Functionalized Carbon Nanotubes: Properties and Applications

YA-PING SUN,* KEFU FU, YI LIN, AND
WEIJIE HUANG

Department of Chemistry and Center for Advanced Engineering Fibers and Films, Howard L. Hunter Chemistry Laboratory, Clemson University, Clemson, South Carolina 29634-0973

ABSTRACT
Carbon nanotubes can be functionalized via amidation and esterification of the nanotube-bound carboxylic acids. The solubility of these functionalized carbon nanotubes makes it possible to characterize and study the properties of carbon nanotubes using solution-based techniques. Representative results concerning the solubility, dispersion, defunctionalization, and optical properties of the functionalized carbon nanotubes are presented. Several examples for the use of functionalized carbon nanotubes in the fabrication of polymeric carbon nanocomposites, the probing of nanotube-molecule interactions, and the conjugation with biological species are highlighted and discussed.

Introduction

The chemical modification and solubilization of carbon nanotubes represent an emerging area in the research on nanotubes-based materials. Several research groups have reported successful functionalization reactions for single-walled (SWNT) and multiple-walled (MWNT) carbon nanotubes.[1–20] These reactions may roughly be divided into two categories: a direct attachment of functional groups to the graphitic surface and the use of the

Ya-Ping Sun received his B.Eng. degree (1982) from the Zhejiang Institute of Technology and his M.S. degree (1985) from Zhejiang University, both in Hangzhou, China. He earned his Ph.D. (1989) at the Florida State University. After postdoctoral training at the University of Texas at Austin, he joined the Department of Chemistry at Clemson University in 1992. He has been Professor of Chemistry since 1999. His research interest is in the development of nanostructures and nanomaterials for optical, electronic, and biomedical applications.

Kefu Fu received his B.S. degree in applied chemistry (1997) from Tongji University in China. He is currently a graduate student at Clemson University, under the direction of Ya-Ping Sun, working toward a Ph.D. degree in chemistry.

Yi Lin received his B.S. degree in polymer chemistry (1996) and M.S. degree in polymer chemistry and physics (1999) from the University of Science and Technology of China. He has been a graduate student working toward a Ph.D. degree in chemistry at Clemson University since 1999, conducting research in Ya-Ping Sun's group on the preparation and characterization of functionalized carbon nanotubes and related nanocomposites.

Weijie Huang earned her B.S. degree in chemistry (1994) from Beijing Normal University in China and her M.S. degree in chemistry (1997, under the supervision of Professor Lan-Sun Zheng) from Xiamen University in China. She is currently a Ph.D. candidate in the Material Science and Engineering program at Clemson University under the direction of Ya-Ping Sun. Her research interest is in the study of carbon and polymeric nanomaterials.

nanotube-bound carboxylic acids. In the first category, Margrave, Smalley, and co-workers reported the fluorination of SWNTs.[2,3] In various alcohol solvents, these functionalized SWNTs were solvated as individual tubes, making it possible to carry out further solution chemistry. Pekker and co-workers reported the hydrogenation of carbon nanotubes via the Birch reduction in ammonia.[15] Other examples include the derivatization of small-diameter (ca. 0.7 nm) SWNTs reported by Tour and co-workers,[13,14] the interactions with anilines reported by Wilson and co-workers,[12] the reactions with nitrenes, carbenes, and radicals reported by Hirsch and co-workers,[19] and the 1,3-dipolar addition reported by Prato and others.[20]

In the second category of functionalization reactions, the nanotube-bound carboxylic acids come from intrinsic or induced defects. The latter refer to the creation of terminal carbons in the shortening of nanotubes, which upon oxidation are converted to carboxylic acids.[1,21,22] Haddon and co-workers first reported the use of the acid groups for attaching long alkyl chains to SWNTs via amide linkages[1] or carboxylate–ammonium salt ionic interactions.[4] Sun and co-workers showed that the esterification of the carboxylic acids can also be applied to functionalize and solubilize nanotubes of any length.[5,10,11] An advantage with the ester linkages is that they can be facilely defunctionalized via acid- or base-catalyzed hydrolysis, allowing the recovery of carbon nanotubes from the soluble samples.[11] There is now ample experimental evidence for the conclusion that the nanotube-bound carboxylic acids are the sites to attach a variety of functional groups for the solubilization of both shortened and full-length carbon nanotubes. These solubilized SWNTs and MWNTs allow solution-based characterizations and investigations.

The two categories of functionalization reactions may have different effects on the structures and intrinsic properties of carbon nanotubes. In this Account, we will focus on the properties of solubilized carbon nanotubes that are obtained from the functionalization of nanotube-bound carboxylic acids. The use of these soluble nanotube samples in nanomaterials development and applications will also be discussed.

1. Properties of Functionalized Carbon Nanotubes

Functionality and Solubility. For the solubilization of carbon nanotubes, the attachment of relatively large functional groups to the nanotubes is required. Since the first report by Haddon and co-workers on the amidation of nanotube-bound carboxylic acids with long-chain alkyl-amines (octadecylamine, for example),[1] a variety of oli-gomeric and polymeric compounds have been used in the functionalization of carbon nanotubes for their solubility in common organic solvents and/or water. Illustrated in Figure 1 are some of the functionalized SWNTs and MWNTs available in our laboratory.
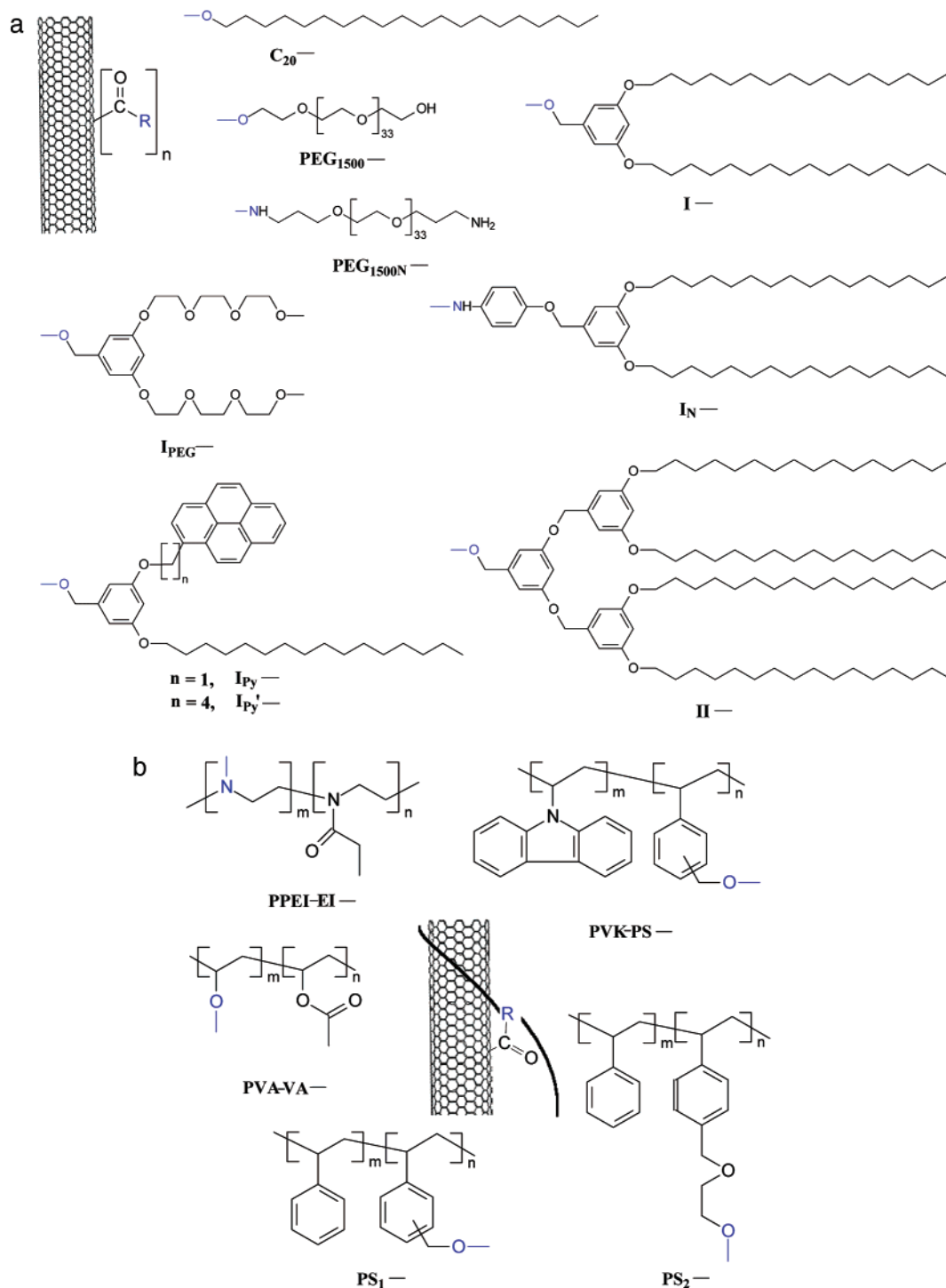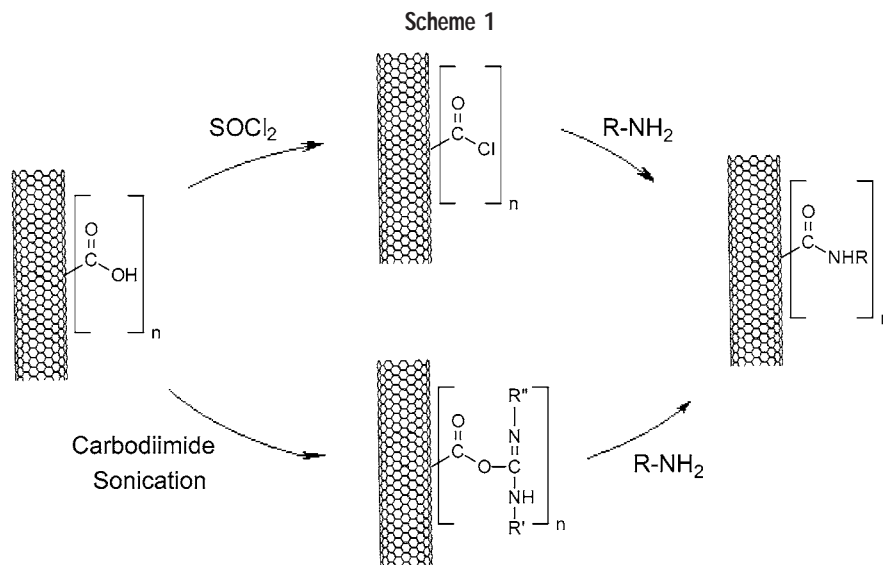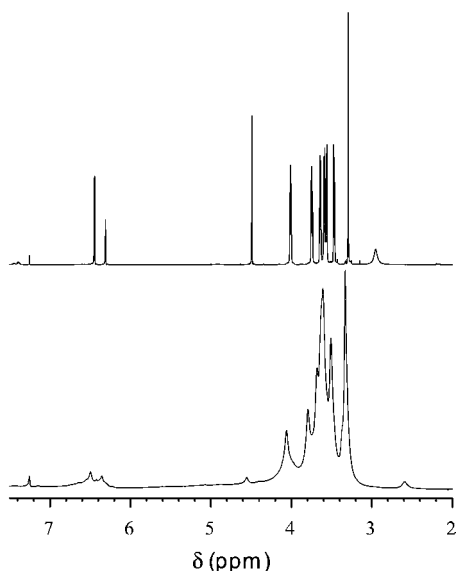
Scheme 1

Solution NMR. The solubilization of carbon nanotubes provides opportunities for solution NMR studies of the nanotubes. However, unlike the successful solid-state ^{13}C NMR characterization of pristine carbon nanotubes,[25] we have not been able to detect any meaningful nanotube carbon signals in the solution ^{13}C NMR measurements of solubilized carbon nanotubes (including ^{13}C-enriched samples). On the other hand, both ^1H and ^{13}C NMR results have provided valuable information on the functional groups in the functionalized SWNT and MWNT samples in solution. For example, the ^1H NMR signals of I_{PEG} become very broad upon the attachment to carbon nanotubes via the esterification of the nanotube-bound carboxylic acids (Figure 2).[10] Results from the determination of NMR nuclei spin–lattice (T_1) and spin–spin (T_2) relaxation times suggest that the broadened proton signals are associated with diamagnetic species of low mobility, namely, the nanotube-attached I_{PEG} moieties.[10]

Microscopy Analysis. The functionalized carbon nanotubes in solution can be deposited directly onto a surface for various microscopy analyses. The results from such analyses offer the most direct evidence for the presence of carbon nanotubes in the soluble samples.

Transmission electron microscopy (TEM) analysis of the functionalized carbon nanotubes is especially useful in providing both an overview at low magnification and a detailed examination at high-resolution. The imaging of functionalized MWNTs is straightforward because of their relatively large sizes (diameters). For example, shown in Figure 3 is a TEM image of an **I**−MWNT specimen prepared via the deposition of the sample solution onto a carbon-coated copper grid. It shows that the soluble sample contains functionalized MWNTs of various lengths and diameters.[26]

The TEM analysis of the functionalized SWNTs is more difficult because of their much smaller sizes (diameters).

FIGURE 2. ^1H NMR spectra of I_{PEG} (top) and I_{PEG}−SWNT (bottom) in CDCl$_3$.
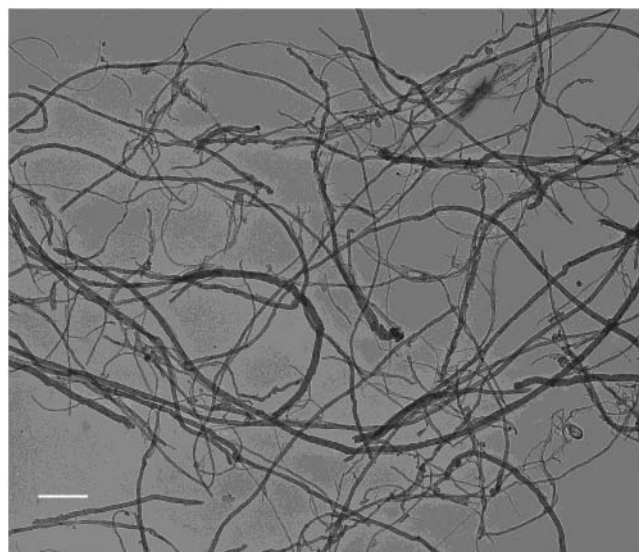
FIGURE 3. A typical TEM image of the **I**−MWNT sample on a carbon-coated copper grid (scale bar = 500 nm). Reprinted with permission from ref 26. Copyright 2002 American Chemical Society.

FIGURE 4. A TEM image of the PPEI-EI—SWNT sample on a holey LaCrO$_3$ stainless steel grid after thermal defunctionalization at 370 °C with air (scale bar = 10 nm).[23]

It is particularly challenging with the samples obtained from more effective functionalization reactions because the nanotubes in these samples are less bundled. The presence of functional groups on the nanotube surface makes it even harder to distinguish carbon nanotubes from the background in TEM images. Therefore, a partial or complete removal of functional groups from the functionalized carbon nanotubes in the specimen typically improves the TEM results significantly. For a PPEI-EI—SWNT sample deposited on a holey LaCrO$_3$ stainless steel grid, the thermal defunctionalization and subsequent evaporation of the functional groups via heating at 370 °C in the presence of air allow much improved TEM imaging of the single-walled nanotubes (Figure 4).[23]

Atomic force microscopy (AFM) has been used extensively in the characterization of functionalized carbon nanotubes. An advantage with the AFM characterization is that there is no severe sample damage such as that caused by the focused electron beam in TEM measurements. Haddon and co-workers used AFM to characterize octadecylamine-functionalized SWNTs before and after chromatographic separation of the soluble sample.[8,9] Their results suggest that the nanoscopic bundling/debundling information can be obtained from the height images in specific areas. The AFM technique can also be used to probe the attachment of large polymeric species to carbon nanotubes, such as the functionalization of SWNTs and MWNTs with natural proteins (Figure 5).[27]

An ultimate imaging of a functionalized SWNT at the atomic-resolution may be achieved by using the scanning tunneling microscopy (STM) technique. For example, results from the STM study of a PPEI-EI polymer-functionalized SWNT suggest that the polymers not only wrap around the nanotube but also follow the chirality of the nanotube.[16] According to the plots for the local density of electronic states, the tip of a PPEI-EI-functionalized carbon nanotube may be described as the addition of low-energy acceptor states to a "bare" nanotube system, namely, that the polymers interact strongly with the tip of the nanotube. The polymers also interact with the nanotube body and sometimes cover the entire nanotube. Of particular interest is the surprising regularity of polymer crystallization on the nanotube, suggesting that the nanotube may serve as a template for the polymer crystallization in the functionalized nanotube sample.[16]

Scanning electron microscopy (SEM) has not been very useful in the imaging of functionalized carbon nanotubes due primarily to the presence of a large amount of organic functionalities. However, SEM has been a valuable tool in the characterization of defunctionalized carbon nanotube samples.[11,17]

Defunctionalization. The carbon nanotubes can be recovered from the soluble samples via defunctionalization. The characterization of the defunctionalized samples provides further evidence for the conclusion that the soluble samples before defunctionalization contain substantial amount of carbon nanotubes. In addition, the gravimetric results associated with the defunctionalization allow an estimate of the carbon nanotube contents in the soluble samples.[17]

There are essentially two kinds of defunctionalization processes: chemical defunctionalization in solution and thermal defunctionalization in the solid state. The defluorination of fluorinated carbon nanotubes in a reaction with anhydrous hydrazine may be considered as a chemical defunctionalization process.[2,3] For soluble carbon nanotube samples that are based on the formation of ester linkages, a classical example for chemical defunctionalization is acid- or base-catalyzed hydrolysis, which re-
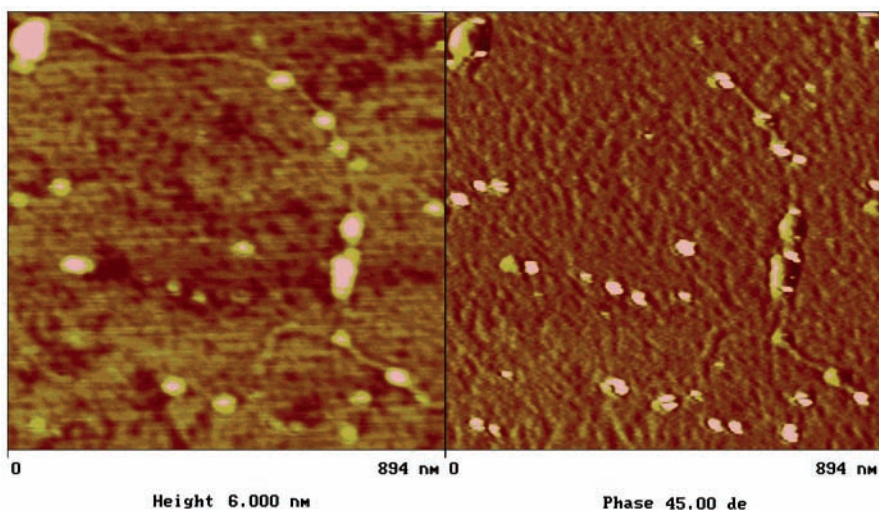
FIGURE 5. Height (left) and phase (right) images from the AFM analysis of the SWNT—BSA conjugate sample on mica substrate. Reprinted with permission from ref 27. Copyright 2002 American Scientific Publishers.

Scheme 2
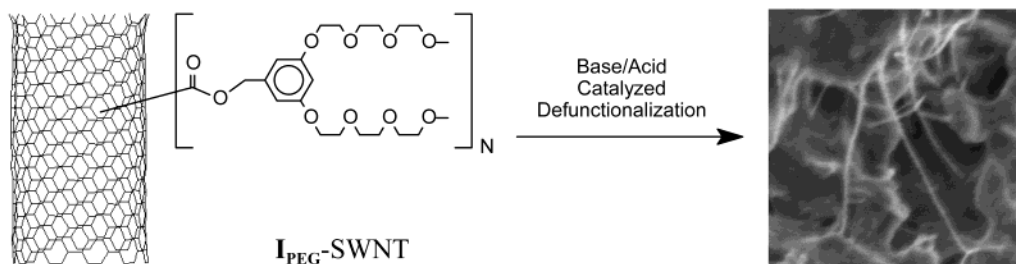
I_{PEG}-SWNT

moves the functional groups from the nanotube surface and results in the precipitation of defunctionalized carbon nanotubes. For example, for the solubilized carbon nanotubes I_{PEG}–SWNT and I_{PEG}–MWNT, the acid-catalyzed hydrolysis can be accomplished by refluxing the soluble samples with a strong acid such as trifluoroacetic acid.[11] The hydrolysis reaction in homogeneous solution yields defunctionalized carbon nanotubes as dark-colored precipitates. The high content of carbon nanotubes in the defunctionalized samples makes it possible to carry out SEM analyses (Scheme 2).[11]

The thermal defunctionalization is less specific but effective for different classes of functionalized carbon nanotube samples. A convenient way to defunctionalize a small quantity of sample is in a thermal gravimetric analysis (TGA) scan with a slow-temperature scanning rate, because most of the organic functional groups are evaporated before the onset of carbon nanotube weight loss (>800 °C in an inert atmosphere and >400 °C in the presence of air). For example, the results in Figure 6 show that the TGA trace of the PPEI-EI–MWNT sample is intermediate between those of the neat polymer and the pristine MWNT sample.[17] According to the TGA results, the thermal defunctionalization of the PPEI-EI–MWNT sample is largely completed at 500 °C in the presence of air. This is confirmed by results from the SEM analysis of the defunctionalized sample (Figure 7).

Optical Properties. Solubilized carbon nanotube samples are highly colored. The absorption spectra of the functionalized carbon nanotubes in solution are generally broad and essentially featureless curves extending into the near-infrared region. Among the scarce results on the absorptivity of carbon nanotubes is an estimate from the gravimetric results associated with the chemical defunctionalization of dendron-functionalized SWNTs.[11] In that experiment, the decrease in UV/vis absorption of the solution as a result of the nanotube precipitation was used to calculate the average absorptivity of carbon nanotubes. For SWNTs, the estimated absorptivity value at 500 nm is ~100 mL mg^{-1} cm^{-1}, about 2 orders of magnitude higher than that of fullerene C_{60} on a per unit weight basis.[11,28]

Fullerenes have been widely studied as nonlinear absorbers in the visible and near-infrared because their absorption cross-sections are larger in the excited state than in the ground state (reverse saturable absorbers).[29-31] An important application of nonlinear absorbers is the limiting of intense pulsed laser irradiation.[29,31] For example, fullerene C_{60} in toluene solution exhibits strong optical limiting responses toward nanosecond laser pulses at 532 nm.[29] Pristine carbon nanotubes in a suspension are also excellent optical limiters,[32-34] but with a different nonlinear scattering mechanism. Since carbon black suspension is often considered as a benchmark for nonlinear scattering optical limiters, it is no surprise that the suspension of pristine carbon nanotubes behaves in a similar fashion.

The solubility of functionalized carbon nanotubes to form homogeneous solutions allows an evaluation of their optical limiting properties from a different perspective.[6]
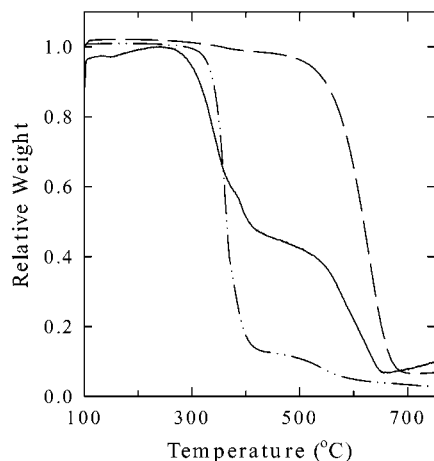
FIGURE 6. TGA traces (measured in the presence of air) of PPEI-EI polymer (— ·· —), pristine MWNT (— — —), and PPEI-EI—MWNT (—) samples. Adapted from ref 17.
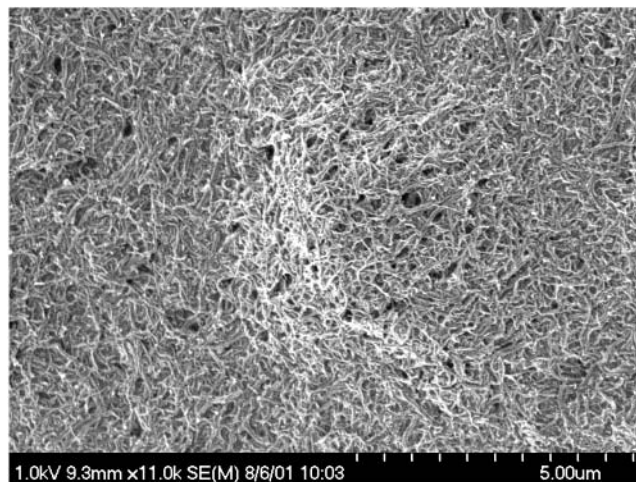
FIGURE 7. A SEM image of the PPEI-EI—MWNT sample after being subject to TGA analysis to 500 °C. Reprinted with permission from ref 17. Copyright 2002 American Chemical Society.
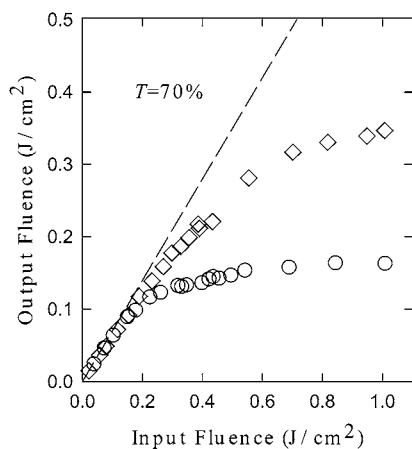
FIGURE 8. Optical limiting responses of the PPEI-EI–SWNT sample in homogeneous chloroform solution (◇) are compared with those of pristine SWNTs in aqueous suspension (○) toward nanosecond laser pulses at 532 nm. Reprinted with permission from ref 6. Copyright 2000 American Chemical Society.

Scattering becomes a minor issue in these carbon nanotube solutions, so that the nonlinear absorption plays a more important role in the optical limiting responses. For example, the transmission spectral profile of a homogeneous chloroform solution of PPEI-EI–SWNT is obviously different from that of an aqueous suspension of SWNTs.[6] In fact, the latter agrees well with the transmission spectral profile of an aqueous suspension of carbon black. Similarly, the optical limiting properties of the functionalized carbon nanotubes are different from those of the corresponding nanotube suspensions. The responses of the functionalized SWNTs in a chloroform solution toward nanosecond laser pulses at 532 nm are considerably weaker than those of an aqueous SWNT suspension of the same linear transmittance (Figure 8).[6] The different optical limiting responses of the carbon nanotubes in solution versus in suspension may be attributed to their different dominating optical limiting mechanisms (nonlinear absorption in the solution vs nonlinear scattering in the suspension).[6,34] In this context, carbon nanotubes may serve as an excellent model system for a fundamental understanding of the two primary optical limiting mechanisms.

Raman spectroscopy has been used widely and successfully in the characterization of pristine carbon nanotubes.[35] However, for functionalized carbon nanotubes, Raman measurements are generally overwhelmed by the strong luminescence background.[10,17,18,36] For example, shown in Figure 9 is an observed Raman spectrum of the PPEI-EI–MWNT sample obtained from the acyl chloride route (Scheme 1), which essentially becomes a luminescence spectrum. In fact, for effectively functionalized and solubilized SWNT and MWNT samples, in which most of the nanotubes are well-dispersed without significant bundling, the Raman spectra measured on a FT-Raman spectrometer at 1064 nm excitation are still covered with strong broad luminescence signals. The luminescence interference is apparently dependent on how well the carbon nanotubes are dispersed in the soluble sample. Generally speaking, the better the nanotube dispersion, the stronger the luminescence interference. As discussed
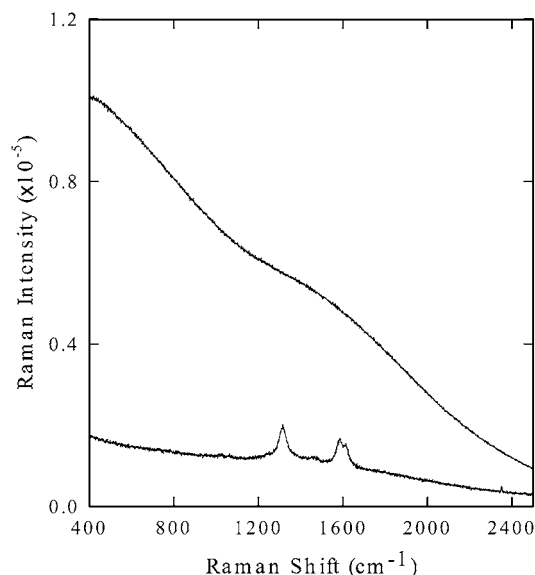
FIGURE 9. Raman spectra (780 nm excitation) of PPEI-EI–MWNT samples obtained from the acyl chloride method (top) and the diimide-activated coupling method (bottom).

in the previous section, for example, the functionalization via amidation with the acyl chloride route is more effective than amidation with the diimide-activated coupling (Scheme 1) for the dispersion of nanotubes in the resulting soluble samples. Consequently, the Raman spectrum of the sample obtained from the amidation reaction using 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDAC) as a coupling agent exhibits less luminescence interference (Figure 9). Nevertheless, if this sample, which contains more bundled nanotubes, is refunctionalized to improve the nanotube dispersion, the Raman spectrum of the resulting better-functionalized nanotube sample is again overwhelmed by the strong broad luminescence.

The defunctionalization, either chemically or thermally, results in a partial or complete reversal of the nanotube
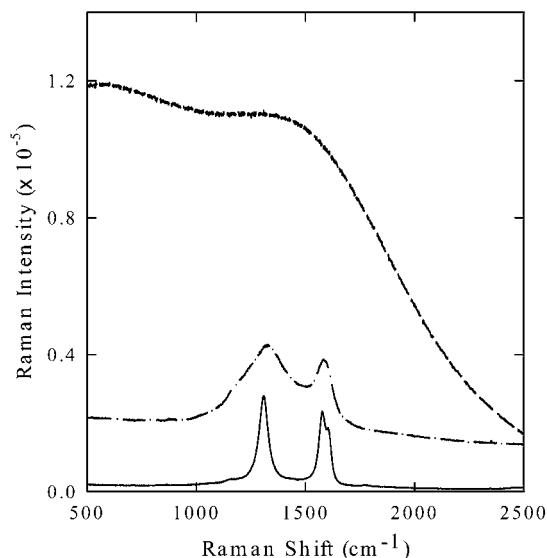
FIGURE 10. Raman spectra (780 nm excitation) of the **I**–MWNT sample before (− − −) and after (− · −) thermal defunctionalization in a TGA scan to 650 °C. The spectrum of the pristine MWNT sample (—) is also shown for comparison.[36]

dispersion achieved in the functionalization. For the dendron **I**-functionalized MWNTs, as an example, the Raman spectrum of the soluble sample is overwhelmed by the luminescence background (Figure 10). Upon the thermal defunctionalization of the sample in a slow TGA scan to 800 °C in the nitrogen atmosphere, the spectrum of the resulting sample shows the characteristic Raman peaks of MWNTs (Figure 10).[36]

The inverse correlation between the Raman and luminescence properties and their dependence on the nanotube dispersion in solubilized carbon nanotube samples are very interesting. Further investigations are required for an understanding of the mechanistic details.

2. Functionalized Carbon Nanotubes for Materials Development and Applications

The solubility of functionalized carbon nanotubes in common organic solvents and/or water allows solution-based techniques to be used in the characterization of the nanotube samples and in the study of the fundamental properties of carbon nanotubes. The same solubility also offers unique opportunities in the development of carbon nanotubes-based materials and in the use of the solubilized carbon nanotubes as starting materials for further chemical and biochemical modifications.

Polymeric Nanocomposites. Embedding carbon nanotubes in polymeric matrices for various nanocomposite materials has been a popular subject in the nanotube research.[37,38] Results from the experimental preparation and fabrication of polymeric carbon nanocomposites based on pristine carbon nanotubes suggest that the dispersion of the nanotubes in polymer matrices is a challenging task. This is a particularly serious issue for nanocomposites that are designed for optical applications because the aggregation of carbon nanotubes, among other problems, reduces the optical quality of the composite materials. The use of solubilized carbon nanotubes offers significant advantages in most cases.[39,40]

The solubility of the dendron- and polymer-functionalized SWNTs and MWNTs (Figure 1) allows the preparation of nanotubes-embedded polymer thin films using a solution casting method.[39,40] For example, the water-soluble functionalized carbon nanotubes can be homogeneously dispersed in poly(vinyl alcohol) (PVA) thin films by following a simple solution mixing and casting procedure. These films are of high optical quality, with their absorption spectra similar to those of the functionalized SWNTs in solution.[39] Luminescence polarization measurements of the thin films suggest that the absorption and luminescence dipole moments of the functionalized carbon nanotubes are intrinsically collinear, with the average of observed luminescence anisotropy values at the positive limit (0.5).[39,41] Since PVA polymer film is often used as a host to align asymmetric chromophores,[41] the carbon nanotubes-embedded PVA films can also be used to align the nanotubes via mechanical stretching. Results from a polarized spectroscopy study of the stretched films show that the electronic transitions of the embedded carbon nanotubes are in the direction of the nanotube long axis.
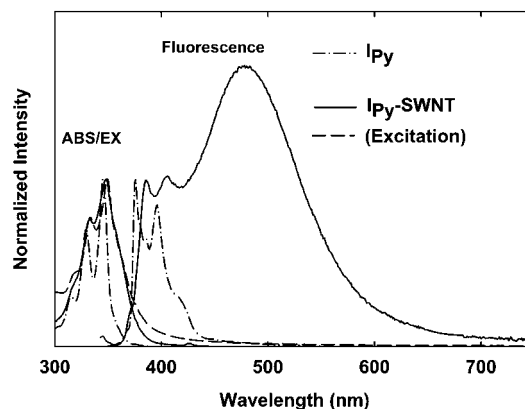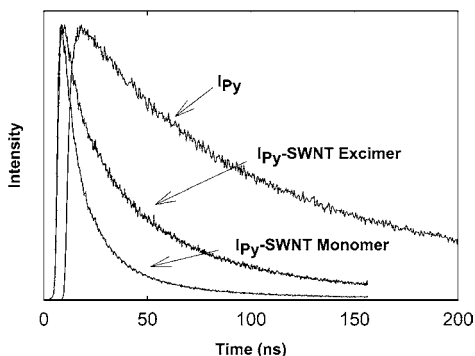

FIGURE 11. Absorption (ABS), fluorescence, and fluorescence excitation (EX) spectra of $\mathbf{I_{Py}}$ and $\mathbf{I_{Py}}$—SWNT in room-temperature toluene. Reprinted with permission from ref 43. Copyright 2002 American Institute of Physics.

Nanotube–Probe Interactions. The interaction between aromatic moieties and the carbon nanotube surface is an important issue. For example, π-stacking interactions were proposed to be responsible for the introduction of proteins into carbon nanotube samples.[42] The functionalized carbon nanotubes may play a valuable role in the study of such interactions. With the incorporation of aromatic probes into the functional groups, interactions between the carbon nanotubes and the attached probes can be evaluated in a dilute solution by using conventional spectroscopic techniques. Specifically, the pyrene-containing dendron-functionalized carbon nanotubes have been used for fluorescence spectroscopic probing of interactions between the nanotubes and the attached pyrene moieties.[43]

The fluorescence properties of $\mathbf{I_{Py}}$—SWNT in solution are characteristic of the formation and decay of pyrene excimers (Figure 11).[43] The excimer formation is "intramolecular" in nature (between pyrene moieties in neighboring $\mathbf{I_{Py}}$ units that are attached to the same nanotube) because the intensity ratio between pyrene excimer and monomer emissions is independent of the solution concentration. The excimer formation is also predominantly dynamic in nature because the excimer emission is suppressed effectively either in a highly viscous polymer blend or in a 77 K glassy medium. The fluorescence decays of $\mathbf{I_{Py}}$ before and after being attached to SWNTs are compared in Figure 12. The faster monomer fluorescence decay in $\mathbf{I_{Py}}$—SWNT may be attributed to the quenching of pyrene excited states by the attached carbon nanotube, which serves as an energy sink in an excited-state energy transfer mechanism. Since the absorption spectrum of the carbon nanotubes overlaps with that of pyrene, the coupling between energy levels of the pyrene moieties and the attached carbon nanotube might be responsible for the proposed energy transfer quenching of pyrene excited states in $\mathbf{I_{Py}}$—SWNT.[43]

Nanotube–Protein Conjugates. The solubilized carbon nanotubes may be used as starting materials for reactions in homogeneous solution. Of particular importance are reactions with biological species, which require the use of water-soluble functionalized carbon nanotubes.

FIGURE 12. Fluorescence decays of I_{Py} and I_{Py}—SWNT (monitored at 380 nm for monomer and 490 nm for excimer) in room-temperature toluene. Reprinted with permission from ref 43. Copyright 2002 American Institute of Physics.

The potential biologically significant applications of carbon nanotubes have already attracted much attention. For example, Sadler and co-workers reported the immobilization of oligonucleotides, enzymes, and proteins on MWNTs.[44] Mioskowski and co-workers used MWNTs for helical crystallization of proteins to take advantage of their shape and exceptional rigidity.[45] Mattson, Haddon, and co-workers also reported on the growth of embryonic rat-brain neurons on MWNTs.[46] The biocompatibility of carbon nanotubes is a significant issue in many of their proposed bio-applications. For the preparation of nanotube-protein bioconjugates, specifically, the different solvation and other requirements for the handling of bioactive molecules and for the processing of carbon nanotubes represent significant challenges.[47] The water-soluble functionalized carbon nanotubes can be used in exchange reactions with natural proteins under the conditions that cause minimum damages to the proteins.[27]

SWNTs and MWNTs that are functionalized with hydrophilic I_{PEG} are readily soluble in water, forming homogeneous aqueous solutions. The ester linkages with the oligomeric functional groups can be replaced by amide linkages with the amino moieties in natural proteins via exchange reactions. For example, the water-soluble I_{PEG}—SWNT sample has been used as a starting material in the exchange reaction with bovine serum albumin (BSA) protein under ambient conditions for the preparation of SWNT—BSA conjugate.[27] The BSA protein contains 60 amino moieties in lysine residues and 26 arginine moieties in guanidino side-chains, amenable to the coupling with the nanotube-bound carboxylic acids. The transformation from the ester linkages in I_{PEG}—SWNT to amide linkages in the SWNT—BSA conjugate is a thermodynamically favorable process. Since the displaced I_{PEG} is an oligomeric species, it can be removed from the reaction mixture via dialysis, which further pushes the reaction toward the direction of the transformation.[27] Additional dialysis in a membrane tubing of very large pore sizes also allows the removal of the residual free BSA after the exchange reaction.

The starting material I_{PEG}—SWNT is also soluble in organic solvents such as chloroform, but the SWNT—BSA conjugate is only soluble in water. Thus, the solubility change becomes a simple indicator for the ester to amide transformation in the exchange reaction. The TEM results confirm that the conjugate sample contains well-dispersed SWNTs. In a closer examination of the SWNT—BSA conjugate using AFM, the height and phase images show that the BSA proteins are intimately associated with a long SWNT (Figure 5).[27]

Results from the electrophoresis analysis of the nanotube—BSA conjugates suggest that the proteins are largely intact after being subject to the exchange reaction conditions.[27] According to the total protein analysis, which targets the amino acid building blocks in proteins, the bioactivities of BSA proteins are apparently preserved upon their attachment to the carbon nanotubes. For example, the SWNT—BSA conjugate sample was analyzed in terms of the modified Lowry procedure for microdetermination of the active protein concentration (tryptophan and tyrosine contents). The results show that the overwhelming majority of the BSA proteins ($86\% \pm 2\%$) in the conjugate sample remain bioactive.[27]

This preparation of nanotube-protein conjugates serves as a demonstration on the potential of water-soluble functionalized carbon nanotubes. The same strategy and methodology may be used to introduce carbon nanotubes into other biologically or biomedically important systems.

In summary, functionalized carbon nanotubes have played and will continue to play an important role in the research and development of nanotubes-based materials and systems. The solubility of the carbon nanotubes associated with the functionalization and chemical modification offers excellent opportunities not only in the characterization and understanding of carbon nanotubes but also in the utilization of carbon nanotubes for various nanomaterials.

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