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Sidewall Covalent Functionalization of Single Wall Carbon Nanotubes Through Reactions of Fluoronanotubes with Urea, Guanidine, and Thiourea

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

Introduction

Single walled carbon nanotubes (SWNTs)[1] have been of immense research interest because of their remarkable mechanical and electrical properties. To utilize them in various applications, one needs to overcome the challenges of solubilization and dispersion and to design an interface to covalently bond the SWNTs to surfaces, polymers, biomolecules, and so forth. The major challenge of SWNT dispersion has been the van der Waals forces between the nanotubes, which cause the formation of large bundles. These bundles create unwanted effects such as decreasing the mechanical strength of polymer composites.[2,3] It is necessary to functionalize the SWNT sidewall to overcome the $\pi-\pi$ 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, dispersion is improved in solutions and in composites which would enable many applications. These goals have been pursued by adopting the nanotube sidewall functionalization strategies through developing a number of covalent and noncovalent methods.[4–10] The enhancement of properties of various application-based composites, coatings, and microelectronic devices 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

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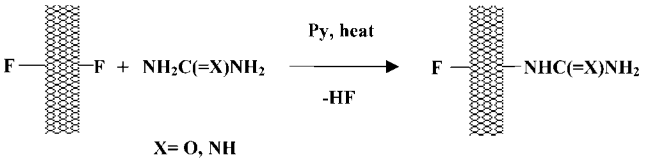
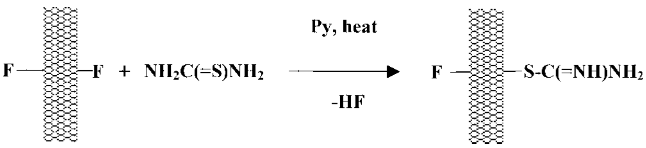
Scheme 1. Derivatization Route for F-SWNT through Reactions with Urea and Guanidine



Scheme 2. Reaction of F-SWNT with Thiourea



substituted by a variety of nucleophilic reagents to produce an array of sidewall functionalized SWNTs. It was particularly shown 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, it is important to 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.

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 (depicted in Schemes 1 and 2). These compounds were chosen because of their low cost, water solubility, and chemical properties prompting their use as chemical synthons for production of plastics, resins, rubber chemicals, rocket propellants, fertilizers, and biomaterials. Besides that, urea, thiourea and guanidine are chaotropic agents which can cause disruption of local noncovalent bonding in molecular structures, particularly, hydrogen bonding in water. This interaction has been studied in protein solutions[25,26] and more recently with SWNTs.[27] Since F-SWNTs are hydrophobic, urea can intercalate nanotube bundles by disrupting the van der Waals forces and self-assemble 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 SWNT sidewalls is expected to result in smaller SWNT bundles and improved dispersion in water and polar organic solvents. The abundance of terminal amide and heteroamide functionalities on the SWNT sidewalls will provide for uses of these modified nanotubes as reactive building blocks in copolymerization and polycondensation with different polymer resins, epoxies, polyurea, urea-formaldehyde, Nylon, and so forth to create an integrated nanocomposites structures with enhanced mechanical properties.

The results of these studies we have only briefly presented at conferences.[21,24] This paper gives a full report of this work.

Experimental Section

Materials. Urea with 99% purity was purchased from Sigma-Aldrich. Guanidine in the form of guanidinium hydrochloride (98% pure) was acquired from Alfa Aesar. Thiourea was purchased from Sigma-Aldrich. F-SWNTs of approximately C_2F stoichiometry, prepared by direct fluorination of SWNTs, were obtained from Carbon Nanotechnologies, Inc. (CNI). The SWNTs are commercially produced by CNI by their proprietary modified HipCO process.

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,* 50 mg of F-SWNTs were mixed with 5 g of urea and ground in a mortar. Then the mixture was placed into a three-neck flask, heated to 150 °C to melt, and stirred in the fume hood at this temperature for 4 h under continuos N_2 gas flow. The hazardous HF gas formed as a byproduct in the reactions studied here was thus safely removed through N_2 purging line. Thereafter, the mixture was cooled to room temperature, deionized water was added into the flask, and the mixture was sonicated for 30 min in a bath sonicator. The solution was then filtered on a Millipore Fluoropore PTFE filter membrane with a 0.22 μm pore size. The product was washed repeatedly with deionized water and ethanol and then dried for 8 h in a vacuum oven at 70 °C to remove any residual water.

In the *solution synthesis* method, applied for preparation of U-F-SWNTs, thiourea-functionalized SWNTs (T-F-SWNT), and guanidine-functionalized SWNTs (G-F-SWNT), 50 mg of F-SWNTs were sonicated in DMF for 20 min, and 500 mg of urea, thiourea, or guanidine hydrochloride, respectively, was added afterward with

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10 drops of pyridine (Py). The latter is known for its action as a catalyst in fluorine substitution reactions[15–17] as a result of the ability to bind HF. The solution mixture was then heated and stirred at two different temperatures, 80 and 100 °C, for 4 and 12 h under nitrogen. Higher temperature conditions were not desirable since thiourea, in particular, decomposes above 135 °C. The mixture was cooled down to room temperature, washed repeatedly with deionized water and ethanol, and dried for 8 h in a vacuum oven at 70 °C to remove any residual solvent. The functionalized SWNT products, U-F-SWNT, T-F-SWNT, and G-F-SWNT, were collected on a filter membrane after washing off unreacted urea, thiourea, and guanidine hydrochloride, respectively, with deionized water and ethanol.

Characterization. To study the chemical changes, the F-SWNTs and the synthesized U-F-SWNT, T-F-SWNT, and G-F-SWNT derivatives were characterized by ATR-FTIR spectroscopy performed using a Thermo Nicolet Nexus 670 FTIR spectrometer on samples pressed into a KBr pellets. X-ray photoelectron spectroscopy (XPS) data for elemental analysis were obtained with PHI Quantera spectrometer using the monochromatic Al Kα radiation source (1486.6 eV) with a power setting of 350 W and an analyzer pass energy of 23.5 eV. To observe the changes in covalent attachment of functional groups to the sidewall, Raman spectra were taken with a Renishaw Microraman system operating with a 780 nm AlGaAs diode laser source. Thermal gravimetric analysis (TGA) was carried out for studying the thermal stability of the new products and understanding the degree of SWNT functionalization by weight loss and shift in derivative peaks. TGA analyses of the products were done in an inert environment using prepurified argon gas with a TA-SDT-2960 TGA-DTA analyzer. To examine surface morphology modification of the SWNT derivatives, we have performed the atomic force microscopy (AFM) analysis on a Digital Instrument Nanoscope IIIA equipped with a silicon tip. For microstructure investigation, we have used the transmission electron microscopy (TEM) imaging of a specimen placed on lacey carbon coated copper grids (size 300 mesh) by using a JEOL JEM-2010 electron microscope operating at an accelerating voltage of 100 kV. A scanning electron microscope (SEM) FEI XL-30 with 2 nm high resolution was also used for taking surface images.

Results and Discussion

Reactions of F-SWNTs with Urea, Thiourea, and Guanidine. The suggested reaction routes are shown in Schemes 1 and 2. Unlike urea and guanidine, which react with the F-SWNTs through their NH_2 groups and form C—N linkages with the SWNT sidewalls after elimination of HF (Scheme 1), thiourea most likely attaches to the sidewall not through the C—N but the C—S bond (Scheme 2). This is deemed possible in view of higher nucleophilicity of sulfur in the >C═S moiety relatively to oxygen in the >C═O and nitrogen in the >C═NH groups.[28,29]

It is well-known that under prolonged heating up to a melting point urea can undergo polymerization as well as decomposition with release of ammonia and formation of isocyanic acid.[30] Therefore, these processes are expected to contribute to the functionalization reaction of F-SWNTs with urea and result in attachment of some polyurea units to the sidewalls of F-SWNTs to form PolyU-F-SWNT derivatives according to the following equations:

$$\text{F-SWNT-NHCONH}_2 + n\text{H}_2\text{NCONH}_2 \rightarrow \text{NH}_3 + \underset{\textbf{PolyU-F-SWNT}}{\text{F-SWNT-NHCONH(CONH)}_n\text{H}} \qquad (1)$$

$$\text{H}_2\text{NCONH}_2 \leftrightarrow \text{NH}_3 + \text{HNCO} \qquad (2)$$

$$\text{F-SWNT-NHCONH}_2 + n\text{HNCO} \leftrightarrow \underset{\textbf{PolyU-F-SWNT}}{\text{F-SWNT-NHCONH(CONH)}_n\text{H}} \qquad (3)$$

These secondary processes can most likely occur to a different degree during the urea melt and solution synthesis conditions employed in the present work. The addition reactions of isocyanic acid in molten urea are reversible according to the recently proposed mechanism for the reaction of oxidized SWNTs with urea melt where formation of some polyurea-derivatized nanotubes was observed.[31] Under the heating and stirring of urea and F-SWNTs in DMF solution in the presence of pyridine for 4 h at 100 °C, providing more homogeneous conditions, the formation of polyurea can become more notable. Other secondary reactions can also occur, particularly hydrolysis of urea moieties in the U-F-SWNTs to produce carbamic acid groups NHC(═O)OH on the SWNT sidewalls as reactive intermediates. The latter can react with isocyanic acid, hence, serving as building blocks for incorporation of urethane units into a PolyU-F-SWNT side chain. In comparison, formation of the polymerization byproduct stemming from the SWNT sidewalls during the functionalization of F-SWNTs with thiourea and guanidine hydrochloride under the similar DMF solution synthesis conditions is not likely.

The reactions of F-SWNTs shown on Schemes 1 and 2 also produce gaseous HF as a byproduct which under urea melt process conditions will most likely completely evaporate, while during the solution process HF can dissolve in DMF and form ammonium-type salts by bonding to certain heteroamide functional groups attached to the SWNTs. The salt formation should be the most evident in the case of G-F-SWNTs due to greater basicity of guanidine as compared to thiourea and urea.[28,29]

FTIR Spectroscopy. The FTIR spectra of functionalized SWNTs are shown in Figure 1. They provide structural information on the functional groups present on the SWNT sidewall before and after the reaction. In the spectrum of the F-SWNT sample the absorption band of the C—F stretch shows up at 1203 cm^{-1}, while the band of activated sidewall C═C stretches is detected near 1539 cm^{-1} in agreement with the IR characterization data on fluorinated HipCO SWNTs.[4–6] In the spectra of derivatized nanotubes, such as U-F-SWNTs, prepared both by melt and by solution syntheses, G-F-SWNTs, and T-F-SWNTs, strong absorption bands at 3400–3430 cm^{-1} attributed to the N—H stretches are seen. Peaks, observed in these spectra in the 1700–1500 cm^{-1} range, characterize the C═O and C═N stretches coupled with the in-plane NH and NH_2 bending vibrations of the (C═O)NH moieties in U-F-SWNTs and (C═NH)NH_2 units in G-F-SWNTs and T-F-SWNTs.[32–34]

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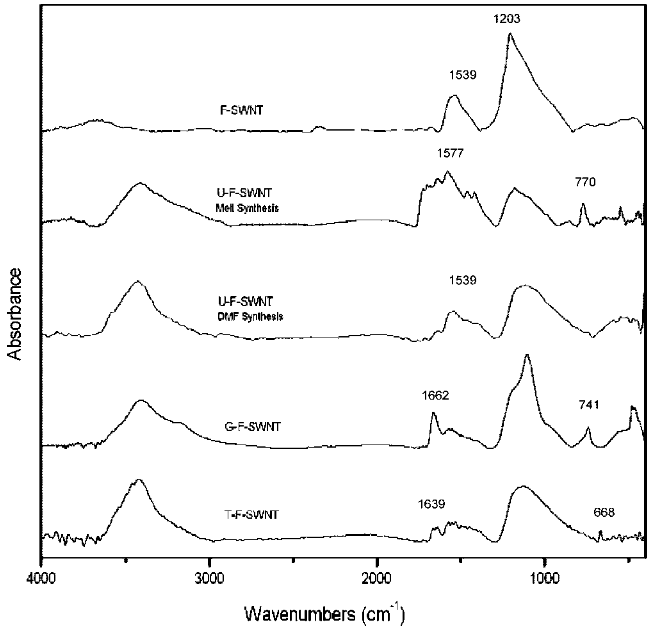

Figure 1. FTIR spectra of derivatized F-SWNTs pressed in KBr pellets.

Medium intensity or shoulder bands appearing in these spectra in the 1500–1350 cm^{-1} region are due to antisymmetric C—N stretching vibrations coupled with the out-of-plane NH_2 and NH modes. The band of the stretching mode of residual sidewall C—F groups is significantly weakened in the spectra of derivatized F-SWNTs because of removal of substantial amount of fluorine through both substitution and partial defluorination reactions in F-SWNTs (Schemes 1 and 2). As the result, this band appears just as a shoulder on a broader band in the 1200–950 cm^{-1} region. Besides C—F stretching mode, out-of-plane NH and NH_2 and symmetric C—N stretching vibrations also contribute into an observed high-intensity of this band. The band at 770 cm^{-1} in the IR spectrum of urea is normally assigned to the CO deformation mode coupled with the antisymmetric NH_2 torsional mode.[32] Therefore, we have assigned the peak appearing in the similar position in the spectra of U-F-SWNTs (Figure 1) to this type of vibration. However, it is noted that the intensity of this peak and other peaks characterizing the $C(=O)NH_2$ moiety (1700 –1350 cm^{-1}) are significantly weakened in the IR spectrum of U-F-SWNT derivative prepared by solution synthesis. This can be attributed to a lesser degree of fluorine substitution taking place in F-SWNTs under solvothermal conditions since this process runs at a lower temperatures (80 and 100 °C) than urea melt process (150 °C) and also can produce PolyU-F-SWNT as a byproduct. This notion is also supported by XPS elemental analysis data and AFM imaging of U-F-SWNT samples.

By comparison with literature data on guanidinium salts,[34] the peak at 741 cm^{-1} in the spectrum of G-F-SWNTs is assigned to the out-of-plane NCNN deformation mode. In the IR spectra of free thiourea the peak at 730–740 cm^{-1} is assigned to the C=S stretching vibration. It was found that this mode shifts to lower wavenumber by about 20–25 cm^{-1} in the coordination compounds of thiourea with $ZnSO_4$ and $CdCl_2$ due to a somewhat weakened C=S bond.[35] For this reason, it is expected that when thiourea bonds covalently to the F-SWNT sidewall through nucleophilic sulfur, the frequency of the C—S single bond stretch in the T-F-SWNTs will downshift further. This argument supports the assignment of the observed peak at 668 cm^{-1} in the spectrum of T-F-SWNTs to this mode.

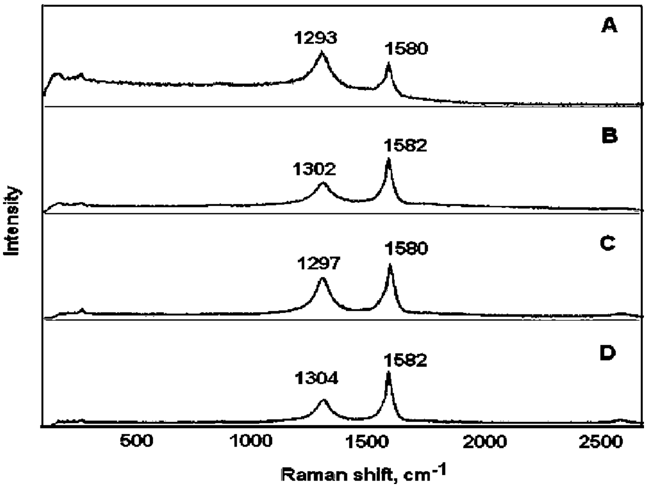

Figure 2. Raman spectra of fluorinated (A) and derivatized nanotubes, U-F-SWNT (B), T-F-SWNT (C), and G-F-SWNT (D).

Raman Spectroscopy. The observed high intensity of the D-peak (1293 cm^{-1}) in the Raman spectrum of F-SWNTs (Figure 2A) reflects the largest content of the sp^3-hybridized sidewall carbons (~37 atom % from XPS data) among all functionalized SWNTs prepared in the present work. In comparison with F-SWNTs, the Raman spectra of derivatized products (Figure 2B−D) show a decreased intensity of the disorder peak (D mode) with respect to the G peak, which is usually attributed to the sp^2 C=C tangential mode. In addition, they also show a clear upshift of the D peak. The intensity of the D peak decreases as a result of the reduction in the number of sp^3 C—C bonded carbons caused by partial defluorination of F-SWNTs when fluorine atoms are stripped off the sidewall in the course of reactions with urea, thiourea, and guanidine. Defluorination results in some recovery of sp^2 C=C bonds between the sites of sp^3 C—X attachment and partial restoration of aromatic π-electron conjugation and graphene symmetry along the length sections of the sidewall which is shown by relative increase in the intensity of G-peak at 1580–1582 cm^{-1} (Figure 2B−D).

The shift in the position of the D peak in the spectra of derivatized F-SWNTs indicates that besides the residual fluorine, other groups, covalently attached to the sidewalls, also contribute to the content of sidewall sp^3 state bonded carbons. Their overall content is sharply reduced relative to F-SWNTs since only a fraction of the C—F bonds undergoes substitution by urea and heteroamide moieties resulting in formation of new sidewall-C-X (X = N or S) covalent bonds

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Table 1. XPS Elemental Analysis Data (atom %) of the Derivatized F-SWNT Products Obtained under Different Reaction Conditions

Product	temp, °C	time, h	XPS C 1s	XPS F 1s	XPS O 1s	XPS S 2p	XPS N 1s
F-SWNT			62.6	35.7	1.6		0.1
U-F-SWNT							
solution synthesis	100	4	78.6	13.2	5.5		2.8
melt synthesis	150	4	65.2	14.7	6.7		13.4
G-F-SWNT	80	4	73.4	24.1			2.5
	100	4	89.9	7.7			2.4
T-F-SWNT	80	4	83.3	14.5		0.7	1.5
	100	4	87.8	10.2		0.7	1.3

according to the reaction Schemes 1 and 2. Of all the Raman spectra, the G-F-SWNT have shown the largest shift from 1293 cm^{-1} in F-SWNT to 1304 cm^{-1}, as seen in Figure 2D. Only a slightly smaller upshift (to 1302 cm^{-1}) was observed for U-F-SWNTs (Figure 2B), while T-F-SWNTs have shown the smallest shift, to 1297 cm^{-1} (Figure 2C). The latter probably indicates that in T-F-SWNTs attachment to the sidewall occurs through the element of a different nature (namely, sulfur) than that in U-F-SWNTs and G-F-SWNTs which are both linked through the C—N bonds to the sidewall carbons. Thus, the Raman spectrum of T-F-SWNTs supports the covalent bonding of thiourea to F-SWNTs (Scheme 2) primarily through the C—S and not the C—N bond.

The Raman spectra of F-SWNTs and their derivatives (Figure 2) also show tiny peaks in the 150–270 cm^{-1} range typical for nanotube breathing modes which normally appear as a medium intensity peak in the spectra of pristine SWNTs. On the basis of our previous studies of a large series of functionalized carbon nanotubes,[5,6,16] the very low intensity of peaks due to this mode can be attributed to a high degree of sidewall modification which hinders the radial breathing oscillation of the nanotube frame.

X-ray Photoelectron Spectroscopy (XPS). The XPS analysis was done on SWNT products obtained under variable reaction conditions using both reaction schemes (Schemes 1 and 2). The elemental analysis data are summarized in Table 1. The high-resolution XPS C 1s and F 1s spectra of functionalized SWNTs are shown in Figure 3. These data provide information on the extent of fluorine removal from F-SWNTs both through displacement by urea, guanidine, and thiourea groups and defluorination reactions. The degree of functionalization of SWNTs can also be estimated from these data. The atomic content of fluorine in F-SWNTs was found to be 37.4 atom % based upon integration of F 1s and C 1s peaks. All derivatized F-SWNTs have shown the reduced content of fluorine. The most notable change in fluorine content with respect to F-SWNTs was found for the G-F-SWNTs (7.7 atom %) prepared through the reaction (Scheme 1) run at 100 °C, while at 80 °C the same reaction yielded the product with F content as high as 24.1 atom %. However, the nitrogen content in the G-F-SWNT derivatives was found not to depend on reaction temperature and remained at about the same level, 2.4–2.5 atom %. The degree of sidewall functionalization (R/C) by guanidine groups was estimated from elemental analysis data (after deduction of atomic percent of carbons bonded to fluorine) and found to decrease with the reaction temperature, from 1:58 to 1:100. This is most likely related to guanidine's high basicity which facilitates the predominant occurrence of defluorination other than nucleophilic substitution of fluorine in F-SWNTs at higher temperatures.

A somewhat similar trend was observed for T-F-SWNTs. XPS data show more fluorine removal from F-SWNTs with the reaction temperature increase and virtually no change in the content of sulfur and nitrogen (Table 1). As in the case of G-F-SWNTs, this is due to a higher degree of defluorination occurring with temperature increase from 80 to 100 °C under solvothermal reaction conditions. The measured S/N atomic ratio of 1: 2 in the reaction product (T-F-SWNT, Scheme 2) supports the attachment of thiourea molecules which are estimated to bond to about 1 in 90 carbons on the SWNT sidewall.

For U-F-SWNTs, prepared by urea melt synthesis, XPS analysis yielded a much higher content of nitrogen (13.4 atom %) as compared to only 2.8 atom % content found in the product prepared through the DMF solution synthesis. The former has also shown an accurate (2:1) nitrogen to oxygen atomic ratio, as expected from stoichiometry of the attached urea groups, while the latter demonstrated a considerably elevated content of oxygen in relation to nitrogen (Table 1), which can be related to the presence of $\{-\mathrm{NC}(=\mathrm{O})\mathrm{O}-\}_x$ units in the PolyU-F-SWNT byproduct formed in DMF under solvothermal synthesis conditions. The XPS elemental analysis data suggest that the urea melt synthesis yields the F-SWNT derivative having the degree of sidewall functionalization by urea molecules as high as 1 in 8 carbons.

In Figure 3A, the high-resolution XPS spectrum of F-SWNTs shows a C 1s peak with maxima at 284.6 and 289.3 eV due to the C=C and C—F bonded carbons and a weak shoulder at 290–292 eV which can be attributed to the CF_2 carbons. In the C 1s spectra of derivatized F-SWNTs (Figure 3B—E) the peak of the C—F bonded carbons at 289.1 eV is significantly decreased in intensity for each derivative indicating that the amount of the bonded fluorine is diminished with functionalization. The position of the C 1s peak at 289.1 eV reflects the predominantly covalent nature of the C—F bond in the F-SWNTs and their derivatives since this peak is located very close to the C—F carbon peak position in the spectra of fluorographite C_2F.[36] This is also confirmed by the observed position of the F 1s peak at 688.0 eV in the XPS spectra of F-SWNTs (Figure 3A) and all

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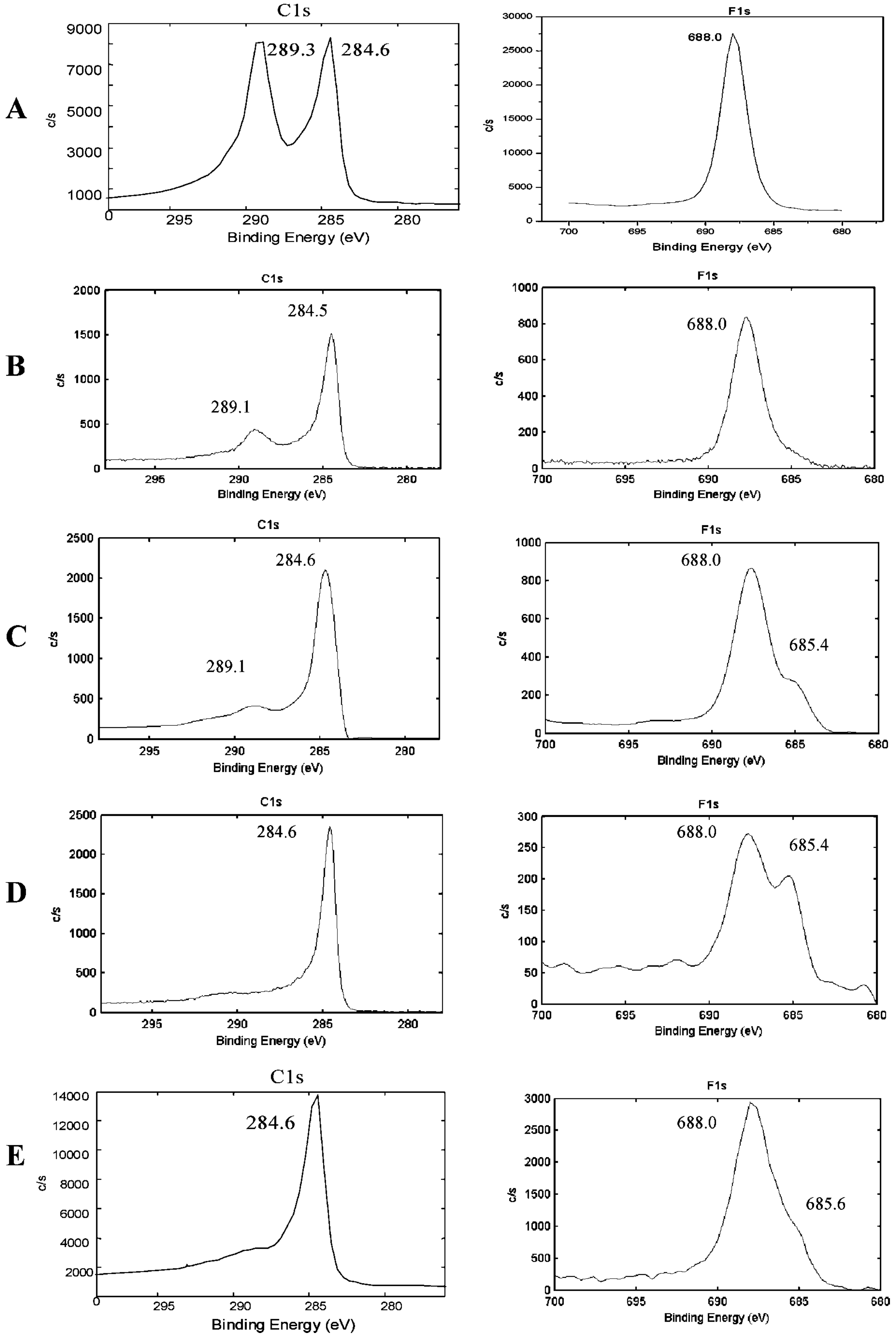

Figure 3. XPS C 1s and F 1s spectra of functionalized SWNTs: F-SWNTs (A), U-F-SWNTs from urea melt synthesis (B) and from DMF solution synthesis (C), and G-F-SWNTs (D) and T-F-SWNTs (E), both prepared at 100 °C.

studied derivatives (Figures 3B−E), where this peak is located only slightly below the maximum value for the covalent C−F bond in PTFE (689 eV).

It should be noted that in the XPS F 1s spectra of U-F-SWNTs, G-F-SWNTs, and T-F-SWNTs, which are all prepared through DMF solution synthesis, an additional shoulder peak at 685.4 eV has appeared. The position of this peak suggests the presence of ionic fluorine most likely from HF which is the reaction byproduct (Schemes 1 and 2) capable of forming salt with the F-SWNT amide and heteroamide derivatives. The shoulder peak at 685.4 eV shown by G-F-SWNT (Figure 3D) has an increased intensity compared to other nanotube derivatives because of higher basicity of guanidine moieties as compared to urea and thiourea. It should be pointed out that the peak due to ionic fluorine does not appear in the XPS F 1s spectrum of U-F-SWNTs (Figure 3B) produced at 150 °C under solvent-free urea melt process conditions when HF entirely evaporates.

Thermal Gravimetric Analysis (TGA). Thermal degradation studies were carried out in an argon flow environment under continuous heating at 10 °C/min up to 1000 °C. The differential weight curve of the F-SWNT precursor, shown in Figure 4A, displays a single degradation peak at 528 °C due to the removal of fluorine which is known to form CF_4 as a major degradation product.[5] The TGA residue of 51 wt % was confirmed to be SWNTs that were defluorinated as evidenced by the decreased D peak and increased G peak intensities in the Raman spectrum (not shown). Urea itself was also subjected to TGA, and it was found that there is a two-step degradation curve for urea, showing two major peaks on the DTA plot, one at 241 °C and the second at 371 °C (Figure 4B). These peaks are most likely due to well-known decomposition of urea into ammonia and isocyanic acid HNCO.[30] The TGA−DTA curves for the U-F-SWNTs (Figure 4C,D) also show a degradation occurring in the 200–350 °C temperature range with the DTA peaks shifted relative 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.[15–17] It was also found that the DTA curve virtually lacked a peak at 400–600 °C, confirming that most of the fluorine was removed from the F-SWNT sidewall. On the basis of weight loss, it was estimated that about 1 in 8 carbons on the U-F-SWNT sidewall are functionalized with urea molecules by melt synthesis, which is in close agreement with the estimation from XPS analysis data. However, this should be considered as an upper limit for the degree of sidewall functionalization by urea since the PolyU-F-SWNT byproduct can also be present in the sample and contribute to weight loss during TGA. The TGA curves for all three F-SWNT derivatives prepared by DMF solution synthesis at 80 °C (Figure 4D−F) show significantly lower total weight loss (20–30%) as compared to urea melt synthesized U-F-SWNTs (∼70%). This should reflect a smaller number of amide and heteroamide functionalities attached to the SWNTs. The DTA curves for these products (Figures 4D−F) exhibit an additional peak at 100–190 °C which can be explained by release of HF from salts formed by amide groups. By taking into account only the weight loss occurring in the 200–400 °C temperature range due to detachment of covalently bonded groups, the degree of sidewall functionalization by DMF solution synthesis can be estimated as approximately 1 in 25 for U-F-SWNTs, 1 in 45 for T-F-SWNTs, and 1 in 20 for G-F-SWNTs. The obvious discrepancy of these numbers with the XPS based estimation is related to a difficulty in accurate quantifying of the weight loss due to residual covalently bonded fluorine on F-SWNT derivatives.

Scanning Electron Microscopy (SEM). The SEM studies helped to reveal the surface morphology and extent of nanotube bundling within bulk nanotube samples. The SEM image of the U-F-SWNTs from melt synthesis given as an example in Figure 5 shows very thin nanotube bundles. It is interesting to note that the SEM investigation 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 the case of U-F-SWNTs, we found no need to coat the sample surface with gold as clear images were obtained even at a magnification of 120 000×.

This indicates that the increased conductivity of F-SWNTs results from their surface modification through urea treatment resulting in both functionalization and partial defluorination of SWNT sidewalls. The modified electrical properties of U-F-SWNTs and other derivatives are currently under investigation.

Atomic Force Microscopy. AFM studies have provided direct evidence for surface modification in derivatized F-SWNTs. The AFM image of the specimen from U-F-SWNTs (Figure 6a), which were prepared from F-SWNTs through a DMF solution synthesis, shows small and large beads on the backbones of some nanotubes. From the cross-section height analysis indicated by the flags in Figure 6a the size of the nanotube with the sidewall-attached beads was estimated to be 6.6 nm. Note that there are different size beads along the backbone of this and some other nanotubes seen on the image. The beads are most likely the result of polyurea formation on the nanotubes producing PolyU-F-SWNT byproduct. The presence of polyurea beads on the nanotubes has also been reported in previous work.[27] The same AFM image (Figure 6a) shows that there are also many shorter length nanotubes without beads on the sidewalls present in the sample.

At the same time, none of the zoomed AFM images of G-F-SWNT (Figure 6b) and T-F-SWNT (Figure 6c,d) samples show beads on the nanotubes indicating that polymerization reactions most likely did not occur during the reaction of F-SWNTs with guanidine and thiourea. The tapping mode analysis of the cross-section profile of the single G-F-SWNT nanotube shows the height of 1.97 nm (Figure 6b) which after deduction of the mean diameter value of the nanotube frame (∼1.2–1.4 nm) yields the expected size of the guanidine moiety covalently attached to the sidewall. The height analysis of the T-F-SWNT single nanotube sample yields a 2.22 nm height across the derivatized nanotube (Figure 6c) and 0.74 nm difference measured

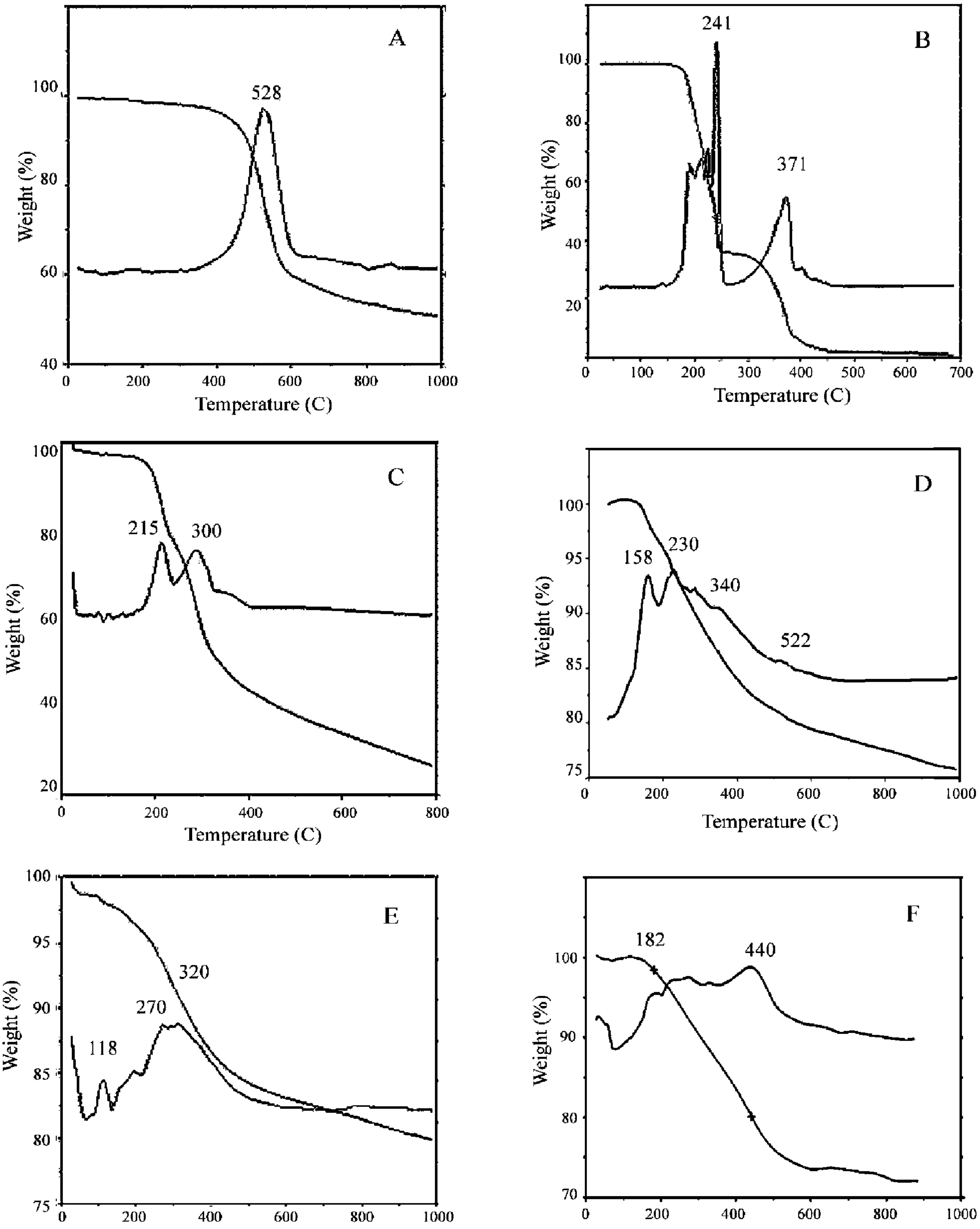

Figure 4. TGA-DTA curves for (A) F-SWNTs, (B) urea, (C) U-F-SWNTs produced by urea melt synthesis, (D) U-F-SWNTs from DMF solution synthesis, (E) T-F-SWNTs, and (e) G-F-SWNTs.

along the backbone area (Figure 6d). The latter value represents the approximate length of the $-S-C(=NH)NH_2$ group attached to the nanotube sidewalls in a "stretched" fashion.

Transmission Electron Microscopy (TEM). Although nanotubes decorated with covalently attached beads of polymerized urea were clearly observed in the AFM images, it appears that no large beads on the nanotubes are seen in our TEM images (Figure 7). This can be accounted for by difference in the procedure of sample preparation for SEM and TEM. The samples for TEM studies are prepared from the functionalized nanotubes after their resuspension by

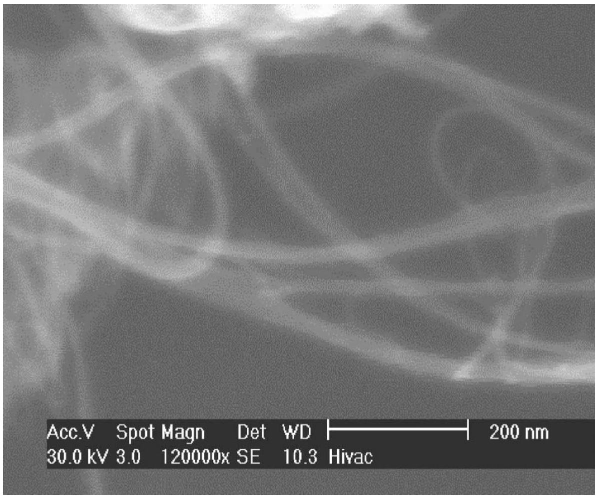

Figure 5. SEM image of U-F-SWNT from melt synthesis.

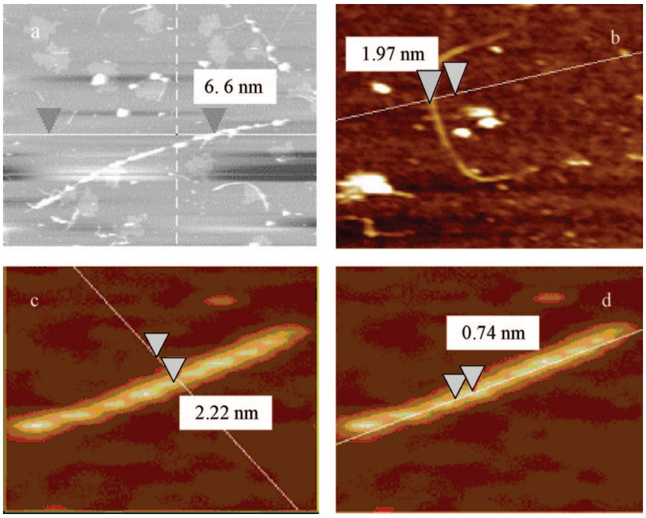

Figure 6. AFM images and height analysis for derivatized F-SWNT samples: (a) U-F-SWNTs from DMF solution synthesis, (b) G-F-SWNTs, (c) T-F-SWNTs, height analysis across the nanotube, and (d) T-F-SWNTs, height analysis along the nanotube backbone.

sonication followed by centrifugation of the suspension and sampling of the top part of the suspension. The TEM image of the F-SWNTs, taken for comparison, is shown in Figure 7a. The presence of many nanotubes still in the form of bundles should be noted. The images of U-F-SWNTs from melt synthesis are shown in Figure 7b. The image shows that U-F-SWNTs are densely functionalized, and more individual nanotubes can be found on this image than on one for the F-SWNTs (Figure 7a). On the sidewall, there is clearly seen plenty of attached molecules of urea sticking out from the nanotubes, like pine needles, as indicated by the black arows in Figure 7b. The presence of more single nanotubes than larger bundles in the TEM sample is another indication of the strong intercalating nature of urea into the larger bundles to produce smaller bundles and singles.

Dispersion in Solvents and Epoxy Systems. To study the effect of functional groups on the nanotubes on dispersion ability in different solvent systems, 5 mg of F-SWNTs and U-F-SWNTs was placed into a 20 mL vial containing either pure deionized water or 5 wt % urea in water solution. The vials were placed into a bath sonicator and sonicated for 15 min. The obtained suspensions were left standing for about 1 h, then the photographs were taken. As shown on pictures in Figure 8, the F-SWNTs, due to their hydrophobic nature, do not disperse and remain on top of water. However, when placed in the 5% urea solution, the F-SWNTs seem to enlarge in volume and migrate to the bottom of the vial. This indicates that even though urea is extremely soluble in water, it still can be drawn to the van der Waals forces within the F-SWNT bundles, intercalate, wrap, and thus separate them, which should result in an enlarged, "swelled" appearance of the sample. It also seems that the hydrophobic nature of the fluorinated tubes has been somewhat overcome by

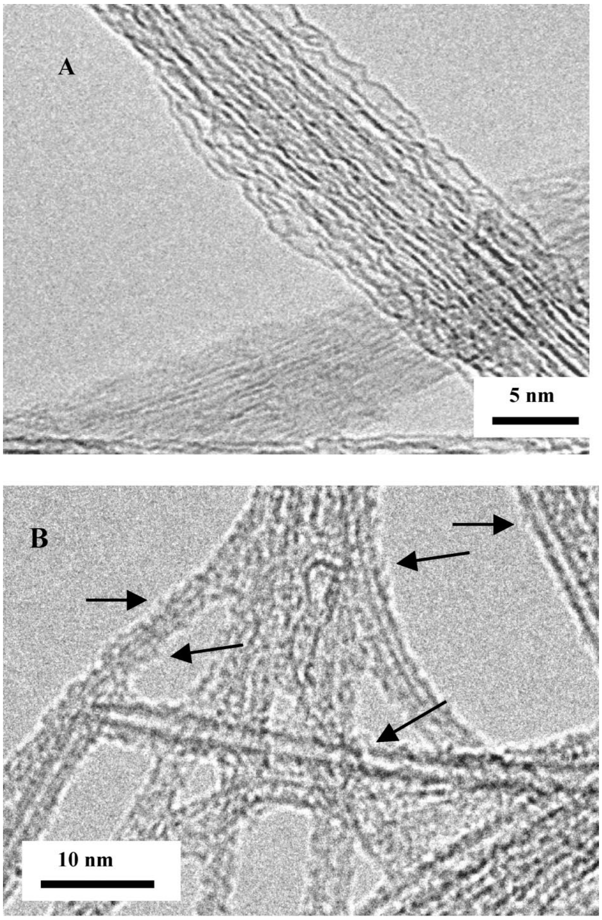

Figure 7. TEM of SWNT derivatives: (A) F-SWNTs with a scale bar of 5 nm, (B) U-F-SWNT with a scale bar of 10 nm. Black arows point at attached molecules of urea sticking out from the nanotubes.

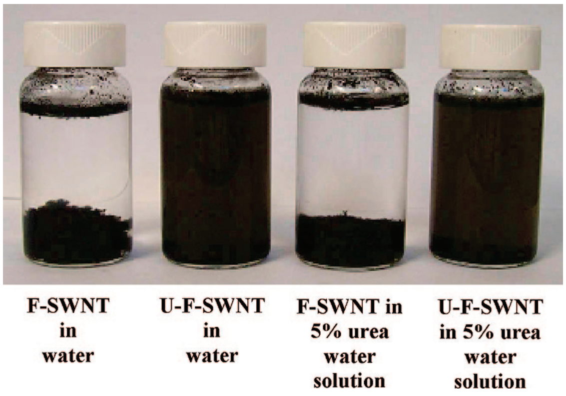

Figure 8. Photographs of F-SWNT and U-F-SWNT dispersed in water and 5% urea solution.

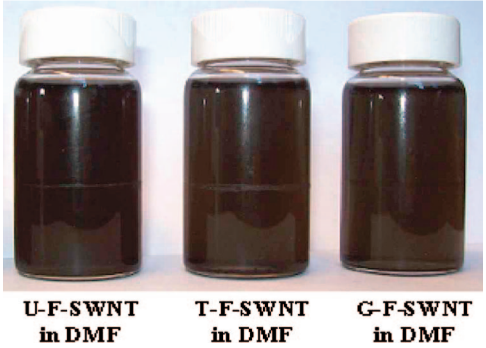

Figure 9. Photographs of F-SWNT amide and heteroamide derivatives dispersed in DMF.

creating a hydrophilic coating by urea over the bundles which under the weight of the coating sank to the bottom of the vial.

U-F-SWNTs show a much better dispersion in water compared to F-SWNTs, as the solution visibly remains homogeneous and dark, exhibiting only a small amount of "swelled" nanotube precipitate on the bottom of the vial (Figure 8). Finally, the U-F-SWNTs in the 5% urea solution produced the best dispersion, as the vial was entirely dark. This dispersion has shown no precipitate even after many months. This is an important result, as it could enable applications of U-F-SWNTs for biomedical research carried out mostly in aqueous environments. Various functionalized nanotubes have been recently used in cancer research,[1–7] and U-F-SWNT would be an ideal candidate for studying interactions with proteins on the surface of cancer cells.

In comparison, T-F-SWNTs and G-F-SWNTs formed much less stable suspensions in water. These derivatives, as well as U-F-SWNTs, however, dispersed well in DMF and showed no or little precipitation after many weeks of standing forming the dark-colored solutions, as seen in Figure 9. They thus showed more stable suspensions than F-SWNTs, for which the dispersion in DMF was observed to become gray colored as a result of partial precipitation seen on the bottom of the vial after two weeks of standing.

To evaluate the potential applications of U-F-SWNTs in composite systems the dispersions in the EPON 862/W Cure epoxy system have been studied. The epoxy system was chosen since urea is known as one of the curing agents for the epoxy resins. For this reason, urea-functionalized SWNTs are expected to serve both as a curing agent and as a modifier of the epoxy properties. Therefore, dispersions of 0.015 and 0.15 wt % U-F-SWNTs in epoxy have been made by mixing followed by ultrasonication. Similarly, F-SWNT/epoxy dispersions have been prepared for comparison. The composite mixtures were characterized by optical microscopy and then cured in a borosilicate glass mold according to a standard procedure used for this type of epoxy system. Thereafter, photographs of the cured samples removed from mold were taken. As shown in Figure 10, U-F-SWNTs (0.015 wt %) clearly show that very uniform dispersions in the liquid epoxy and in the cured solid composite sample have been obtained. On the contrary, F-SWNTs appear as agglomerated particles both in uncured and in cured composite samples. With the concentration increased to 0.15 wt %, U-F-SWNT also maintains very good dispersion in the epoxy (not shown) both before and after curing. The achieved good dispersion is indicative of a high degree of debundling of U-F-SWNTs and strong interfacial interaction with the epoxy matrix. This should lead to enhancement of mehanical properties of epoxy composites processed with U-F-SWNTs. These preliminary results facilitate the continuing work on processing, fabrication, and property testing of this type of composites which is in progress.

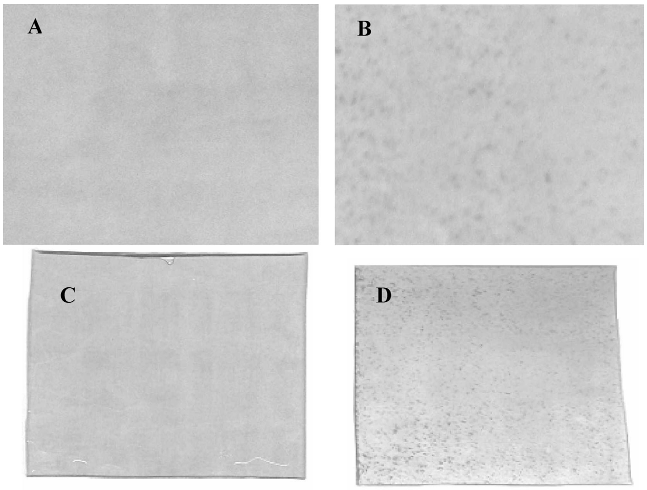

Figure 10. Dispersions of 0.015 wt % U-F-SWNTs (A, C) and F-SWNTs (B, D) in the EPON 862/W Cure epoxy system. A, B: Optical microscope 20× images taken before curing. C, D: Photographs of the cured samples.

Conclusion

In this work we have shown that F-SWNTs have been successfully functionalized with urea, guanidine, and thiourea moieties which become covalently bonded to the F-SWNT sidewalls as the result of partial substitution of fluorine. Covalent bonding has been confirmed by the use of several materials characterization techniques that showed that the local environment of the fluorine atoms has been modified through these new developed functionalization methods. Raman spectra have shown shifts in the D peak indicating that other groups have been attached to the sidewall. Also, decrease in the D peak intensity correlates with the thermal defluorination and recovery of the sp^2 $C{=}C$ bonds between the sites of $C{-}X$ ($X = N, S$) bonding of studied molecules to the nanotube sidewalls. FTIR spectra indicated the presence of the characteristic bands of the amide and heteroamide groups as well as decreased intensity of the peaks due to $C{-}F$ stretch. TGA-DTA weight loss curves confirm that fluorine in the F-SWNTs has been mostly removed and displaced by urea, guanidine, and thiourea, thus producing bifunctionalized SWNT derivatives. XPS analysis data have also confirmed the derivatization of F-SWNTs and residual fluorine presence which depended on the functionalization method and reaction conditions used. AFM has shown that urea can form beads of polyurea on the SWNT sidewall when F-SWNTs are derivatized through the DMF solution method. TEM imaging has directly exposed urea molecules stemming from the sidewalls of derivatized F-SWNTs. The dispersion of new SWNT derivatives, U-F-

SWNT, T-F-SWNT, and G-F-SWNT, in water and DMF has been investigated and stable suspensions produced. Very good dispersions of U-F-SWNTs in liquid and cured epoxy systems have also been demonstrated. This opens to door to creation of fully integrated nanocomposite systems achieved through interfacial covalent bonding of SWNTs to polymer matrices.

From the synthetic chemistry point of view, the development of solvent-free one-step urea melt synthesis will add to the number of green chemistry methods of functionalizing nanotubes. The demonstrated new methods help to create bifunctionalized nanotubes in a facile manner. From the applications standpoint, electrical resistivity measurements are in progress for all derivatives as well as fabrication and mechanical property testing of composite samples. The new derivatives with their amide terminal groups also will be useful in nanotube−FET devices and for gas sensing applications. The ability to disperse in aqueous systems will generate new research aimed at biological applications of urea, thiourea, and guinidine functionalized carbon nanotubes. Improved dispersion of nanotubes attained through urea functionalization leads to their potential application as mechanical strength reinforcers in epoxy, polyurea, urea-formaldehyde, Nylon, and other polymer composites.

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