the urea-F-SWNTs, among the three derivatives, have shown the highest stability in water and aqueous urea solutions, thereby creating new opportunities for biomedical applications with nanotubes. These bifunctional derivatives will aid in creating an interface between the SWNT's and polymers, which will result in much stronger composites. The three derivatives are easily and rapidly synthesized, and the method can be easily scaled up for applications such as creating an integrated polymer network for stronger composites, coatings, for use in biomedical applications and nanoelectronic devices.

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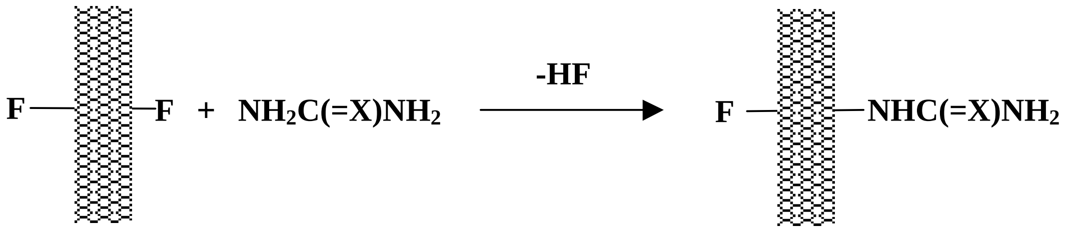
Introduction

Single walled nanotubes (SWNTs)[1] have been of immense research interest due to their remarkable mechanical and electrical properties. To utilize them in various applications, one needs to overcome the challenges of solubilization, dispersion, and design an interface to covalently bond the SWNTs to surfaces, polymers, biomolecules, etc. The major challenge to SWNT dispersion has been the Van der Waals forces between the nanotubes, which cause the formation of large bundles. These bundles create such unwanted effects as decreasing the mechanical strength of polymer composites[2,3]. It is necessary to functionalize the SWNT sidewall in order to overcome the π-π stacking interactions and Van der Waals forces between the SWNTs within the bundles, and thereby dramatically increase the availability of individual SWNTs. When SWNTs are in smaller bundles or as singles, better dispersion in solutions and in composites can be achieved which will enable many applications. These goals have been pursued by adopting the nanotube sidewall functionalization strategies through developing a number of covalent and non-covalent methods[4-10]. The enhancement of properties of various application-based composites, coatings, and electronics, particularly requires the covalent sidewall functionalization of SWNTs, which is capable of creating the efficient interface between the SWNTs and the matrix.

Fluorination of SWNTs was the first covalent sidewall functionalization method to produce the highly individualized and soluble nanotubes[5,11]. The introduction and use of fluorinated nanotubes (F-SWNT) has already resulted in increased dispersion in composites[12-14]. It has also been shown that fluorinated SWNTs can be further derivatized due to a higher reactivity than the pristine SWNTs[4-6]. The fluorine in the C-F bond of F-SWNT can be readily substituted by a variety of nucleophilic reagents to produce an array of sidewall functionalized SWNTs. It was shown in particular that the reactions of F-SWNT with terminal alkylidene diamines provide a convenient route to amino functionalized SWNTs through the sidewall C-N bond forming reactions[15-17]. These results have facilitated the use of the other substituted amino compounds, such as aminoalcohols, aminothiols, aminoacids, and aminosilanes, for preparation of the SWNTs sidewall functionalized with the terminal OH, SH, COOH and silyl groups by the similar one-step route[18-21]. It should be noted that in comparison with the widespread approach to functionalization, which is based upon etching of nanotube surface by oxidative acids[22,23], the method of direct fluorination and subsequent substitution of fluorine generally causes no destruction to the SWNT sidewalls. This is critical for maintaining the mechanical strength of the SWNT frame. Therefore, search for broader applicability of the C-N functionalization method[15-17] to the synthesis of diverse family of SWNT derivatives by studying new reagents capable of displacing fluorine in F-SWNTs is important.

We have recently studied the functionalization of SWNTs with the terminal amide and heteroamide functional groups via the reactions of F-SWNTs with urea, thiourea and guanidine (Scheme 1). These compounds were chosen due to their availability at low cost, water solubility and chemical properties prompting their use as chemical synthons in the production of polymers and biomaterials. Besides that, urea and guanidine are chaotropic agents which can cause disruption of local non-covalent bonding in molecular structures, particularly, hydrogen bonding in water. This type of interactions of urea have been studied in proteins solutions[25] and more recently with SWNTs[26]. Since F-SWNTs are hydrophobic, urea can intercalate into the nanotube bundles by disrupting the Van der Waals forces within such bundles, and self-assembles around SWNTs until unbundling occurs. Similar behavior is commonly noted in urea-based protein folding solutions[25]. For these reasons, the covalent attachment of simple amide and heteroamide moieties to the SWNTs sidewall is expected to result in disrupted SWNT bundles and improved dispersion in water and polar organic solvents. The results of these studies we have only briefly presented at conferences.[21,24] In this paper full report of this work is provided.

Scheme 1. Derivatization route for F-SWNT precursor through reactions with urea, thourea and guanidine



X= O, S, and NH

Experimental Section

Materials. Urea with 99% purity was purchased from Sigma-Aldrich. Guanidine hydrocloride (98% pure) was acquired from Alfa Aesar. Thiourea was purchased from Sigma-Aldrich. F-SWNTs of approximately C_2F stoichiometry were obtained from Carbon Nanotechnologies, Inc.

Methods. *Urea-functionalized SWNTs* (U-F-SWNTs) were prepared from F-SWNTs by using two methods, solvent-free urea melt synthesis, and solution synthesis. In the *urea melt synthesis*, 50mg of F-SWNTs were mixed with 5g of urea and grinded in a mortar. Then the mixture was placed into a three-neck flask, heated to 150°C to melt and stirred at this temperature for 4 hours under nitrogen. Thereafter, the mixture was cooled to room temperature, and then washed repeatedly with de-ionized water and ethanol and filtered on a Millipore Fluoropore PTFE filter membrane with a .22 μm pore size. The U-F-SWNTs were then dried overnight in a vacuum oven at 70°C. In the *solution synthesis*, 50mg of F-SWNTs were sonicated in DMF for 20 minutes and 500mg of urea added afterwards with 10 drops of pyridine. The mixture was heated and stirred at 100°C under nitrogen for 4 hours. After completion of the reaction, the product was collected on a filter membrane after washing off unreacted urea with water and ethanol.

Solution synthesis was also applied for preparation of thiourea-functionalized SWNTs (T-F-SWNT) by sonicating 50mg F-SWNT in 100ml DMF, followed by addition of 500mg of thiourea, and ten drops of pyridine. The solution mixture was then heated and stirred at 80°C-100°C under nitrogen for 4-12 hours. Higher temperature conditions were not possible since thiourea decomposes above 135°C. The derivatized tubes were then cooled to room temperature and washed repeatedly with de-ionized water and ethanol, and dried overnight in a vacuum oven at 70°C. The guanidine-functionalized SWNTs (G-F-SWNT) derivative was prepared by sonicating 50mg of F-SWNTs with DMF for 20 minutes, then 500mg of guanidine hydrochloride and ten drops of pyridine were added to the solution. The mixture was heated to 100°C and stirred under nitrogen for 4 hours. Afterwards, the SWNT were similarly washed and dried overnight in a heated vacuum oven.

Characterization. F-SWNTs and the synthesized U-F-SWNT, T-F-SWNT, and G-F-SWNT derivatives were characterized by Raman spectroscopy using Reinshaw Microraman, ATR-FTIR, TGA, (XPS) PHI Quantera was used to determine elemental analysis. TGA was done in inert environment using pre-purified argon gas, (AFM) Digital Instrument Nanoscope IIIA with Silicon tip, (TEM) JEM 2010 Transmission Electron Microscope (Cryo-TEM), and (SEM) FEI XL-30 Environmental SEM high resolution (2nm) thermal field emission electron microscope were used for surface imaging.

Results and Discussion

Raman spectroscopy. The Raman spectra of the SWNT derivatives (Figure 1B-D) show a decreased intensity and shift of the disorder peak (D mode) as compared to the F-SWNTs precursor (Figure 1A). The decreased intensity of the D peak is due to the reduction of the number of sp^3 C-C bonded carbons, as some of the fluorine atoms are removed from the sidewall and substituted through the predominant C-N covalent bond formation according to the reaction scheme (Scheme 1). By attaching the urea and heteroamide molecules, which are much larger than the fluorine atom, there is a recovery of sp^2 bonds between the sites of C-N attachment. The shift in the D peak indicates that another group is covalently attached to the sidewall. Of all the Raman spectra, the G-F-SWNT have shown the greatest shift, from 1293.3 cm^{-1} in F-SWNT to 1304.4 cm^{-1}, as seen in Figure 1D. The graphitic peak (G peak) which is indicative of sp^2 bonding, is located at 1580 cm^{-1} for the F-SWNT, and this is shown in Figure 1A. The G peak increases in intensity for all derivatives, and this results from the reappearance of the long-range symmetry of the SWNT sidewall.

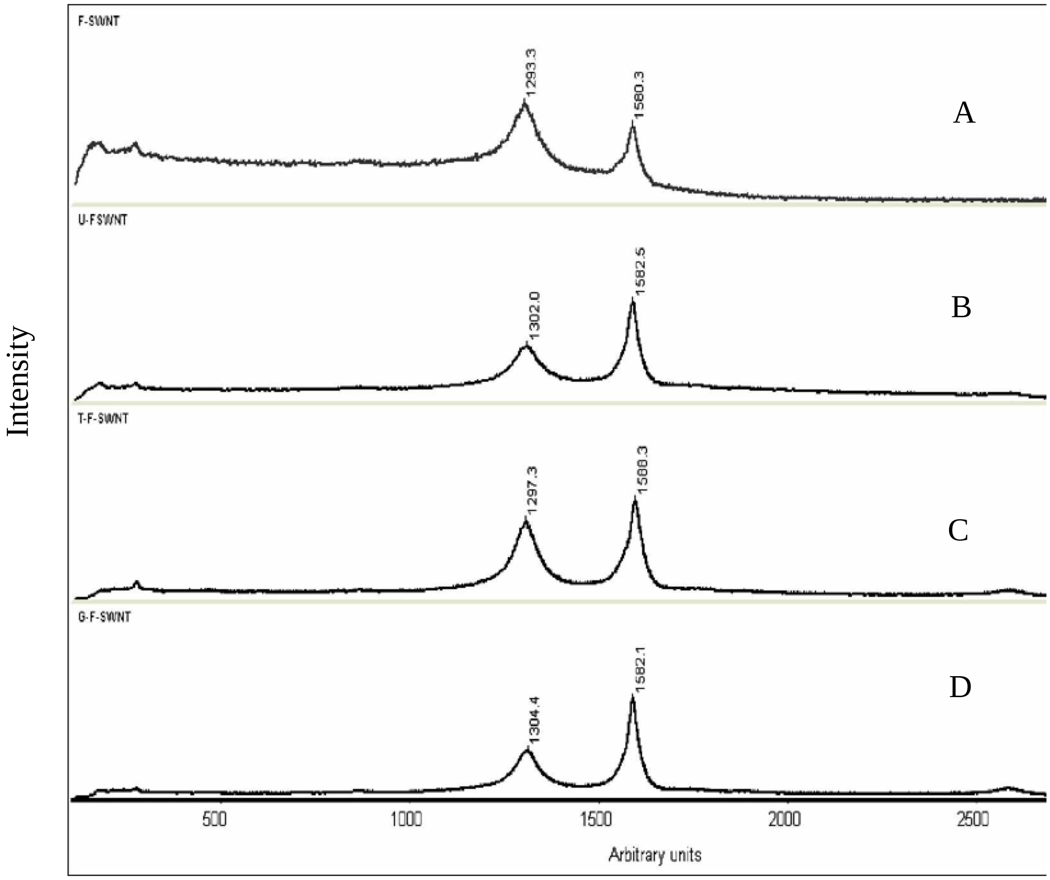


Figure 1. Raman spectra of fluorinated (A) and derivatized nanotubes, U-F-SWNT (B), T-F-SWNT (C), and G-F-SWNT (D).

FTIR spectroscopy. The ATR-FTIR spectra of functionalized SWNTs are shown in Figure 2. They provide structural information on the functional groups that were covalently attached to the SWNT sidewall after the reaction. In the spectrum of F-SWNT (Figure 2A) the C-F stretch bands appear at 1185 cm^{-1}, while the band for activated C=C stretches is seen near 1558 cm^{-1}. The U-F-SWNTs show a broad peak at 3134 cm^{-1}, which is attributed to the N-H stretch, a peak at ~1675 cm^{-1} and a band at 1052 cm^{-1} which result from the C=O and C-N stretching vibrations in the terminal amide groups. The C-F band has a significantly reduced intensity and appears as a shoulder on the band attributed to the C-N stretch (Figure 2B). The IR spectrum of G-F-SWNT derivative (Figure 2C) exhibits very broad band of N-H stretch in the 3050-3450 cm^{-1} region, peaks at 1652 and 1082 cm^{-1} due to the C=N and C-N stretches, respectively, in the guanidine moiety attached to the SWNT. The C-F band also shows a reduced intensity in this spectrum. In the IR spectrum of T-F-SWNT derivative, shown in Figure 2D, the peak of the C=S stretch for thioamide moiety is believed to appear in the region of 800-980 cm^{-1} where the peak observed at 967 cm^{-1} is the likely candidate for this assignment. The intensity of the C-F band is dramatically reduced after functionalization of the F-SWNT.

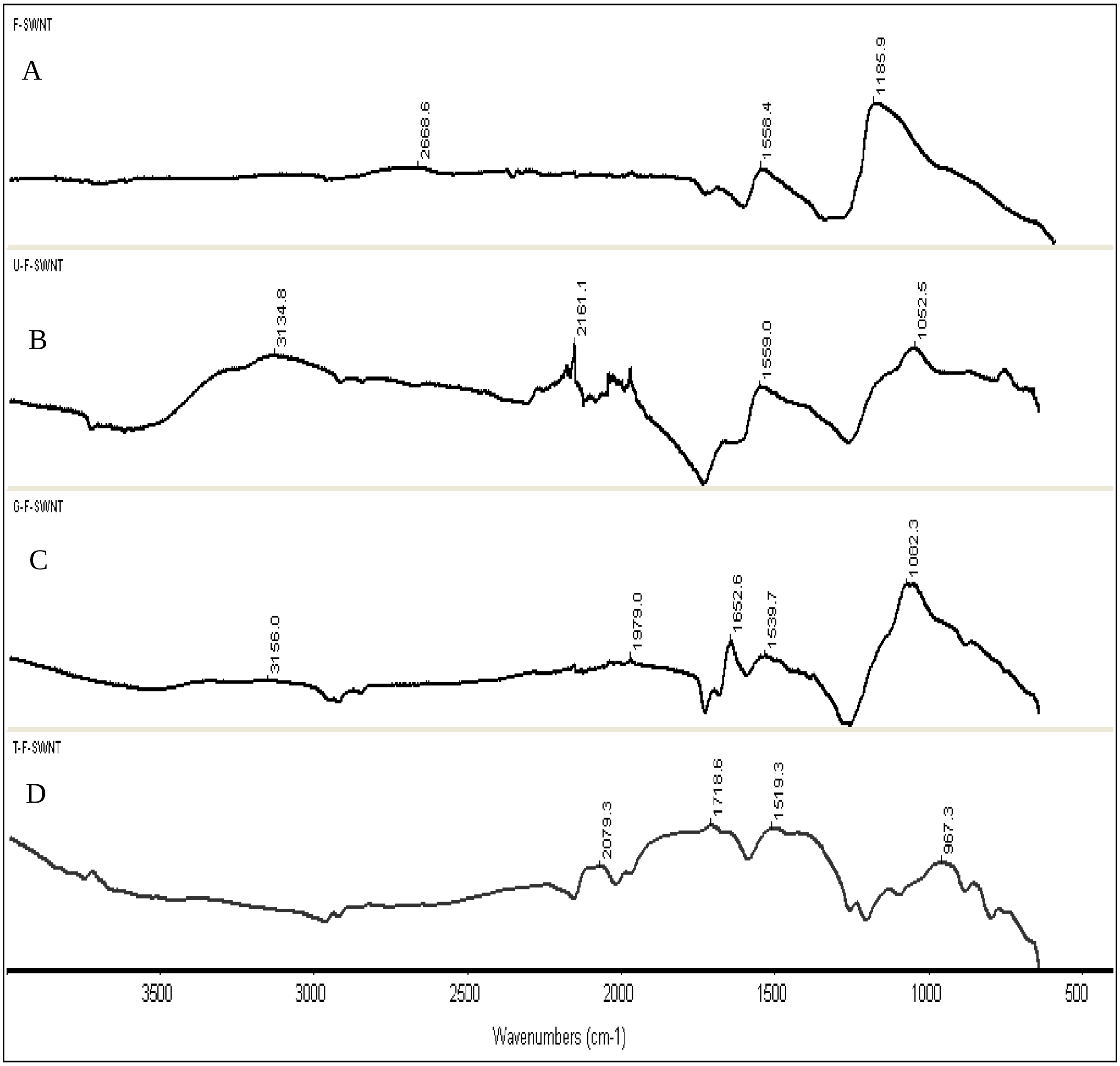


Figure 2. ATR-FTIR spectra of derivatized F-SWNT: (A) F-SWNTs, (B) U-F-SWNT, (C) G-F-SWNT, (D) T-F-SWNT.

Thermal gravimetric analysis (TGA). TGA experiments were carried out in argon environment that was heated to up to 1000°C at 10°C/min. The differential weight curve of the F-SWNT precursor is shown in Figure 3a, which shows a single degradation peak at 528°C in which fluorine is removed from the sidewall as CF_4. There was still 51% residual weight which was confirmed to be SWNTs that were defluorinated as evidenced by the decreased D peak and increased G peak in Raman spectroscopy (not shown). Urea itself was also subjected to TGA, and it was found that there is a two-step degradation curve for urea, one at 241°C and the second at 371°C, this is shown in Figure 3b. These peaks are most likely due to well-known decomposition of urea into ammonia and isocyanic acid HNCO. As for the U-F-SWNT, the differential curve (Figure 3c) also shows a two-step degradation with the peaks in the 200-300 ºC temperature range and shifted relatively to urea itself. This indicates that urea moieties are attached to the SWNTs by covalent sidewall C-N bonds which cleave in U-F-SWNTs in the same temperature region as sidewall amino functionalized SWNTs. It was estimated that there are 1 in 8 carbons of the F-SWNT sidewall that are functionalized with urea molecules. Furthermore, it was shown that all three derivatives virtually lacked a peak at 528°C, confirming that most of the fluorine was removed from the F-SWNT sidewall. Since the F-SWNTs were prepared in excess of urea (at a taken ratio of 10:1), there were sufficient amide or heteroamide groups to displace the fluorine and attach to the SWNTs.

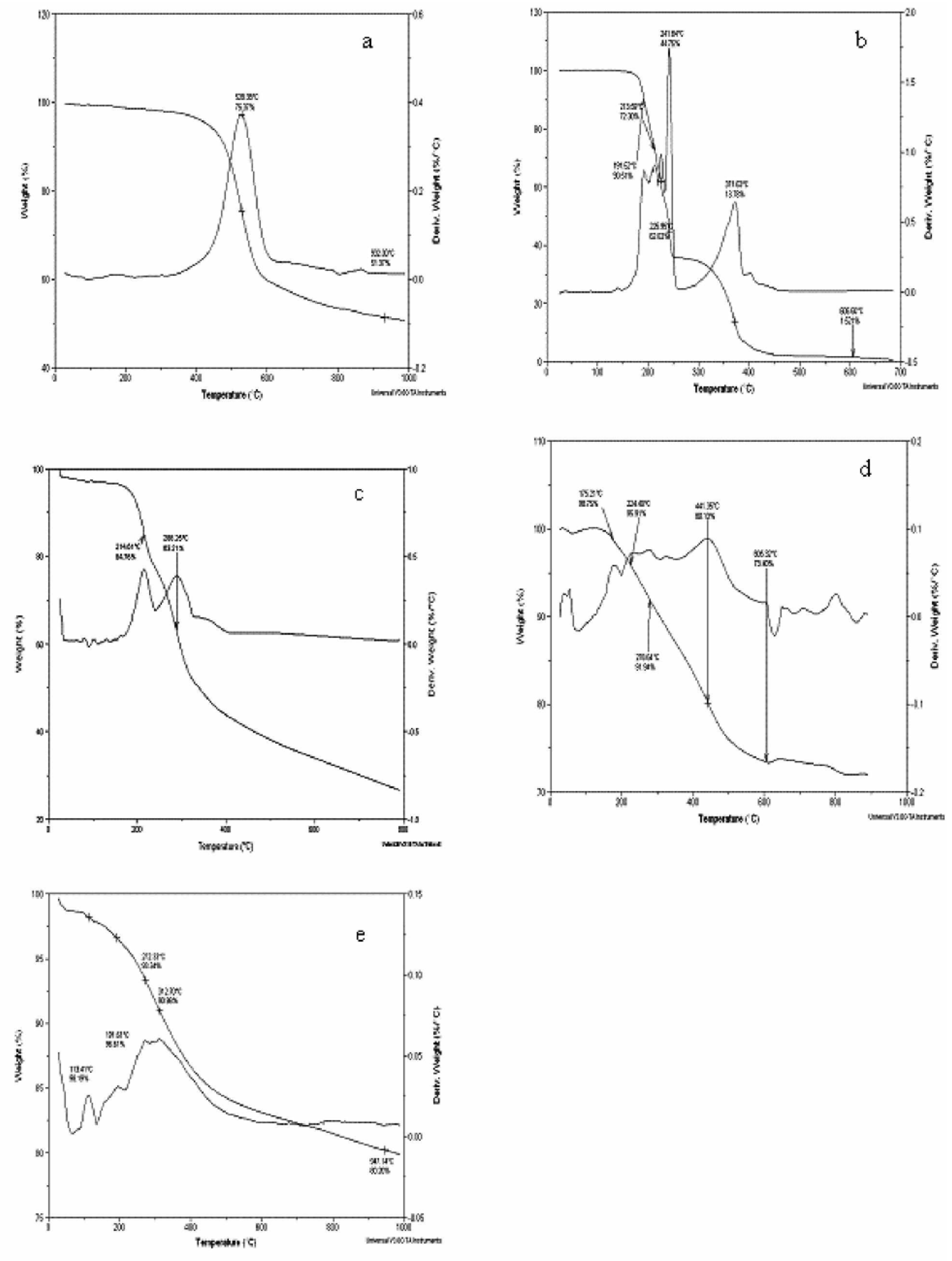

a
529.38°C
75.97%
932.30°C
51.37%
Weight (%)
Deriv. Weight (%/°C)
Temperature (°C)
Universal V3.6D TA Instruments
b
241.84°C
44.75%
213.69°C
72.30%
191.52°C
90.51%
225.95°C
62.82%
371.62°C
13.78%
606.60°C
1.52%
Weight (%)
Deriv. Weight (%/°C)
Temperature (°C)
Universal V3.6D TA Instruments
c
214.61°C
84.76%
288.25°C
63.21%
Weight (%)
Deriv. Weight (%/°C)
Temperature (°C)
d
175.21°C
98.75%
224.40°C
95.91%
441.35°C
80.10%
606.32°C
73.40%
280.64°C
91.94%
Weight (%)
Deriv. Weight (%/°C)
Temperature (°C)
Universal V3.6D TA Instruments
e
272.81°C
93.34%
312.30°C
90.96%
191.61°C
96.61%
113.47°C
98.19%
947.14°C
80.20%
Weight (%)
Deriv. Weight (%/°C)
Temperature (°C)
Universal V3.6D TA Instruments

Figure 3. TGA-DTA curves for (a) F-SWNT, (b) Urea, (c) U-F-SWNTs produced by urea melt synthesis, (d) G-F-SWNT, (e) T-F-SWNT.

Scanning electron microscopy (SEM). An SEM of the U-F-SWNTs is shown below in Figure 4. SEM of these U-F-SWNTs has exposed their modified electrical properties. Usually, F-SWNTs have a high resistivity, and they must be made conductive for SEM imaging by coating with gold. In this case, there was no need to coat the U-F-SWNTs with gold as clear images were obtained even at a magnification of 120,000X. This indicates that increased conductivity results from the urea functionalization. The modified electrical properties of these derivatives are currently under investigation.

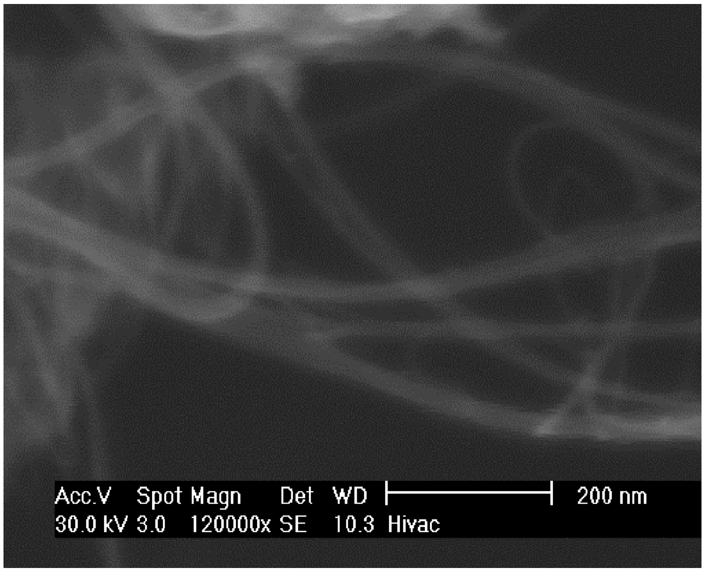


Figure 4. SEM image of Urea-F-SWNT.

Atomic force microscopy. AFM studies of the U-F-SWNTs, which were prepared from F-SWNTs in DMF through a solution synthesis, have large beads on the backbone, and this is shown in Figure 5a. The size of the bead, which is indicated by the black flags in Figure 5a, corresponds to the white flags in the height analysis of the image in Figure 5c, where the height is 6.6nm. Note that there are different sizes of beads along the backbone of the nanotubes, this is shown in Figure 5b. The beads are most likely the result of polyurea and/or a salt complex. The presence of beads on the nanotubes has also been seen in previous research*. We note that although there is beading present in the AFM, there appears to be no large beads in our TEM images. The lack of beading in the TEM samples results from the tubes being re-suspended, sonicated, and centrifuged for TEM analysis.

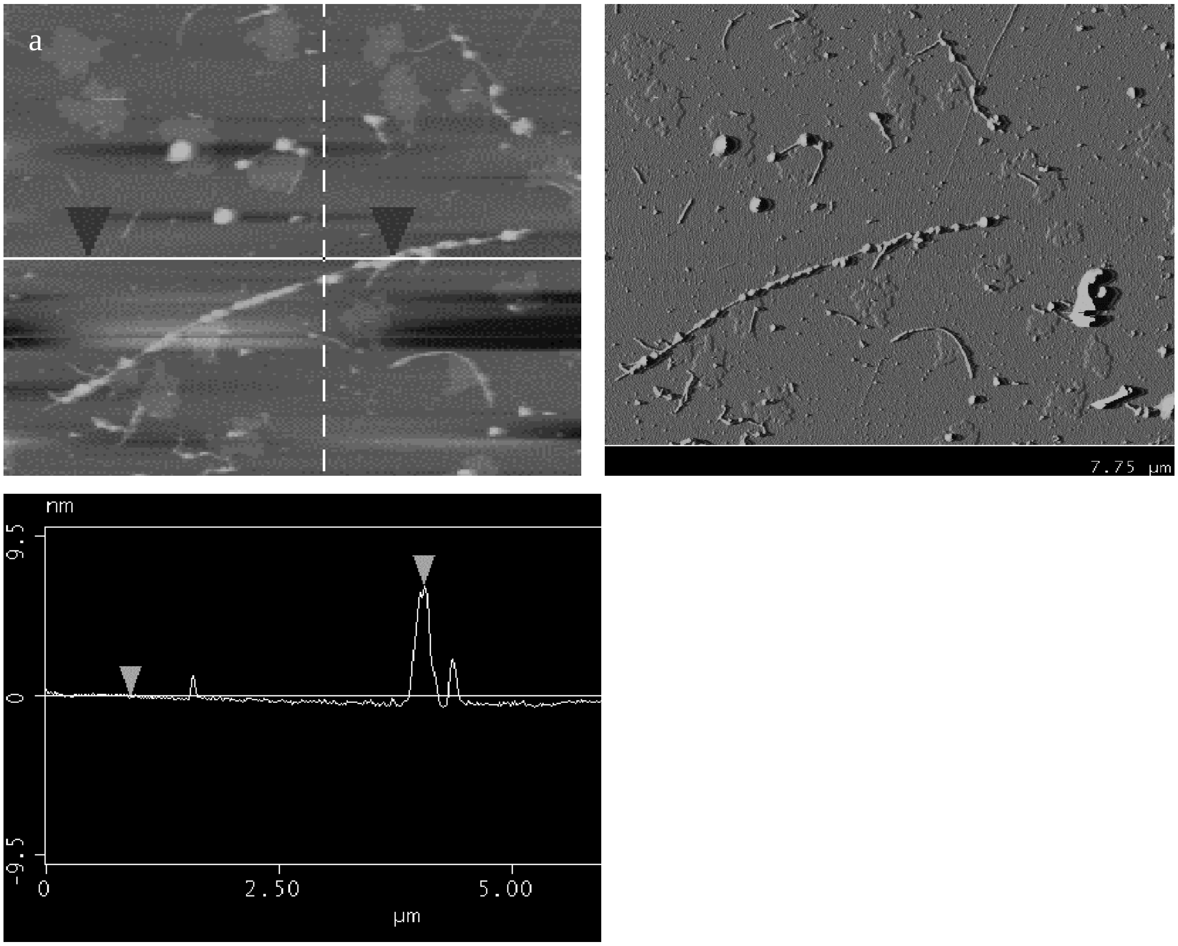


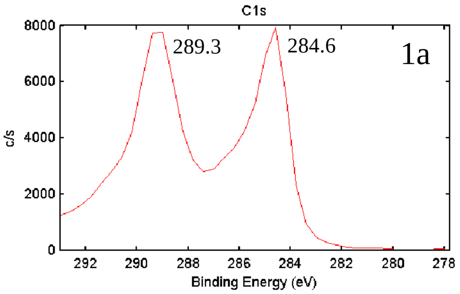
Figure 5. AFM images and height analysis, (a) height image, (b) amplitude data, (c) height analysis of a bead along the backbone of a nanotube bundle, the white flags in (c) correspond to the dark flags in (a).

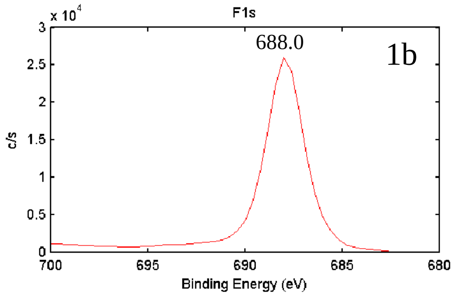
X-ray photoelectron spectroscopy (XPS). In order to determine which method was optimal for high yield of functionalization of SWNTs, XPS analysis was done on all products, even those from different reaction schemes. The XPS data are summarized in Table 1. The atomic content of F1s in F-SWNTs was found to be 37.4%. Among derivatized F-SWNTs, the most notable change in fluorine content with respect to F-SWNTs was found for the G-F-SWNTs (7.7 at.%). For U-F-SWNTs, it was found that urea melt had a higher atomic percent content of nitrogen (10.8 at. %, measured by N1s peak) compared to only the 2.8 at. % content found in the product prepared through the DMF solution synthesis. It is known that thiourea itself can exist in two tauomer forms, $S=C(NH_2)_2$, and isothiourea $HS=CNHNH_2$, and is not thermally stable at temperatures 135°C. This would account for the low presence of sulfur and the higher presence of N1s in the thiourea reaction schemes. The products with the asterix in Table 1 are shown by the XPS spectra in Figure 9, which specifically highlight the C1s and F1s peaks.

Table 1. Comparison of Different Methods and Conditions for Synthesis of dDerivatized F-SWNTs and XPS Elemental Analysis (At. %) of the Products

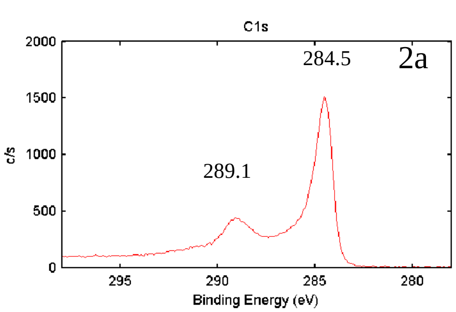
	Temp °C	Time (Hours)	XPS %C1s	XPS %F1s	XPS %O1s	XPS %S2p	XPS %N1s
F-SWNT			62.6	37.4			
Urea/DMF	100	4	78.6	13.2	5.5		2.8
Urea melt*	150	4	64.3	11.7	13.1		10.8
Guanidine	80	4	73.4	24.2			2.5
Guanidine*	100	4	89.9	7.7			2.4
Thiourea*	80	12	87.5	11.0		0.2	1.3
Thiourea	80	4	83.0	15.3		0.7	1.1
Thiourea	100	4	84.6	14.0		0.9	0.9

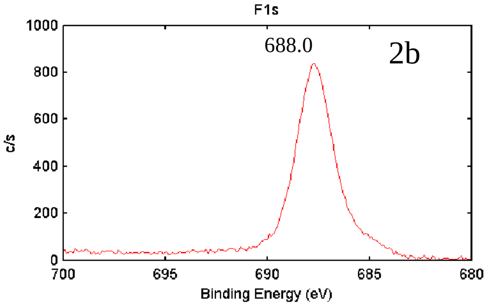
In Figure 9, we see the peak of carbons of the C-F bond at 289.3 eV and the C=C bonded carbons at the lower energy of 284.6 eV, which has been previously observed in the XPS spectrum of the control sample of the F-SWNTs that are shown in Figure 6-1a. The peak at 289.3 eV is significantly decreased in intensity for each subsequent derivative, and this indicates that the amount of the covalently bonded fluorine is diminished with functionalization. The single F1s peak at 688.0 eV of the control in Figure 10-1b is due to the covalent C-F bonding. We also note that for the U-F-SWNTs in the DMF, and for both the G-F-SWNTs and the T-F-SWNT derivatives, there is an additional peak at 684.5 eV. This suggests that the there is ionic fluorine present probably from some amount of HF forming salt with the amide derivatives. It should be noted that the development of this peak occurs only with the reactions in which DMF was used, however there is a high degree of substitution in the U-F-SWNT melt process; there is also evidence of a shoulder at this peak region. Nevertheless the intensity of the potential salt formation is clearly shown in the derivatives that were synthesized in DMF. It is with G-F-SWNT that had the most intense peak at 685.4 eV, which would make guanidine HCl the most reactive with F-SWNT.



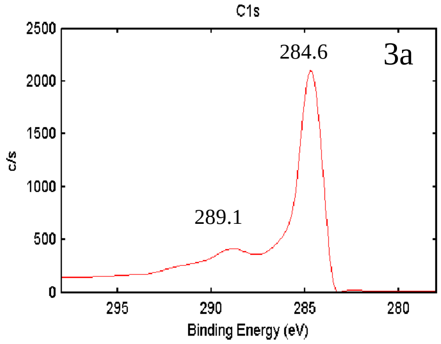


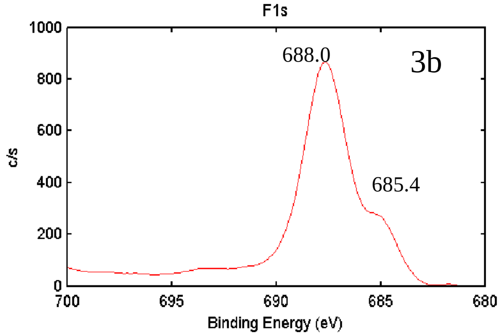
F-SWNT





U-F-SWNT melt





U-F-SWNT in DMF

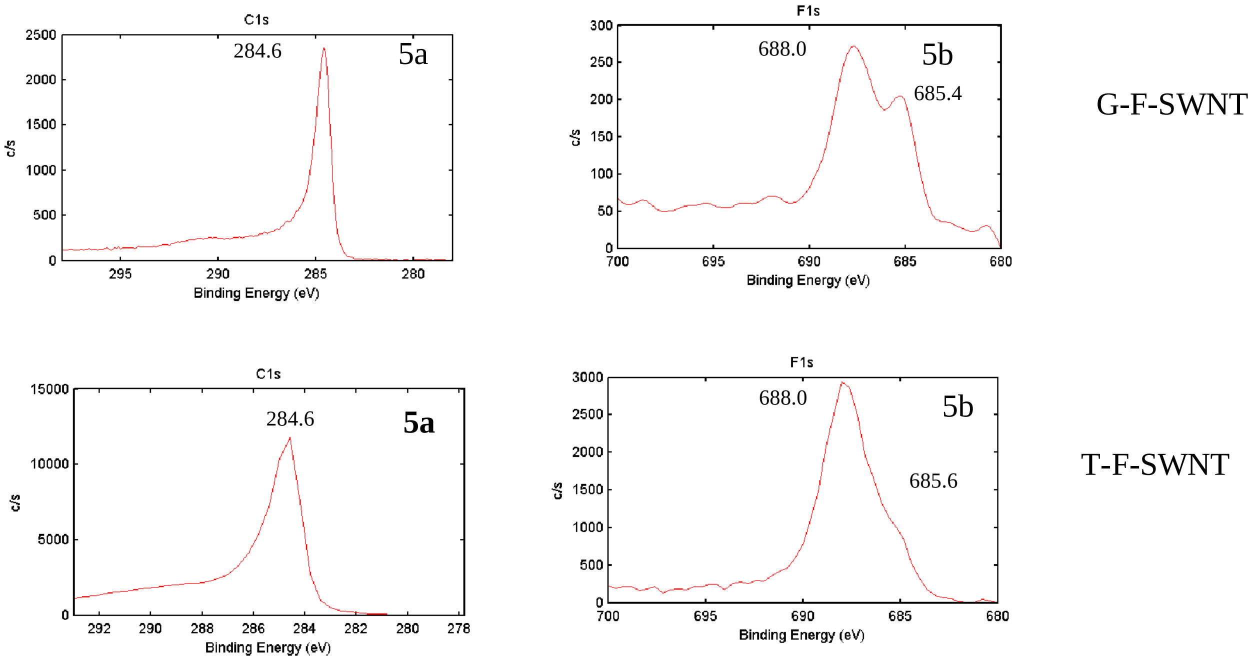
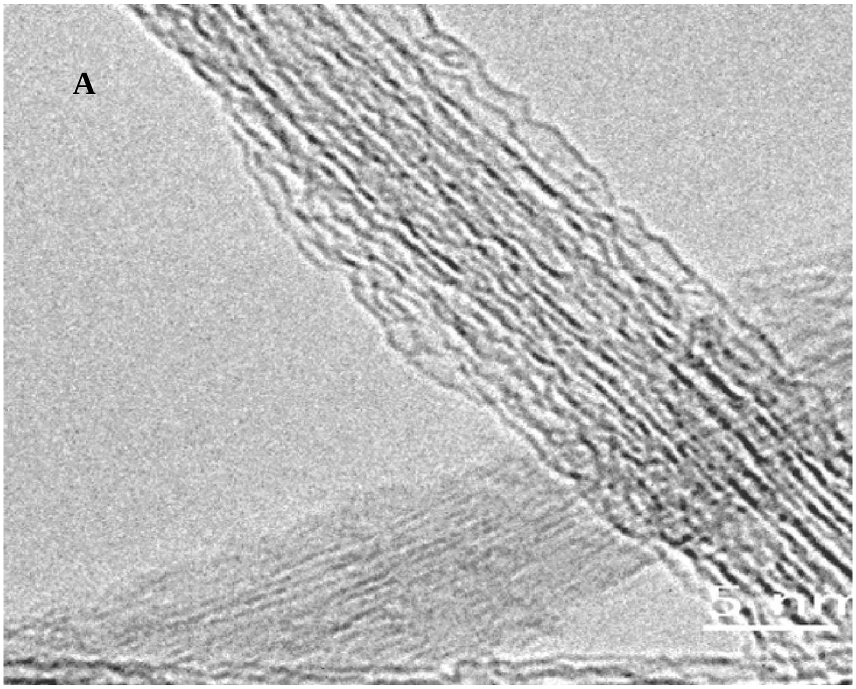
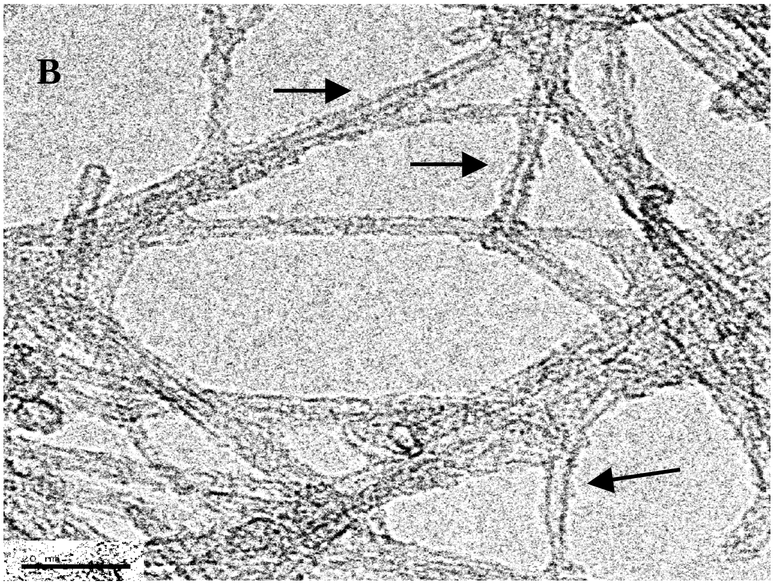


Figure 6. XPS peaks of a) C1s and b) F1s 1) F-SWNT control, 2) U-F-SWNT melt, 3) U-F-SWNT in DMF 4) G-F-SWNT, 100ºC for 4 hours, and 5) T-F-SWNT 80ºC for 12 hours.

Transmission electron microscopy (TEM). The TEM of F-SWNT is shown in Figure 7a. Note the existence of many nanotubes in the form of bundles. The image of U-F-SWNT from melt synthesis is shown in Figures 7b and 7c. U-F-SWNT are densely functionalized and there are more singles shown here than for the F-SWNT. On the sidewall, there are molecules of urea sticking out from the nanotube, like pine needles, as indicated by the black arows in 7b abd 7c. The presence of more singles than larger bundles is another indication of the intercalating nature of urea into the larger bundles which has ahown here to produce smaller bundles and singles.


A
5 nm


B
20 nm

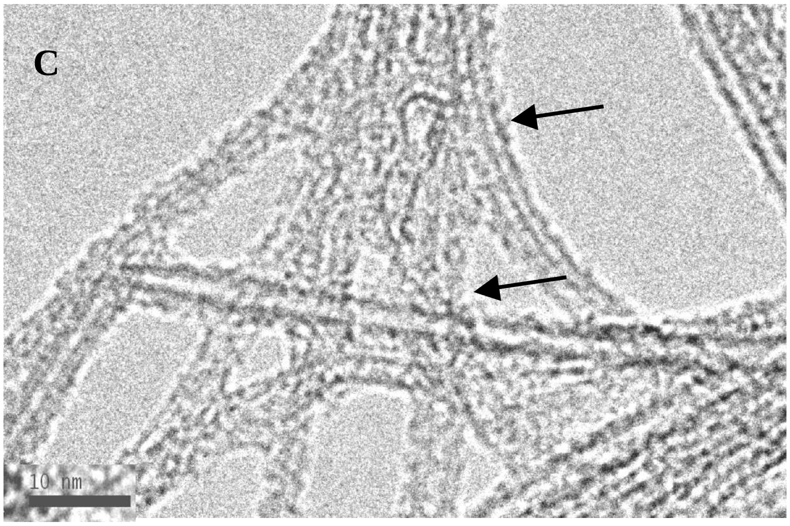


Figure 7. TEM of SWNT derivatives: (A) F-SWNTs with a scale bar of 5 nm, (B) U-F-SWNT with a scale bar of 20nm, and (C) U-F-SWNT with a scale bar of 10 nm.

Dispersion in solvents. To see the effect of the derivatives in solvents, 5mg of F-SWNT and U-F-SWNT were placed into a small vial containing either de-ionized water or 5 wt. % urea in de-ionized water solution. The vials were then sonicated in a bath sonciator for 15 minutes, and a picture was taken of the vials one hour later, which is shown in Figure 8. The F-SWNT, due to their hydrophobic nature, stayed on top of the water. However, when placed in the 5%urea solution, the F-SWNT seemed to enlarge and migrate to the bottom of the vial. This would indicate that even though urea which is extremely soluble in water, was still drawn to the Van der Waals forces within the F-SWNT bundles and were able to intercalate the bundles and wrap them, thus separating them, resulting in an enlarged, “swelled” appearance.

It seemed the hydrophobic nature of the fluorinated tubes was overcome, by creating a hydrophilic coating over the bundles, and from pure weight of the coating as well, these bundles sank to the bottom of the vial. U-F-SWNT had a better dispersion in water compared to F-SWNT, as the solution was much darker, however there was again “swelled” tubes on the bottom of the vial. Finally, the U-F-SWNT in the 5%urea solution had the best dispersion, as the column was entirely dark. This is important, as it would enable U-F-SWNT to be used for biomedical research, since these tubes can be used in an aqueous environment.

In Figure 9 below, 5mg of the F-SWNT and derivatives were each placed in 20ml of DMF, sonicated for 15 minutes and a photo was taken one hour later. It is shown that the vial with U-F-SWNT is the darkest. For the F-SWNT suspension, the dispersion is not very dark, and the “swelled” bundles that have dropped out of DMF are shown in the bottom.

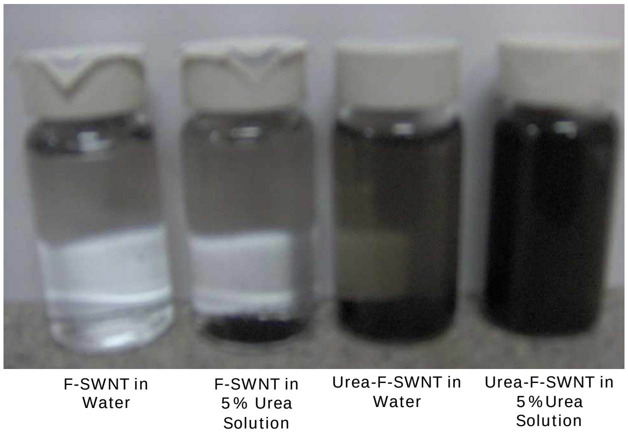


Figure 8. Picture of F-SWNT and U-F-SWNT in water and 5% urea solution.

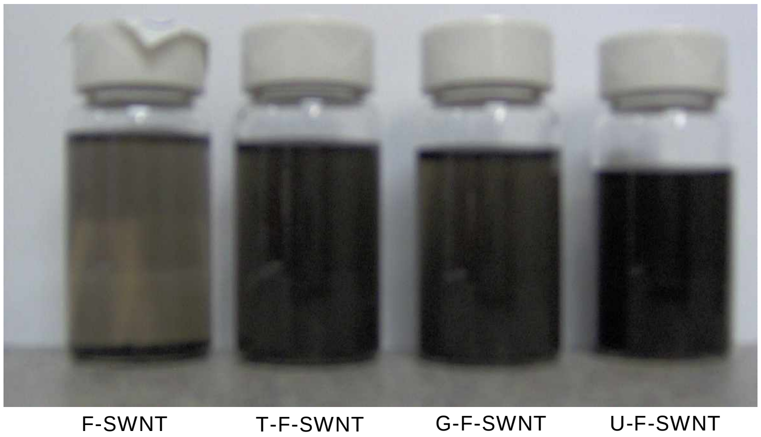


Figure 9. Picture of F-SWNT and derivatives in DMF.

Conclusion.

It has been shown that F-SWNT has been successfully bifunctioanlized with urea, guanidine HCl and thiourea forming covalent bonds to F-SWNT. Covalent bonding has been shown by the use of several techniques that illustrate the local environment of the fluorine atoms has changed with these new developed methods. Raman spectra have shown shits in the D peak which would indicate another group has attached itself to the sidewall, also the decrease of the D peak that correlates to the return of the sp^2 bonds in between the sites of C-N bonding of the nanotubes and derivatives. FTIR has shown the presence of the amino and related structures as well as the decreased intensity of the C-F peaks. TGA has shown the derivative weight loss curves which show that fluorine in bulk is not present and the 2-step loss of urea and derivatives from the F-SWNT. AFM has shown how urea beads up on the sidewall when prepared with DMF. XPS has shown residual fluorine presence and had quantified the effect of the new developed methods. TEM has shown urea molecules from urea melt process. Images of the dispersion in solutions have been presented. The development of solvent free synthesis will add to green chemistry methods of functionalizing nanotubes. Resistivity measurements are in progress for all derivatives. These new methods create bifunctionalized tubes in a facile manner. The ability to disperse in aqueous systems will generate new research and biological applications. The new derivatives with their amino terminal groups also will be useful in nanotube-FET devices and have potential in epoxy composites.

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