

FEATURE ARTICLE

Covalent Functionalization of Single-Walled Carbon Nanotubes for Materials Applications

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Covalent functionalization of single-walled carbon nanotubes (SWNTs) has significantly expanded the utility of the nanotube structure. Covalent sidewall functionalization has been employed to increase the solubility of these materials, which allows for the manipulation and processing of these otherwise insoluble nanotubes. Increased solubility leads to better dispersion in polymeric systems. Functionalization can be performed selectively wherein the metallic SWNTs react faster than the semiconductors. This has allowed a separation of carbon nanotubes by type. Covalent sidewall functionalization also allows nanotube-based composite formation where the functional group is well mixed with the polymer matrix. This has led to dramatic increases in the modulus of elastomers while retaining their elongation-at-break properties.

I. Introduction

Covalent functionalization of single-walled carbon nanotubes (SWNTs) has given scientists and engineers the ability to manipulate these astonishing structures in ways that would otherwise be unattainable.¹ SWNTs consist of only carbon and can be considered theoretically to be a graphene sheet rolled into a seamless cylinder.² Nanotubes are the strongest material known. SWNTs are ladder polymers (i.e., more than one bond needs to be broken to cleave the backbone). Typical ladder polymers are fully joined by only two repeating bonds. However, depending on the tube type, SWNTs have 10–20 carbon–carbon bonds per repeat unit that would need to be broken for polymer strand rupture to occur. Furthermore, each of those 10–20 carbon–carbon bonds has a bond order of ca. 1.3. And because the carbon–carbon bond is among the strongest bonds in the universe, it is unlikely that we will ever find more robust polymeric chains. Beyond their amazing mechanical properties, they also exhibit extraordinary optical, electrical, and thermal

properties.³ Unfortunately, many of the optical, electrical, and thermal properties are extended π -conjugation-dependent; therefore, covalent functionalization causes a loss of these qualities.

SWNTs are synthesized in a variety of ways with the two most prevalent being laser ablation of a metal-doped graphite target (laser oven)⁴ and gas-phase catalytic growth from carbon monoxide (HiPco)⁵ or other carbon sources such as methane or mixed carbon/H₂ sources. All known preparations of SWNTs give mixtures of nanotube chiralities, diameters, and lengths. The diameter and vector of a carbon nanotube is defined by two integers, n and m . When $n - m = 3q$, where q is an integer that does not equal 0, the nanotube is semimetallic with a band gap on the order of millielectronvolts; when $n - m = 0$, the nanotube is metallic with a band gap of 0 eV and is referred to as an armchair-type nanotube. All other nanotubes ($n - m \neq 3q$) are semiconductors with a band gap of ca. 0.5 to 1 eV. Prepared lengths of carbon nanotubes can vary anywhere from 50 nm to 2 cm long.⁶ Carbon nanotubes are highly polarizable, smooth-sided compounds with attractive interactions of 0.5 eV per nanometer of tube-to-tube contact. Because of these extreme

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TABLE 1: Common SWNT Sidewall Functionalization Methodologies

methodology	addend	characterization techniques	degree of functionalization	highest solubility
diazonium ^{23,27,29,31}	aryl	UV/vis/NIR, Raman, TGA, XPS, ATR-IR, AFM, TEM	1 addend in every 10 carbons in SDS/water and 1 addend in every 25 carbons in organic solvent or neat	0.8 mg/mL in DMF
diazonium in oleum ³⁰	aryl	UV/vis/NIR, Raman, TGA, XPS, ATR-IR, AFM, TEM	1 addend in every 20 carbons	0.25 mg/mL in H ₂ O
fluorination ³⁴	fluorine	ATR-IR, AFM, STM, VTP-EIMS, UV/vis/NIR, Raman, TGA	1 addend in every 2 carbons	1 mg/mL in 2-propanol
radical chemistry ³⁷	alkyl	Raman, ATR-IR, UV/vis/NIR, TGA	1 addend in every 6 carbons	not given
dissolving metal reduction (Billups reaction) ³⁸	alkyl, aryl	TEM, AFM, Raman, ATR-IR, TGA-MS	1 addend in every 17 carbons	not given
azomethine ylides (Prato reaction) ³⁹	pyrrolidine	UV/vis/NIR, Raman, TEM	1 addend in every 100 carbons	50 mg/mL in CHCl ₃
nitrene ⁴⁰	aziridene	XPS, AFM, TEM, NMR, UV/vis/NIR, Raman	1 addend in every 50 carbons	1.2 mg/mL in DMSO
Bingel reaction ⁴¹	cyclopropane	AFM, ¹⁹ F NMR, XPS	1 addend in every 50 carbons	not given
dichlorocarbene ⁴²	cyclopropane	mid-IR, Raman, EDS, UV/vis/NIR, AFM, thermal	1 addend in every 25 carbons	not given

cohesive forces, SWNTs exist as bundled structures that are often referred to as ropes.⁷ This bundling or roping phenomenon contributes to the bulk materials having limited solubility and poor dispersion in polymers.^{8,9} In fact, pristine carbon nanotubes tend to agglomerate in polymer hosts, which often weakens the mechanical strength of these composite materials.¹⁰ Another problem associated with pristine nanotubes in composites and blends is the lack of interfacial bonding (SWNT to matrix material), which leads to fiber pullout during stress, followed by catastrophic failure. Bundling also convolutes the optical and electronic property characterizations. Covalent functionalization can provide “handles” for dispersion in host polymers and in exfoliation of the bundles, ultimately paving the way for important discoveries that would be unrealized without functionalization.

Noncovalent functionalization of SWNTs, such as wrapping of the nanotubes with surfactants, led to the discovery of carbon nanotube fluorescence-based identification.¹¹ This discovery led to the remarkable optical assignment of the semiconductors by their *n* and *m* values.¹² Several covalent functionalization strategies exist such as defect site creation and functionalization from the defects,¹³ creating carboxylic acids on the endcaps of carbon nanotubes and subsequent derivatization from the acids,^{14,15} and covalent sidewall functionalization.¹⁶ This paper focuses on covalent sidewall functionalization of SWNTs and discusses how this methodology generates the ability to solubilize and disperse these nanotubes into polymer matrices.⁹ Covalent sidewall functionalization can even be performed selectively (i.e., metallic nanotubes can be modified without affecting the semiconductors¹⁷). Functionalized SWNTs also lead to the creation of novel composite materials and elastomers where the issues of fiber pullout and interfacial bonding are addressed.^{18,19}

II. SWNT Preparation and Characterization

SWNTs prepared from laser ablation,²⁰ HiPco,²¹ or related gas-phase growth methods are typically contaminated with amorphous carbon and metal particles. The as-prepared material, in general, is purified by an oxidative treatment to remove amorphous carbon and an acid treatment to remove metal particles. Functionalization can be performed on the raw or purified material as well as material individualized in aqueous surfactants (vide infra). Covalently functionalized SWNTs are

characterized by several analytical techniques that we recently reviewed.²² Absorption and resonance Raman spectroscopy are employed to ensure that the functionalization is covalent and occurs at the sidewalls, not merely at defect sites or at the ends of the SWNTs. Once covalent sidewall functionalization is confirmed, thermogravimetric analysis (TGA) and X-ray photoelectron spectroscopy (XPS) are used to determine the degree of functionalization. Use of these techniques is difficult unless the modified carbon nanotubes are purified. Imaging techniques such as atomic force microscopy (AFM), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) are used to analyze the diameter of the bundles or individuals, and AFM gives a good indication of the average lengths of the nanotubes.

III. Functionalized SWNTs

A. Functionalization Methodologies. Several SWNT sidewall functionalization methodologies now exist, and they all have one thing in common: a highly reactive intermediate is necessary to attack the carbon nanotubes. Table 1 lists common functionalization protocols available to researchers who desire modified carbon nanotubes. The first methodology developed by the authors is functionalization of carbon nanotubes with substituted benzenediazonium salts. This can be performed in several ways including electrochemical reduction of the salt²³ as well as treating surfactant-wrapped nanotubes^{11,24–26} with the salt in aqueous solution.^{27,28} The arenediazonium species can be used directly or formed in situ by mixing an aniline and isoamyl nitrite (or sodium nitrite) with the SWNTs in organic solvents,²⁹ oleum (H₂SO₄ with dissolved SO₃),³⁰ or without any solvent.³¹ The solvent-free process is particularly attractive for large-scale functionalizations because previously developed procedures required ca. 2 L of solvent per gram of SWNTs due to the poor dispersion of SWNTs. Additionally, the solvent-free process could be performed in the same equipment used for polymer blending, thereby streamlining the overall functionalization/blending protocol.

The methodology that gives the most highly functionalized SWNTs is functionalization by adding preformed arene diazonium salts to micelle-coated carbon nanotubes at pH 10; the micelle most often being generated from the surfactant is sodium dodecyl sulfate (SDS).²⁷ The micelle-coated material generated according to the published procedure gives noncovalently

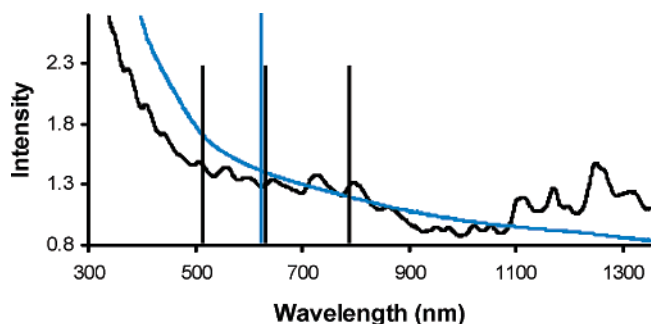


Figure 1. Absorption spectra of SDS-coated SWNTs (black) and heavily functionalized carbon SWNTs (blue). Hence, functionalization causes the loss of the van Hove singularities in the absorption spectra, which is a key tool for the verification of functionalization.

wrapped SWNTs as individuals (unbundled). Functionalization of this material is rapid according to UV/vis/NIR (Figure 1), and the material is heavily functionalized according to Raman spectroscopy (Figure 2) and TGA. In fact, SWNTs functionalized in this way have approximately 1 in 10 carbons on the

sidewalls bearing an aryl moiety; this ratio varies slightly depending on the substituent on the arene ring of the diazonium salt. After only 10 min, all of the van Hove singularities in the absorption spectra are lost (Figure 1), and after purification of this reaction, Raman analysis shows carbon nanotubes with the disorder mode (D band, 1290 cm^{-1}) higher in intensity than the tangential mode (1590 cm^{-1}), which is some of the most heavily functionalized material known. Analysis by AFM (Figure 3) of the functionalized material, dispersed from *N,N*-dimethylformamide (DMF), shows the carbon nanotubes with a dramatic decrease in the bundling; therefore, SWNTs functionalized as individuals tend to disperse as individuals in organic solvent. This gives a profound increase in solubility in DMF of functionalized carbon nanotubes (0.8 mg/mL)²⁷ as compared to that of pristine carbon nanotubes (0.07 mg/mL).³² This increase in solubility allows the functionalized material to be solvent blended into host polymers. For comparison, micelle-coated carbon nanotubes that are not functionalized are washed to remove the surfactant, rapidly rebundling (Figure 4). Analysis by TEM (Figure 5) confirms that the functionalized SWNTs

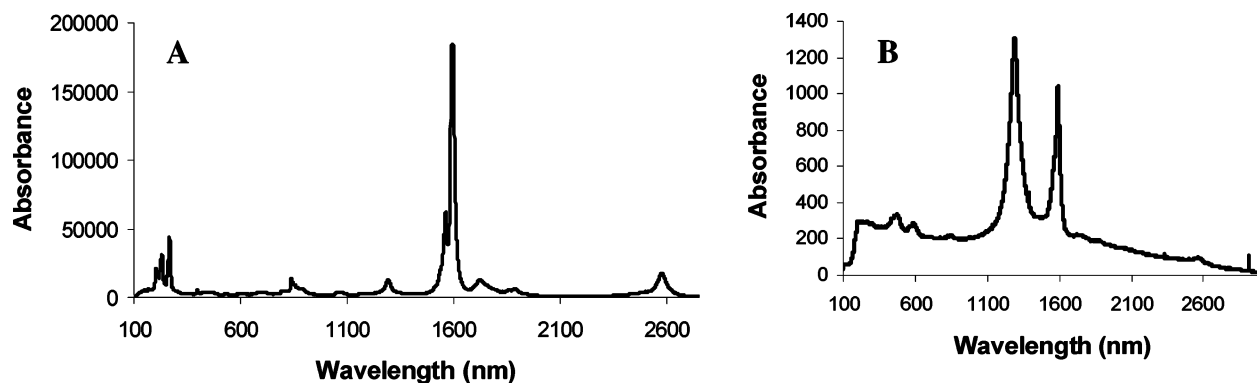


Figure 2. Raman (780-nm excitation) of (A) pristine SWNTs and (B) heavily functionalized individual carbon nanotubes.

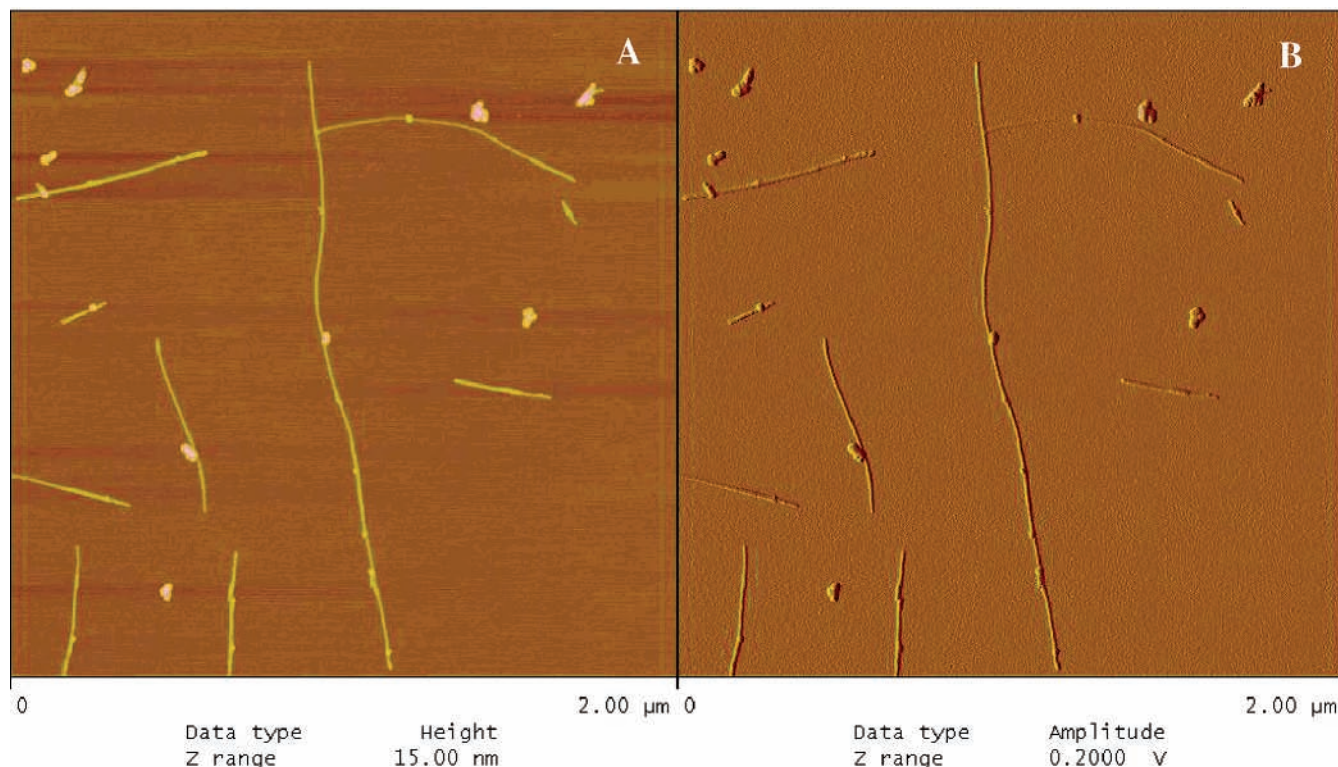


Figure 3. AFM analysis (spin coated onto freshly cleaved mica) by (A) height and (B) amplitude of 4-*tert*-butylbenzene functionalized individual SWNTs that had been treated as SDS-wrapped SWNTs in water. These functionalized SWNTs were washed free of their SDS wrapping prior to imaging, yet they remain unbundled throughout their entire lengths.

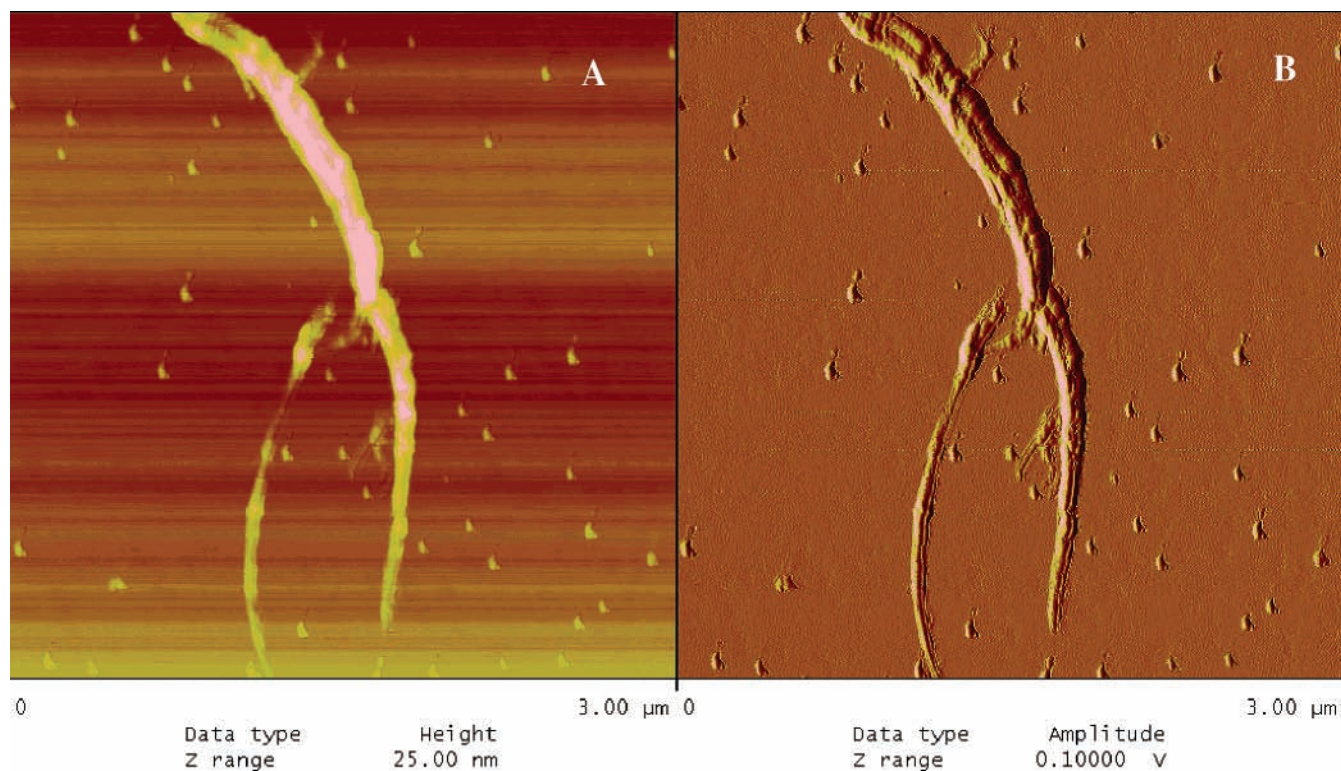


Figure 4. AFM analysis (spin coated onto freshly cleaved mica) by (A) height and (B) amplitude of unfunctionalized SWNTs that were washed free of their SDS wrappings. Notice their tendency to rebundle, unlike the functionalized SWNTs in Figure 3.

are predominately dispersed as individuals in organic solvent, and they are not prone to rebundling, thus overcoming the original 0.5 eV/nm attractive interactions. Also note in Figure 5 the roughened SWNT surface due to arene functionalities.

There is a significant downside to the SDS-wrapping protocol, however. The procedure for obtaining individual SDS-wrapped SWNTs is laborious because of multiple sonications and centrifugations being required. A day's work can afford only about 15 mg of the SDS-wrapped SWNTs. Nonetheless, until recently, wrapping SWNTs with surfactants was the only means of obtaining unbundled nanotubes.

Interestingly, oleum, a superacid medium, has recently been used by Pasquali, Smalley, and co-workers to spin SWNT fibers.³³ Using this protocol, the SWNTs are dispersed as individuals, and there is no need to sonicate or centrifuge the mixtures. Following that lead, we showed that the functionalization of SWNTs in oleum (Table 1) provides nanotubes that are individualized.³⁰ The functionalized nanotubes show little tendency to rebundle. Moreover, the products are even soluble in water because of concomitant arene sulfonic acid formation.

Fluorination of carbon nanotubes was developed by Margrave and co-workers.³⁴ Typically, purified carbon nanotubes are added to a reactor and treated with fluorine gas to provide highly fluorinated SWNTs, and this material is also sold commercially. The methodology gives heavily functionalized carbon nanotubes according to Raman analysis and TGA with increased solubility in organic solvents.³⁵ Fluorine appended to the sidewall can be displaced with various nucleophiles such as organolithium and Grignard reagents to give nanotubes functionalized with organic moieties.³⁶

Another radical process was developed³⁷ where highly reactive alkyl radicals are generated by the addition of a radical source in the presence of an alkyl iodide typically to form the alkyl radical that reacts with carbon nanotubes. This gives highly functionalized material as well.

More excitingly, the Billups reaction, involving the treatment of SWNTs with lithium metal in liquid ammonia, a modified Birch-type protocol, was recently disclosed to generate ultrahighly lithiated SWNTs (ca. 1 lithium atom per 2.2 carbon atoms) that can be further treated with numerous electrophiles including alkyl halides, aryl halides, and even vinyl monomers.³⁸ A most interesting feature of the Billups reaction is that it affords predominantly individualized SWNTs because the lithium intercollates between the SWNTs of the bundles. Therefore, the rule of thumb is that if the SWNTs are dispersed as individuals in the reaction medium (as in oleum or Li/NH₃) they will react as individuals and remain unbundled. Finally, the Billups reaction could be a predecessor to a new form of unprecedented ultrahighly lithiated carbon materials for battery and related storage applications.

Interestingly, a functionalization methodology developed by Prato and co-workers³⁹ affords SWNTs that, albeit lightly functionalized relative to the above protocols, are reported to be exceedingly soluble in organic solvents (50 mg/mL, Table 1). This methodology involves a 1,3-dipolar cycloaddition of an azomethine ylide generated in situ from an amino acid and aldehyde. Three other methods that use highly reactive intermediates to functionalize carbon nanotubes are nitrene decomposition, the Bingel reaction, and dichlorocarbene formation as developed by Hirsch,⁴⁰ Green,⁴¹ and Haddon,⁴² respectively (Table 1). These are the same reagents that were developed for reactions on C₆₀; therefore, there is some commonality of reactive patterns between SWNTs and C₆₀. The characterization tools and the reported solubility values for the functionalized SWNTs are summarized in Table 1.

B. Selective Functionalization and Separation. Another aspect of functionalization chemistry is that there are covalent and noncovalent functionalization protocols that show preferential reactivity toward the metallic nanotubes over the semiconductor SWNTs. Such selective reactions include diazonium

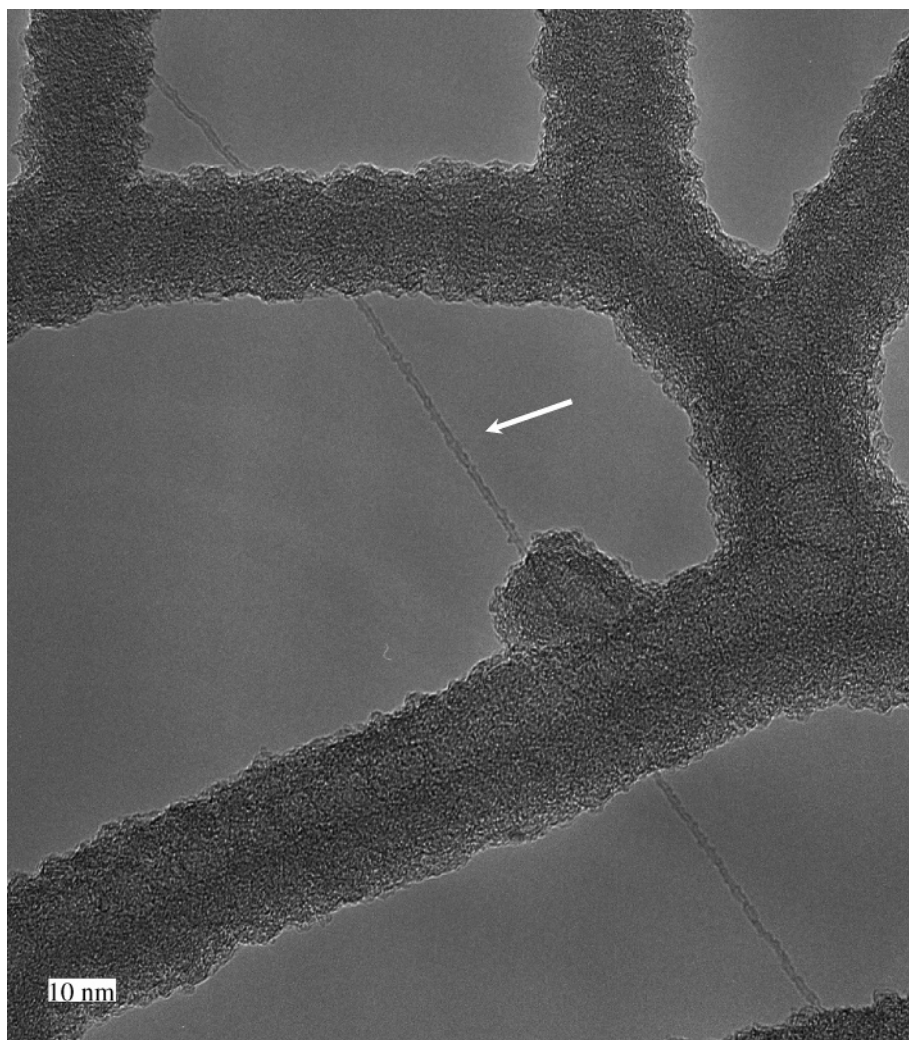


Figure 5. TEM of a functionalized carbon nanotube (arrow) on a lacey carbon grid. There is no tendency to rebundle for the 4-*tert*-butylbenzene functionalized SWNT.

chemistry,¹⁷ dichlorocarbene reactions,⁴² and osmylation⁴³ for covalent functionalization and selective absorption of bromine,⁴⁴ amines,⁴⁵ and DNA⁴⁶ for selective noncovalent methodologies. This is important because it now gives researchers the ability to manipulate carbon nanotubes by band gap and thus begin to separate the metallic from the semiconducting SWNTs.^{44–47}

SWNTs that are SDS wrapped as individuals in aqueous solutions and titrated with a benzenediazonium salt show a profound difference between the rate of functionalization of the metallic and semimetallic SWNTs over the functionalization rate of semiconductor SWNTs. Under carefully controlled conditions, the selective functionalization with benzenediazonium salt even shows differences in the rate of reaction between the metallic and semimetallic nanotubes.⁴⁸ The selective nature of the functionalization reaction is apparent from the absorption spectra (Figure 6). The three peak grouping in the region from 480 to 620 nm corresponds to metallic and semimetallic nanotubes; the rest of the transitions correspond to semiconductors. After the addition of 12 equiv of diazonium salt for every 1000 C atoms on the nanotube, these transitions are lost, and the semiconductor transitions are unaffected. Raman spectra also show that the same trend wherein metallic carbon nanotubes react at a much faster rate than the semiconductors (Figure 7). The selective functionalization reaction was monitored by Raman excitation at 532 nm. This wavelength probes the metallics and one semiconductor, the (9, 2) SWNT. (Recall, as

described above, $9 - 2 = 7$, which is not a multiple of 3; therefore, the (9, 2) tube is a semiconductor.) Even upon the loss of all of the radial breathing modes for the metallic SWNTs, the (9, 2) semiconducting SWNT remains largely unaffected.

The selective functionalization was recently used to separate the metallic nanotubes from the semiconductors.⁴⁷ This was realized by selectively reacting a nonpolar addend onto the side wall of the metallic carbon nanotubes and then reacting the semiconductors with a polar arene moiety. Silica gel column chromatography was performed on the now chemically distinguished SWNT types, and the nonpolar component was collected, thermalized (which has been shown to remove the addends to regenerate the pristine SWNTs),²⁸ and analyzed. The thermolysis is typically performed with TGA by heating to 750 °C in an inert atmosphere such as nitrogen or argon.^{17,22,23} Raman analysis of the regenerated material showed that this separation did, in fact, give an SWNT sample greatly enriched in the metallic nanotubes. This is most apparent by comparing the Raman spectra (at 633-nm excitation) of the starting mixture (Figure 8) against the enriched component (Figure 9). This wavelength of excitation probes both the metallic and semiconducting nanotubes; therefore, of the common Raman excitation wavelengths, 633-nm excitation gives valuable information about both nanotube types. Clearly, the separated material is greatly enriched in the (13, 4) semimetallic carbon nanotube and the (9, 9) metallic species.²² Thus, selective functionalization

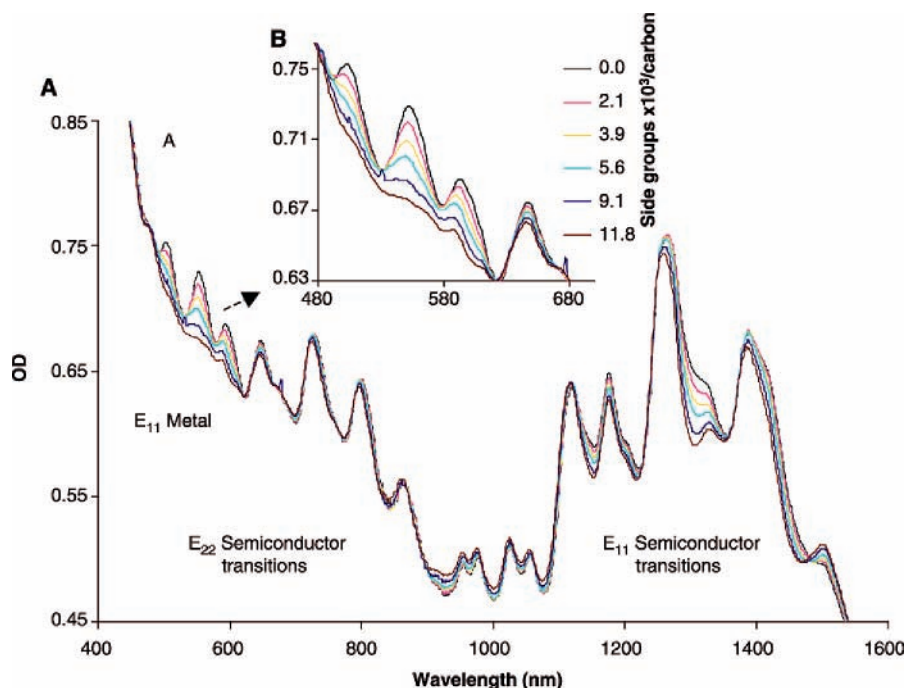


Figure 6. Progressive loss of the van Hove absorption bands of the three metallic/semimetallic peaks in the region from 480 to 600 nm^{-1} during the slow addition of an arene diazonium salt. The semiconducting SWNTs' bands remain largely unaffected.

and separation offers prospects for interesting electronic and optoelectronic applications of SWNTs once the covalent functionalities are removed by thermolysis. Further effects on the Raman band intensities based on morphological changes are being studied.

C. Carbon Nanotube-Modified Composites. Polymer-based composites and blends, where polymers serve as the matrixes for inorganic, organic, or carbon fillers, have had enormous impact as engineering materials, and they are widely used in commercial products. Often carbon black, glass fibers, and/or phenolic resins are incorporated into the polymer hosts resulting in significant improvements in mechanical properties including impact strength and tensile and compressive moduli (stiffness) over that of the nonfilled polymer. As stated previously, SWNTs exhibit extraordinary mechanical properties,^{1,49,50} such as tensile strengths of 50–200 GPa, estimated Young's moduli of 1–5 TPa, and high strains (ca. 5–6%) at break.⁵¹ Furthermore, when released from strain, bent SWNTs recover their original form without direct fracture.⁵² On the basis of these extraordinary mechanical properties and the large aspect ratio (typically ca. 500–1000) associated with individual tubes, SWNTs are excellent candidates for the development of nanoreinforced polymer composite materials,^{9,53} complementing or substituting the traditional carbon black and glass fiber fillers. Moreover, the functionalized SWNTs show further promise because their miscibility at >1 wt % levels in the polymer host is often enhanced relative to that of the unfunctionalized SWNTs.

Research on nanotube composites has concentrated, for the most part, on polymer multiwalled nanotube (MWNT)-based materials^{54–57} wherein they exhibit mechanical properties that are superior to those of conventional polymer-based composites because of their considerably higher intrinsic strengths and moduli and the fact that the stress-transfer efficiency can be 10 times higher than that of traditional additives.⁵⁶ However, polymer–SWNT composites show even more promise than the MWNT-based nanocomposites as potential high-performance engineering materials.^{58,59} For instance, dynamic mechanical analysis (DMA) studies of in-situ polymerized poly(methyl

methacrylate), PMMA–SWNTs, demonstrated that the tensile modulus increased by more than a factor of 2 with only 0.1 wt % SWNTs added.⁶⁰ These improvements are far in excess of that observed in the PMMA–MWNT nanocomposites. Independent experiments on PMMA–SWNTs at low nanotube concentrations (<1 wt %) indicate that the polymer is intimately mixed with the nanotubes. Furthermore, measurements of the melt rheology of polystyrene–SWNT nanocomposites indicate a substantial increase in the viscosity and elasticity of the system at low shear rates even at 1 wt % SWNT loadings.^{9,53} The low-frequency linear oscillatory shear moduli for polystyrene–functionalized-SWNT nanocomposites demonstrate a transition from liquidlike to solidlike behavior associated with the formation of a percolated network structure, whereas that for the unfunctionalized SWNT and polystyrene remains liquidlike for nanocomposites with 3 wt % SWNT.^{9,53} The formation of such a percolated nanoparticle network structure is a consequence of the dispersion of the functionalized SWNTs, the effective aspect ratio of the SWNTs, and perhaps most importantly the strength of the polymer/functionalized-SWNT interaction. Thus, functionalization greatly increases the dispersion of SWNTs in polymer matrixes, and the functional moiety increases the interfacial bonding or entanglement. This is in sharp contrast to unfunctionalized SWNTs where dispersion and interfacial bonding or entanglement is minimal.

Elastomers are another class of composites that could be profoundly influenced by SWNT additions. Elastomers are used commercially in a wide range of applications in market segments including rubber tires, which is the largest consumer of natural and synthetic rubber. The North American synthetic rubber industry had a volume of 2.2 million metric tons in 2002.⁶⁰ Traditionally, additives are applied within elastomers to make them have a higher tensile modulus (stiffness), but the result is generally a concomitantly large reduction in the strain-at-break (the stretch point at which the polymer will break). For the sake of illustration, polyisoprene shows a strain-at-break of ca. 10 (i.e., 1000%) or higher, meaning that it can stretch to 10 times its original length with nearly a complete return to its original

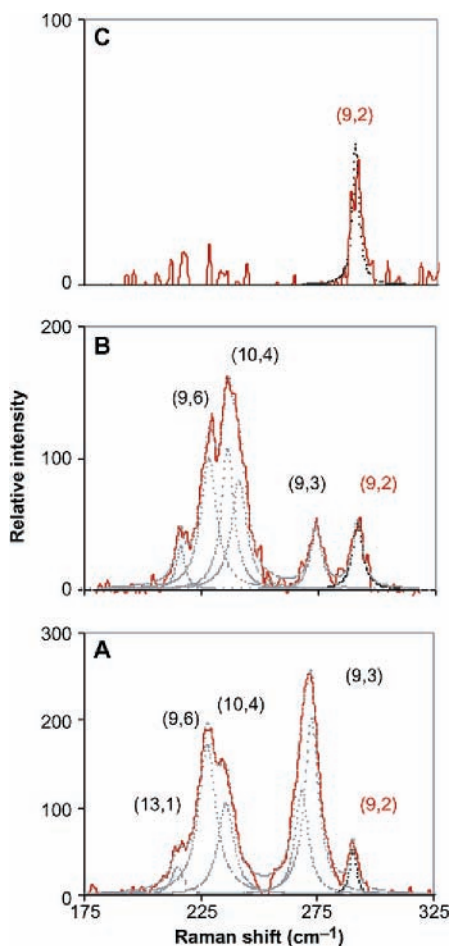


Figure 7. Raman (532-nm excitation) of (A) radial breathing modes of the starting SWNTs, (B) after the addition of 6 equiv of 4-chlorobenzene diazonium salt, and (C) after the addition of 25 equiv of the diazonium salt. Only the semiconductor transition ($n - m = 7 \neq 3q$) remains, whereas the semimetallic transitions ($n - m = 3q$) are lost.

state upon release. By adding 30–50 wt % of carbon black, the tensile modulus could increase 10-fold but the strain-at-break could fall to 1.25 (125%), hence it would no longer respond as an elastomer but as a thermoplastic in dynamic mechanical properties. The development of high-strength elastomers with high breaking strains and low densities are crucial in many applications including tires, belts, hoses, seals, O-rings, and so forth that affect industries such as automotive, engine, aerospace, oil drilling, and refining. Therefore, to be able to

SCHEME 1: Functionalized Carbon Nanotubes Used to Make the SWNT-PDMS Composite

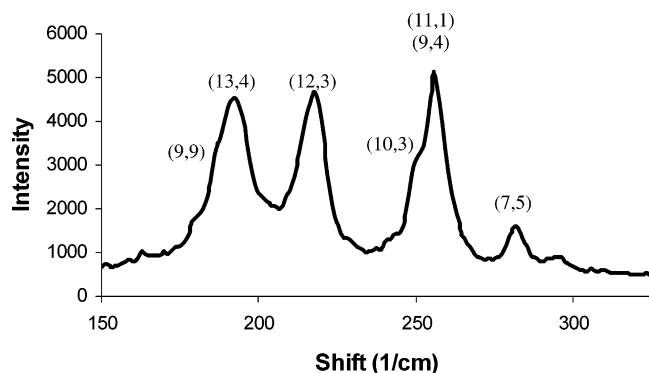
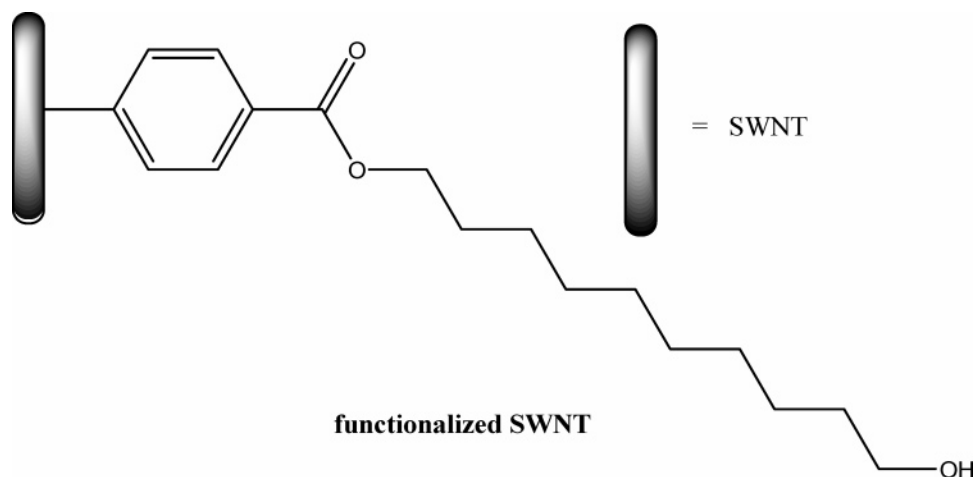


Figure 8. Raman (633-nm excitation) of the starting SWNTs with the radial breathing modes assigned to specific tube types.

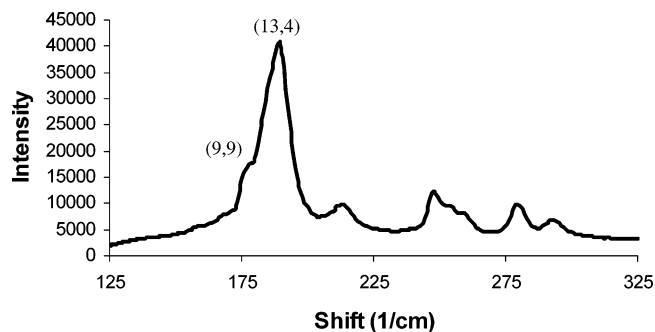


Figure 9. Raman (633-nm excitation) analysis of the separated SWNT material enriched in metallics after functionalization, chromatography on silica gel, and thermolysis.

stiffen elastomers while retaining the strain-at-break properties is highly desirable.

We have recently developed model functionalized SWNT (Scheme 1) reinforced networks of an amine-terminated poly(dimethylsiloxane) (PDMS) that typifies the extraordinary effects of functionalized SWNT-filled elastomeric composites.⁶¹ Typical data for the tensile stress vs strain for one such nanocomposite along with a comparable PDMS network with roughly the same cross-link density (based on solvent swelling) are shown in Figure 10. A comparison of the tensile modulus and the elongation-at-break for a series of nanocomposites is shown in Figure 11. Note that the functionalized SWNT material (Scheme 1) was prepared by the dry functionalization process that produces small bundles,³¹ and even greater enhancement is expected with unbundled, functionalized SWNTs. These results are remarkable because the tensile modulus and strength are

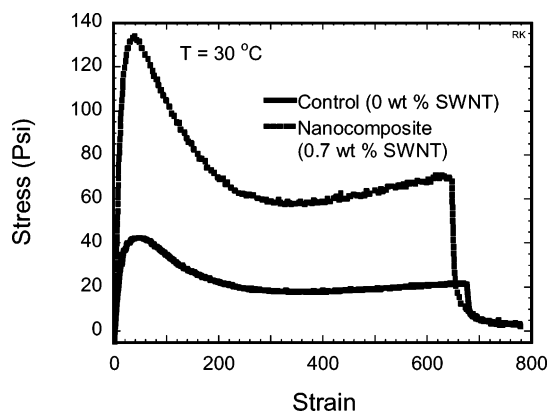


Figure 10. Tensile testing of a 0.7 wt % functionalized SWNT filled PDMS nanocomposite compared to a similarly cross-linked PDMS network that contains no nanotubes. The sample was stretched at a rate of 2 mm/min in a mini-Instron tester.

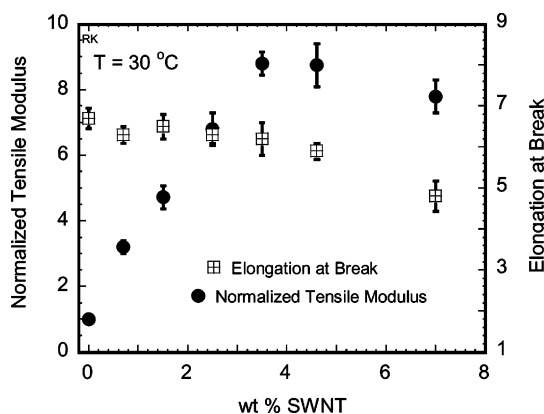


Figure 11. Composition dependence and elongation-at-break for the functionalized PDMS nanocomposite shown in Figure 10.

considerably increased whereas the strain-at-break is largely unchanged. The area under the curves in Figure 10 is proportional to the energy needed to cause polymer failure. Furthermore, the data suggest an optimal network structure at 3–4 wt % addition of the functionalized SWNT (Figure 11). There is no other elastomer additive system known that can so dramatically increase the tensile modulus with so little effect on the strain-at-break, underscoring the applicability of functionalized SWNT composites. One needs only a compatibilizing nanotube functionalization pendant for efficient polymer blending and miscibility, and it should be readily extendable to a wide range of elastomers and network-forming polymers including high-temperature epoxies.¹⁹ When considering polymeric pendants emanating from the functionalized SWNTs (and in the extreme, every polymer chain in the composite being bound to a nanotube), it may require pendants that have molecular weights similar to the molecular weight of the polymer or else miscibility will be disfavored because of an unfavorable entropy of mixing. However, this could be overcome enthalpically by using polymeric pendants that are known to mix well with the polymer host.

In light of the above considerations, for their full potential to be realized, SWNT sidewall functionalization must be achieved, thereby generating reinforced polymer and composites material.^{9,53,61} Not only does functionalization give nanotubes with increased solubility in organic solvent, but these modified nanotubes disperse far better in polymers than do the unfunctionalized SWNTs. Agglomeration must be overcome to give well-dispersed material, and because the or-

ganic moieties prevent bundling, agglomeration is lessened and dispersion is increased. Also, functionalization with an appropriate “handle” gives carbon nanotubes with increased interfacial bonding to the polymer, thereby lessening fiber pull-out during mechanical stress. In multicomponent, cross-linked composite material, such as elastomers, carbon nanotubes with an appropriate addend can be covalently attached to the host, thereby creating greatly fortified, novel nanocomposite structures that maintain elongation-to-break with increased modulus.

IV. Conclusions

Covalent functionalization of carbon nanotubes gives researchers the ability to manipulate these entities in typical organic solvents or even in solvent-free conditions. Functionalization can be done on the as-generated SWNT bundles to afford functionalized SWNT bundles. However, using protocols that disperse the SWNTs as individuals in the reaction medium (such as wrapping with surfactants, using oleum, or Li/liquid ammonia), functionalization can ensure individual unbundled SWNTs. These unbundled entities should prove to be the optimal additives for nanocomposites. Because selective reaction chemistries are now available that can react preferentially with SWNTs on the basis of nanotube type (n, m value), functionalization allows the manipulation and separation of highly enriched SWNT fractions. Covalent sidewall functionalization also overcomes the issues of poor interfacial bonding and dispersion in host polymeric matrixes, thus routes to unprecedented ultrahigh performance blends and composites are being realized.

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