CARBON NANOTUBES AND NANOCOMPOSITES FOR THERMAL AND ELECTRICAL APPLICATIONS

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CARBON NANOTUBES AND NANOCOMPOSITES FOR THERMAL AND ELECTRICAL APPLICATIONS

A Dissertation
Presented to
the Graduate School of
Clemson University

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy
Chemistry

by
Wei Wang
May 2008

Accepted by:
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Prof. Igor Luzinov
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ABSTRACT

The known electrical and thermal properties of carbon nanotubes have prompted many predictions on their extraordinary potentials for ultimately performing polymeric nanocomposites. In this dissertation, chemical modification and functionalization of carbon nanotubes have been demonstrated as being effective for high-quality polymeric carbon nanotube composites, especially with our approach of using polymers that are structurally identical or maximally similar to the matrix polymers in the nanotube functionalization. For example, a poly(N-vinyl carbazole) (PVK) copolymer containing pendant hydroxyl groups was synthesized for the functionalization of single-walled carbon nanotubes (SWNTs). The shared solubility of the functionalized nanotube samples with PVK matrix polymer enabled the wet-casting of high-quality PVK-SWNT nanocomposite thin films for an evaluation of their enhanced charge dissipation under photo illumination.

For desired electrical properties, not only the dispersion of carbon nanotubes in the polymer matrix is important to the performance, but also the use of only metallic nanotubes may offer solutions in some of the more demanding applications. Here demonstrated is that the bulk-separated metallic SWNTs offer superior performance (consistently and substantially better than the as-produced nanotube sample) not only in conductive composites with both poly(3-hexylthiophene) and PEDOT:PSS matrixes, but also in transparent conductive coatings of neat SWNTs.
DEDICATION

This dissertation is dedicated to my beloved wife, Karen, for her sacrifice, love and unconditional support.
ACKNOWLEDGMENTS

I would like to thank my advisor, Professor Ya-Ping Sun. His knowledge, guide, seriousness, diligence and philosophy in the science greatly affected me as a graduate student, which I have benefited from and shall certainly very much appreciate for my future career.

I am especially grateful to my other Ph.D. committee members, Prof. Gautam Bhattacharyya, Prof. Igor Luzinov, and Prof. Rhett Smith, for their time and active help in the completion of this dissertation.

I am grateful to all those who loved and supported me. In particular, I would like to thank my wife, Karen, and my parents, Mrs. Xiaoju Jin and Mr. Huahe Wang. My special thanks go to Dr. Yi Lin, who was the first one showing me the excellence of the scientific culture of the Dr. Sun’s research group. I would also like to give my special thanks to Prof. Su-Yuan Xie, a visiting professor from Xiamen University, whom I am very fortunate to work with from 2003 to 2005. Also my thanks go to other members in Dr. Sun’s research group for their help, kindness and friendship. In particular current members: Dr. M. J. Meziani, Dr. Fushen Lu, Dr. Li Cao, Lingrong Gu, Xin Wang, Monica Veca and the past members: Dr. Bailin Chen, Tara Elkin, Dr. Shiral Fernando, Barbara Harruff, Darron Hill, Dr. Huaping Li, Dr. Yang Liu, Brad Martin, Dr. Pankaj Patak, Shelby Taylor, Dr. Liangwei Qu, Dr. Puyu Zhang, and Dr. Bing Zhou.

Finally, I would like to thank Dr. Alex Kitaygorodskiy at Clemson, Dr. Larry Allard at ORNL, and Dr. John Connell at NASA Langley Research Center for fruitful collaborations.
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INTRODUCTIONARY REMARKS

My graduate research has been focusing on the design, synthesis, and characterization of functionalized carbon nanomaterials, especially carbon nanotubes, and on the electrical and thermal properties of these nanomaterials and their related potential applications.

Carbon nanotubes are newly discovered carbon allotropes with unique cylindrical hollow structures. As one-dimensional nanomaterials, carbon nanotubes represent an excellent combination of various exceptional physical properties, including high mechanical strength (e.g. measured Young's modulus of carbon nanotubes of 1.4 TPa and tensile strength of above 100 GPa), rich electronic properties (the existence of both semiconducting and metallic nanowires), good thermal conductivity (theoretical value well above diamond), as well as ultra-low density and chemical/thermal stability. Enormous potential has thus been envisioned for carbon nanotubes in a wide range of applications, such as nano-electronics devices, polymeric nanocomposites with enhanced mechanical, electrical, and thermal properties, chemical or biological sensors, and so on. However, due to the large surface area and severe bundling effects, carbon nanotubes are neither soluble nor dispersible in any organic solvent, which greatly limits their usages in above mentioned applications. Therefore, there have been extensive investigations in the scientific community on the development of chemical modification and functionalization techniques to make the nanotubes more processible. Of particular interest are those that result in the solubilization of the carbon nanotubes. The nanotube functionalization reactions could be either noncovalent or covalent in nature. In noncovalent
functionalization, the functional molecules, such as surfactants, interact with the nanotube surface via van der Waals forces. While for covalent functionalization, the addition to the nanotube graphitic sidewall generally involves highly reactive species, e.g. aryl diazonium compounds. A more versatile alternative in covalent functionalization is to target the nanotube surface defects, which are typically in the form of carboxylic acids due to the oxidative acid treatment used in the nanotube purification procedures. We have prepared a review on the various approaches in the functionalization and solubilization of carbon nanotubes (Chapter 1).

In our group, we have been focused on the defect-derived carboxylic acids for the covalent functionalization of carbon nanotubes because of the well-established reaction schemes (esterification or amidation reactions) and the fact that electronic structures of the nanotubes are largely preserved during the functionalization process. We have found the approach to be simple and effective, with the functionalized carbon nanotubes being readily soluble in organic and/or aqueous solution, thus enabling convenient solution-phase processing for various applications. Furthermore, we have developed a more elegant strategy of using polymers that are structurally identical or maximally similar to the matrix polymers for the nanotube functionalization to ensure the full compatibility of the functionalized carbon nanotubes with the polymer matrix. For example, we have applied the strategy to the covalent functionalization of carbon nanotubes with derivatized poly(vinyl carbazole) (PVK) for their homogeneous dispersion into the PVK matrix (Chapter 2). The resulting nanocomposites of high optical properties exhibited interesting photoconductive properties.
A similar review on carbon nanotubes serving as ideal filler materials for polymeric nanocomposites is also provided in Chapter 1, so are different fabrication methods for polymeric carbon nanotube composites and their electrical and thermal properties and applications.

Single-walled carbon nanotube (SWNT) may, depending on its chirality, be either metallic or semiconducting. The coexistence of metallic and semiconducting SWNTs in as-produced nanotube samples has been a bottleneck for many widely pursued applications, especially those more demanding ones, such as nano-electronic devices and electrically conductive nanocomposites. Therefore, the separation of SWNTs based on their electronic structures is an important and potentially highly valuable task. We have developed a bulk separation method based on selective interactions of large planar aromatic molecules with semiconducting SWNTs for their solubilization in organic solvents, and we have used the separated metallic SWNTs in the preparation and fabrication of conductive polymeric nanocomposites (Chapter 3). The results with poly(3-hexylthiophene) and PEDOT:PSS as polymer matrices demonstrated unambiguously that the nanocomposites with the separated metallic SWNTs are consistently and substantially better in performance than those with pre-separation purified SWNTs.

We have also made significant effort in the use of the separated metallic SWNTs for transparent conductive thin films, targeting potentially competitive performance to that of the presently dominating indium tin oxide (ITO) coatings. Results from a number
of different fabrication methods with different nanotube samples are compared and discussed in Chapter 4.
1.1. Introduction

Carbon nanotubes are newly discovered carbon allotropes, with unique cylindrical hollow structures of extremely large aspect ratios.\(^1\)\(^2\) One may conceptually visualize their structures by taking single or multiple graphene sheets and rolling them up into seamless tubes.\(^3\) Depending on the number of the graphene layers, carbon nanotubes are further categorized into single-walled (SWNT), double-walled (DWNT), and multiple-walled (MWNT) nanotubes. The distance between the coaxial graphene layers in MWNTs is about 0.34 nm, which is close to that in graphite. For SWNTs, the rolling up of a graphene sheet will need to match carbon atoms on the edges, which can be described by a chiral vector, \(C_h\),\(^3\)\(^4\)

\[
C_h = na_1 + ma_2
\]  

(1)

where \(a_1\) and \(a_2\) are unit vectors along the hexagonal lattice, and \(n\) and \(m\) are numbers of the steps along the vectors. In fact, \((n,m)\) is commonly referred to as the chiral index for a specific SWNT. When \(n = m\), the nanotube is an “arm chair”, while \(n = 0\) or \(m = 0\), the nanotube is a “zigzag”. All other SWNTs are called “chiral” nanotubes (Scheme 1.1).\(^5\) It
is now well established that a SWNT is either metallic (including semi-metallic) or semiconducting, depending on its chirality. For an arm chair SWNT \((n = m)\), the conductance and valence bands in the electronic density of states (DOS) overlap, so that the nanotube is metallic. If \(n-m = 3q\) and \(q \neq 0\) (where \(q\) is an integer), the corresponding SWNTs are semi-metallic, with a small band gap of several mili-eV’s. For \(n-m \neq 3q\), the nanotubes are semiconductors with a significant band gap near the Fermi level. Statistically (without any bias toward either type in the production), the ratio between metallic and semiconducting SWNTs should be 1 to 2. For MWNTs, the coaxial layers may be of different chiralities with negligible inter-layer electronic coupling, and as a result, MWNTs generally exhibit metallic characteristics.

There are now many ways to produce carbon nanotubes, including electric arc-discharge, laser ablation, and various chemical vapor deposition (CVD) techniques such as the CoMoCat process and the HiPco process. The production generally involves vaporizing carbon targets or decomposing carbon stocks, and sequentially rearranging carbon atoms into tubular structures by the assistance of catalysts. The as-produced carbon nanotubes are typically several hundred nanometers to several microns in length. The average diameter and diameter distribution of SWNTs are dependent on their production methods, while diameters of MWNTs generally vary in the range of 10 to 100 nm. For example, SWNTs produced from arc-discharge and laser ablation methods are relatively more uniform in diameter (typically 1.2-1.4 nm), while those from the HiPco method have broad diameter distributions (0.7-1.3 nm). As pesudo-one-dimentional nanostructures of very high surface areas, carbon nanotubes, SWNTs in particular, are
Scheme 1.1 (a) The two chiral vectors $a_1$ and $a_2$ on a graphene sheet; (b) an arm chair SWNT (8,8); (c) a zigzag SWNT (8,0); and (d) a chiral SWNT (10,-2). (From ref. 5.)
generally severely bundled due to the strong van der Waals force (on the order of 0.5 eV/nm). Most electron microscopy images of pristine or purified SWNTs are typically those of nanotube bundles (Figure 1.1).

Carbon nanotubes are often described as the ultimate nanofibers for their superior mechanical properties. However, their electrical and thermal properties are just as unique and impressive. According to estimates from theoretical calculations, metallic SWNTs should have exceptionally high electrical conductivity of up to $10^6$ S/cm, higher than that of copper metal at room temperature. Experimental measurements on single or bundled SWNT yielded somewhat lower value, on the order of $10^4$ S/cm. Carbon nanotubes are also excellent thermal conductors. Theoretical calculation predicted that an isolated (10,10) SWNT should have a very high thermal conductivity of 6,600 W/mK at room temperature. Experimentally, though not as high as predicted, the thermal conductivity of an individual MWNT was found to be about 3,000 W/mK. These superior properties of carbon nanotubes, combined with their high aspect ratio and uniquely high mechanical performance, make them ideal fillers in polymeric nanocomposite materials for electrical and thermal applications.

1.2 Polymeric/carbon nanotubes composites

Ever since the discovery of carbon nanotubes, there has been much interest in their uses for polymeric carbon nanotubes composites. However, despite their widely acknowledged and discussed superior properties and performance potentials, carbon nanotubes are not readily dispersed into polymeric matrices for the desired...
Figure 1.1 TEM image showing bundled SWNTs. (From ref. 8.)
nanocomposite materials. In fact, the homogeneous dispersion of carbon nanotubes, especially SWNTs, has been a major challenge in the development of polymeric carbon nanotube composites. The nanotubes are severely bundled or aggregated, and are essentially insoluble in any solvent systems, hindering any solution phase processing. Among early examples, polymeric carbon nanotube composites were fabricated via simple mixing, either in solution or in the melt state, with the aid of high shear forces such as sonication. However, the preparation based on simple polymer-nanotube blends typically results in composites of relatively poor dispersion of the nanotubes, which compromises the predicted or expected performance.\textsuperscript{25} Other mixing methods such as dry powder mixing,\textsuperscript{26} latex mixing,\textsuperscript{27} and coagulation\textsuperscript{28} have been adopted in an effort to improve the nanotube dispersion, though each method has its own limitation. The results are generally far from satisfactory.

Improved polymeric carbon nanotube composites were prepared by using \textit{in situ} polymerization, namely to polymerize monomers in the presence of carbon nanotubes.\textsuperscript{29} In fact, most of the epoxy-nanotube composites, which represent the earliest examples for using carbon nanotubes in polymeric nanocomposites, were fabricated with this method.\textsuperscript{30} Experimentally, carbon nanotubes were firstly dispersed in low molecular weight precursors, followed by adding hardening agents to cure the polymer to have the dispersed nanotubes “locked” inside the polymer matrix.
1.2.1 Functionalization of carbon nanotubes.

There have been extensive investigations on the chemical modification and functionalization of carbon nanotubes to make them more processible.\textsuperscript{31-35} Of particular interest are those that result in the solubilization of the carbon nanotubes, thus enabling conventional wet processing and fabrication of the relevant polymeric nanocomposites. The functionalization could be noncovalent or covalent in nature. In the noncovalent functionalization, the functional molecules are anchored onto the nanotube surface via van der Waals forces for the solubilization of the functionalized nanotubes in organic solvents or aqueous media. Several classes of functional molecules based on different kinds of noncovalent interactions have been examined, including hydrophobic (sodium dodecyl sulfate (SDS),\textsuperscript{36,37} poly(vinyl pyrrolidone),\textsuperscript{38} etc.) and π-π interactions (pyrenes,\textsuperscript{39} poly(arylene ethynylene)s,\textsuperscript{40} etc.). Some polymers such as poly(phenylene vinylene) derivatives\textsuperscript{41,42} or biological species such as DNA\textsuperscript{43} have also been used to functionalize carbon nanotubes presumably by conformational matching. For covalent functionalization, there are primarily two different routes. One is the addition reaction to the nanotube graphitic sidewall, involving generally highly reactive species such as fluorine,\textsuperscript{44} aryl diazonium compounds,\textsuperscript{11} nitrenes,\textsuperscript{45} azomethine ylides,\textsuperscript{46} etc. A more versatile alternative is the targeting of the defect-derived carboxylic acid groups on the nanotube surface,\textsuperscript{31-35,47,48} which are often associated with the oxidative conditions used in the nanotube purification procedures. These carboxylic acid groups, typically accounting for a few percents of the nanotube carbons, may be functionalized with
molecules or polymers bearing amino or hydroxyl moieties in classical reactions such as amidation and esterification.

The functionalized carbon nanotubes could be dispersed homogeneously into a polymer matrix via solution-phase processing, where the matrix polymer and functionalized nanotubes are both soluble in a common solvent. For example, Grady, et al.\textsuperscript{49} prepared polypropylene-SWNT composites from mixing solutions of polypropylene and octadecylamine (ODA) -functionalized SWNTs. However, there is a potentially significant problem with such use of functionalized carbon nanotubes because, generally speaking, the amount of functional groups required for the solubility of carbon nanotubes is substantial. These small-molecule functional groups are often unwanted, potentially acting as “impurities” in the intended polymeric nanocomposites to negatively affect their properties and performance.

One strategy to improve the compatibility is to use polymer functionalized carbon nanotubes for polymeric nanocomposites. Among several approaches to attach polymers to carbon nanotubes is the “grafting-to” method, where the polymer is attached to the nanotube surface via covalent bonding. For example, Wu, et al. generated polymeric anions on poly(N-vinyl carbazole) (PVK) and polybutadiene backbone by reacting the polymers with organometallic reagents such as sodium hydride or butyl lithium, and then attached the polymeric anions to SWNTs in classical nucleophilic reactions.\textsuperscript{50} Also popular has been the “grafting-from” method, where the chemically modified nanotube is used as the initiator for polymerization. For example, Viswanathan, et al. used excess sec-butyl lithium to generate carbanions on the nanotube surface, so that both free sec-
butyl lithium and the nanotube-bound carbonions could initiate polymerization reactions upon the addition of styrene monomers to achieve improved compatibility of the nanotubes with the polystyrene matrix.\textsuperscript{51} Recently, several research groups reported further modification to the grafting-from method.\textsuperscript{52-54} As shown in Scheme 1.2, the nanotube-bound initiators were prepared for grafting various polymers onto nanotube surface via atomic transfer radical polymerization (ATRP). Kong, \textit{et al.}\textsuperscript{52} and Qin, \textit{et al.}\textsuperscript{53} functionalized MWNTs and SWNTs, respectively, with hydroxyl containing ATRP initiators via esterification reactions at nanotube surface defect sites. These nanotube-bound initiators were then used for the polymerization of different monomers, including styrene,\textsuperscript{52} methyl methacrylate,\textsuperscript{53} and butyl methacrylate.\textsuperscript{54} Most of these polymer-functionalized carbon nanotubes, in which the polymer structures were more controllable, were found to be soluble in common organic solvents.

1.2.2 Matrix polymers as functionalization agents for enhanced compatibility.

The selection of right functionalization agents is obviously important to the properties of the functionalized carbon nanotubes and ultimately to the performance of the resulting polymeric carbon nanotube composites. In order not to introduce foreign materials (essentially impurities) into the targeted nanocomposites, the best strategy is to select and use functionalization agents that are structurally identical or maximally similar to the matrix polymers.\textsuperscript{63} It not only helps the homogeneous dispersion of the functionalized carbon nanotubes, but also prevents any possibilities of microscopic phase separation in the resulting nanocomposites. By targeting the defect-derived carboxylic
Scheme 1.2 Polymerization on nanotube surface via ATRP. (From ref. 52.)
Scheme 1.3 Representative polymers for the functionalization and solubilization of carbon nanotubes (with the matrix polymer structural motifs and groups for functionalization reactions highlighted). (From ref. 63.)
acid groups on the nanotube surface, Sun and coworkers prepared functionalized carbon nanotubes of a variety of monomeric and polymeric functional groups (Scheme 1.3).\textsuperscript{55-63} The emphasis on covalent functionalization at the defect sites has been due to the fact that nanotube electronic structures are largely preserved post-functionalization.\textsuperscript{63} These functionalized carbon nanotubes are mostly soluble in common solvent systems, allowing convenient wet processing in the fabrication of desired polymeric nanocomposites.

A good example of such strategy was the functionalization of carbon nanotubes with poly(vinyl alcohol) (PVA).\textsuperscript{57} The pendant hydroxyl groups in the polymer were used for the esterification of the nanotube defect-derived carboxylic acids, thus providing direct matrix-filler bonding. Because the carboxylic acids were associated with only a small fraction of the nanotube carbons, the electronic structures of the nanotubes were preserved both in the functionalized sample and in the final composite films, as reflected in their respective optical absorption spectra (Figure 1.2). The electronic transitions corresponding to the van Hove singularity pairs in the density of states of semiconducting (S\textsubscript{11}, ~1800 nm; S\textsubscript{22}, ~1000 nm) and metallic (M\textsubscript{11}, ~700 nm) SWNTs remained largely unchanged. The significant solubility of PVA-functionalized carbon nanotube in hot water allowed easy fabrication of impurity-free PVA-carbon nanocomposite films at different nanotube loadings. A low loading of the functionalized sample (1 wt\%) dispersed in PVA polymer matrix hardly changed the crystallinity, but the Young’s modulus and yield stress increased by about 25% and 40%, respectively, from those of the PVA polymer, indicating efficient load transfer as a result of the excellent interfacial
Figure 1.2 Optical absorption spectra of PVA-functionalized SWNTs (red curve) and a free-standing PVA-SWNT nanocomposite thin film fabricated from the same sample (blue curve). (From ref. 57.)
bonding. The favorable matrix-filler interactions also allowed the effective alignment of the carbon nanotubes in PVA thin films via mechanical stretching.\textsuperscript{64}

Other polymers containing PVA moieties, such as poly(ethylene-\textit{co}-vinyl alcohol) (EVOH, see Scheme 1.3),\textsuperscript{62} were covalently attached onto SWNTs via the same esterification reaction. The common solubility of EVOH-functionalized SWNTs and neat EVOH in a polar solvent like DMSO made it possible to conveniently fabricate EVOH/SWNT nanocomposite films of variable nanotube contents via wet casting. This represents another example of homogeneously dispersing carbon nanotubes into polymeric matrices without introducing any other dispersion materials.

A combination of this strategy on nanotube dispersion and solubilization by using matrix polymers with the grafting-from method was applied to the preparation of nylon/carbon nanotube composites without any unwanted foreign materials.\textsuperscript{61,65} For the functionalization of SWNTs with nylon-6, the precursor \(\varepsilon\)-caprolactam for nylon-6 was first attached to the nanotubes via amide linkages.\textsuperscript{61} The grafting-from was the anionic ring-opening polymerization (AROP) from the nanotube-bound \(\varepsilon\)-caprolactam into the bulk that contained the same monomer (Scheme 4). The functionalized samples were found to share solubility with nylon-6 polymer in formic acid, which thus allowed intimate mixing of the nanotubes and nylon-6 in various proportions for processing in solution or melt.

In the same strategy, polymers with amino or hydroxyl end groups have also been used for the functionalization of carbon nanotubes without introducing potential impurities into the final nanocomposites. More specifically, an amine-terminated
Scheme 1.4 Reaction scheme for the preparation of nylon-6-functionalized SWNTs. (From ref. 61.)
polyimide (PI-NH$_2$, see Scheme 1.3) synthesized from the condensation of 4,4’-(hexafluoroisopropyldene) diphthalic anhydride with 1,3-bis(3-aminophenoxy)benzene was covalently grafted to carbon nanotubes via the amidation of the surface defect-derived carboxylic acids.$^{58}$ The polyimide PI-NH$_2$ was designed to be structurally identical to the matrix polyimide on which the targeted nanocomposites was based. The shared solubility of the PI-NH$_2$-functionalized carbon nanotubes with the matrix polyimide in a polar solvent like DMF and their intimate miscibility in solution allowed the relatively convenient wet-casting of the desired high-quality (optically transparent and homogenous) nanocomposite thin films (Figure 1.3).$^{58}$

Other than directly preparing polymers that contain amine or hydroxyl groups for the nanotube functionalization, these functional groups could also be introduced into some polymers under consideration without fundamentally altering their structures. For example, the commercially available poly(propionylethlenimine) (PPEI) could be partially hydrolyzed to introduce a controlled fraction of secondary amine moieties. The resulting copolymer poly(propionylethlenimine-\textit{co}-ethylenimine) (PPEI-EI) (see Scheme 1.3) has been very effective in the functionalization of carbon nanotubes under various sets of reaction conditions, with the functionalized samples of excellent solubility characteristics in common organic solvents and water.$^{66-69}$ For example, the PPEI-EI-functionalized carbon nanotubes were intimately miscible and fully compatible with the parent PPEI and other polymers such as PVA for nanocomposites.$^{70}$ In fact, fluorescent PPEI-EI-functionalized SWNTs were homogenously embedded in PVA film and visualized in confocal microscopy imaging without obvious deviation. Upon mechanical
Figure 1.3 Pictures of four nanocomposite films of polyimide (the polymer structure shown) with different contents of SWNTs on a piece of paper printed with the logo of Clemson University (for a demonstration of the optical transparency). (From ref. 58.)
stretching, while the nanotubes remained well dispersed, their preferential alignment along the stretching direction was well illustrated in the confocal images.70

Most copolymers used in this strategy have been specifically prepared from co-monomers in polymerization reactions. For the desired compatibility, a copolymer could be designed such that the major co-repeating units are the same as those in the matrix polymer, with minor co-repeating units containing amino or hydroxyl moieties for linkages with the nanotube defect-derived carboxylic acid groups. For the important commercial polymer, polystyrene, as an example, polystyrene random copolymers with derivatized styrene units (in Scheme 1.3, ~7% for PS\textsubscript{OH}, ~11% for PS\textsubscript{OH'}, and ~20% for PS\textsubscript{NH2}) were synthesized from radical copolymerization of styrene and corresponding styrene derivatives.55,56 The units with pendant hydroxyl groups were introduced for the purpose of nanotube functionalization, and the results confirmed the effectiveness of the approach. The functionalized carbon nanotube samples exhibited similar solubility characteristics to those of polystyrene homopolymers, which allowed wet processing of polystyrene-carbon nanotube composite blends and films. The successful fabrication of optically high-quality nanocomposite thin film reflects the excellent compatibility of functionalized carbon nanotubes with polystyrene.55

In the strategy to functionalize carbon nanotubes with copolymers that are structurally similar to the matrix polymers, the minor co-monomers could be slightly different in molecular structure from the major co-repeating units. Their fractions in the copolymers are generally kept small enough to minimize potentially negative effects on the compatibility of the copolymers with the corresponding matrix polymers. One
example was the incorporation of 3,5-diaminobenzyl alcohol as a co-monomer in the condensation for polyimide. The resulting polyimide copolymer (Scheme 1.3, PIOH with one pendant hydroxyl group per seven repeating units) was similarly effective in the functionalization and solubilization of carbon nanotubes (in comparison with the amino-terminated polyimide PI-NH2 discussed above) for high-quality polyimide-carbon nanocomposite films.

1.2.3 Benefits and issues.

The functionalization and solubilization of carbon nanotubes offer significant benefits to the preparation of high-quality polymeric carbon nanotube composites. Among the two somewhat related major benefits are improvements in the exfoliation of carbon nanotubes (especially SWNTs) into individual tubes or thin bundles and in the processibility, both of which enable the homogeneous dispersion of carbon nanotubes in the selected polymer matrix for optimal performance. For nanocomposites in specific applications, such as thin films of sufficient electrical conductivity to mitigate static charges, the use of functionalized carbon nanotubes allows a significant reduction in the nanotube loading, and thus minimizes any potential negative effects on other properties of the polymeric nanocomposites (high optical quality and transmittance, for example).

The characterization of polymeric nanocomposites with well-dispersed carbon nanotubes posts additional challenges beyond those for pristine or functionalized nanotube samples. Scanning and transmission electron microscopy techniques are useful,
Figure 1.4 Photoluminescence spectra (450 nm excitation) from (a) SWNTs dispersed with the aid of polyimide in DMF, (b) the polyimide-functionalized SWNTs (PI-NH₂-SWNT) in DMF solution with similar nanotube content to that in (a), (c) a film from the suspension of SWNTs, and (d) a film from the PI-NH₂-SWNT solution. The insets are photographs (top), and confocal images (bottom, 458 nm excitation, 469 nm detection; scale bars = 5 mm). (From ref. 63.)
though special sample preparation procedures such as microtomy are often required.\textsuperscript{58,61,64} Even for microtomed slices, while the imaging of functionalized MWNTs embedded in polymer matrices is still relatively straightforward, the same for SWNTs can be very difficult, requiring special effort such as the use of holy-carbon grids and so on.\textsuperscript{73} Complementary to electron microscopy, optical spectroscopic techniques have been effective in the characterization of carbon nanotubes. For SWNTs functionalized at surface defect sites, their near-IR electronic transitions are largely preserved either in the functionalized samples or after being dispersed into the polymeric matrices. Therefore, optical absorption spectroscopy serves as a convenient tool in the characterization of SWNTs in polymeric nanocomposites. At a more quantitative level, the functionalized SWNTs exhibit absorption bands that are blue-shifted and narrower in width as an effect of de-bundling.\textsuperscript{73} The same effect is believed to move the G-band toward a higher frequency in the Raman spectrum of SWNTs.\textsuperscript{73,75-77} Particularly interesting and useful is the fact that carbon nanotubes upon the functionalization at surface defect sites exhibit strong visible and near-IR luminescence.\textsuperscript{66,74} Mechanistically, the photoluminescence is attributed to excited state energy trapping sites associated with passivated nanotube surface defects. The effective exfoliation of carbon nanotubes for being dispersed primarily as individual nanotubes (thus minimal inter-tube quenching effect) is a necessary prerequisite to observe such luminescence. Therefore, the defect-derived luminescence may be used as a tool to probe the dispersion of functionalized carbon nanotube in polymeric matrices.\textsuperscript{70,73,74,78} In a recent demonstration,\textsuperscript{73} the nanocomposites with functionalized carbon nanotubes (PI-NH\textsubscript{2}-SWNT) exhibited strong luminescence,
whereas those with purified SWNTs at the same nanotube loading were essentially non-emissive in the visible and near-IR regions (Figure 1.4).

1.3 Electrical properties and applications

Carbon nanotubes are dispersed into polymeric matrices for desired electrical properties of the resulting nanocomposites. A variety of potential applications for these nanocomposites, ranging from static charge dissipation to electromagnetic interference (EMI) shielding, have been explored and investigated. For the latter, polymeric nanocomposites dispersed with conductive carbon nanotubes are more advantageous than conventional metal-based EMI shielding materials in several aspects, such as corrosion resistance, light weight, flexible, and low costs, with comparable performance. The nanocomposite with 15 wt% SWNTs loading was found to have EMI shielding efficiency of about 50 dB at 10 MHz and 15-20 dB in the range of 0.5-1.5 GHz.

1.3.1 Electrical conductive polymeric/carbon nanotube composites.

For superior electrical properties, the dispersion of carbon nanotubes in polymeric nanocomposites is an important parameter. As discussed earlier, since pristine carbon nanotubes are bundled and insoluble, their exfoliation and solubilization via chemical modification and functionalization are often required. Generally enhanced performance with the use of non-covalently or covalently functionalized carbon nanotubes has been demonstrated. For example, Ramasubramaniam, et al. used poly(phenylene ethylene) (PPE) to wrap SWNTs. These PPE-functionalized (non-covalently) SWNTS were
soluble in many organic solvents, enabling solution-phase processing for the fabrication of polystyrene/SWNT (with PPE wrapping) nanocomposites (Figure 1.5a). The resulting polystyrene nanocomposites exhibited low percolation threshold with much improved electrical conductivity, 6.89 S/cm at 7 wt% nanotube loading, higher by 5 orders of magnitude than that of a similar polystyrene/SWNT nanocomposite prepared from in situ polymerization. Various potential applications of these polymeric nanocomposites were proposed and discussed (Figure 1.5b).

The non-covalent functionalization has its advantages in preserving the electrical properties of carbon nanotubes with minimal damage to the nanotube surface. However, the use of dispersion agents that are different from matrix polymers may potentially negatively affect other nanocomposite properties, such as mechanical strength and long term stability. Covalent functionalization of carbon nanotubes at the surface defect sites also largely preserves the electrical properties of carbon nanotubes, thus representing another popular approach in the development of polymeric nanocomposites for potential electrical applications. For example, Li, et al. functionalized MWNTs with alkyl alcohols of various alkyl chain lengths (Scheme 1.5) to demonstrate that the increased solubility of functionalized MWNTs could improve nanotube dispersion in the polymer matrix, and therefore result in higher electrical conductivity in the corresponding nanocomposites. Interestingly, at the same nanotube loading, the conductivity of polysulfone nanocomposite with hexadecyl alcohol-functionalized MWNTs was higher by almost 4 orders of magnitude than that of the nanocomposite with butyl alcohol-functionalized MWNTs. Again, the use of functionalization agents significantly differing
Figure 1.5 (a) SEM images of the polystyrene/PPE-functionalized SWNTs (5 wt%) composite film; (b) The room-temperature electrical conductivity of polystyrene/PPE-functionalized SWNTs composites vs. nanotube concentration in the composites and their potential applications. (From ref. 85.)
Scheme 1.5 MWNTs functionalized with alcohols of various alkyl chain lengths. (From ref. 86.)
from matrix polymers could result in various degrees of phase separation in the nanocomposites. The incompatibility of alkyl alcohols with polysulfone matrix could be responsible for the conductivity inhomogeneity in the nanocomposites. A more elegant strategy is to design and prepare functionalized carbon nanotubes in which the functional agents are structurally identical or largely similar to the selected matrix polymer for intimate mixing and compatibility, as demonstrated by Wang, et al. specifically on polymeric carbon nanotube composites for desired electrical properties.

In the work by Wang, et al., a PVK copolymer with minor units containing pendant hydroxyl groups (PVK$_{OH}$, Scheme 1.3) was synthesized for the covalent functionalization of SWNTs. The PVK copolymer-functionalized SWNTs were readily soluble in common organic solvents, with the solution miscible with that of PVK polymer. The excellent compatibility of the functionalized nanotubes with the PVK matrix enabled the fabrication of high-quality nanocomposite thin films for studies of optical properties. These nanocomposite films were found to be significantly photoconductive (enhanced charge dissipation under photo-illumination).

Similarly, a polythiophene copolymer, poly[3-(2-hydroxyethyl)-2,5-thienylene] (PHET), was synthesized for the functionalization of MWNTs (Scheme 1.6). The resulting polythiophene nanocomposite with 50 wt% PHET-functionalized MWNTs was found to be 28 times more conductive than the nanocomposite of the same nanotube loading but prepared from simple ultrasonic mixing of PHET with unfunctionalized MWNTs, demonstrating the importance of nanotube homogeneous dispersion and
Scheme 1.6 The functionalization of SWNTs with a derivatized polythiophene. (From ref. 87.)
compatibility with matrix polymer to the electrical conductivity of corresponding nanocomposites.

In the use of polymer-functionalized carbon nanotubes for polymeric nanocomposites of enhanced electrical conductivity, a potentially significant issue is the possibility for the polymeric functional groups to form an insulating layer on the nanotube surface, which could decrease the electrical conductivity of the nanotube. For example, Bekyarova, et al. reported that the chemical functionalization of SWNTs with ODA and poly(m-aminobenzensulfonic acid (PABS) resulted in a reduction in the electrical conductivity of nanotube by 2-3 orders of magnitude, with an associated increase in the percolation threshold by a factor of 5.88

There are many potential applications of polymeric nanocomposites from the homogeneous dispersion of carbon nanotubes. While the electrical conductivities of resulting nanocomposites are generally not high (especially at relatively low nanotube loadings), they are sufficient for dissipating static charges in the corresponding polymer matrices that are otherwise insulating. A classical case was the successful use of SWNTs to impart electrical conductivity in polyimide and related polymeric materials suitable for space applications, such as solar sails and ultra-thin membranes for lightweight space structures.89-94 In the work by Smith, et al.,93 amide acid polymers with alkoxyisilane groups as end-caps were employed to functionalize SWNTs in hydrolysis reaction. The functionalized SWNTs were mixed with the selected matrix polymers in solution at different concentration ratios for the casting of optically transparent thin films. The
Figure 1.6 (a) Surface resistance and surface and volume resistivities of polyimide/functionalized-SWNTs nanocomposites (from ref. 93); and (b) the composite film after a crumple test showed no surface resistivity change (From ref. 94).
percolation threshold was estimated to be 0.03-0.04 wt% SWNTs in the nanocomposite films (Figure 1.6a). At the nanotube loadings only slightly above the percolation threshold (such as 0.05 wt%), the electrical conductivity in the nanocomposite films was sufficient for effective dissipation of static charges, while other film properties including excellent optical transparency and flexibility were preserved.\textsuperscript{93} In a follow-up study by the same group,\textsuperscript{94} a crumple test was performed to show how the robustness and stability in electrical conductivity of the polymeric nanocomposites benefited from the improved mechanical properties with the embedding of SWNTs. As illustrated in Figure 1.6b, the observed surface resistivity of the nanocomposite films remained largely unchanged despite their being subjected to the harsh mechanical manipulation.\textsuperscript{94}

1.3.2 Separated metallic SWNTs for enhanced performance.

In the development of polymeric carbon nanotube composites, SWNTs are often considered as being more superior for desirable properties of the nanocomposites such as high optical quality and transparency, lower carbon loading, mechanical properties, etc.\textsuperscript{20-25} For electrical properties and applications, metallic and semiconducting SWNTs are produced as mixtures by all of the available production methods, but only the metallic ones are highly conductive. More disappointing is the fact that metallic SWNTs generally represent the minority fraction in the mixtures. Therefore, post-production separation of metallic SWNTs from their mixtures with semiconducting SWNTs has been pursued by a number of research groups,\textsuperscript{4,95-97} with various strategies that exploit the generally subtle physical and chemical differences between metallic and semiconducting SWNTs.\textsuperscript{98-121} A
few relatively more effective post-production separation methods are highlighted as follows.

The dielectrophoresis\textsuperscript{98,99} and DNA wrapping\textsuperscript{43,100,101} both exploit the relatively higher polarizability of metallic SWNTs for separation, though these methods are limited to very small quantities of nanotubes. In a more recent development, Arnold, \textit{et al.} reported the use of ultra-centrifugation to separate single-strand DNA- or surfactant-wrapped SWNTs in solutions with density gradient media (Scheme 1.7).\textsuperscript{102,103} The method represents an interesting improvement over others in the same category, but the limitation with the small amount of sample that could be processed remains.

Selective removal of either metallic or semiconducting SWNTs from their mixtures may be accomplished in the current-induced electrical breakdown\textsuperscript{104} laser irradiation\textsuperscript{105,106} or specific chemical reactions.\textsuperscript{107-115} In those reactions, metallic SWNTs are generally higher in reactivity than their semiconducting counterparts because of the higher electron density at the Fermi level. While most of reaction conditions favor metallic SWNTs, reversing the reactivity order was also possible by doping metallic SWNTs with hole-doping agents like H\textsubscript{2}O\textsubscript{2}.\textsuperscript{115} As suggested by theoretical calculation, H\textsubscript{2}O\textsubscript{2} would selectively shift the Fermi level to the first van Hove singularity band in semiconducting SWNTs to result in their higher chemical reactivity.\textsuperscript{115} The enriched metallic SWNTs could be recovered from the mixture with dopant by high temperature annealing. It should be noted, however, that thermally annealed SWNT samples are generally so severely aggregated that their further processing or dispersion may become an extremely challenging task.
Scheme 1.7 A schematic illustration on the use of surfactant encapsulation and gradient density sorting for enriched metallic and semiconducting SWNTs. (From ref. 103.)
Bulk separation (on the order of milligram to gram quantity) is necessary for the evaluation of separated metallic and semiconducting SWNTs in polymeric nanocomposites. Several techniques amenable to bulk separation have been explored.\textsuperscript{4,116-123} Papadimitrakopoulos and coworkers reported that the functionalization reaction of ODA with purified SWNTs under typical thermal reaction conditions preferred semiconducting ones over their metallic counterparts, thus to allow the recovery of enriched semiconducting and metallic SWNTs from the solubilized and precipitated fractions, respectively.\textsuperscript{116-118} Maeda, \textit{et al.} found similar phenomenon in the use of smaller amine molecules including octylamine, propylamine, and iso-propylamine to functionalize SWNTs,\textsuperscript{119,120} though it is puzzling how these small amines were capable of solubilizing the nanotubes.

Sun and coworkers developed a bulk separation method by exploiting the selective interactions of relatively large planar aromatic molecules with semiconducting SWNTs for their solubilization in organic solvents.\textsuperscript{4,121} The originally reported work was based on the use of a tetra-substituted free-base porphyrin, 5,10,15,20-tetrakis (hexadecyloxyphenyl)-21\textit{H},23\textit{H}-porphine (THPP, Scheme 1.8).\textsuperscript{4} In a relatively simple procedure, THPP was mixed with purified SWNTs (from arc-discharge or laser ablation production) in an organic solvent. Upon sonication, the soluble fraction and insoluble residue were found to be enriched with semiconducting and metallic SWNTs, respectively.\textsuperscript{4} Other planar aromatic molecules have been evaluated for the bulk separation, among which the pyrene derivative 1-docosyloxyethyl-pyrene (DomP) is particularly effective.\textsuperscript{121-123} The separation is efficient and scalable (already at gram
Scheme 1.8 The separation of metallic and semiconducting SWNTs based on selective interactions of large aromatic molecules, as reported in ref. 4.

5,10,15,20-Tetrakis(hexadecyloxyphenyl)-21H,23H-porphine
quantity). As for the quality of the separation, the metallic fraction can be enriched to contain at least 85% of metallic SWNTs (in reference to the starting population of 1/3), while the other fraction to reach a semiconducting purity beyond 95%.

The same group has demonstrated recently that the separated metallic SWNTs did offer much enhanced performance in nanocomposites with conductive polymers. In a comparison of polythiophene carbon nanotube composites that are dispersed with the separated metallic SWNTs vs those with pre-separation purified SWNTs, the former consistently exhibited substantially better electrical conductivity. The improvements were more significant at higher nanotube loadings, (see Figure 3.4 in chapter 3), suggesting that the electrical conductivity in the nanocomposites was governed by available conductive channels, namely the amount of metallic SWNTs. In fact, the relationship between the calculated actual concentrations of metallic SWNTs in the nanocomposites and their corresponding observed electrical conductivities adhered to the percolation theory.

The potential of the bulk-separated metallic SWNTs in transparent conductive nanocomposite thin films was explored with PEDOT:PSS as the matrix polymer. In the study, PEDOT:PSS was processed as an aqueous dispersion. For solvent compatibility, DMSO was used to disperse nanotubes. The suspension of the nanotubes in DMSO was mixed with the aqueous PEDOT:PSS solution, and the mixture was used for fabricating the transparent conductive coating on glass substrate via spraying. Two PEDOT:PSS-SWNT mixtures with one containing 10% (wt/wt) the separated metallic fraction and the other 10% (wt/wt) the pre-separation purified nanotube sample were prepared, so was an
aqueous solution of neat PEDOT:PSS (also containing the same amount of DMSO) as reference. Depending on the amount of solution or mixture sprayed, the coating thickness varies, as reflected by the variation in optical transmittance at 550 nm. The surface resistivity results compared in Figure 3.5 (see Chapter 3) demonstrate clearly the enhanced electrical conductivity with the separated metallic SWNTs in the transparent conductive films.

In the development for alternatives to the currently dominating indium tin oxide (ITO) technology, PEDOT:PSS transparent conductive films have been demonstrated for some successful uses in organic optoelectronic devices. For example, the organic photovoltaic cell with PEDOT:PSS electrode was found to be only 15% less in efficiency when compared to the same cell with a classic ITO electrode. A strategy already discussed in the literature on further improving the performance of transparent PEDOT:PSS electrode is the incorporation of SWNTs. The results from the recent work by Wang, et al. suggest that the use of bulk separated metallic SWNTs might offer the necessary conductivity enhancement without sacrificing the optical transparency to make the resulting PEDOT:PSS/SWNT composite films competitive to ITO coatings for transparent electrodes and other applications.

1.4. Thermal conductive nanocomposites

Carbon nanotubes are excellent thermal conductors, but their uses as fillers in polymeric matrices have not yielded the kind of highly thermal conductive nanocomposites that one might expect. A key difference between polymeric carbon
nanotube composites for enhanced electrical and thermal properties is that the latter is not
governed by the percolation phenomenon.\textsuperscript{130} Nevertheless, since polymers are usually
poor thermal conductors, with thermal conductivity on the order of 0.1 W/mK, the
incorporation of carbon nanotubes still offers significant thermal conductivity
improvements in the resulting nanocomposites.

Several groups have prepared polymeric nanocomposites with carbon nanotubes
for the investigation of their thermal conductive properties.\textsuperscript{131,132} For example, Biercuk, \textit{et}
al. dispersed SWNTs into epoxy to increase thermal conductivity.\textsuperscript{131} At 1 wt\% loading of
nanotubes, the room-temperature thermal conductivity of the nanocomposite was about
0.5 W/mK, more than doubling that of the neat epoxy. Significantly less improvement
was observed in the epoxy composite with vapor-grown carbon fibers (VGCF) at the
same filler loading level (Figure 1.7). Similarly, Kashiwagi, \textit{et al.} reported that the
thermal conductivity of the polypropylene nanocomposite with 5 wt\% MWNT was about
0.3 W/mK at room temperature, roughly 30\% higher than that of pure polypropylene.\textsuperscript{132}
These seemingly unimpressive improvements in thermal conductivity have been typical
in other polymeric nanocomposites with SWNTs or MWNTs at similar nanotube
loadings.

Carbon nanotubes are pseudo-one-dimensional nanostructures, and their thermal
properties are highly anisotropic, with much higher thermal conductivity along the
nanotube axis. In order to take advantage of the anisotropically high thermal
conductivity, Huang, \textit{et al.} fabricated composite films with aligned carbon nanotubes by
\textit{in situ} inject molding of silicone elastomers onto CVD-grown nanotube arrays (Figure
Figure 1.7 Thermal conductivity enhancements in epoxy/carbon nanocomposites with different SWNT or VGCF concentrations. (From ref. 131.)
Figure 1.8 SEM images of aligned carbon nanotube composite films prepared by *in situ* inject molding method: (a) side view; and (b) top view. (From ref. 133.)
The film with 0.3 wt% nanotube loading, upon reactive-ion etching treatment to expose nanotube tips, exhibited thermal conductivity of 1.21 W/mK, 2.2 times that of the pure silicone elastomer. The thermal conductivity enhancement was attributed entirely to the embedded nanotube arrays.

Mechanistically, the high interfacial thermal resistance in polymeric carbon nanotube composites is believed to be a limiting factor. Since the heat transportation in the nanocomposites is carried out by phonons with different frequencies, the phonons slow down at the polymer-nanotube interface due to material characteristics such as the polymer being largely amorphous in nature, resulting in high interfacial thermal resistance. Huxtable, *et al.* applied a picosecond transient absorption technique to estimate the interfacial thermal conductance in polymer-nanotube composites, with the estimated conductance as small as 12 MW/m²K. Therefore, the development of highly thermal conductive polymeric carbon nanotube composites may be dependent on ways to reduce the high interfacial thermal resistance. One possible way is the chemical functionalization of carbon nanotubes, because the covalent bonding between carbons on the nanotube surface and polymers in the matrix could facilitate the phonon transportation at the interface. However, the flip side of the covalent bonding on nanotube surface is that it may act as phonon scattering center to reduce the intrinsic thermal conductivity of the carbon nanotube. Therefore, the effect of chemical functionalization on thermal conductivity needs to be carefully investigated. According to the calculation by Padgett, *et al.*, the random chemical functionalization of 1% of the carbon atoms on a nanotube with phenyl groups would reduce the thermal conductivity of
the nanotube by more than a factor of 3.\textsuperscript{137} The lower thermal conductivity was attributed to decreased phonon scattering length. As shown in Figure 1.9, there is a faster convergence for functionalized carbon nanotubes, implying that the phonon scattering length in a functionalized tube is shorter than in a pristine one.\textsuperscript{137} Similarly, Shenogin, \textit{et al.} performed molecular dynamics simulation to examine the impact on thermal conductivity of carbon nanotubes upon their being chemically bound to the polymer matrix.\textsuperscript{138,139} In their results, the thermal conductivity remained nearly constant at about 1,700 W/mK as 1\% of the nanotube carbons were functionalized, while the thermal interfacial resistance was reduced by 3-4 times as a result of the covalent functionalization. It was found that the net effect of functionalization on thermal conductivity was dependent on the nanotube aspect ratio. For aspect ratios in the range of 100-1000, the functionalization led to thermal conductivity of the nanotube higher by a factor of two (Figure 1.10).

On the issue of thermal conductivity enhancement in polymeric carbon nanotube composites, the experimental and simulation results discussed above seem to suggest the need for an optimal density of covalent links on nanotube surface, at which the desired reduction in interfacial resistance could be realized without scarifying too much the intrinsic thermal conductivity of the nanotubes. As for the effect of aspect ratio, longer nanotubes and thus larger aspect ratios are always desirable for thermal conductivity enhancement.\textsuperscript{140-142} However, while SWNTs are each of a very large aspect ratio, they are often tangled and bundled, resulting in lower effective aspect ratios.\textsuperscript{142} More rigid and
Figure 1.9 Thermal conductivity vs. nanotube length for various degrees of chemical functionalization (♦: 0%, ○: 0.25%, △: 1%, ■: 5% and ▲: 10% functionalized). (From ref. 137.)
randomly oriented carbon nanotubes in low conductivity organic matrix for un-functionalized and highly functionalized carbon nanotubes. (From Figure 1.10 Calculated thermal conductivity of composite with 1% randomly oriented carbon nanotubes in low conductivity organic matrix for un-functionalized and highly functionalized carbon nanotubes. (From ref. 138.)
straight MWNTs, such as those synthesized by aligned CVD method,\textsuperscript{143} could be competitive as fillers for thermal conductive nanocomposite materials. These principles seem easier to appreciate, but more difficult to evaluate and materialize, with only a limited number of relevant experimental investigations.\textsuperscript{144,145}

Ghose, et al. tested experimentally some of the strategies discussed above.\textsuperscript{144} In their experiments, functionalized MWNTs were mixed with commercially available polyimide (Ultem\textsuperscript{TM} 1000) in DMAC solution at various concentrations ranging from 5 to 20 wt\% effective nanotube contents. The resulting blends were molded into pellets in which the nanotubes were randomly orientated. These pellets of nanocomposites with functionalized MWNTs exhibited higher thermal conductivity values than did those with pristine MWNTs. The performance was also dependent on the degree of surface functionalization in the functionalized nanotube samples. For nanocomposites with the same 20 wt\% nanotube loading, the one from the functionalized MWNTs with surface functionalization density controlled at 6\% had a thermal conductivity of 0.8 W/mK, while the other with 15\% functionalization density had a higher thermal conductivity of 1.1 W/mK. This is more than double the thermal conductivity value of the composite with pristine MWNTs, and a more than 900\% increase over that of the pure Ultem polymer.\textsuperscript{144}

The same group also demonstrated the anisotropic thermal conductive properties in Ultem nanocomposites with aligned MWNTs (Figure 1.11), where the nanotube alignment was a result of the melt extrusion processing.\textsuperscript{144} The observed thermal conductivity of the nanocomposite at 20 wt\% nanotube loading was 2 W/mK in the direction of the nanotube alignment, higher than that of the same nanocomposite with
Figure 1.11 SEM image of melted press Ultem/MWNT at 20 wt% (the arrow indicating direction of nanotube alignment). (From ref. 144.)
randomly oriented MWNTs, but only 0.2 W/mK in the direction perpendicular to the alignment.

Functionalized carbon nanotubes are more readily aligned in polymeric nanocomposites for their being well-exfoliated and dispersed. Therefore, as demonstrated by Wang, et al., the nanocomposites could be mechanically stretched to align the embedded nanotubes for much enhanced thermal conductivity in the alignment direction. In the study, PVA-functionalized SWNTs were used to prepare PVA nanocomposite films with different nanotube contents. Then, the films were mechanically stretched to align the embedded nanotubes. The nanotube alignment was characterized by polarized luminescence and electronic microscopy techniques (Figure 1.12a). According to results from the in-plane thermal diffusivity measurements, the PVA nanocomposite film with 10 wt% functionalized SWNTs had a post-stretching increase of 3.4 times in thermal diffusivity along the stretching direction (Figure 1.12b).

As discussed in the beginning of this section, while much effort has been made, which has resulted in many valuable insights into the development of highly thermal conductive polymeric carbon nanocomposites, the use of carbon nanotubes through their chemical modification or various other manipulations or arrangements for the predicted ultimate performance still remains a significant challenge.

1.5. Summary

The known electrical and thermal properties of carbon nanotubes have prompted many predictions on their extraordinary potentials for ultimately performing polymeric
Figure 1.12 (a) SEM image of mechanically stretched PVA/functionalized-SWNTs (10 wt%) nanocomposite film with a draw ratio of 5.5; and (b) the in-plane thermal diffusivity results of PVA/functionalized-SWNTs nanocomposite films with different nanotube concentrations with (■) and without (□) the mechanical stretching.
nanocomposites. However, the experimental materialization of these predictions has proven to be more complex in the development of nanocomposites for electrical properties and more challenging in those for high thermal conductivity. Nevertheless, chemical modification and functionalization of carbon nanotubes have been demonstrated as being effective for high-quality polymeric carbon nanotube composites, especially with the elegant approach of using polymers that are structurally identical or maximally similar to the matrix polymers in the nanotube functionalization. For desired electrical properties, the dispersion of carbon nanotubes in the polymer matrix is important to the performance, and the use of only metallic nanotubes may offer solutions in some of the more demanding applications (such as transparent conductive coatings or films). For highly thermal conductive polymeric nanocomposites, on the other hand, the feasibility of using carbon nanotubes to achieve the desired performance has yet to be convincingly demonstrated experimentally.
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CHAPTER TWO

SYNTHESES, CHARACTERIZATION, AND NANOCOMPOSITE THIN FILMS OF POLY(N-VINYL CARBAZOLE) FUNCTIONALIZED SINGLE-WALLED CARBON NANOTUBES

2.1 Introduction

Polymeric photoconductive materials have found many important applications\(^1\). Among well-known photoconductive polymers is poly(N-vinyl carbazole) (PVK), which is commonly used with a dopant to increase charge generation efficiency in the visible and beyond. A variety of dopants have been developed, such as nanoscale semiconductors and fullerenes\(^2,3\). Recently, the use of single-walled carbon nanotubes (SWNTs) in nanocomposites with photoconductive polymers has attracted much attention\(^4\text{-}12\). The broad absorption of SWNTs over the visible and near-IR wavelength regions may allow their use as nanoscale dopant for broadband photosensitization. The nanotubes above certain concentration in polymeric nanocomposites are also expected to form a percolation network for enhanced electrical conductivity, which may facilitate the charge transportation in photoconductors such as PVK-SWNT.

A significant challenge in the preparation of PVK-SWNT and other polymeric nanocomposites is the homogeneous dispersion of nanotubes in the polymer matrix, which is hindered by the bundling and insolubility of the nanotubes. In fact, the dispersion is particularly important in the fabrication of photoconductive nanocomposites
because of the requirement for high optical quality to facilitate efficient light absorption (minimizing light scattering). The recent development in the solubilization of carbon nanotubes has suggested that SWNTs can be de-bundled in solution upon their functionalization, amenable to their homogeneous dispersion into polymer films via simple wet-casting\textsuperscript{13-28}. Especially attractive is the use of polymers in the nanotube functionalization that are either identical to or structurally minimally altered from the matrix polymers, thus to ensure full compatibility in the resulting nanocomposites. For example, Hill, et al. functionalized carbon nanotubes with polystyrene copolymers and then dispersed homogeneously the solubilized nanotubes into the polystyrene matrix\textsuperscript{16,17}. Similarly, Qu, et al. synthesized an amino-terminated oligomeric polyimide to functionalize carbon nanotubes via the amidation of the nanotube surface-bound carboxylic acids. The soluble functionalized nanotube samples were mixed with neat polyimide polymer in solution for the fabrication of high-quality nanocomposite thin films\textsuperscript{19}.

Here we report on a similar application of the strategy to disperse SWNTs into PVK polymer matrix in a fully compatible fashion. The nanotubes were functionalized with a PVK-based copolymer containing a small fraction of styrene units bearing pendant hydroxyl groups, which were designed for the esterification of the nanotube surface-bound carboxylic acids. The functionalized SWNTs were found to share solubility with PVK in common organic solvents, which allowed the solution-phase mixing and the subsequent wet-casting of PVK-SWNT nanocomposite thin films. Results from the sample characterization and a qualitative evaluation for enhanced charge dissipation in
the nanocomposite under light illumination are presented and discussed.

2.2 Experimental section

2.2.1 Materials

*p*-Chloromethylstyrene (90%), sodium hydride (NaH, 60%, dispersed in mineral oil), and ethylene glycol (99+%) were purchased from Acros, 9-vinyl carbazole and 2,2'-azobis(isobutyronitrile) (AIBN, 98%) from Adrich, and thionyl chloride (SOCl₂) and poly(N-vinyl carbazole) (PVK, \(M_W = 100,000\)) from Alfa Aesar. 4-(4'-Vinylphenyl)-3-oxabutanol (VPOB) was synthesized from *p*-chloromethylstyrene and ethylene glycol as previously described\(^{16}\). Styrene was obtained from Baker and was carefully distilled before use. Deuterated chloroform for NMR measurements (containing tetramethylsilane as internal standard) was supplied by Cambridge Isotope Laboratories.

The SWNT sample was produced by using the arc-discharge method\(^{29}\) in Prof. A. M. Rao’s laboratory at Clemson University. The as-produced sample was purified by the oxidative acid treatment in a procedure already reported in the literature\(^{16}\). Briefly, a suspension of SWNTs (500 mg) in aqueous HNO₃ (2.6 M, 100 mL) was refluxed for 48 h, followed by centrifuging to discard the supernatant. The remaining solids were washed repeatedly with deionized water until neutral and then dried under vacuum.

2.2.2 Measurements

UV/vis/near-IR absorption spectra were recorded on Shimadzu UV3100 and Thermal-Nicolet Nexus 670 FT-NIR spectrometers. Raman spectra were obtained on a
Renishaw Raman spectrometer equipped with a 50 mW diode laser source for 785 nm excitation and CCD detector. Mass spectroscopy was conducted on a Bruker Daltonics AutoflexII MALDI-TOF instrument, with 2,5-dihydroxybenzoic acid as the matrix. NMR measurements were performed on a JEOL Eclipse +500 NMR spectrometer. Thermogravimetric analysis (TGA) was carried out on a Mettler-Toledo TGA/SDTA851e system. Scanning electron microscopy (SEM) images were obtained on a Hitachi S-4700 field-emission SEM system. Transmission electron microscopy (TEM) analyses were conducted on Hitachi HD-2000 TEM/STEM system. Atomic force microscopy (AFM) was performed on a Molecular Imaging PicoPlus system equipped with a multipurpose scanner of maximum scanning area of 100 × 100 μm². The height analyses of AFM images were assisted by SPIP software distributed by Image Metrology. The electrical charge dissipation experiments were carried out on a John Chubb Instrumentation JCI 155v4 charge decay test unit.

2.2.3 Poly(N-vinyl carbazole-co-p-(4-(4'-vinylphenyl)-3-oxabutanol)) (PKS)

In a typical experiment, a toluene solution (100 mL) of VPOB (1 g, 5.6 mmol) and 9-vinyl carbazole (10.8 g, 56 mmol) was mixed with a toluene solution (10 mL) of AIBN (92 mg, 0.56 mmol). The mixture was stirred at 80 °C for 12 h under argon protection. After being concentrated, the reaction mixture was precipitated into cold petroleum ether. The solids from filtration were washed with petroleum ether, and then dissolved in chloroform for a repeat of the purification via precipitation. The copolymer PKS was obtained as a white powder (8.35 g, 70% yield). For the molecular weight of
PKS, the result of $M_w \sim 12,000$ (polydispersity $\sim 2.3$) from gel permeation chromatography (GPC, linear polystyrene standards) was supported by that of $M_n \sim 6,000$ from MALDI-TOF.

2.2.4 Functionalization of SWNTs

In a typical experiment (Scheme 2.1), a purified SWNT sample (75.2 mg) was refluxed in SOCl$_2$ (25 mL) for 24 h, followed by the removal of excess SOCl$_2$ under vacuum. Separately, PKS (500 mg) in a minimal amount of THF was added through a syringe to slurry of NaH (800 mg) in THF (125 mL) with constant stirring. After refluxing for 2 h, the slurry was mixed with the SOCl$_2$-treated SWNT sample. The mixture was stirred under nitrogen protection at room temperature for 48 h. The suspension thus obtained was centrifuged at 3,000 g to collect the dark-colored supernatant. The solid residue was extracted repeatedly with THF, coupled with centrifugation. All of the soluble fractions were combined, and then the solvent THF was evaporated. The solid sample was re-dissolved in chloroform and precipitated into cold hexane. Upon washing with deionized water and drying under vacuum, the PKS-functionalized SWNT sample was obtained as greyish black powders.

2.2.5 Chemical defunctionalization

In a typical experiment, to a solution of PKS-functionalized SWNT sample in THF (6 mg/mL, 5 mL) was added trifluoroacetic acid (5 mL). The mixture was refluxed under nitrogen protection for 10 h, resulting in the formation of dark-colored precipitates.
Scheme 2.1 Functionalize SWNTs with PKS copolymer.
Upon centrifuging, the solids were collected, washed repeatedly with chloroform, and then dried carefully for characterization.

2.2.6 PVK-SWNT nanocomposite films

In a typical experiment for film with high nanotube content, a solution of PKS-functionalized SWNTs in chlorobenzene (20 mg/mL, 2 mL) was prepared. To the solution was added a PVK homopolymer sample (200 mg). Upon vigorous mixing, the viscous solution was spin-coated (Laurell Model WS-400A-6TFM/LITE) onto a pre-cleaned ITO-coated glass substrate (1 min at 500 rpm, 30 s at 1,500 rpm, and then 30 s at 2,500 rpm). The resulting thin film was dried at 80 °C for 6 h.

2.3 Results and discussion

The PKS copolymer is majority PVK, with only ~10 mol% VPOB units according to the $^1$H NMR signal integration. Since it is known that defects on nanotube surface are converted to carboxylic acids upon oxidative acid treatment$^{30,31}$, they may be targeted by the pendant hydroxyl groups in VPOB units to form ester linkages. In the esterification reaction through the acyl chloride route, the presence of excess NaH is apparently necessary$^{32,33}$. It not only serves as an acid trap but also eliminates any trace amount of water in the reaction mixture. In fact, the reaction without NaH was found to be inefficient, with only very limited solubilization of nanotubes under otherwise the same experimental conditions.
The PKS-functionalized SWNT sample is readily soluble in many common organic solvents (such as THF, chloroform, chlorobenzene, DMF, and DMSO) to form dark-colored but visually clear solutions, in contrast to the colorless solutions of PKS and PVK. The optical absorption spectra (Figure 2.1) of the PKS-functionalized SWNT sample were measured in a DMSO solution and also in the solid-state because of the strong solvent interference for the longer wavelength region beyond 1,500 nm. The absorption bands at ~1,800 nm and ~1,000 nm are characteristic of the electronic transitions associated with the first \( S_{11} \) and second \( S_{22} \) pairs of van Hove singularities in the density of states for the semiconducting SWNTs, and the band at ~700 nm corresponds to the absorption of the metallic SWNTs \( M_{11} \). Thus, it seems that the electronic structures of SWNTs are preserved upon the functionalization targeting the nanotube surface defect sites. This is consistent with what have already been reported in the literature\(^{16-19,31}\).

The Raman spectrum of the PKS-functionalized SWNT sample is shown in Figure 2.2, where there is obviously overwhelming luminescence interference. The luminescence in functionalized carbon nanotube samples has been attributed to well-passivated nanotube surface defects\(^{34-36}\), namely that structural defects on nanotubes may act as traps for the photoexcitation energy, and these energy trapping sites may be stabilized by the functional groups to be responsible for the observed broad luminescence. As discussed in the literature\(^{37}\), there is strong experimental evidence suggesting that the functionalization is required for the observation of the nanotube
Figure 2.1 Optical absorption spectra of the PKS-Functionalized SWNT sample.
Figure 2.2 Raman spectra of the PKS-Functionalized SWNT sample before (top) and after (bottom) thermal defunctionalization.
defects-derived luminescence and that a better dispersion of nanotubes in their functionalization enhances the luminescence and, consequently, results in more significant interference in Raman measurements. The correspondence of luminescence enhancement to improved nanotube dispersion is understandable because of the known inter-tube quenching effect associated with the bundling of the nanotubes\textsuperscript{34-38}. Thus, the observed overwhelming luminescence interference in the Raman spectrum is an indication that the nanotubes were well-dispersed in the PKS-functionalized SWNT sample. As expected, a removal of the functional groups in the thermal defunctionalization of the functionalized nanotube sample eliminated the luminescence interference, with the Raman spectrum of the resulting sample exhibiting the characteristic SWNT features: D*-band at 2,580 cm\textsuperscript{-1}, G-band at 1,590 cm\textsuperscript{-1}, D-band at 1,310 cm\textsuperscript{-1}, and the radial breathing mode at 167 cm\textsuperscript{-1} (Figure 2.2).

The PKS-functionalized SWNTs were evaluated on mica surface in AFM analyses, for which the specimen was prepared by preserving the nanotube dispersion in solution as much as possible. In the preparation, a dilute solution of the PKS-functionalized SWNTs in chlorobenzene was sprayed onto a heated mica substrate to facilitate the desired rapid solvent evaporation. Shown in Figure 2.3 is a typical AFM image of the sample. There are apparently abundant nanotubes in the specimen, with their lengths ranging from 100 nm to 2 \textmu m. However, the nanotubes are grouped into features that are 1-2 nm in thickness according to the height analysis (Figure 2.3). It may be argued that the functionalized SWNTs are dispersed individually or in thin bundles while...
Figure 2.3 An AFM image (top) of the PKS-functionalized SWNT sample. The height analysis plot (bottom) is from left to right along the line in the image.
in solution, but assembled on surface in the preparation of the specimen due probably to surface tension-related issues and interactions between the polymeric functional groups.

The PKS-functionalized SWNTs were thermally defunctionalized to allow an estimate of the nanotube content in the sample. In a TGA scan (Figure 2.4), the functional groups were removed from the nanotube surface at 500 °C in an inert atmosphere, leaving behind mostly clean SWNTs according to the subsequent SEM analysis (Figure 2.5). The nanotube content in the sample was estimated to be ~20 wt% (Figure 2.4). On the other hand, TGA was also used to evaluate the insoluble residue from the functionalization reaction. Before the analysis, the residue sample was washed repeatedly with THF, in which PKS is highly soluble, to remove any unattached PKS. According to the result shown in Figure 2.4, the polymeric functional groups accounted for 20-30 wt% of the insoluble residue. These PKS species were likely attached to those nanotubes that were insufficiently functionalized to attain solubility.

The functionalization reaction was under conditions designed for the esterification of the nanotube surface-bound carboxylic acids (Scheme 2.1). There has been little success in literature to provide direct evidence on such a mode of functionalization. Nevertheless, indirect evidence may be obtained from the chemical defunctionalization to hydrolyze the ester linkages. The defunctionalization of the PKS-functionalized SWNTs was achieved under the reaction conditions for acid-catalyzed hydrolysis, resulting in the precipitation of the defunctionalized nanotubes. According to the SEM analysis of the recovered nanotube sample (Figure 2.6), the defunctionalization was incomplete, namely that the precipitated were mostly under-functionalized SWNTs as a
Figure 2.4 TGA traces (N₂, 10 °C/min) of the PKS-functionalized SWNT sample (——) and the insoluble residue from the functionalization reaction (--.--.--).
Figure 2.5 An SEM Image of the PKS-Functionalized SWNT sample after thermal defunctionalization in TGA scan.
Figure 2.6 An SEM image of the PKS-functionalized SWNT sample after the chemical defunctionalization.
Figure 2.7 Chlorobenzene solutions of PKS-functionalized SWNTs and PVK homopolymer mixtures with nanotube contents of ~3 wt% (left) and ~0.1 wt% (right) before spin-casting.
result of the partial removal of the polymeric functional groups \(^{16,18,32,33}\). There was apparently a significant amount of soft materials (remaining PKS polymers) in the SEM specimen.

The shared solubility of PKS-functionalized SWNTs with PVK homopolymer in chlorobenzene allowed their intimate mixing in solution (Figure 2.7). The selection of chlorobenzene as a solvent for wet-casting was for its intermediate boiling point (thus suitable vapor pressure under ambient conditions). The PVK-SWNT nanocomposite thin film on the ITO-coated glass substrate appeared homogeneous and optically transparent. The film contained around 3 wt% of SWNTs, estimated from the nanotube content in the PKS-functionalized SWNT sample.

The charge dissipation properties of the PVK-SWNT nanocomposite thin film (less than 1 µm in thickness and highly transparent) in the dark and under the illumination of white light were compared. The film surface was charged by a corona in the charge decay test unit, followed by monitoring the charge decay. As shown in Figure 8, the decay was much faster under the illumination than in the dark, with \( \tau_{\text{light}} \sim 0.7 \text{ s} \) vs \( \tau_{\text{dark}} \sim 1.4 \text{ s} \), where \( \tau \) represents the time for the surface charge to decay to \( 1/e \) of the initial value. It should be noted that the charge decay in the dark is relatively fast, in comparison with that in neat PVK film, which was likely due to the presence of conductive nanotubes (metallic SWNTs, in particular) as well-dispersed fillers in the nanocomposite film.

PVK is a well-known hole-transport polymeric material. The dispersion of SWNTs in PVK matrix apparently enhances the charge dissipation under photo-
Figure 2.8 Charge decays of the PKS-SWNT nanocomposite thin film in dark (○) and under illumination of white light (V).
illumination\textsuperscript{6}. In nanotubes themselves, photoconductivity has been observed and investigated\textsuperscript{40-45}. However, the role of nanotubes in the PVK-SWNT nanocomposite here might be as photoinduced charge generators (like C\textsubscript{60} in PVK matrix), but the mechanistic details on such activities remain to be explored in further investigations.

2.4 Conclusion

In summary, a specifically designed PVK copolymer with pendant hydroxyl groups was synthesized and used to functionalize SWNTs, yielding a soluble functionalized SWNT sample. The sample was thoroughly characterized by using various spectroscopic and microscopic methods. The solubility of PKS-functionalized SWNTs in the same solvent for PVK homopolymer enabled well-mixing in solution and the subsequent spin-casting of the PVK-SWNT nanocomposite thin film of a high optical quality. The charge dissipation in the nanocomposite was apparently enhanced under light illumination.
References


CHAPTER THREE

SEPARATED METALLIC SINGLE-WALLED CARBON NANOTUBES FOR CONDUCTIVE NANOCOMPOSITES

3.1 Introduction

Since the discovery of single-walled carbon nanotubes (SWNTs), there has been much excitement on their superior and in many cases unique properties,\(^1,2\) including their being ballistic conductors.\(^3\) In reality, the high electrical conductivity is associated only with metallic SWNTs, but all of the available production methods for SWNTs yield mixtures of metallic and semiconducting nanotubes. Moreover, metallic SWNTs generally represent the minority fraction in the mixtures (statistically 1:2 for metallic:semiconducting).\(^1,2\) Thus, post-production separation of metallic and semiconducting SWNTs has been pursued by a number of research groups,\(^4-6\) with various strategies based on physical and chemical means.\(^7-12\) We reported earlier a separation method that is uniquely suited for SWNTs produced from the arc-discharge and laser ablation techniques.\(^11\) The separation is based on the observation that semiconducting SWNTs are selectively solubilized via non-covalent interactions with planar aromatic molecules, such as derivatized free-base porphyrin (Scheme 3.1) or pyrene with long alkyl chains (to facilitate the solubilization of the non-covalently attached nanotubes in common organic solvents).\(^11\) Thus, the metallic and semiconducting fractions are obtained from the residue and supernatant, respectively, in
the solubilization-based separation process. While there has been much discussion on
great potentials and promises of bulk separated metallic or semiconducting SWNTs,\textsuperscript{4-6} experimental demonstration of such has been scarce.\textsuperscript{13} Here we report the use of the bulk separated metallic fraction from arc-discharge SWNTs in conductive polymeric
nanocomposites to demonstrate unambiguously the superior performance of metallic SWNTs.

3.2 Experimental section

3.2.1 Materials

Regioregular poly(3-hexylthiophene) (P3HT, $M_w = 50,000$, polydispersity index = 1.3 - 1.6) was purchased from Rieke Metal, Inc., and poly(3,4-ethylene-
dioxythiophene)/poly(styrene sulfonate) (PEDOT:PSS, Baytron PH500, ~1 wt\% solid content) from H. C. Stark. Solvents THF, DMSO, and DMF were obtained from
Mallinckrodt and distilled before use, and chlorobenzene was from Acros.

1-Docosyloxymethyl pyrene (DomP) was synthesized and characterized according to the procedures and methods reported previously.\textsuperscript{18}

The SWNT sample from the arc-discharge production method was supplied by Carbon Solutions, Inc. The as-received sample was purified by a combination of thermal oxidation and oxidative acid treatments as reported previously.\textsuperscript{17} Briefly, the sample (1 g) was heated in a furnace to 300 °C in air for 30 min and then refluxed in diluted nitric acid (2.6 M, 500 mL) for 24 h. The solid was collected via centrifugation, washed repeatedly
Scheme 3.1 Scheme of SWNT separation.
with deionized water until neutral pH, and then dried in vacuum oven to obtain the purified sample (330 mg).

3.2.2 Measurements

Optical absorption spectra were recorded on Shimadzu UV3100 and UV3600 spectrophotometers. Raman spectra were measured on Renishaw Raman spectrometer (50 mW diode laser for 785 nm excitation) and Jobin Yvon T64000 Raman spectrometer (Melles-Griot 35 mW He-Ne laser for 632.8 nm excitation). The latter was also equipped with triple monochromator and Olympus BX-41 microscope. Scanning electron microscopy (SEM) images were obtained on Hitachi S4700 field emission system.

Current-voltage (I-V) relationships for the nanocomposite thin films were determined by using the traditional four-probe method with Keithley 2400 multimeter controlled by Lab Tracer 2.0 software (Keithley Instruments, Inc.) and a probe station (Multiheight probe, Jandel). Electrical conductivity values were calculated according to $\sigma = \frac{\pi}{ln2} \frac{I}{V} t$, where $t$ is the specimen thickness. Surface resistivity values were calculated according to $R_s = \frac{ln2}{\pi} \frac{V}{I}$.

3.2.3 Separation

In a typical experiment, a purified SWNT sample (150 mg) was added to a solution of DomP in dry THF (10 mg/mL, 30 mL). The mixture was homogenized (Fisher Scientific Power Gen 125) for 1 h and then sonicated (VWR Model 250D) for 24 h. The mixture was centrifuged at 1,380 g for 15 min to remove the supernatant. The
residue containing enriched metallic SWNTs was refluxed in THF for 24 h, and then washed repeatedly with THF until the solution from the washing exhibiting no pyrene absorption.

3.2.4 Nanocomposite films

In typical fabrication of P3HT/SWNT films, the purified or separated metallic SWNT sample (2.5 mg) was suspended in chlorobenzene (5 mL) and homogenized for 10 min. It was mixed with a solution of P3HT (47.5 mg) in chlorobenzene, and the mixture was homogenized for 20 min and then sonicated for 24 h. The drop-casting of the P3HT/SWNT composite thin films on clean glass slides were performed in a glove box under nitrogen atmosphere. The films were dried in vacuum before conductivity measurements.

For PEDOT:PSS/SWNT films, the selected SWNT sample (5 mg) was suspended in DMSO (45 mL) with homogenization for 10 min and then sonication for 1 h. The suspension was mixed with aqueous PEDOT:PSS solution (5 mL). The mixture was sonicated for 1 h, followed by centrifuging at 2,256 g for 10 min to remove any solid residues. The supernatant was used for spray-coating onto glass substrates that were maintained at 150 °C. The resulting films were dried in vacuum before optical transmittance and surface resistivity measurements.
3.3 Results and discussion

The nanotube sample produced from the arc-discharge method was purified by using oxidative acid treatment in procedures that are well-established in the literature.\textsuperscript{16,17} The separation experiment for the purified SWNTs was carried out under conditions similar to those reported previously,\textsuperscript{11} except for the use of 1-docosyloxyethyl pyrene (DomP, Scheme 2.1) as the planar aromatic agent.\textsuperscript{18} The separated metallic fraction was recovered by thoroughly removing any residual separation agent. Results from electronic microscopy analyses revealed no significant difference of the separated metallic fraction from the pre-separation purified SWNTs (Figure 3.1).

The resonance Raman spectrum (632 nm excitation) of the separated metallic fraction exhibits much more pronounced BWF (Breit-Wigner-Fano) feature in the G-band region than that of the pre-separation purified sample (Figure 3.2),\textsuperscript{19} suggesting substantial enrichment of metallic SWNTs in the separated fraction. More quantitatively, the optical absorption spectral features (Figure 3.2) due to the electronic transitions between the van Hove singularity pairs of semiconducting SWNTs were carefully measured, which allowed an estimate of the content of metallic SWNTs in the separated fraction: \textsuperscript{4} about 2.5 times of that in the pre-separation purified sample or about 82% if the content in the latter is at the statistical limit of 1/3.

The separated metallic fraction was dispersed in regioregular poly(3-hexylthiophene) (P3HT) for P3HT/SWNT nanocomposite films of improved electrical conductivity. In the film fabrication experiment, nanotubes were added to a solution of
Scheme 3.2 Molecular structure of (a) DomP, (b) THPP, (c) P3HT, and (d) PEDOT:PSS.
Figure 3.1 SEM images of (a) the pre-separation sample and (b) separated metallic SWNTs (scale bar = 300 nm).
Figure 3.2 Optical absorption spectra of the pre-separation sample (---) and separated metallic SWNTs (-----), and their corresponding Raman G-bands (632 nm excitation) in the inset.
P3HT in chlorobenzene, and the resulting mixture in a dark green color appeared homogenous and stable (without precipitation). For the comparison between the separated metallic fraction and the pre-separation purified SWNTs, two mixtures of P3HT with 10% (wt/wt) respective nanotube samples were cast into a pair of thin films in a glove box (under nitrogen to prevent any oxidation or chemical doping). The absorption spectral features of the nanocomposite films in the visible exhibited no meaningful difference from those of the blank P3HT film, suggesting no ground-state complex formation between the polymers and SWNTs. The results from SEM analyses were also similar between the films, both with no nanotubes visible on the film surface. However, when the films were stretched to failure, SWNTs at the torn edges could be observed in the SEM imaging of both films.

As compared in Figure 3.3 for the two films of the same 10% (wt/wt) nanotube content, the one with the separated metallic fraction is obviously more conductive than the other with pre-separation purified SWNTs. The electrical conductivity calculated from the $I$-$V$ curves of the composite films is $10^{-2}$ S/cm for the former and $2.3 \times 10^{-3}$ S/cm for the latter, compared with the conductivity of $10^{-6} - 10^{-7}$ S/cm for blank P3HT films.

P3HT/SWNT composite films with various loadings (up to 20% by weight) of separated metallic fraction and pre-separation purified nanotube sample were fabricated and evaluated for their electrical conductivity results. The comparison in Figure 4a shows clearly that the films with the enriched metallic SWNTs are consistently more conductive than those with the pre-separation mixture at the same nanotube sample loadings. In fact, the increase in conductivity is more than an order of magnitude with the use of separated
Figure 3.3 $I$-$V$ curves for the P3HT/SWNT composite films (10 wt% nanotubes for both) with pre-separation purified SWNTs (□) and separated metallic SWNTs (○). Dashed lines represent the best fits from linear regression.
Figure 3.4 The electrical conductivity results of P3HT/SWNT composite films depending on (a) different amounts of pre-separation (□) and separated metallic (○) nanotube samples, and (b) their corresponding effective metallic SWNT contents in the films (dashed line: the best fit in terms of the percolation theory equation).
metallic fraction at 20% (wt/wt) nanotube sample loading in the films (Figure 4a). It seems that the film conductivity is dictated by available conductive channels, namely the amount of metallic SWNTs. Thus, the actual contents of metallic SWNTs in the nanocomposite films are calculated from the known compositions in both the separated metallic fraction and the pre-separation purified nanotube sample. As shown in Figure 4b, the relationship between the actual contents of metallic SWNTs in the films and the film electrical conductivity values follows the percolation theory,\textsuperscript{22,23}

\[ \delta = |x - x_c|^\alpha \]  

(1)

where \( \delta \) is the electrical conductivity, \( x \) the content of metallic SWNTs, \( x_c \) the percolation threshold where the transition takes place, and \( \alpha \) the critical exponent for the conductivity (an index for system dimensionality, theoretically 1.3 and 1.94 for ideal 2D and 3D systems, respectively).\textsuperscript{22} The best fit in Figure 4b corresponds to \( x_c \) of 0.74\% (wt/wt) and \( \alpha \) of 1.92. It makes sense that these films behave like 3D systems because the film thickness (about 1 micron) is considerably greater than the average diameters of the dispersed SWNTs or their bundles.\textsuperscript{24}

P3HT is highly colored, so that the films with and without embedded nanotubes are of poor optical transparency in the visible region. In order to prepare optically transparent conductive thin films, poly(3,4-ethylene-dioxythiophene):poly(styrene-sulfonate) (PEDOT:PSS) was used as matrix. The films were made ultra-thin, essentially thin coatings on glass substrate (Figure 3.5 inset), to facilitate the optical transparency.
Figure 3.5 The surface resistivity results of PEDOT:PSS/SWNT films on glass substrate with the same 10 wt% nanotube content (○: pre-separation purified sample and ▼: separated metallic SWNTs; and for comparison, ●: blank PEDOT:PSS without nanotubes) but different film thickness and optical transmittance at 550 nm. Shown in the inset are representative films photographed with tiger paw print as background.
The film (coating) thickness was controlled in terms of the optical transmittance at 550 nm.

The same approach of solution-phase dispersion and then wet-casting was applied to the fabrication of PEDOT:PSS/SWNT nanocomposite coatings on glass substrate. As well-established, PEDOT:PSS was processed as an aqueous dispersion. For solvent compatibility, DMSO was used to disperse nanotubes. The suspension of the nanotubes in DMSO was mixed with the aqueous PEDOT:PSS solution, and the mixture was used for fabricating the transparent conductive coating via spraying. Two PEDOT:PSS-SWNT mixtures with one containing 10% (wt/wt) the separated metallic fraction and the other 10% (wt/wt) the pre-separation purified nanotube sample were prepared, so was an aqueous solution of neat PEDOT:PSS (also containing the same amount of DMSO) as reference. Depending on the amount of solution or mixture sprayed, the coating thickness varies, as reflected by the variation in optical transmittance at 550 nm. These coatings were measured carefully for their surface resistivity values. The results compared in Figure 3.5 demonstrate clearly the enhanced electrical conductivity with the separated metallic SWNTs in the transparent conductive films.

In the development for alternatives to the currently dominating indium tin oxide (ITO) technology, PEDOT:PSS transparent conductive films have been demonstrated for some successful uses in organic optoelectronic devices. For example, the organic photovoltaic cell with PEDOT:PSS electrode was found to be only 15% less in efficiency when compared to the same cell with a classic ITO electrode. A strategy already discussed in the literature on further improving the performance of transparent
PEDOT:PSS electrode is the incorporation of SWNTs. The results presented above suggest that the use of bulk separated metallic SWNTs might offer the necessary conductivity enhancement without sacrificing the optical transparency to make the resulting PEDOT:PSS/SWNT composite films competitive to ITO coatings for transparent electrodes and other applications.

3.4 Conclusion

In summary, semiconducting SWNTs could be extracted from the purified nanotube sample through their preferential interactions with planar aromatic species, yielding substantially enriched metallic SWNTs. When dispersed in conductive polymer thin films, the metallic SWNTs enhance the electrical conductivity of the resulting nanocomposites significantly more than the starting purified nanotube sample. The results not only validate the post-production separation approach, but also demonstrate unambiguously the great potentials of metallic SWNTs in conductive nanocomposites and other relevant applications.
References


13. Arnold, M. S.; Green, A. A.; Huvat, J. F.; Stupp, S. I.; Hersam, M. C. Nat. Nanotech. 2006, 1, 60-65. In addition, there were reports on selectively etching away metallic SWNTs to leave the semiconducting ones for field-effect transistor devices.9c,14, 15


CHAPTER FOUR

SEPARATED METALLIC SINGLE-WALLED CARBON NANOTUBES FOR
TRANSPARENT CONDUCTIVE FILMS

4.1 Introduction

Transparent conductive films are essential components in many electrical and optoelectronic devices,\textsuperscript{1} including transistors, flat panel displays, touch screens and solar cells. However, the current commercially available technology, which uses indium tin oxide (ITO) thin film, has some significant deficiencies, including expense, incompatibility with plastic substrates and lack of flexibility.\textsuperscript{2-6} A single-walled carbon nanotube (SWNT) comprises a single sheet of graphite rolled into a seamless cylinder with diameter on the order of a nanometer.\textsuperscript{7,8} This essentially one-dimensional nanostructure has a length-to-diameter ratio in excess of 10,000 with a theoretical electrical conductivity estimated as high as \(10^4\sim10^6\ \text{S/cm}\.\textsuperscript{9,10}\) The combination of a large aspect ratio and high electrical conductivity has made SWNTs the subject of intense investigation as a possible successor to ITO for transparent conductive films.\textsuperscript{11-22} Compared to traditional ITO films, SWNTs films are advantageous in that they are made from readily available inexpensive carbon nanomaterials and have the highly desirable properties of both flexibility and bendability.\textsuperscript{11} Additionally, the fabrication process can be accomplished at room temperature without requiring expensive vacuum procedures.
Two major methods are available for fabricating SWNT film on different substrates at room temperature: the vacuum filtration method and the wet coating method (including bar coating, spray coating, spin coating, etc.) Even though SWNTs from different sources show large discrepancies in the electrical performance, the state of art performance of transparent conductive SWNTs films is currently about 200 Ω/square with 80% optical transparency at 550 nm.

While the surface resistivity of transparent conductive SWNT films is still higher than ITO films of comparable thickness, current experiments show that SWNT films, especially those fabricated on flexible substrates, can replace traditional ITO films in various applications, such as electrochromic devices (ECD), organic light-emitting diodes (OLED), photovoltaic devices, field effect transistors (FET), sensors, EMI shielding, supercapacitors and batteries. The early results suggest that devices fabricated with SWNTs films perform comparably to those made from ITO films. Indeed, transparent conductive SWNTs films used as hole transport layers in organic photovoltaic devices have resulted in a conversion efficiency of approximately 2.5%.

However, for an optimized device performance, lower surface resistivity (at 10-50 Ω/square) must be achieved. Consequently, current research on transparent conductive SWNTs films has been focused on further improving their electrical conductivity. One possible strategy of increasing conductivity involves the use of pure or enriched metallic SWNTs, since the high electrical conductivity is associated only with metallic SWNTs. Unfortunately, all current production methods for SWNTs have yielded a mixture of metallic and semiconducting nanotubes, with metallic SWNTs representing
the minor fraction in the mixture (with a statistically one-third ratio in a given sample). Moreover, the resistance of metallic-metallic nanotube interconnects in the nanotube films has been shown to be much less than the resistance of metallic-semiconducting and semiconducting-semiconducting junctions, due to the presence of Schottky barrier.\textsuperscript{46} Thus, using separated metallic SWNTs for transparent conductive films can significantly reduce the surface resistivity of the resulting films. Several post-production separation methods have been developed to separate metallic and semiconducting SWNTs based upon their physical and chemical differences.\textsuperscript{45,47-59} We recently reported a bulk separation method based upon the selective solubilization of semiconducting SWNTs via non-covalent interactions with planar aromatic molecules, such as derivatized free-base porphyrin\textsuperscript{56} or pyrene\textsuperscript{60,61} with long alkyl chains (to facilitate the solubilization of the non-covalently attached nanotubes in common organic solvents). Thus, the metallic and semiconducting fractions are obtained from the residue and supernatant, respectively, in this solubilization-based separation process. The noncovalent nature of the process enables the adsorbed molecules to be easily washed off by repeated refluxing after the separation to recover nanotubes with clean surfaces. Hence, the process is potentially scalable.

Here, we report the fabrication of transparent conductive SWNTs films by using bulk separated metallic nanotubes. This chapter also provides a comparison of different film fabrication methods (direct spraying, dipping and vacuum filtration) and various nanotube samples (e.g. purified arc-discharge nanotubes, purified laser ablation nanotubes and commercial acquired SWNTs) in terms of SWNT film morphology,
electrical conductivity and optical transparency. Results obtained in this study are also compared with those in the literature.

4.2 Experimental Section

4.2.1 Materials

Graphite powder (CVP grade) was supplied by Bay Carbon, carbon cement was obtained from Dylon Industries, and powdery Ni (2.2-3.0 μm, 99.9%) and Co (1-6 μm, 99.8%) were purchased from Alfa Aesar.

Nitric acid was purchased from Fisher Scientific. Solvents tetrahydrofuran (THF) and dimethyl formamide (DMF) were obtained from Mallinckrodt and distilled prior to use. Surfactant sodium dodecyl sulfate (SDS) was purchased from EMD.

1-Docosyloxymethyl pyrene (DomP) was synthesized according to the procedures reported previously. The raw arc-discharge produced SWNTs sample was supplied by Carbon Solutions, Inc. The laser ablation produced SWNT samples were synthesized in our lab. The commercial available purified arc-discharge nanotubes (P3 SWNTs) were provided by Carbon Solution, Inc. and used as received. The raw arc-discharge produced SWNT and laser SWNT samples were purified by a combination of thermal oxidation and oxidative acid treatments as reported previously. The sample (1 g) was furnace-heated to 300 °C in air for 30 min and then refluxed in diluted nitric acid (2.6 M, 500 mL) for 24 h. The solid was collected via centrifugation, washed repeatedly with deionized water until neutral pH, and then dried in a vacuum oven to obtain a purified sample (330 mg).
Scheme 4.1 Chemical structure of SDS.
4.2.2 Measurements

Optical absorption spectra were recorded on Shimadzu UV3100 and UV3600 spectrophotometers. Raman spectra were measured on a Renishaw Raman spectrometer (50 mW diode laser for 785 nm excitation) and a Jobin Yvon T64000 Raman spectrometer (Melles-Griot 35 mW He-Ne laser for 632.8 nm excitation). The Jobin Yvon spectrometer was also equipped with a triple monochromator and an Olympus BX-41 microscope. Scanning electron microscopy (SEM) images were obtained using a Hitachi S4800 field emission system, and transmission electron microscopy (TEM) images were obtained using a Hitachi HD2000 thin film characterization system. Thermogravimetric analysis (TGA) was conducted with a TA Instruments TGA Q500 system.

Current-voltage ($I$-$V$) relationships for the nanotube films were determined via the traditional four-probe method with a Keithley 2400 multi-meter controlled by Lab Tracer 2.0 software (Keithley Instruments, Inc.) and a probe station (Multi-height probe, Jandel). Surface resistivity values were calculated according to equation (1):

$$R_s = \frac{\ln 2}{\pi} \left(\frac{U}{I}\right)$$  \hspace{1cm} (1)

4.2.3 SWNT synthesized by laser ablation

The laser ablation method was used for the synthesis of SWNTs (Figure 4.1).\textsuperscript{62} The laser source was a Spectra Physics Quanta-Ray PRO-290 Q-switched Nd:YAG laser.
operated at 10 Hz (2 J/pulse at 1,064 nm and 9 mm beam diameter). In a typical experiment, the ablation target was prepared by mixing graphite (2.32 g), Ni (0.236 g), and Co (0.236 g) with graphite cement (2.40 g) for hot-pressing (130 °C) into a pellet (about 10 mm thick and 18 mm in diameter), followed by baking at 180 °C for 5 h in air, curing at 810 °C for 8 h, and annealing at 1,200 °C for 30 h in an argon flow (50 sccm, atmospheric pressure). The furnace temperature was set at 1,150 °C, with a steady argon flow (62 sccm, 75 kPa), in the ablation experiment. After two hours, the rubber-like carbon nanotube soot from the laser ablation was collected on the water cooled collector.

The purification procedure of the laser ablation SWNT sample was similar to that discussed above for the arc discharge SWNT sample.

4.2.4 Nanotube separation

In a typical experiment, a purified SWNT sample (150 mg) was added to a solution of 1-Docosyloxyethyl pyrene (DomP) in dry THF (10 mg/mL, 30 mL). The mixture was homogenized (Fisher Scientific Power Gen 125) for 1 h, sonicated (VWR Model 250D) for 24 h, and centrifuged at 1,380 g for 15 min to remove the supernatant. The precipitate fraction was then subjected to another two rounds of reaction with DomP. The final residue containing enriched metallic SWNTs was refluxed in THF for 24 h, and then washed repeatedly with THF until the solution from the washing exhibited no pyrene absorption.
Figure 4.1 The setup of laser ablation apparatus for SWNTs synthesis.
4.2.5 Carbon nanotubes films by direct spray

In a typical fabrication of carbon nanotubes films, the purified or separated metallic SWNT sample (2 mg) was suspended in dry DMF (20 mL). The mixture was homogenized for 30 min and then sonicated for 24 h. The final suspension was used without centrifugation. The solution was then spray-coated onto glass substrates that were maintained at 200 °C under argon protection. The resulting films were dried in a vacuum oven before optical transmittance and surface resistivity measurements.

4.2.6 Carbon nanotubes films by dipping

In a typical fabrication of carbon nanotube films, the purified or separated metallic SWNT sample (10 mg) was suspended in deionized water (25 mL) and then mixed with a SDS surfactant (0.025 g). The mixture was then sonicated for 16 h and centrifuged for 20 min at 2256 g to remove undispersed solid residues. The solution was then spray-coated onto glass substrates that were maintained at 150 °C under argon protection. Air dried films were carefully dipped into deionized water and held for 5 min without stirring to remove the surfactant. This dipping process was repeated three times, and the resulting films were dried in vacuum before optical transmittance and surface resistivity measurements.

4.2.7 Carbon nanotubes films by vacuum filtration

In typical fabrication of carbon nanotube films, the purified or separated metallic SWNT sample (5 mg) was suspended in deionized water (125 mL), with surfactant SDS
(1.25 g). The mixture was then sonicated for 16 h and centrifuged for 20 mins at 2256 g to remove undispersed solid residues. The homogenous and stable solution was vacuum-filtrated using alumina filters (Whatman, Inc., 2 inch diameter, and 200 nm pore size) of different volumes. The filtered film was rinsed thoroughly with deionized water to remove surfactants until no bubbles were visible. The films were then dried in a vacuum oven before conductivity measurements.

To remove alumina filters, the filter membrane with the nanotube film on top was placed face up in a Petri-dish filled with concentrated NaOH solution (great care was taken to prevent the solution from wetting the nanotube film). After 1-2 hours, the alumina filter dissolved completely, leaving the thin nanotube film floating on the solution. The film was then carefully transferred onto a clean glass slide, and washed with deionized water several times until neutral pH. The films were dried in a vacuum oven before optical measurements.

4.3 Results and Discussion

4.3.1 Nanotubes separation

The nanotube samples produced from both the arc-discharge method and laser ablation method were purified via oxidative acid treatment using well-established procedures in the literature. TGA was used to estimate the nanotube purity of the purified samples, which was approximately 90% for both samples.

P3 SWNTs (commercially available purified arc discharge nanotubes) sample was supplied by Carbon Solution, Inc. (labeled carbonaceous purity between 80-90%, see the
SEM and TEM images in Figure 4.2). Here, purified arc discharge SWNTs, purified laser ablation SWNTs, and P3 SWNTs are denoted as P-SWNT, L-SWNT, and P3-SWNT, respectively. The separation experiment for all three nanotube samples was carried out under conditions similar to those reported previously\textsuperscript{60,61} with the use of DomP as the planar aromatic agent. The separated metallic fraction was recovered by thoroughly removing any residual separation agent after the separation. Results from electronic microscopy analyses reveal no significant difference of the separated metallic fraction from the pre-separation purified SWNTs. Separated metallic fractions of P-SWNT, L-SWNT, and P3-SWNT are denoted as mP-SWNT, mL-SWNT, and mP3-SWNT, respectively.

Substantial enrichment of metallic SWNTs in the separated metallic fraction was found by both resonance Raman and NIR optical absorption spectroscopy.\textsuperscript{45,61} More quantitatively, the NIR optical absorption spectral features, due to the electronic transitions between the van Hove singularity pairs of semiconducting SWNTs (S\textsubscript{11} band), permit an estimate of the content of metallic SWNTs in the separated fraction. Compared with the starting purified sample, separated metallic SWNTs exhibited significantly diminished S\textsubscript{11} and S\textsubscript{22} bands, and an enhanced M\textsubscript{11} band. By assuming the starting sample has 1/3 of metallic nanotubes and 2/3 of semiconducting nanotubes, we are able to estimate the metallic SWNTs enrichment in the separated fractions by comparing the integrated peak area of the S\textsubscript{11} band. Table 4.1 provides a summary of these metallic nanotube enrichment results for mP-SWNT, mL-SWNT, and mP3-SWNT.
Figure 4.2 TEM image of (a) P-SWNT, (c) L-SWNT, and (e) P3-SWNT; SEM images of (b) P-SWNT, (d) L-SWNT, and (f) P3-SWNT.
Table 4.1 Summary of semiconducting/metallic nanotube percentages for purified SWNTs, mP-SWNT, mL-SWNT, and mP3-SWNT. (* indicates the statistic percentage without production bias.)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Semiconducting SWNTs (%)</th>
<th>Metallic SWNTs (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Purified SWNTs*</td>
<td>67</td>
<td>33</td>
</tr>
<tr>
<td>mP-SWNT</td>
<td>18</td>
<td>82</td>
</tr>
<tr>
<td>mL-SWNT</td>
<td>24</td>
<td>76</td>
</tr>
<tr>
<td>mP3-SWNT</td>
<td>21</td>
<td>79</td>
</tr>
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</table>
4.3.2 Transparent conductive films by SWNTs

4.3.2.1 Direct spray

The common practice in fabricating transparent conductive carbon nanotube films involves the dispersion of nanotubes into solvents with the assistance of dispersion agents, usually surfactants. However, any coating of surfactant molecules onto nanotube surface can drastically reduce the electrical properties of resulting nanotube film.\textsuperscript{64} Therefore the direct preparation of separated metallic SWNTs into homogenous and stable dispersion is preferable. The solvent of choice for such purpose is DMF for its well known ability to disperse SWNTs directly.\textsuperscript{65} For comparison, both P-SWNT and mP-SWNT were used to prepare films by the same procedure. Nanotube samples were dispersed in DMF with the aid of homogenization and sonication with a typical nanotube concentration yield of 0.1 mg/mL. After sonication, the final nanotube dispersion was used directly without centrifugation, and a spray gun was used to spray solution onto the heated glass substrates (~200 °C) under argon atmosphere. Figure 4.3 shows a picture of slides coated with nanotubes via this spraying method.

Figure 4.4 shows SEM images of P-SWNT films with different thicknesses that were achieved by spraying a volume of 5 mL, 10 mL, 15 mL, and 20 mL nanotube dispersion. According to these SEM images, the nanotubes are randomly laid upon the glass substrate without preferential orientation, and overlapping with one another to interconnected network. As the volume of sprayed solution increases, the coverage of interconnected nanotubes on the glass slide increases. By manually counting the diameter of the nanotubes within these SEM images taken at different locations, the average
Figure 4.3 A picture of typical nanotube coated slides by direct spraying. (left: slide fabricated with 10 mL P-SWNT dispersion solution; right, slide fabricated with 10 mL mP-SWNT dispersion solution).
Figure 4.4 SEM images of P-SWNTs films with different thickness by spraying a volume of (a) 5 mL, (b) 10 mL, (c) 15 mL, and (d) 20 mL nanotube dispersion solution; (e) diameter distribution of P-SWNT in the film.
nanotube bundle size in the nanotube film was determined to be approximately 19 nm with statistical fitting (Figure 4.4e). SEM analyses from mP-SWNT films yielded similar results.

Surface resistivities of both P-SWNT and mP-SWNT films were measured using the classic four probes method. Film thickness, intuitively, is proportional to the volume of dispersion solution used. However, due to unknown amounts of sample lost during the spraying process, constructing an accurate relationship between film thickness and the volume of the solution sprayed is quite difficult. Instead, film thickness was evaluated by its optical transparency, which is the ratio of the transmitted and incoming radiation power at a specific wavelength. Here, the film optical transparency is characterized by the optical transmittance at 550 nm for comparison with examples in the literature. Figure 4.5 shows the relationship between surface resistivity of the nanotube film and its corresponding optical transparency. Apparently, with decreased optical transparency, both nanotube films made from P-SWNT and mP-SWNT decrease in surface resistivity. However, the results compared in Figure 4.5 show little difference between films made by purified and separated metallic nanotubes, with both exhibiting a surface resistivity of approximately 20 KΩ/square at 80% optical transparency. One possible reason for this resistivity is that the nanotubes, especially separated metallic SWNTs, are difficult to disperse homogenously in DMF to either the level of individual nanotubes or the level of thin bundles, as reflected in the SEM results. During the separation process, nanotubes go through extensive de-bundling and exfoliation, so that dye molecules can anchor on their surfaces. Once these dyes molecules are removed upon separation, nanotubes are again
aggregated due to strong van der Waals force. Without dispersion agents, both purified SWNTs and separated SWNTs remain as rather large and undispersed bundles. Therefore, the intrinsic difference between these two samples has yet to be uncovered.

4.3.2.2 Dipping

To explore the full potential of separated metallic SWNTs, dispersion agents, such as surfactant molecules, were introduced for a better dispersion of nanotubes. An important issue was the removal of the surfactant molecules after the dispersion. One simple solution is called dipping method, in which SWNTs are first dispersed into an aqueous surfactant solution. The resulting dispersion solution was directly sprayed onto heated glass substrates (~150 °C) to prepare nanotube films. The removal of surfactant coated on the nanotube surface was achieved by dipping the nanotube coated glass into deionized water three times. The appropriate concentration of surfactant is critical in this dipping removal process. For the anionic surfactant, sodium dodecyl sulfate (SDS), it has a CMC concentration of 0.17-0.23 wt%. If the concentration of SDS in nanotube dispersion solution was greater than the CMC concentration, nanotube film was observed to peel off immediately from the glass substrate during immersion in water. Therefore, to ensure a good adherence between the nanotube film and the glass substrate, SDS solution of 0.1 wt% of was used. Figure 4.6 shows these P-SWNT films with various thicknesses prepared by the dipping method. The middle line represents the water level during the dipping process. Only the top portion of the slide was immersed.
SEM was used to investigate the morphology of the nanotube films prepared with the dipping process. Figure 4.7 shows SEM images of the film made of P-SWNTs before and after dipping process. Before being dipped in deionized water, the nanotube film exhibits a composite-like morphology, with surfactant molecules wrapping around the nanotubes. After the dipping process, most of the surfactants are washed away, with nanotubes remaining on the surface of the glass slide and forming a random interconnecting network. However, the removal of surfactant is by no means complete. Many spaces exist between the nanotube networks in which surfactant molecules remain trapped. Since SDS molecules are not electrically conductive, static charges generated by the interaction of the electron beam with the sample accumulate on the region where the surfactant molecules are located. This is clearly illustrated by the bright spots in the view of SEM image.

Dipping these nanotube films in deionized water dramatically affects their film optical transparency and electrical property. Figure 4.8 shows the optical transparency comparison of a P-SWNTs film before and after dipping in deionized water. The optical transparency of the film increases from 77.76% to 91.38% after the dipping process while the surface resistivity of the film decreases from 134 KΩ/square to 11 KΩ/square, by more than 10 times. Further extended dipping failed to improve the film optical transparency and electrical property, which also compromised the integrity of the film.

Films with various thicknesses were prepared by spraying different volumes of the SDS nanotube dispersion solution. For P-SWNT, the surface resistivity of the film after dipping is about 3 KΩ/square at 80% optical transparency (Figure 4.9), resulting in
Figure 4.5 The relationship between surface resistivity of the nanotube film fabricated by direct spraying and its corresponding optical transparency. (□: P-SWNT and ○: mP-SWNT)
Figure 4.6 Picture of P-SWNT films with various thicknesses by dipping method. (The arrow indicates the interface between sprayed film and dipped film.)
Figure 4.7 SEM images of P-SWNT film fabricated by dipping method. (a) Before dipping in the water; (b) after dipping in the deionized water three times.
Figure 4.8 Optical transparency comparison of a P-SWNTs film before (----) and after dipping (——) in deionized water.
Figure 4.9 The relationship between surface resistivity of the nanotube film fabricated by dipping method and its corresponding optical transparency. (□: P-SWNT and ○: mP-SWNT)
an approximate 6-7 times improvement over films prepared with the same material using the direct spray method. However, the difference between P-SWNT and mP-SWNT is still quite marginal. Nanotube films made from mP-SWNT exhibited a surface resistivity approximately 40% lower than that of P-SWNT, which is quite possibly due to a low concentration of surfactant. At a concentration below CMC, not enough surfactant molecules are available to disperse the nanotubes. Therefore, most of nanotubes in the separated metallic sample still remain as large bundles, thus reducing the number of effective conductive paths in the conductive network.

4.3.2.3 Vacuum filtration

Much higher concentrations of surfactant are necessary to further debundle nanotubes in our separated samples. Yet the problem remains as to how to effectively remove the surfactant molecules subsequent to the film fabrication process. Vacuum filtration may be the method for accomplishing this task. Vacuum filtration, used to fabricate transparent conductive carbon nanotube films, involves a three-step process: (1) vacuum filtering surfactant-assisted nanotube dispersion with a filtration membrane, such as porous alumina; (2) washing off the surfactant molecules; and (3) transferring the nanotube film from the filtration membrane to other substrates (glass or PET). Removal of surfactant was achieved by repeatedly washing the filtrated films with deionized water until no bubble was observed. The lack of weight loss in TGA at approximately 230 °C under nitrogen atmosphere for the final washed film (Figure 4.10) verifies that the surfactant was removed.
For comparison, both the P-SWNT and mP-SWNT were used to prepare two separate films using identical preparation procedures. Films with various thicknesses were prepared by filtering different volumes of the nanotube dispersion. Figure 4.11 shows a typical example from P-SWNT film on an alumina filter prepared via the vacuum filtration method. For both P-SWNT and mP-SWNT, the original nanotube concentration in the dispersion was 0.04 mg/mL. During the centrifuge process, large bundles and undispersed nanotubes were removed from the solution, leaving a clear and homogenous solution. To estimate the exact amount of nanotube used for each film, the weight of the thickest film was carefully measured to calculate the starting nanotube dispersion concentration after centrifuge, which was approximately 0.016 mg/mL for P-SWNT and 0.02 mg/mL for mP-SWNT. As shown in Figure 4.12, the surface resistivity of the film can be varied over a wide range by controlling the amount of nanotubes used. These results demonstrate clearly an enhanced electrical conductivity with the separated metallic SWNTs in the nanotube films. The surface resistivity of separated metallic SWNTs films was observed to be at least 3-4 times lower than their purified counterparts with the same amount of nanotubes. In the densest films, a surface resistivity as low as 30-40 Ω/square is achieved for mP-SWNT, even though its rather low transparency.

The advantages of the vacuum filtration method include the ability to create more homogenous nanotube films that possess superior conductivity due to their homogeneity and a better packing of the nanotubes. The film homogeneity is due to the natural compensation in the filtration process, in which the already deposited nanotubes reduce the flow of the nanotube suspension to allow more nanotubes deposit into other less
dense areas of the film. The compact packing process, which ensures a maximal overlap between nanotubes, is a direct result of vacuum-pressing during the filtration process. Figure 4.13a shows a SEM image of a P-SWNT film fabricated using the vacuum filtration method. The SEM image clearly illustrates a definite similarity of the film to those created using both the spraying method and dipping method. The vacuum filtration method, like the direct spraying and dipping methods, also have nanotubes randomly laid upon the film surface. However, the nanotube surfaces observed after using this method are quite clean and the packing of the nanotubes is much more compact. The most striking feature of this image is the bundle size of the nanotubes, which is approximately 7.5 nm in diameter (Figure 4.13b), much smaller than the usual bundle size of SWNTs found in films fabricated by the other two methods, which was approximately 19 nm in diameter. The bundle size reduction may be the direct result of excessive amount of SDS surfactant molecules in the nanotube dispersion solution, which can effectively wrap around nanotubes during the sonication and stabilize those nanotubes that are debundled. SEM analyses from mP-SWNT films show a similar effect of reduced bundle size. This reduced bundle size enables separated metallic nanotubes to show their distinct advantage over starting purified samples on electrical properties.

To build a relationship between optical transparency and the amount of nanotubes used in the film, nanotube films with various thicknesses were carefully transferred from
Figure 4.10 TGA traces for (-----) P-SWNT films fabricated by vacuum filtration method and (---) SDS surfactant. (10 °C/min, 60 mL/min N₂)
Figure 4.11 A picture of a P-SWNT film on alumina filter by vacuum filtration method.
Figure 4.12 The relationship between surface resistivity of the nanotube film fabricated by vacuum filtration method and its corresponding weight of SWNTs. ( □: P-SWNT and ○: mP-SWNT)
Figure 4.13 (a) A SEM image of P-SWNTs film fabricated by vacuum filtration method; (b) diameter distribution of P-SWNT in the film.
Figure 4.14 (a) Optical transmittance spectra of P-SWNT films with different thicknesses (----) and ITO film (──); (b) the relationship between optical transmittance and corresponding weight of nanotubes. The dashed line is the best fitting of experimental data.
filter membranes to glass slides by using a concentrated NaOH solution to dissolve the alumina membrane. Figure 4.14a shows the optical transmittance spectra of P-SWNT films with different thicknesses in the range of 400-800 nm. Compared to the optical transmittance of traditional ITO films, P-SWNT films have a more uniform transmittance over the whole visible region, with relatively lower transmittance in the blue and UV region that contribute to the scattering. For films with a 63% optical transparency, the corresponding amount of nanotubes used is 0.08 mg. According to Beer’s law,

\[
A = \log \left( \frac{I_1}{I_0} \right) = -\varepsilon dc
\]  

(2)

Therefore,

\[
T = \frac{I_1}{I_0} = e^{-dc} = e^{-aM}
\]  

(3)

where T is the optical transmittance, and M is the weight of nanotubes. The best fitting of experimental data using equation (3) is shown in Figure 4.14b. From the fitting, the nanotube film with 80% optical transparency is estimated to require 0.05 mg nanotubes. If the density of the nanotubes is 1.59 g/cm³, the corresponding nanotubes film thickness is 25 nm.

4.3.2.4 Comparison of different fabrication methods

Table 4.2 compares the various fabrication methods for transparent conductive nanotube films used in this study.
<table>
<thead>
<tr>
<th>Fabrication method</th>
<th>Electrical performance by purified nanotubes</th>
<th>Electrical performance by separated metallic nanotubes</th>
<th>Enhancement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direct spraying</td>
<td>20 KΩ/square @ 80 % optical transparency</td>
<td>20 KΩ/square @ 80 % optical transparency</td>
<td>None</td>
</tr>
<tr>
<td>Dipping</td>
<td>3 KΩ/square @ 80 % optical transparency</td>
<td>2 KΩ/square @ 80 % optical transparency</td>
<td>40 %</td>
</tr>
<tr>
<td>Vacuum filtration</td>
<td>1000 Ω/square @ 63 % optical transparency</td>
<td>250 Ω/square @ 63 % optical transparency</td>
<td>300-400 %</td>
</tr>
</tbody>
</table>

Table 4.2 Comparison of different fabrication methods for transparent conductive nanotube films.
Vacuum filtration is clearly the best method for fabricating nanotube transparent conductive films. Compared to either the direct spraying method or the dipping method, the vacuum filtration method is superior in three distinct aspects. First, the vacuum filtration process itself guarantees the homogeneity of the films. As the nanotubes accumulate in a certain area, the deposited nanotubes will reduce the flow of the solution in this region and thusly allow more nanotubes to deposit in less dense area. Second, during the filtration process, nanotubes are randomly laid upon the membrane with a maximal overlap and compact packing. These characteristics in turn yield enhanced electrical conductivity and mechanical properties. Third, unlike previous methods, the nanotube film thickness can be readily controlled by controlling both the concentration and volume of the solution filtered.

More importantly, vacuum filtration method can ensure that nanotubes are effectively debundled during the fabrication process. The excessive amount of surfactant molecules wrap around nanotube surface to stabilize individual nanotubes or nanotube thin bundles, which are continuously generated during the exfoliation process. Therefore, this method is compatible for use with separated metallic SWNTs, which are even more difficult to disperse than purified SWNTs due to the extended sonication process. The unique configuration of vacuum filtration permits the removal of surfactants using a water washing process, while simultaneously maintaining both the integrity and quality of the host film. The ability to effectively remove all surfactant molecules after the film fabrication process guarantees a total restoration of the electrical conductivity of the nanotubes.
4.3.2.4 Comparison of different SWNTs samples

With the vacuum filtration established as the best method to fabricate transparent conductive nanotube films, different nanotube samples, namely P3-SWNT, L-SWNT and their separated metallic parts were evaluated for electrical performances.

Transparent conductive nanotube films were fabricated with P3-SWNT and mP3-SWNT using the vacuum filtration method. The fabrication procedure is very similar to that used for P-SWNT, except P3-SWNT and mP3-SWNT were instead substituted. Figure 4.15 shows the surface resistivity results from these nanotube films.

Transparent conductive films fabricated with P3-SWNT exhibit excellent electrical property. The surface resistivity of the film reaches 150 Ω/square at 0.1 mg nanotube loading level, approximately 6-7 times lower than in similar films made from P-SWNT. However, mP3-SWNT films showed no further enhancement in surface resistivity compared to their starting purified samples. Indeed, the electrical performance is somewhat worse for thinner films. An increase in the nanotube loading results in almost no difference between films from two different nanotube samples.

Raman and NIR results from mP3-SWNT and P3-SWNT (see section 4.3.1) confirmed a significant enrichment of metallic SWNTs in mP3-SWNT sample, even though the separation efficiency is slightly lower than that of P-SWNT. SEM/TEM images (shown in section 4.3.1) show no apparent difference between P3-SWNT and P-SWNT: both have an ample amount of nanotube in the sample. Since electronic microscopy cannot provide the comprehensive evaluation of the composition in the
Figure 4.15 The relationship between surface resistivity of the nanotube film fabricated by vacuum filtration method and its corresponding weight of SWNTs. (□: P3-SWNT and ○: mP3-SWNT)
Figure 4.16 TGA traces of (a) P3-SWNT and (b) P-SWNT. Dashed lines are derivatized analyses. (10 °C/min, 60 mL/min air)
nanotube sample, TGA is used to estimate the nanotube purity in both samples. Figure 4.16 shows that both P-SWNT and P3-SWNT have 10 wt% metal impurities, which are consistent with the statement in section 4.3.1. The shape of the TGA scan also reveals that for P-SWNT, there is only a single weight-loss at 500 °C, which is widely accepted to be the burning of the SWNTs in the air.\textsuperscript{66}

However, two weigh-loss stages occur over the scanning temperature range for P3-SWNT. Derivatized analysis shows two weight losing peaks, centered at 500 °C and 700 °C, respectively. The first peak is attributed to SWNTs as previously discussed, while the second one is believed to be graphite or graphite nanoplatelets. Indeed, a control TGA experiment of pure graphite confirms that decomposition air temperature of the graphite to be 700 °C. Graphite is a common impurity in nanotubes, especially nanotubes produced by the arc-discharge method. Because it cannot be removed during normal oxidation purification process, graphite is likely to remain if it comprises a portion of the starting raw material. Thus, even though the labeled purity of P3-SWNT is 80-90%, the true composite is actually 60% SWNTs with 20% graphite or graphite nanoplatelets. Because these nanoplatelets are 2D materials with high electrical conductivity, the unusually high graphite content in P3-SWNT may contribute to its high electrical performance. Conversely, graphite complicates the separation process. Since graphite does not possess the same chirality as nanotubes, planar conjugated molecules such as DomP used in this work, cannot differentiate them. Therefore, both mP3-SWNT and P3-SWNT contain a similar amount of graphite impurities and the electrical conductivity of nanotubes is not enhanced by separation.
Transparent conductive nanotube films were also fabricated with L-SWNT and mL-SWNT using the vacuum filtration method. The surface resistivity results shown in Figure 4.17 indicate that L-SWNT performs similarly to P-SWNT with a surface resistivity of 1500 $\Omega$/square at 0.1 mg nanotube loading.

Upon separation, mL-SWNT shows a notable enhancement in surface resistivity (800 $\Omega$/square at 0.1 mg nanotube loading), which is an approximate two-fold improvement as compared to its purified counterpart. However, the enhancement observed for separated laser ablation nanotubes significantly less than the mP-SWNT. Of particular note is the lower separation efficiency of the L-SWNT as compared with the P-SWNT. Because L-SWNT has a slightly different diameter distribution than P-SWNT, the separation for arc discharge SWNTs may need to be modified to maximize the separation efficiency for laser ablation nanotubes. Also, L-SWNT is known for its surface perfection and strong bundles, which can further reduce the separation efficiency.

4.3.3. Comparison with literature results

Table 3.4 summarizes the literature results of transparent conductive SWNTs film which are compared with the results obtained in his study. From the comparison, it is quite clear that the electrical performance of transparent conductive nanotube films strongly depends on both the nanotubes and the fabrication method. For purified arc-discharge SWNTs (similar electrical property with HiPco SWNTs and CVD SWNTs), reported values range from 500 to 6000 $\Omega$/square at 80% transparency. The simple spray nanotube dispersion method in an alcohol solution achieved the best results.\textsuperscript{21} Indeed, the
Figure 4.17 The relationship between surface resistivity of the nanotube film fabricated by vacuum filtration method and its corresponding weight of SWNTs. (□: L-SWNT and ○: mL-SWNT)
<table>
<thead>
<tr>
<th>Fabrication Method</th>
<th>Materials</th>
<th>Surface Resistivity (Ω/square)</th>
<th>Transmittance @ 550 nm</th>
<th>Ref. No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bar coating</td>
<td>Purified CVD SWNT</td>
<td>6 K</td>
<td>88% on PET</td>
<td>Ref 20</td>
</tr>
<tr>
<td>Dip coating</td>
<td>Purified Laser SWNT</td>
<td>80</td>
<td>80% on PET</td>
<td>Ref 18</td>
</tr>
<tr>
<td>Spray coating</td>
<td>Purified Arc SWNT</td>
<td>~500</td>
<td>80% on glass</td>
<td>Ref 21</td>
</tr>
<tr>
<td>Spray coating</td>
<td>Hipco SWNT, Laser SWNT</td>
<td>2 K (Hipco) 1 K (Laser)</td>
<td>80% on PET</td>
<td>Ref 19</td>
</tr>
<tr>
<td>Spray coating</td>
<td>Arc SWNT</td>
<td>4 K</td>
<td>N/A</td>
<td>Ref 64</td>
</tr>
<tr>
<td>Vacuum filtration</td>
<td>Purified laser SWNT</td>
<td>30</td>
<td>70% on alumina filter</td>
<td>Ref 12</td>
</tr>
<tr>
<td>Vacuum filtration</td>
<td>Purified Hipco SWNT</td>
<td>1 K</td>
<td>85% on alumina filter</td>
<td>Ref 13</td>
</tr>
<tr>
<td>Vacuum filtration and transfer</td>
<td>P3 SWNT</td>
<td>200</td>
<td>80% on PET</td>
<td>Ref 14</td>
</tr>
<tr>
<td>Vacuum filtration</td>
<td>P-SWNT</td>
<td>1000</td>
<td>63% on glass</td>
<td>This work</td>
</tr>
<tr>
<td>Vacuum filtration</td>
<td>mP-SWNT</td>
<td>250</td>
<td>63% on glass</td>
<td>This work</td>
</tr>
<tr>
<td>Vacuum filtration</td>
<td>P3 SWNT</td>
<td>150</td>
<td>63% on glass</td>
<td>This work</td>
</tr>
<tr>
<td>Vacuum filtration</td>
<td>L-SWNT</td>
<td>1500</td>
<td>63% on glass</td>
<td>This work</td>
</tr>
<tr>
<td>Vacuum filtration</td>
<td>mL-SWNT</td>
<td>800</td>
<td>63% on glass</td>
<td>This work</td>
</tr>
<tr>
<td>ITO on glass</td>
<td></td>
<td>10-50</td>
<td>85%</td>
<td></td>
</tr>
<tr>
<td>ITO on PET</td>
<td></td>
<td>50-200</td>
<td>80%</td>
<td></td>
</tr>
<tr>
<td>PEDOT:PSS</td>
<td></td>
<td>500</td>
<td>80%</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.3 Summary of literature results of transparent conductive SWNTs film and comparison with results obtained in this work and benchmark values of ITO and PEDOT:PSS.
findings from our study actually correlate those in the literature. For P-SWNT, the surface resistivity is approximately 1000 Ω/square at 63% optical transparency for SWNT films fabricated via the vacuum filtration method. The surface resistivity of the film decreases 3-4 times when using mP-SWNTs and the projected value of about 500 Ω/square at 80% transparency makes mP-SWNTs a superior nanotube material for use in transparent and conductive nanotube films.

Laser ablation SWNTs are believed to possess a high electrical conductivity due to fewer imperfections on their surfaces.67 In the literature, there are actually great many discrepancies between the results from these different research groups. Both 30-80 Ω/square at high transparency12 and about 1000 Ω/square at 80% transparency19 have been reported thus far. The result from our study, which is approximately about 1-2 KΩ/square, actually agrees with the latter. While the mL-SWNT can be used to improve surface resistivity, the results are still far below the 30-80 Ω/square reported in the literature.

P3 SWNTs have consistently showed a 200 Ω/square at an 80% transparency.14 While this study has confirmed those findings, the existence of graphite impurities prevents a further improvement of the electrical properties of P3 SWNTs via separation.

4.3.4 Feasibility of SWNT transparent conductive films

The feasibility of creating and using SWNT transparent conductive films is ultimately determined by their fundamental technical attributes of surface resistivity and optical transparency. SWNT transparent conductive films in their current developmental
stage are comparable to commercially available technologies such as ITO on plastic substrate and PEDOT:PSS coating (see Table 4.3). However, the literature results and this study both indicate a need for further performance improvement. SWNT transparent conductive films are also superior to either ITO or PEDOT:PSS in that they possess a uniform optical transmittance over the entire visible spectrum, and good thermal and chemical resistance.

SWNT transparent conductive films are also cost effective. The results of this study show that 80% transparency SWNT film has an average thickness of approximately 25 nm. Thus, it is possible to fabricate such films with a surface area of 20 m$^2$ by using only 1 gram of nanotubes with an appropriate setup! Moreover, if the price of nanotubes is about $100/g, the material cost of SWNT film, not including substrate and fabrication, is only $5/m$^2$, which is far less than ITO films, plus the fact that cost of these nanotube can dramatically decrease once the production scale is increased. However, a potential technical difficulty preventing the use of SWNTs in transparent conductive films involves film transfer and large area fabrication. Because these SWNTs require such a thin film, transferring it from the filter membrane to other substrates while preserving its integrity remains extraordinarily difficult. While stamping is a viable alternative to this transfer process,$^{14}$ it is unsuitable for the possible industrial scale production of large area SWNTs films. This process is also incompatible with the printing or roll-to-roll process which is expected to use in flexible electronics.
4.4 Conclusion

In summary, semiconducting SWNTs can be extracted from the purified nanotube sample through their preferential interactions with planar aromatic species, yielding substantially enriched metallic SWNTs in bulk quantity. The metallic SWNTs can significantly enhance the electrical conductivity of the nanotubes film much more than the starting purified nanotube sample. These results not only validate the post-production separation approach, but also demonstrate unambiguously the great potential of metallic SWNTs in transparent conductive film applications.
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344-347.


SUMMARY AND CONCLUSION

The known electrical and thermal properties of carbon nanotubes have prompted many predictions on their potentials for ultimately performing polymeric nanocomposites. However, the experimental materialization of these predictions has proven to be more complex in the development of nanocomposites for electrical properties and more challenging in those for high thermal conductivity. Nevertheless, that chemical modification and functionalization of carbon nanotubes have been demonstrated as being effective for fabricating high-quality polymeric carbon nanotube composites, especially with our approach of “matrix functionalization”, which uses polymers that are structurally identical or maximally similar to the matrix polymers in the nanotube functionalization.

For desired electrical properties, the dispersion of carbon nanotubes in the polymer matrix is important to the performance. For example, we have applied the “matrix functionalization” strategy to fabricate high quality PVK SWNT nanocomposites for potential photoconductivity application. We designed and synthesized a PVK copolymer with styrene unit containing hydroxyl group. The PVK unit ensured maximal compatibility with the matrix PVK polymer, and hydroxyl group on styrene unit was used to functionalize carbon nanotubes via esterification reaction. The ratio between PVK and styrene unites was purposely kept at 10:1 to minimize the negative effect on the compatibility. The PVK functionalized SWNTs sample was thoroughly characterized by using various spectroscopic and microscopic methods. The shared solubility of
functionalized nanotube sample with PVK matrix polymer in the same solvent enabled their intimately mixing in solution and subsequent spin-casting of high optical quality nanocomposite thin film. Photo-induced charge decay measurement showed that the charge dissipation in the nanocomposite film was apparently enhanced under light illumination.

For highly thermal conductive polymeric nanocomposites, on the other hand, the feasibility of using carbon nanotubes to achieve the desired performance has yet to be convincingly demonstrated experimentally. To investigate the effect of chemical functionalization on thermal conductive nanocomposites, we synthesized PVA functionalized SWNTs to prepare PVA nanocomposite films with different nanotube concentrations. Even though the improvement on thermal conductivity of resulting random PVA nanocomposites was marginal, the functionalized carbon nanotubes were more readily aligned in nanocomposites by mechanical stretching due to their excellent dispersion. Therefore, aligned PVA nanocomposites showed much enhanced in-plane thermal diffusivity in the aligned direction.

SWNT may, depending on its chirality, be either metallic or semiconducting. The coexistence of metallic and semiconducting SWNTs in as-produced nanotube samples has been a bottleneck for many widely pursued applications, especially those more demanding ones, such as nano-electronic devices and electrically conductive nanocomposites. Therefore, the separation of SWNTs based on their electronic structures is an important and potentially highly valuable task. We have developed a bulk separation method based on selective interactions of large planar aromatic molecules with
semiconducting SWNTs for their solubilization in organic solvents. As a result, substantially enriched metallic SWNTs can be obtained after semiconducting SWNTs being extracted from the purified nanotube sample by this method. When dispersed in conductive polymer (both P3TH and PEDOT:PSS) thin films, the metallic SWNTs enhance the electrical conductivity of the resulting nanocomposites significantly more than the starting purified nanotube sample. The results not only validate the post-production separation approach, but also demonstrate unambiguously the great potentials of metallic SWNTs in conductive nanocomposites and other relevant applications.

Furthermore, the use of SWNTs for transparent conductive films has attracted a lot of attention recently. Compared to other technologies, such as traditional ITO films, SWNTs films are advantageous due to their low cost and much desirable flexibility and environmental stability. Our research has been focused on further improving electrical conductivity of transparent conductive SWNTs films by using separated metallic nanotubes. We compared different film fabrication methods (direct spraying, dipping and vacuum filtration) and various nanotube samples (e.g. purified arc-discharge nanotubes, purified laser ablation nanotubes and commercially acquired SWNTs) in terms of SWNT film morphology, electrical conductivity and optical transparency. The results clearly demonstrated that the metallic SWNTs could significantly enhance the electrical conductivity of the nanotubes film much more than the starting purified nanotube sample. These results promise the great potentials of metallic SWNTs in transparent conductive film applications. The SWNT transparent conductive films in their current developmental stage are comparable to commercially available technologies such as ITO on plastic.
substrate and PEDOT:PSS coating. However, both the literature results and this study indicate a need for further performance improvement. One recent development in the literature is to use chemical doping to further improve the electrical conductivity of SWNT films. But doping stability is still an open issue. Additionally, SWNT transparent conductive films are superior to either ITO or PEDOT:PSS in that they possess a uniform optical transmittance over the entire visible spectrum. Combined with low cost, flexibility, and good thermal/chemical resistance, SWNTs films represent a promising alternative technology for transparent conductive films.
APPENDIX A

Glossary

AIBN 2,2’-Azobis(isobutronitrile)
AROP Anionic ring-opening polymerization
ATRP Atomic transfer radical polymerization
CMC Critical micelle concentration
CVD Chemical vapor deposition
DOMP 1-Docosyloxyethyl-pyrene
DOS Density of states
DWNT Double-walled carbon nanotube
ECD Electrochromic device
EMI Electromagnetic interference
EVOH Poly(ethylene-co-vinyl alcohol)
FET Field effect transistor
ITO Indium tin oxide
MWNT Multi-walled carbon nanotube
ODA Octadecylamine
OLED Organic light-emitting diode
P3HT Poly(3-hexylthiophene)
PABS Poly(m-aminobenzensulfonic acid)
PEDOT:PSS Poly(3,4-ethylene-dioxythiophene):poly(styrene-sulfonate)
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>PHET</td>
<td>Poly[3-(2-hydroxyethyl)-2,5-thienylene]</td>
</tr>
<tr>
<td>PI</td>
<td>Polyimide</td>
</tr>
<tr>
<td>PPE</td>
<td>Poly(phenylene ethylene)</td>
</tr>
<tr>
<td>PPEI</td>
<td>Poly(propionylethylenimine)</td>
</tr>
<tr>
<td>PPEI-EI</td>
<td>Poly(propionylethylenimine-\textit{co}-ethylenimine)</td>
</tr>
<tr>
<td>PS</td>
<td>Polystyrene</td>
</tr>
<tr>
<td>PVA</td>
<td>Poly(vinyl alcohol)</td>
</tr>
<tr>
<td>PVK</td>
<td>Poly(vinyl carbazole)</td>
</tr>
<tr>
<td>PVP</td>
<td>Poly(vinyl pyridone)</td>
</tr>
<tr>
<td>SDS</td>
<td>Sodium dodecyl sulfate</td>
</tr>
<tr>
<td>SOCl$_2$</td>
<td>Thionyl chloride</td>
</tr>
<tr>
<td>SWNT</td>
<td>Single-walled carbon nanotube</td>
</tr>
<tr>
<td>THPP</td>
<td>5,10,15,20-Tetrakis(hexadecyloxyphenyl)-21(H),23(H)-porphine</td>
</tr>
<tr>
<td>VGCF</td>
<td>Vapor-grown carbon fibers</td>
</tr>
<tr>
<td>VPOB</td>
<td>4-(4”-Vinyl phenyl)-3-oxabutanol</td>
</tr>
</tbody>
</table>
APPENDIX B

Coauthored publications during my graduate study (2003-2007)


2005, 44, 4594-4598.


Charge transport in transparent single-wall carbon nanotube networks

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Abstract

We report the electric-field effects and magnetotransport in transparent networks of single-wall carbon nanotubes (SWNT). The temperature dependence of conductance of the network indicates a 2D Mott variable-range hopping (VRH) transport mechanism. Electric field and temperature are shown to have similar effects on the carrier hops and identical exponents for the conductance of the network are obtained from the high electric field and temperature dependences. A power-law temperature dependence with an exponent 3/2 for the threshold field is obtained and explained as a result of the competing contributions from electric field and phonons to the carrier hop. A negative magnetoresistance (MR) is observed at low temperatures, which arises from a forward interference scattering mechanism in the weak scattering limit, consistent with the VRH transport.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The charge transport in single-wall carbon nanotube (SWNT) systems can vary from diffusive to ballistic, depending upon the extent and nature of disorder. Although high quality individual SWNT often show ballistic transport, as disorder increases variable-range hopping (VRH) conduction is widely observed [1–3]. A comparison of the roles played by temperature and electric field can throw light onto the nature of hopping transport. Such an investigation is particularly interesting for carbon nanotube systems because the nature of localization is non-trivial due to the presence of extended wavefunctions along the individual tube (or bundle of tubes). While electric field is predicted to play a role identical to that of temperature for hopping transport in amorphous and doped crystalline semiconductors, similar investigations
are required in nanotube systems in order to understand the hopping process in which both dimensionality and disorder play important roles [4]. The effects of magnetic field at low temperatures also offer intriguing physics for SWNT systems and can provide further insight into the nature of scattering processes for the carriers undergoing hops [5].

In this paper, the low-temperature electric and magnetic field effects are reported on optically transparent networks of SWNTs. The recent interest generated in these novel materials originates not only from the interesting physics they offer but also from their potential applications as transparent flexible electrodes and transistors in organic electronics [6]. The transparencies of these networks are already comparable to those of conventional transparent electrodes, indium–tin oxide, and an understanding of the transport phenomenon is essential towards making them viable alternatives to the latter. Hopping transport has been recently reported in these networks, with metallic fraction of tubes playing an important role in conduction [1]. In the present work, we report on various aspects of charge transport in transparent SWNT networks including the dependence of network conductance on temperature, electric and magnetic fields at low temperatures, towards evolving a consistent picture for transport.

2. Experimental details

The SWNTs were prepared by the carbon-arc method and comprised of metallic and semiconducting tubes in the ratio of 1:2 (i.e. 33% of the tubes are metallic). The nanotubes were dispersed in dimethylformamide (DMF) via homogenization followed by sonication for 60 min. The dispersion solution was sprayed onto a heated glass slide held at 150 °C [7]. The SWNTs are randomly oriented in an interconnected network with high optical transparency (>85% at 550 nm wavelength) and a scanning electron microscope (SEM) image of the network is shown in Figure 1. The SWNTs have a bundle diameter of 10–20 nm and an average length of over 1 μm.

The pulsed voltage–current (V–I) and magnetic field measurements were performed in a Janis variable-temperature cryogenic system equipped with a 11 T superconducting magnet. The sample is immersed directly in a vapour or liquid helium bath. This together with the fact that the nanotube network is dilute (i.e. packing fraction is low 20–25%) ensures good thermal contact between the entire network and the bath. The contact geometry used in the measurements was the conventional ‘collinear’ four-probe type with a contact separation of 1 mm, such that an ‘average’ network property was measured. The nonlinear V–I

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3. Results and discussion

Measurements were performed on samples showing optical transparency of 85–90% at 550 nm wavelength and the typical results are presented below. Our network shows hopping transport (figure 2(a)) with a resistivity ratio, $R_{15}/R_{400} ≈ 50$, and the exponent for hopping conduction is found by evaluating the reduced activation energy $W(T) = -\frac{d}{d\ln T} \ln R(T)$ as shown in the inset of figure 2(a). The graph yields an exponent of 0.38, close to 1/3 as seen from the
negative slope of the W-plots. This value favours a 2D Mott VRH conduction for the network described by the equation for conductance [8]:

\[ G(T) = G_0 e^{\lambda/(T_b/T)^p} \]  

where \( p \approx 0.38 \approx 1/3 \), \( G_0 \) is characteristic of the sample, \( k_B T_b = 3/(\beta^2 N(0)d) \), \( \lambda \) is the localization length, \( N(0) \) is the density of states (DOS) at the Fermi level and \( d \) is the sample thickness. Note that the metallic DOS at the Fermi level should be rescaled to account for the volume packing-fraction of tubes [9]. Disorder is present along the individual nanotubes or along tube and bundle boundaries, and both are relevant to the hopping transport. The value of \( T_b = 292 \) K is obtained from the W-plots, \( W = -p \ln T + \lambda/(\ln T) \), and an estimate of localization length can be obtained using (1), \( \lambda \approx 9 \) nm. This value can be correlated to the typical size of nanotube-bundles [9]. Figure 2(b) shows the linear relationship between \( \ln R \) and \( T^{-1/3} \).

The conductance of the network, \( G = J/E \), is plotted as a function of applied pulsed electric field in figure 3. The conductance is nearly constant at low electric fields, especially at higher temperatures, and it increases at higher fields till it becomes nearly temperature-independent. At lower temperatures \( T < 4.2 \) K the conductance increases by nearly two orders of magnitude for \( E \approx 500 \) V cm\(^{-1} \). Non-ohmic conductivity of the type seen in our system can result from a redistribution of carrier energy under the effect of electric field [9].

For hopping conduction the field dependence was shown to be \( I = I_0 e^{\lambda/(E/E_0)^p} \), with \( E_0 \) being a characteristic constant of the system [4]. However, the electric-field dependence is better described by an equation more similar to (1) [10–12]:

\[ G(E) = G_0 e^{\lambda/(E/E_0)^p} \]  

These equations are strictly valid in the limit of \( T \to 0 \) K. Our analysis shows that for our network the conductance-expression (2) is a more appropriate description for the electric-field dependence than the current-expression. To analyse the field-dependence, we calculate the field scaling function, \( \beta_T = -\ln G/\ln E = \Delta(\ln G - \ln G_0) \) for the lowest temperatures [10]. The field scaling function together with the temperature scaling function \( \beta_T = -\ln G/\ln T = p(\ln G - \ln G_0) \) is plotted as a function of \( \ln G \) in figure 4(a) [13]. The value of exponent \( \Delta \) obtained is \( 0.36 \approx 1/3 \) at the lowest temperature, virtually identical to the temperature exponent. Indeed we find that the slope of \( \beta_T \) (at high field) is nearly the same as the slope of \( \beta_T \). This result suggests that strong electric field plays a role similar
to temperature for the low-temperature hopping transport in our network. The applied field modifies the energy of hop between two states by an amount $eER\cos\theta$ where $R$ is the separation of the two states, $e$ is the electronic charge and $\theta$ is the angle between field and direction of hop. At high fields for hops in the field direction, electrons can hop without thermal activation by phonons when $eER \approx W$, where $W$ is the thermal hopping energy \cite{12}. Note that the slope of $\beta_G$ versus $\ln G$ is negative at higher temperatures and lower fields. Therefore the assumption of single parameter scaling (with electric field alone) is not completely valid for $T > 0$ and only holds at high fields. Additionally we note that the value of $G_{HF}$ (246 $\mu$S from 2.6 K data) is close to the value of $G_{HF}$ (295 $\mu$S), further supporting the identical effects of field and temperature in the limits of low temperature and low bias respectively.

The $G$-$E$ plot in figure 5 suggest the presence of a threshold field above which the response is non-linear. We define a threshold field ($E_{th}$) for the field response as the value of electric field for which $\Delta G/G(0) \approx 0.2$, where $G(0)$ is the field-independent conductance in the low-field regime. An empirical relation $E_{th} = 0.65T^{0.5}$ is obtained from the slope of the double logarithmic plot of $E_{th}$ versus $T$ in figure 4(b). The exponent of $E_{th}$ does not significantly depend upon the precise way the threshold field is defined; for e.g. $\Delta G/G(0) \approx 0.5$ yields a slope of 1.6 $\approx 3/2$. The threshold field increases with temperature, since higher fields are required to overcome the contribution from phonons. Above $E_{th}$, the carriers start to gain
more of their energy from the electric field than from thermal excitations, until finally the transport becomes activationless at high fields. For 2D Mott VRH, the optimum hopping distance $R \sim T^{-1/2}$ and the average hopping energy $W \sim R^{-2}$, so a simple calculation suggests that the dependence of $E_{opt}$ on temperature will be linear, our exponent is somewhat higher, possibly because the above description holds strictly only at zero bias [12]. We also observe that the quantity $eE_{opt} W \sim \Omega(1)$ when $E \sim E_{opt}$. It is further seen that this empirical relation is nearly independent of applied transverse magnetic fields up to 11 T and it is therefore intrinsic to the role of electric field in hopping conduction and not dependent on the scattering and interference processes associated with magnetic field, as described below.

A negative magnetoresistance (MR) was observed for the network at low temperatures as shown in figure 5(a). For systems close to the metal–insulator transition, the negative MR is often inferred from the suppression of quantum corrections to the conductivity, under magnetic field, i.e. negative MR in weak localization. The interpretation must, however, be consistent with the nature of charge transport. In our disordered network, the temperature and electric-field data support VRH conduction and the magnetotransport must also be analyzed within the same framework. A negative MR in the VRH regime has been suggested to arise from a forward interference scattering process. In this model by Nguyen et al., the application of a magnetic field removes the destructive interference between multistate hops [14]. The MR is linear with field in the low-intermediate-field region and linear fits to our data in this region are shown in
figure 5(a). At 4.2 K there is an additional positive contribution from a different mechanism and a term quadratic in field must also be included along with the linear term in order to obtain a satisfactory fit. This quadratic positive contribution most likely arises from the localization originating from wavefunction shrinkage under magnetic field [15]. However, the fits are not fully satisfactory down to zero-field and this minor contribution can be explained due to the complex nature of the scattering process at very low fields [16]. An analytically simpler version of Nguyen’s model by Schmacher considers only a single intermediate hopping site and this model also predicts the temperature dependence of the negative MR in the weak scattering limit, given as [17]:

$$\ln(\rho(B)/\rho(0)) = -kBT^s = -C_2B$$

where $k$ is a constant, $B$ is the magnetic field, $C_2$ is the coefficient of magnetic field and $s$ is an exponent close to 1; in the case of strong scattering the MR is expected to be temperature-independent. To evaluate the exponent, the temperature dependence of $C_2$ obtained from the above fits is plotted in figure 5(b) on a double logarithmic scale. The slope gives the exponent $s = 0.71 \pm 0.02$, a value slightly lower than the theoretical prediction.

4. Conclusion

Measurements of the low-temperature electric and magnetic field dependence of conductance in transparent SWNT networks are presented. A 2D Mott VRH is observed for the network and a scaling function analysis shows an identical exponent $(-1/3)$ for both high electric field and low temperatures. The charge transport analysis that includes temperature, electric and magnetic field dependences is presented within a consistent framework. Temperature and electric field are shown to play identical roles in the hopping transport. A power-law relation for the temperature dependence of $E_{bg}$ is obtained with an exponent $-3/2$ and is understood to result primarily from the increased contribution of field to the hopping process in comparison to the phonon contribution. A negative MR is observed at low temperatures arising from a forward interference scattering process, and an inverse power-law temperature dependence for this MR suggests a weak scattering process in the system.

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References


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Diameter-Selective Fractionation of HiPeO Single-Walled Carbon Nanotubes in Repeated Functionalization Reactions


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The functionalization reaction of the diamine-terminated oligomeric poly(ethylene glycol) with a purified HiPeO single-walled carbon nanotube sample was repeated multiple times to yield the corresponding number of soluble fractions and the final insoluble residue. According to results from the characterization with various instrumental techniques, these soluble fractions and the final residue all have different nanotube diameter distributions. A general conclusion is that the functionalization and stabilization are selective toward smaller diameter nanotubes, regardless of their being semiconducting or metallic. Mechanistic implications, especially with respect to the post-production separation in terms of the nanotube metallicity, are discussed.

Introduction

A single-walled carbon nanotube (SWNT) is characterized by a pair of chiral indices ($n, m$), which determine the tube diameter ($d$) in terms of the relationship as follows.

$$d = \sqrt{\frac{|3m^2 + n(3n + 3m)}{\phi(C, C)}} \cdot \phi(C, C)$$

where $\phi(C, C)$ is the nearest neighbor carbon-carbon distance. The indices also define the metallicity of the nanotube: a semiconducting SWNT with $n$ and $m = m + n$ and a metallic SWNT with $n = 0$. Various production methods for SWNTs generally yield mixtures of different chiralities. In fact, it is well known that the SWNTs from the high-pressure CO disproportionation (HiPeO) process are of a particularly broad distribution in tube diameters (~0.7-1.3 nm).

There have been significant efforts on post-production separation of SWNTs aimed toward their ultimate „purification” in terms of chiralities, with especially heavy emphasis on harvesting semiconducting- or metal-rich-enriched SWNTs. Interestingly, with only a few exceptions, the reported post-production separation experiments have been carried on HiPeO-SWNTs. The separation effort exploits potentially selective interactions of functional molecules with semiconducting or metallic SWNTs. For example, Tour, Smalley, and co-workers reported that some highly reactive species such as diazonium salts were preferentially added to the sidewalls of metallic HiPeO-SWNTs. 

Similar preferential additions of nitronium ions and fluorine gas were reported recently by others. The approach used by Longincourt and co-workers used the approach of using long-chain molecules bearing amino residues to remove some semiconducting HiPeO-SWNTs from the purified mixture, where the basis of separation was apparently the selectivity of the functionalization agent octadecylamine (OPA) toward semiconducting nanotubes for their solubilization. Maeda et al. reported recently that an opposite selectivity could be achieved with the use of smaller amine molecules such as o-tolylamine and pyrrolidine, namely that metallic instead of semiconducting nanotubes were enriched in the supernatant. On the other hand, the reactivity and interactions of a nanotube with other species are known to be dependent on the tube diameter (or the graphene curvature corresponding to pyramidalization and $\pi$-orbital misalignment). In fact, there is an inverse relationship between the nanotube reactivity and diameter, with the smaller SWNTs being more reactive. Therefore, a significant issue in the post-production separation of SWNTs is the highly interplay between the selectivity toward the tube diameter and the selectivity toward the semiconducting or metallic characteristics. According to reports on the reactivity-based post-production separation, the nitronium ion attack prefers smaller diameter metallic SWNTs, while the oxidation reaction is selective toward smaller diameter SWNTs regardless of metallicity. Also, the selective interactions of ODA molecules with semiconducting SWNTs were found to be more pronounced with the nanotubes of smaller diameters. We reported previously an investigation on repeated functionalization reactions to sequentially extract soluble fractions from arc-discharge-produced SWNTs. Despite the intrinsically narrow diameter distribution in the starting nanotube sample, the functionalization results with the use of diamine-terminated oligomeric poly(ethylene glycol) (PEG) as a functionalization agent suggest a clear preference of the functionalization reaction toward smaller diameter SWNTs. 

In the work presented here, the same approach and similar experimental conditions were applied to the repeated functionalization reactions with HiPeO-SWNTs, in which the diameter-selective fractionation in the solubilization became more evident. The results from the characterization of the functionalized samples are described, and their implication to the effort on using similar functionalization reactions for post-production separation of semiconducting and metallic SWNTs is discussed.
Experimental Section

Materials. Diamine-terminated oligomeric poly(ethylene glycol) (H₂NCH₂CH₂CH₂OCH₂CH₂CH₂NH₂ with a = 35, or PEG₃₅) and sodium dodecyl sulfate (SDS) were purchased from Aldrich, and desalted chloroform and D₂O were purchased from Cambridge Isotope Laboratories. Distilled deionized water (cellulose membrane) with a molecular weight cutoff of ~12,000 was obtained from Sigma-Aldrich.

The HiPco-SWNT sample was supplied by Carbon Nanotechnologies, Inc. and was purified by using a procedure adapted from what is available in the literature. In the purification, the as-supplied nanotube sample (500 mg) was treated with intermittent microwave (800 W) for 20 cycles of 60 s on and 300 s off, followed by refluxing in diluted nitric acid solution (2.6 M, 250 mL) for 12 h. Upon centrifugation (1380g) to discard the supernatant, the sol was repeatedly washed with distilled water until neutral pH was obtained, and then the sample was dried under vacuum to yield the purified HiPco-SWNT sample (~250 mg).

Measurements. Several centrifuge machines were used for low- (Fisher Scientific, Centrifuge Model 220) and high-speed centrifugation (Beckman-Coulter Optima L90K ultracentrifuge with a type 50 Ti fixed-angle rotor). UV/visible/NIR absorption spectra were recorded on a Shimadzu UV-3600 spectrophotometer. Raman spectra were obtained on a Raman Raman spectrometer equipped with a 50 mW diode laser source for 785 nm excitation. A Jobin-Yvon T64000 spectrometer equipped with a triple monochromator, a research-grade Olympus BX-41 microscope, a liquid-nitrogen-cooled CCD detector, and two excitation sources (He-Ne laser for 568 nm and Spectra-Physics 40 mW argon-ion laser for 514 nm excitations). Thermogravimetric analysis (TGA) experiments were performed on a Mettler-Toledo TGA/DSC1 system. Transmission electron microscopy (TEM) digital images were obtained on Hitachi H-7650 TEM and Hitachi HD-2000 STEM/TEM systems.

Functionalization Reactions. In a typical experiment, a mixture of purified HiPco-SWNTs (225 mg) and PEG₃₅ (3.8 g) was heated to 120 °C and stirred under nitrogen protection for 4 days. After the reaction, the mixture was cooled to room temperature and then extracted repeatedly with water for the solubile fraction. Each extraction involved the addition of deionized water (15 mL) and then centrifuging at 1380g to collect the colored supernatant. Typically five repeats were necessary until the supernatant became colorless. The combined solubile fraction was dried via dialysis (molecular weight cutoff of ~12,000) against fresh deionized water for 3 days, and then evaporated to remove water. The insoluble residue after the repeated extractions was dried under vacuum for the next round of functionalization reaction.

In each subsequent functionalization reaction, the same PEG₃₅/nanotube weight ratio of 17/1 was used, and so were the reaction conditions. The reaction mixture was extracted in the same procedure to separate the soluble fraction from the insoluble residue.

All solubile fractions from the repeated functionalization reactions and the final insoluble residue were dried for their various characterization experiments.

Results and Discussion

The functionalization of HiPco-SWNTs with PEG₃₅ was under thermal reaction conditions mechanically; there is presumably the formation of a zwitterionic bond between the amine group in PEG₃₅ and the nanotube-bound carbonyl acid (due to the oxidation of carbon nanotube defects), though none of the different direct adsorption of PEG₃₅ species on the nanotube graphitic surface may also play a significant role in the solubilization of the nanotube. Nevertheless, the functionalization of HiPco-SWNTs with PEG₃₅ for the nanotube solubilization was relatively robust. The solid-state samples for the solubile fractions from the repeated functionalization reactions could readily be dissolved in water or various polar organic solvents. These aqueous or organic solutions were stable over an extended period of time (at least several months), again demonstrating the robustness of the functionalization and solubilization.

Fractionation. A total of five solubile fractions were collected from the five repeats of functionalization reactions. The amount of nanotubes solubilized in each functionalization reaction varied, with the first and second reactions solubilizing 32% and 28% of the starting HiPco-SWNTs, respectively (Table 1). By the fifth reaction, the amount of nanotubes solubilized decreased to 2% of the starting HiPco-SWNTs (Table 1), suggesting no need for further repeats.

The nanotube contents in the solubile fractions and the final residue (listed in Table 1) were determined by using TGA. Shown in Figure 1 are typical TGA traces for the samples. At a heating rate of 10 °C/min in nitrogen atmosphere, the PEG₃₅ weight loss started at 350 °C, while the defunctionalized HiPco-SWNTs remained stable. Quantitatively, the amount of recovered nanotubes from the five solubile fractions and the final residue totaled 235 mg (about 71% in the soluble fractions and 29% in the final residue), in reasonable agreement with the amount of starting HiPco-SWNTs (225 mg). As detailed in Table 1, the nanotube contents in the solubile fractions decreased significantly in subsequent functionalization reactions after the first two repeats, indicating the inhomogeneous nature of the starting purified HiPco-SWNT sample with respect to functionalization and solubilization.

<table>
<thead>
<tr>
<th>fraction</th>
<th>nanotube content (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>71 (70%)</td>
</tr>
<tr>
<td>2</td>
<td>65 (28%)</td>
</tr>
<tr>
<td>3</td>
<td>57 (22%)</td>
</tr>
<tr>
<td>4</td>
<td>41 (17%)</td>
</tr>
<tr>
<td>5</td>
<td>35 (15%)</td>
</tr>
<tr>
<td>final residue</td>
<td>5 (2%)</td>
</tr>
</tbody>
</table>

* Determined by TGA in inert (nitrogen) atmosphere. * Shown in parentheses are weight percents against the total amount including all fractions and the final residue.

Figure 1. TGA traces (N₂, 10 °C/min) of the first (···) and second (-----) solubile fractions and the final residue (····).
The different fractions share some similar material properties. For example, TEM techniques were used to characterize the soluble fractions and the final residue. In the sample preparation, a drop of diluted aqueous solution of the soluble fraction (or aqueous suspension for the final residue) was placed onto a carbon or holey carbon-coated copper grid, followed by solvent evaporation. The TEM images of the soluble fractions show no meaningful differences, as compared in Figure 2. For the final residue, the TEM image suggests that the nanotubes are in larger bundles than those in the soluble fractions, as one might expect.

The soluble fractions were also evaluated by using 1H NMR. At a relatively dilute concentration of 10 mg/mL in D2O, the observed spectra of the fractions appear similar, each with a broad signal centered at ~3.6 ppm (Supporting Information). This is readily assigned to the ethylene protons in the PEG-solvent functional groups. The broadness of the peak is consistent with the functional groups being attached to SWNTs, which are species with large molecular weights and low mobilities.24

Diameter Selectivity. The optical spectroscopy results of the soluble fractions and the final residue suggest significant diameter preference in the reported functionalization reactions, resulting in different diameter distributions of HiPco-SWNTs in the various fractions.

The solution-phase optical absorption spectra of the soluble fractions (except for the fifth fraction due to limited sample quantity) were measured in D2O to avoid spectral interference in the near-IR region. The solutions were prepared by direct dissolving the solid samples into D2O. Similarly, the starting purified HiPco-SWNT sample and the final residue were suspended in D2O with the assistance of SDS (6.5 mg/mL), which is a surfactant widely used in the literature for optical spectroscopy of SWNTs.25 These solutions and suspensions in D2O (all with 2 mg/mL nanotubes-equivalent concentrations) were centrifuged at 137,000g for 2 h before the optical spectral measurements. As shown in Figure 3, the spectrum of the starting purified sample is resolved with spectral features typical of HiPco-SWNTs after similar purification treatment.26 The peak features at 900–1600 nm and 550–900 nm are commonly assigned to groups of electronic transitions corresponding to the first and second pairs of van Hove singularities in the density of states (DOS) for various semiconducting SWNTs (denoted as S11 and S21, respectively, and note that at 400–650 nm corresponding to first transitions of various metallic SWNTs (denoted as M11).13,14,127 The absorption spectra of the solubilized samples remain similarly resolved with S11, S21, and M11 peak features in their respective spectral ranges (Figure 3), suggesting that the nanotube electronic structures are retained in the functionalization with PEG-2000. This is consistent with previously reported results on the PEG-2000 functionalization of SWNTs from previous production methods.25,26

A closer examination of the absorption spectra reveals significant and systematic changes in the detailed spectral peak features from fraction to fraction, reflecting the underlying variations in diameter distributions of the HiPco-SWNTs. For the S21 bands, more features of the first soluble fraction are at shorter wavelengths (roughly below 1200 nm) in comparison with those of the starting purified sample. In the later soluble fractions, however, more significant spectral features are in the longer wavelength region (especially above 1200 nm). The changes in S21 bands are in a similar trend, with those of the first soluble fraction featured more in the 650–750 nm region, while those of later fractions are more in the 750–900 nm region (Figure 3). It is known that electronic transition energies of SWNTs are inversely related to the nanotube diameters. Thus, the absorption results suggest that the smaller diameter semiconducting SWNTs were preferentially solubilized in the earlier fractions.

The diameter-selective fractionation in the repeated functionalization reactions is more evident in the results of resonance Raman spectroscopy. The Raman measurements were performed at multiple excitation wavelengths of 785 nm (1.58 eV), 632 nm (1.96 eV), and 514 nm (2.41 eV). In order to avoid the
known luminescence interference with functionalized nanotube samples, the soluble fractions and the final residue were thermally defunctionalized (heated to 600 °C and kept for 2 h in inert atmosphere) before the Raman characterization.

For the starting purified sample, the Raman spectrum at 785 nm excitation exhibits typical features of the G-band at 1592 cm⁻¹, D-band at 1330 cm⁻¹, and radial breathing modes (RBMs) in the 100–300 cm⁻¹ region (Figure 4), in agreement with those reported previously. Here the 785 nm excitation is in resonance with mostly semiconducting HiPco-SWNTs of various diameters but with few of their metallic counterparts. Also shown in Figure 4 are Raman spectra of the soluble fractions and the final residue with the same 785 nm excitation. The G-band features are similar among all these samples, with the bands being relatively narrow and symmetrical. However, there are systematic changes in the RBM region, with the spectra of the fullerene fractions enriched with higher frequency features (corresponding to smaller diameter semiconducting SWNTs) and with those of the later fractions and the final residue with lower frequency features (corresponding to larger diameter semiconducting SWNTs). For example, the spectrum of the first soluble fraction shows the 264 cm⁻¹ peak higher in intensity than peaks in the 188–216 cm⁻¹ and 217–242 cm⁻¹ regions, but the spectrum of the fifth soluble fraction exhibits a nearly opposite peak intensity pattern (those of the other fractions are apparently intermediate between the two) (Figure 4). In the spectrum of the final residue, only peaks at 189 and 206 cm⁻¹ could be observed. It is known that the RBM peak frequency (ω_RBM, cm⁻¹) is inversely related to the corresponding SWNT diameter (d, nm) in terms of the equation ω_RBM = 223.5d + 12.5 (see also Supporting Information). Thus, the initial functionalization reaction in multiple rounds was obviously selective toward the smaller diameter nanotubes among the population of semiconducting HiPco-SWNTs.

The Raman spectra were also measured with 632 and 514 nm excitations (coupled with the use of a triple monochromator) for a closer examination of the low-frequency region, despite the fact that different HiPco-SWNTs (from those with 785 nm excitation) are in resonance with these excitation wavelengths. The RBM features in the spectra exhibit systematic changes in a trend similar to that found with the 785 nm excitation. Generally, the earlier fractions are with more intense high-frequency RBM features, and the later fractions and the final residue are with more intense lower-frequency RBM features.
G-band results with 632 and 514 nm excitations are consistent with the enrichment of larger diameter HiPco-SWNTs (indicating semiconducting and metallic ones, respectively) in the later soluble fractions and the final residue.

Optical absorption spectra and resonance Raman results with three different excitation wavelengths apparently suggest that the functionalization reaction of PEOPEm with the purified HiPco-SWNT sample is selective towards those nanotubes of smaller diameters, regardless of their being semiconducting or metallic. This may have significant implications to the effort on the post-production separation of semiconducting and metallic SWNTs.

Mechanistic and Other Implications. A characteristic feature of as-supplied or purified HiPco-SWNTs is the broad distribution of nanotubes of different diameters. Therefore, it is hardly surprising that the diameter selectivity becomes an issue in various functionalization reactions. For the thermal reduction conditions used in this study, the preference of PEOPEm molecules toward smaller diameter HiPco-SWNTs is probably associated with their direct adsorption onto the nanotube surface. The role of such noncovalent but specific interactions in the stabilization of carbon nanotubes has been suggested for other long-chain functionalization agents with primary amine moieties. As for the selectivity toward smaller diameter HiPco-SWNTs, the specific interactions responsible for the direct adsorption may be mechanistically similar to those found in the addition of highly reactive species to the nanotube sidewalls.

The diameter selectivity in functionalization reactions (including the adsorption) could potentially alter the population balance between semiconducting and metallic nanotubes if the two nanotube types were of different diameter distributions, which could thus result in the observation of enrichment in one over the other in various reaction mixtures or fractions. Hypothetically, should the starting sample be populated with more smaller diameter semiconducting nanotubes than their metallic counterparts, the preferential solubilization of the former would obviously leave more metallic nanotubes in the insoluble residue, and vice versa. Therefore, it might be possible, at least in principle, that the interplay between diameter and metallicity fractions in the functionalization and solubilization of HiPco-SWNTs with long-chain amine compounds like PEOPEm and CDA could be driven primarily by the diameter selectivity. This is an interesting topic that deserves further investigations.

In summary, the repeated functionalization reactions of PEOPEm molecules with purified HiPco-SWNTs resulted in multiple soluble fractions and the final insoluble residue. These fractions have different nanotube diameter distributions from that found in the starting purified HiPco-SWNT sample. A general conclusion is that the first nanotubes solubilized are smaller diameter ones, regardless of their being semiconducting or metallic. The results reported here and those already in the literature suggest that because of the intrinsically broad diameter distribution in HiPco-SWNTs, diameter selectivity plays an important role in the reactions or specific interactions designed or exploited for the post-production separation of the nanotubes into semiconducting and metallic enriched fractions. Further experimental investigations on the existing and other amine-bearing functionalization or dispersion agents are required for a better understanding of the various selectivities.

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Polymeric nanocomposite films from functionalized vs suspended single-walled carbon nanotubes

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Abstract

The reported work was to demonstrate that the defect-derived photoluminescence in functionalized single-walled carbon nanotubes could be exploited in probing the dispersion of these nanotubes in polymeric nanocomposites because the luminescence emissions are sensitive to the degree of nanotube bundling and surface modification. The polyimide-SWNT nanocomposite thin films obtained from nanotubes with and without functionalization were compared. The spectroscopic results suggest that despite a similar visual appearance in the two kinds of films, the nanotube dispersion must be significantly better in the film with functionalized nanotubes, as reflected by the strong photoluminescence. In fact, the nanotubes embedded in polyimide matrix that can be readily characterized by Raman spectroscopy are non-luminescent, while those that are difficult for Raman are strongly luminescent. Therefore, Raman and photoluminescence serve as complementary tools in the investigation of nanocomposites concerning the nanotube dispersion related properties.

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Keywords: Carbon nanotubes; Nanocomposites; Photoluminescence

1. Introduction

Polymeric nanocomposites with single-walled carbon nanotubes (SWNTs) as fillers have received much recent attention for their widely predicted superior electronic, thermal, and mechanical properties [1–3]. An important issue in the development of such nanocomposites is the dispersion of SWNTs, since as-produced SWNTs are severely bundled and entangled due largely to the strong inter-tube van der Waals interactions [1]. There is hardly any solubility of the nanotubes in common solvents, which substantially impairs their processability. Thus, the direct incorporation of as-produced SWNTs into polymer matrices usually results in poor nanotube dispersion in the nanocomposites, with the actual performance significantly worse than expected [4]. In order to improve the dispersion, so as to maximize the transformation of the nanotube properties to the resulting nanocomposites, the functionalization of SWNTs has been identified as an effective approach [3–6]. For example, Lin et al. reported that poly(vinyl alcohol) (PVA) could be used to functionalize SWNTs for their exfoliation and solubilization and that the functionalized nanotube sample could be homogeneously dispersed into PVA matrix for high-quality nanocomposites without introducing any unwanted foreign materials [7].

In a different approach, selected polymers and common surfactant molecules have been used to aid the suspension of SWNTs in various solvents [8–10]. It has been shown that polyimide is particularly effective in stabilizing the nanotube suspension, and the resulting suspension can be used to fabricate polyimide–SWNT nanocomposites, which are also free from other agents [11]. The nanocomposites thus prepared are visually similar to those obtained from functionalized nanotube samples, despite their expected significant difference with respect to the dispersion of the embedded SWNTs.
Commonly employed nanoscale characterization techniques such as high-resolution electron microscopy may in principle be applied to an evaluation of the dispersion issue, though the preparation of specimens for the microscopy analyses can be challenging. For example, the microtome process to obtain ultra-thin slices of the nanocomposite often distorts the original distribution of embedded nanotubes in the polymer matrix [12]. As a result, optical spectroscopy methods including especially Raman are widely pursued for the characterization of polymer-SWNT nanocomposites in a convenient and rapid fashion [13–15]. However, Raman is not so useful in the investigation of nanocomposites obtained from homogeneously dispersed functionalized carbon nanotubes because of overwhelming interference of photoluminescence from these nanotubes [6,16].

In this work, we wanted to demonstrate that the photoluminescence in functionalized SWNTs could be exploited in probing the dispersion of these nanotubes in polymeric nanocomposites because the luminescence emissions are sensitive to the degree of nanotube handling and surface modification. In fact, the nanotubes embedded in polymer matrix that can be readily characterized by Raman are non-luminescent, while those that are difficult for Raman are strongly photoluminescent. Therefore, Raman and photoluminescence may serve as complementary tools in the investigation of nanocomposites concerning the nanotube dispersion-related properties. The polyimide-SWNT nanocomposite films obtained from nanotubes with and without functionalization are compared. The films have also been examined by electron microscopy techniques to support the spectroscopic results.

2. Experimental section

2.1. Materials

4,4′-(Hexafluoroisopropylene)diphthalic anhydride (99%) was purchased from Aldrich, 1,3-bis(3-aminophenoxy)benzene and 4,4′-(hexafluoroisopropylene)-diphthalic anhydride with a calculated excess of the former to ensure the amino group termination and the control of the polymer molecular weight to approximately 5000 [18]. The functionalization of SWNTs by PI-NH2 was achieved in carbodiimide (EDAC)-activated amidation reaction of the terminal amino groups in PI-NH2 with the defect-derived carboxylic acid groups on the nanotube surface, as reported previously [18] (Scheme 1).

2.4. Nanocomposite films

For film with suspended SWNTs, a purified SWNT sample (5 mg) was dispersed in DMF (3 mL) and homogenized (PowerGen 125) for 1 h under flowing N2. A DMF solution of the CP-2 polyimide (1 mL, 125 mg/mL) was added to the nanotube suspension under constant stirring, and the mixture was sonicated (VWR Aquasonic 150 HT) for 12 h. The resulting suspension was further stirred to slowly evaporate the solvent until the total volume reduced to approximately 2 mL. The viscous suspension thus obtained was cast onto a glass substrate with an adjustable film applicator (Gardco), and kept in flowing N2 for 24 h. The film was further cured under the same atmosphere at 100 °C for 1 h, 150 °C for 1 h, 200 °C for 1 h, and finally dried in vacuum at 60 °C for 48 h.

For film with functionalized SWNTs, a DMF solution of PI-NH2-SWNT (3 mL, 33 mg/mL) was added dropwise to a DMF solution of CP-2 (4 mL, 500 mg/mL) under constant stirring. The mixture was vigorously agitated until
homogeneous, followed by essentially the same casting and drying procedures as described above.

3. Results and Discussion

3.1. Purification and functionalization of SWNTs

The commercially available SWNT sample was purified by using an established procedure of first heat treatment (300 °C) in air and then refluxing in diluted nitric acid (2.6 M) to remove amorphous carbonaceous impurities and residual metal catalysts from the sample [17]. According to discussion in the literature concerning the effectiveness of the procedure [19,20], the purification should be adequate for the purpose of preparing polymeric nanocomposites used in this work.

The purified SWNT sample was used in the functionalization with PI-NH₂. The target of functionalization was the amidation of nanotube-bound carboxylic acid groups, which are known to be present in the oxidative acid-treated sample [6,21]. The functionalized nanotube sample PI-NH₂-SWNT was characterized by using various instrumental techniques to have the results calibrated with those reported previously [18]. For example, the ¹H NMR signals of the terminal amine protons in PI-NH₂-SWNT were at 5.9–6.1 ppm, shifted upfield from those in the PI-NH₂ spectrum (6.0–6.4 ppm) due to effects of the large aromatic ring currents in the attached carbon nanotubes [18]. The PI-NH₂-SWNT sample was readily soluble in many organic solvents including THF and DMF to form dark-colored solutions. The solution-phase optical absorption spectrum of the sample in DMF exhibited features at ~1800 cm⁻¹ (despite the interference from solvent background) and ~1600 cm⁻¹, corresponding to electronic transitions between the first (S₁) and second (S₂) van Hove singularity pairs in semiconducting SWNTs, respectively (Fig. 1(a)). The first electronic transition of metallic SWNTs (M₁) could also be detected at ~700 cm⁻¹ (Fig. 1(a)). The observation of these characteristic absorption features is consistent with the expectation that the functionalization of SWNTs targets the defect-derived carboxylic acid moieties on the nanotube surface. This mode of functionalization is known to preserve the electronic absorption properties of SWNTs [21].

It is known that SWNTs without functionalization may be dispersed into polar solvents with the aid of surfactants or polymers such as poly(phenylene vinylene) [22] and poly(vinyl pyrrolidone) [8], due presumably to non-covalent interactions. The polyimide CP-2 is somewhat special in this regard [11], such that SWNTs are readily suspended in a DMF solution of CP-2, and the suspension appears homogeneous. The absorption spectrum of the suspended SWNTs is also shown in Fig. 1. However, while the suspension is stable and looks similar to the solution of the functionalized sample PI-NH₂-SWNT (similar absorption spectra as well, Fig. 1(a)), the molecular level structures and properties of the suspended and functionalized SWNTs must be different. A clear indication for such difference is in the results of nanotube photoluminescence, which is associated with passivated surface defects in exfoliated carbon nanotubes [6,16,23–25]. As compared in Fig. 1. (a) Optical absorption spectra of PI-NH₂-SWNT in DMF solution (—) and polyimide-assisted SWNT suspension in DMF (—·—). (b) Optical absorption spectra of nanocomposite films from the functionalized (——) and suspended (—·—) SWNTs.
suspended nanotube samples were controlled to the nanotube loading of 1% by weight and a similar thickness of about 80 μm. As shown in Fig. 1(b), optical absorption spectra of both films exhibit the characteristic S₁₁ (around 1000 nm) and S₂₁ (around 1000 nm) bands for semiconducting SWNTs and also the M₁₁ absorption (around 700 nm) for metallic SWNTs, similar to those of the PI-NH₂-SWNT solution and suspended SWNTs in DMF (Fig. 1(a)). These spectral features confirm the expected preservation of electronic structures for the SWNTs embedded in the CP-2 polymer matrix.

In a closer examination of the absorption spectra, the S₁₁ and S₂₁ bands of the film with functionalized SWNTs are somewhat narrower in bandwidth than those of the film with suspended SWNTs, and the former are also slightly blue-shifted (Fig. 1(b)). These subtle changes in absorption spectral features are consistent with the improved dispersion of the functionalized SWNTs in the polymer matrix. As proposed in the literature [27], van der Waals interactions between nanotubes in a bundle help the overlap between electronic transition states and reduce the band gap of the nanotubes. Therefore, the exfoliation of bundled SWNTs brought about by functionalization gives rise to a better dispersion in the nanocomposite film resulting in narrower and blue-shifted band gap absorption bands.

The improved dispersion of the functionalized SWNTs in the nanocomposite film is reflected by the observation of strong photoluminescence in the visible (Fig. 3), as it is known that the nanotube defect-derived luminescence emission is sensitive to the exfoliation and surface passivation of the nanotubes [16]. Generally speaking, a better functionalization of SWNTs means more effective surface passivation of the defect sites and leads to more homogeneous dispersion (less bundling), which correspond to enhanced photoluminescence emissions with minimized inter-tube quenching [16]. For the film obtained from the suspended SWNTs, although the macroscopic appearance showed no dramatic difference from that of the film with functionalized SWNTs, the nanoscopic structure of the film must be different. The nanotube bundles in the original

Fig. 3. Luminescence emission spectra (550 nm excitation) of the films from (a) suspended SWNTs and (b) PI-NH₂-SWNT. Shown in the insets are corresponding confocal microscopy images of the films (638 nm excitation, 2469 nm detection, scale bar = 5 μm).

3.2. Nanocomposite films

The solution of PI-NH₂-SWNT and the suspension of purified SWNTs, both in DMF, were used in the fabrication of polyimide (CP-2)-SWNT nanocomposite films via wet-casting. The fabrication procedures were largely similar between the two samples (except for the homogenization and sonication required for the suspended SWNTs), and the resulting films also appeared similar. Since the nanotube contents in the functionalized and suspended samples were known (from quantitative ¹H NMR signal integration [18] and the amount of added nanotubes, respectively), the nanotube contents in the resulting nanocomposite films were obtained by quantifying the amount of blank CP-2 polymer used in the preparation of the mixtures for wet-casting. The films from both the functionalized and suspended nanotube samples appeared similarly optically transparent when the nanotube loading was low or the films were ultra-thin.

The color of the films was dependent on the nanotube content and also the film thickness. The films with higher nanotube contents appeared black. For a better comparison, the two kinds of films obtained from the functionalized and
suspension were likely carried over into the nanocomposite film, and the bundled SWNTs embedded in the CP-2 polymer matrix were essentially non-luminescent (Fig. 3). Therefore, the measurement of defect-derived luminescence emissions serves as a convenient and non-destructive technique in the evaluation and analysis concerning the degree of nanotube dispersion in polymeric nanocomposites qualitatively or even quantitatively (by comparing different films or the use of standards).

The strong photoluminescence in functionalized nanotube samples is known to interfere with Raman analyses of these samples in an overwhelming fashion [6]. In fact, the better the nanotube functionalization and dispersion, the stronger the interference becomes. The Raman results on the two kinds of polyimide (CP-2)-SWNT nanocomposite films were as expected. For the film with functionalized SWNTs, the nanotube Raman signals could be detected only with the use of lower laser power at the expense of sensitivity, making the characteristic features of SWNTs poorly defined on top of a huge luminescence background in the observed Raman spectrum (Fig. 4). This is consistent with the film being strongly photoluminescent, as discussed above (Fig. 3). The film with suspended SWNTs, on the other hand, was non-luminescent, so that characteristic Raman features of the embedded SWNTs were clearly observed. With a subtraction of the luminescence background, the G-band and D-band features for functionalized SWNTs in the film can be identified at 1593 and 2642 cm\(^{-1}\), respectively, which are at slightly higher frequencies than those for the suspended SWNTs in film (1587 and 2631 cm\(^{-1}\), respectively). Therefore, it might be argued that there is the commonly acknowledged enhancement in polymer-nanotube interactions [13-15] in the film with functionalized SWNTs. With probably similar effect, the radial breathing mode (RBM) feature at 179 cm\(^{-1}\) for the film with functionalized nanotubes is also at a slightly higher frequency than that of the film with suspended nanotubes (170 cm\(^{-1}\)).

In order to allow a more direct evaluation on the nanotube dispersion in the films, micromantic techniques were employed to obtain ultra-thin (about 100 nm) slices. An SEM image for a slice from the film with functionalized SWNTs is shown in Fig. 5, which seems consistent with a well-dispersion of the nanotubes in the film. The slice was also evaluated by using high-resolution TEM. The specimen was highly sensitive to the electron beam, which instantly created nanoscopic gaps in the film slice. There were mostly individual SWNTs bridging the gaps, as shown in Fig. 5. However, for the film with suspended SWNTs, the slices from micromantic were of poor quality, inadequate for any conclusive SEM and TEM analyses.

Alternatively, the polyimide nanocomposite films with the functionalized and suspended SWNTs were both stretched to failure, and the fracture edges were examined by using SEM for the morphological characteristics (generally reflecting the
nanotube dispersion and load transfer efficiency in the films) [28,29]. As shown in Fig. 6, the fracture surface morphology is different between the two films. For the film from suspended SWNTs, there are plenty of exposed nanotube thick bundles on the fracture surface (the appearance of more nanotubes than what might be expected from the film composition probably due primarily to the nanotube bundles being pulled out of the polymer matrix in the stretching and also to inhomogeneous distributions of nanotubes in the film). This is obviously not the case at the fracture edge of the film from functionalized SWNTs. Despite the same overall nanotube loading, the homogeneous dispersion and better polymer wetting of functionalized SWNTs in the film are likely responsible for the apparently different fracture surface morphology (Fig. 6).

In summary, the polyaniline–SWNT nanocomposite thin film prepared from polyaniline–functionalized SWNTs was compared to that from purified SWNTs in polyaniline-assisted suspension. At the same nanotube contents and film thicknesses, the visual appearance was hardly different between the two kinds of films. However, the nanotube dispersion must be significantly better in the film with functionalized SWNTs, as reflected by the strong photoluminescence in the luminescence emission spectroscopy and confocal microscopy results of the film. The results from other characterization techniques including optical absorption, Raman, and electron microscopy are consistent with the conclusion on the better dispersion of functionalized SWNTs in the film for improved compatibility with the matrix polymer and more efficient load transfer. Further studies to compare the two kinds of films for more specific material properties (such as mechanical [28], thermal, and electrical) and performance should be interesting.

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References


Solubilization of boron nitride nanotubes

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A successful attempt in the functionalization and solubilization of boron nitride nanotubes (BNNTs) is reported, and a functionalization mechanism based on interactions of amino functional groups with nanotube surface borons is proposed.

There has been much recent interest in boron nitride nanotubes (BNNTs) for their electronic, thermal, and mechanical properties, which are very close to or even superior to those of carbon nanotubes. For example, BNNTs are semiconductors with a wide band-gap (4.5 eV) independent of the nanotube chirality or morphology. The thermal conductivity, oxidation resistivity, thermal and chemical stability, and yield resistance of BNNTs are higher than those of their carbon analogue. Among widely discussed unique applications of BNNTs are their use as nanoscale semiconductors operating in oxidative environments at high temperatures and as insulating nanocomposites of high thermal conductivity.

Most investigations in the literature were focused on BNNTs in the solid state, because these nanotubes, like their carbon counterparts, are generally insoluble in common organic and aqueous media. For carbon nanotubes, the research effort on their functionalization and solubilization has stimulated and enabled the exploitation of the properties and applications that are not accessible in the solid state, such as the dispersion of carbon nanotubes in polymer nanocomposites and the compatibility with biological systems. Similarly significant efforts on the research of BNNTs may be expected from the introduction of the nanotubes into homogeneous solution. We report here a successful attempt in the solubilization of BNNTs. The solubilization was based on interactions of amino groups in oligomeric diamine-terminated poly(ethyleneimine) (PEI) with the BNNT surface, conceptually similar to those proposed in the solubilization of carbon nanotubes. The solubilization procedure and results from the characterization of BNNTs before and after the solubilization are presented and discussed.

BNNTs were synthesized by the carbon nanotube synthesis reaction, in which purified multiple-walled carbon nanotubes (MWNTs, Nanostructure & Amorphous Materials, Inc.) were used as a template to react with boron oxide (powder, 99.8%, Alfa Aesar) and hydrazine monooxide (National Wickersam Supply Company) in a quartz chamber at high temperature (1200 °C), followed by thermal treatment (780 °C) in low-pressure air to remove the residual carbon from the sample. The X-ray photoelectron spectroscopy (XPS, Kratos AXIS Hf5) analysis of the sample yielded a B:N ratio of 1.05:1, with the slight excess of boron due to residual boron oxide. Upon further purification by repeated washing with hot water to remove boron oxide, the content of BNNTs in the sample was at least 75% by weight, comparable with those reported in the literature.

The thermogravimetric analysis (TGA, Mettler-Toledo TGA/SDTA851E) result of the sample in air is shown in Fig. 1. The weight increase at high temperatures was due to the oxidation of boron in the BNNTs, and the amount of increase (c. 25%) was consistent with the estimated BNNT content in the sample.

The presence of BNNTs in the sample was confirmed by scanning electron microscopy (SEM, Hitachi S-4700) and transmission electron microscopy (TEM, Hitachi H-9000) characterization. The SEM image in Fig. 2 (top) shows abundant nanotubes. The TEM image in Fig. 2 (bottom) shows a thin film of BNNTs on the liquid nitrogen substrate, which is supported by the excellent solubility of the functionalized BNNTs in water.

The BNNTs were solubilized via functionalization with amine-terminated oligomeric poly(ethyleneimine) (PEI) (Scheme 1). In a typical experiment, a sample of BNNTs (42 mg) was mixed with PEI (800 mg), and the mixture was kept at 100 °C and kept at that temperature for 3 days under nitrogen protection. Upon cooling to ambient temperature, the reaction mixture was extracted repeatedly with diethyl ether, followed by centrifuging at 3000 g. According to the weight of the solid residue, the major portion of the starting BNNTs was solubilized in water as a result of the functionalization with PEI (Scheme 1).

The functionalized BNNTs are soluble in water and organic media compatible with PEI. While BNNTs are colorless, the attachment of PEI in the functionalized BNNTs changed the sample color to brown (Fig. 3). Both the functionalization procedure and the characterization of BNNTs before and after the functionalization are presented and discussed.

Fig. 1 A TGA trace of the BNNT sample (air, 10 °C min⁻¹), where the weight increase is due to the addition of oxygen.
the solution color are likely due to interactions of the PEG 
aminogroups with nanotubes, as proposed in Scheme 1. 
According to results from control experiments, the amino moiety 
in the functionalization agent is necessary for the functionalization 
and solubilization of BNNTs. In fact, there was no solubilization 
at all when the nanotube sample was simply heated in neat 
dionized water under the same experimental conditions. Similarly, 
no meaningful solubilization was found with the use of alcohol-
terminated or methoxy-terminated PEG (PEG-OH and 
PEG-CH2OH, respectively) as the functionalization agent.

![SEM and TEM images of the purified BNNTs](image1)

**Fig. 2** SEM (top) and TEM (bottom) images of the purified BNNTs.

![Scheme 1](image2)

**Scheme 1**

![FT-IR spectra of the starting (a) and recovered (b) BNNT samples in a KBr matrix.](image3)

**Fig. 4** The FT-IR spectra of the starting (a) and recovered (b) BNNT samples in a KBr matrix.

The functionalization of BNNTs with PEG_{3000} was reversible. 

The brown-colored solution of PEG_{3000}-functionalized BNNTs 
was placed in a membrane tubing (molecular weight cutoff 
\( \sim 12000 \)) for dialysis against fresh deionized water. In less than 
2 days, the color disappeared and the solution turned into a 
suspension (Fig. 3), from which colorless BNNTs were recovered 
almost quantitatively via simple low-speed centrifuging. As shown 
in Fig. 4, the FT-IR (Thermo-Nicolet Nexus 670) spectral features 
of the recovered BNNTs are generally the same as those of the 
starting BNNTs (except for several small peaks due to residual 
PFG_{7000}) with the characteristic peaks at 1380 cm\(^{-1}\) and 
800 cm\(^{-1}\) due to N-N vibrations parallel and perpendicular to 
the nanotube axis, respectively.

Additional experiments were performed to confirm that the 
solution color was indeed associated with the PEG_{3000}-BNNT 
interactions. One was to precipitate the PEG_{3000}-functionalized 
BNNTs from the brown-colored solution via high-speed centrifuging. At 25000 g for 30 min, brownish precipitates were 
observed, and the solution became only slightly yellowish, 
suggesting that the color was attached to the nanotubes.
another experiment, the PEG_{1000}-functionalized BNNTs were dialyzed against an aqueous solution of the PEG_{1000} with matching concentration. No meaningful precipitation or change in solution color were observed after the dialysis. Thus, the color must be a part of the functionalization, as proposed in Scheme 1.

The dispersion of the PEG_{1000}-functionalized BNNTs was examined by both TEM and AFM (Molecular Imaging PicoPlus). For the TEM specimen, a small drop of an aqueous solution of the functionalized BNNTs was placed on a holey-carbon-coated copper grid, followed by solvent evaporation. As shown in the TEM image in Fig. 5, the nanotubes are well-dispersed. The sample for AFM measurement was deposited on a mica substrate. However, the presence of abundant functionalized group PEG_{1000} made the imaging somewhat difficult. Thus, the specimen was treated at 400 °C in air for 1 h to remove some of the attached PEG_{1000} molecules from the sample. The subsequent AFM image of the thermally treated specimen exhibits island-like structures on the nanotube surface (Fig. 5), which may be attributed to the remaining PEG_{1000} functional groups.

In summary, BNNTs could be introduced into homogeneous aqueous and organic solutions via the functionalization with oligomeric PEG molecules bearing amino moieties. The color change of the sample from colorless to brown upon the functionalization was identified as being associated with interactions between the PEG amino groups and the nanotube surface. Both the solubilization and the color change were found to be reversible, which could be interpreted mechanistically as being due to the formation and dissociation of amine-boron ionic bonds. The solubilization via functionalization may add a new dimension in applications of BNNTs, such as their homogeneous dispersion in nanocomposite materials for unique thermal and optical properties.

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MATERIALS AND INTERFACES

Polymeric Nanofibers from Rapid Expansion of Supercritical Solution

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The use of the supercritical fluid technique, rapid expansion of a supercritical solution into a liquid solvent (RESOLV), to process polymers into nanofibers (less than 100 nm in diameter) is reported. It is found that the polymer concentration in the pre-expansion supercritical solution plays a critical role in determining the dominating product morphology between nanoparticle and nanofibers. For the CO2-soluble poly(heptadecafluoroctyl acrylate) (PHFDCA), as an example, the rapid expansion of the polymer solutions in supercritical CO2 with low and high PHFDCA concentrations into an ambient aqueous NaCl solution produces exclusively nanoparticles and nanofibers, respectively. The RESOLV processing of poly(methyl methacrylate) (PMMA) and biodegradable polymer poly(ε-lactic acid) (PLA) in supercritical CO2–co-solvent system into nanofibers is also described and discussed.

Introduction

Nanofibers are ultra-fine solid fibers (100 nm or less in diameter) notable for their characteristic features such as large surface area and superior mechanical properties. The current production of nanofibers is primarily by electrospinning,1 though other techniques have been developed for specific systems and applications.2–5 For example, template-guided polymerization methods including the use of zeolite channels,6 nanoporous membranes,4 micelles,7 and liquid crystals8 have been applied to the preparation of nanofibers. The advantages and limitations of these methods have been evaluated and discussed,1,2,7 and the development of new and versatile techniques, especially those for the production of clean, uniform, and template-free polymeric nanofibers, still represents a significant research interest.

Rapid expansion of supercritical solution (RESS) is a supercritical fluid processing technique investigated extensively for the production of polymeric particles and fibers.9–12 In traditional RESS, the solute is dissolved in a supercritical fluid to form a solution, followed by the rapid expansion of the solution across an orifice or a capillary nozzle into ambient air. The high degree of supersaturation accompanying the rapid pressure reduction in the expansion results in homogeneous nucleation and thereby the formation of well-dispersed particles.13–17 Results from mechanistic studies of different solute systems by the RESS process indicate that both nano- and micro-sized particles are present in the expansion jet, though microparticles are generally obtained as primary products due to the particle growth processes of efficient condensation and coagulation.13,16,17

In RESS under well-controlled conditions, polymeric fibers of micrometers or larger diameter may be obtained as primary products.8–12 We have modified the traditional RESS by expanding the supercritical solution into a liquid solvent instead of ambient air, or the rapid expansion of a supercritical solution into a liquid solvent (RESSOLV).18–20 We have shown that the RESOLV process produces exclusively polymeric particles of less than 100 nm in diameter.3,9,25 Mechanically, the use of a liquid at the receiving end of the rapid expansion in RESOLV probably inhibits or disrupts the condensation and coagulation in the expansion jet, thus effectively quenching the rapid particle growth processes. Under the rapid expansion conditions suitable for the fiber formation, the same quenching effect in RESOLV should make it possible to obtain primarily polymeric nanofibers. Here we report that this is indeed the case, namely that nanofibers of less than 100 nm in diameter can be produced from various polymers in RESOLV with the use of relatively concentrated supercritical solutions for the rapid expansion.

Experimental Section

Materials. Poly(heptadecafluoroctyl acrylate) (PHFDCA, Mn = 254 000 g/mol and polydispersity index = 3) was kindly provided by Prof. Robert Knick (Chemical Engineering, University of Pittsburgh, Pittsburgh, PA). Poly(methyl methacrylate) (PMMA, Mn = 55 000 g/mol) and sodium chloride (NaCl) were purchased from Aldrich. The polymer samples were used as received.
was obtained from Fisher Scientific, and was distilled over molecular sieves and then filtered before use. Carbon dioxide (high purity SFC grade) was supplied by Air Products. Water was deionized and purified by being passed through a Labconco WaterPro water purification system.

RESOLV. The experimental setup for the preparation of polymeric nanofibers is similar to what has been reported previously. In a typical experiment, a relatively concentrated solution (up to 5 wt %) of the selected polymer in CO₂ was prepared in the syringe pump. The solution was pushed through the heating unit (copper block wrapped with stainless steel tubing) to reach the desired supercritical temperature before the expansion nozzle. The nozzle was a fused-silica capillary held in a stainless steel tubing (60 μm i.d. and 20 mm long). The rapid expansion was through the nozzle into the chamber containing an ambient solution or solvent in which the polymer is insoluble.

For polymers of low solubility in supercritical CO₂, a co-solvent was added to the syringe pump in the proportion of the supercritical solution for rapid expansion.

Measurements. Scanning electron microscopy (SEM) analyses were performed on a Hitachi S4700 Field Emission SEM and a Hitachi HD-2000 STEM system by using the STEM mode of the instrument. The specimen for SEM imaging was prepared by depositing a few drops of a dilute suspension onto carbon tape, followed by evaporating the solvent under ambient condition, and then coating the sample with platinum to minimize charging effects.

Results and Discussion

The polymer PHDFDA is readily soluble in liquid and supercritical CO₂, making it possible to use relatively concentrated solutions for rapid expansion in RESOLV. For example, a solution of PHDFDA in CO₂ with a high concentration of 5 wt % was prepared in the syringe pump and heated to 40 °C before the expansion nozzle. The rapid expansion was carried out at a preexpansion pressure of 250 bar through the capillary nozzle into an ambient aqueous NaCl solution (1.5 M). Since PHDFDA is insoluble in water, the polymer precipitated out of the aqueous receiving solution. A small aliquot of the aqueous solution suspended with the precipitates was used to prepare a specimen for SEM analysis. The SEM images show that the primary products from the RESOLV process are bundles of PHDFDA nanofibers with diameters less than 100 nm (Figure 1).

The product morphology from RESOLV is apparently dependent on the PHDFDA concentration in the pre-expansion supercritical CO₂ solution. At a much lower supercritical pressure (0.5 wt %, for example), the RESOLV process produces primarily PHDFDA nanoparticles suspended in the aqueous receiving solution, as reported previously. Similar concentration effect on product morphology in traditional RESS has been investigated and discussed extensively. For example, Lee and Shin found in their RESS processing of several polymers and copolymers that the experimental parameters affected significantly the product morphology of fibers vs. particles. They reported that the formation of fibers was promoted by a high polymer concentration under otherwise similar RESS conditions. Anidobé and Thies also reported that the concentration of supercritical solution is an important parameter determining the product morphology and that a higher concentration resulted in the formation of fibers rather than particles in their RESS processing of cellulose acetate.

In the RESOLV experiments reported here, the product morphology was not very sensitive to the preexpansion solution concentration over a relatively narrow concentration range. For example, similar PHDFDA nanofibers were obtained under the same RESOLV conditions except for a lower preexpansion concentration of 2 wt % PHDFDA in supercritical CO₂ (Figure 2). Qualitatively, the nanofiber diameters are not significantly affected by the concentration changes. However, the samples corresponding to lower concentrations seem to contain more PHDFDA nanoparticles. Further decreases in the preexpansion concentration toward that used in the previously reported preparation of PHDFDA nanoparticles (0.5 wt %) resulted in much increased particle contributions in the produced nanofiber-nanoparticle mixtures.

The presence of salt (NaCl) in the aqueous receiving solution seems beneficial to the dispersion of the produced PHDFDA nanofibers, and the benefit appears more significant than that in the stabilization of suspended PHDFDA nanoparticles. When neat water instead of aqueous NaCl solution was used at the receiving end of the rapid expansion, there was more severe aggregation of the nanofibers. SEM images of the sample thus prepared exhibit bundles in which the presence of individual PHDFDA nanofibers becomes less obvious.

The polymer PHDFDA is essentially insoluble in many polar and nonpolar solvents such as methanol and hexane, so that RESOLV could also be carried out by using these solvents at the receiving end of the rapid expansion. In the experiment of rapidly expanding a concentrated supercritical CO₂ solution of PHDFDA into

Figure 1. SEM images of the PHDFDA nanofibers from RESOLV with the rapid expansion of a concentrated polymer solution (5 wt %) into an aqueous NaCl solution.
polymers are only marginally soluble in CO₂ at our operating temperatures and pressures, a co-solvent ethanol was added to CO₂ in the syringe pump to increase the polymer solubility. It is known that PMMA is reasonably soluble in supercritical CO₂–ethanol co-solvent system. With an ethanol content of 10% (v/v), the PMMA concentration used in the RESOLV experiment was 1.1 mg/mL at 350 bar (as one phase). The rapid expansion was at 80 °C through the 50-micrometer capillary nozzle into an ambient aqueous NaCl solution (0.5 M). There was similar formation of precipitates from which a specimen was prepared for SEM analysis. The SEM images show PMMA nanofibers in a network-like configuration (Figure 4). For PLA polymer, the supercritical solution concentration was 50 mg of PLA in 50 mL of CO₂–ethanol (10%, v/v) mixture at 350 bar. The rapid expansion was also at 80 °C through the same capillary nozzle into an ambient aqueous NaCl solution (0.5 M). Again, the SEM images of the precipitates formed in the RESOLV processing show networked PLA nanofibers (Figure 5).

The results presented above clearly suggest that the RESOLV technique can be used to process various polymers into nanofibers. Mechanistically, the fiber formation in RESOLV is likely similar to that in the traditional RESS, namely that there is chain overlap between polymers in the solution being pushed through the nozzle and that the large velocity gradient in the nozzle shears the polymer-enriched droplets into fibers. In both rapid expansion processes (RESS and RESOLV), nanoscale fibers are likely formed initially in the expansion jet as the primary product morphology. For the particle production in traditional RESS, it is suggested in the current mechanism that coagulation and condensation are responsible for the growth of the initially formed nanoscale particles into micrometer-
sized particles to be the primary end product. Likewise, the same condensation and coagulation of initially formed nanoscale fibers are probably behind the observation of only micrometer-sized or larger fibers from the traditional RESS process. In the same context, the role of the liquid receiving solution in suppressing the particle growth to yield exclusively nanoparticles in RESOLV is similar in preserving nanofibers to be the observed primary product in this work. Thus, the traditional RESS produces polymeric microfibers under corresponding fibers when experimental conditions are favorable to the fiber product morphology, whereas the RESOLV produces polymeric nanoparticles and also nanofibers under the selected conditions reported here. Here the receiving liquid in RESOLV inhibits or disrupts the condensation and coagulation is unclear. We speculate that the much lower diffusivity in liquid (air in traditional RESS) may significantly slow the aggregation of the initially formed nanoscale particles or fibers in the expansion jet. Further experimental and theoretical investigations are required to look into the mechanistic details.

There might be many experimental parameters affecting the product morphology in RESOLV, as in the traditional RESS, though the focus in this work was on the obviously important role of the supercritical solution concentration. It does appear that a change in the concentration alone and otherwise the same processing conditions is sufficient to determine the dominating product morphology between nanoparticles and nanofibers in RESOLV. This is particularly clear in the RESOLV processing of PHDFDA. In the PHDFDA concentration range of 0.3–2 mg/mL in supercritical CO2, the observed product morphology undergoes the transition from exclusively nanoparticles to predominantly nanofibers. The production of nanofibers is more straightforward at higher PHDFDA concentrations (such as 5 wt%). For PMMA and PLA, the use of a co-solvent introduces additional complication into the system, though details on the mechanistic implications remain to be explored. However, the role of solution concentration is still critical even in the presence of a co-solvent. Under experimental conditions similar to those described above for the formation of PMMA and PLA nanofibers in RESOLV, the use of solutions with significantly lower polymer concentrations for the rapid expansion yielded primarily PMMA and PLA nanoparticles. Shown in Figure 6 is an SEM image of the aggregated PMMA nanoparticles from RESOLV (pre-expansion PMMA concentration of 0.1 mg/mL) that precipitated from the receiving aqueous solution. The reported RESOLV processing for the production of polymeric nanofibers is in principle limited only by the solubility of the polymer in a selected supercritical solvent system. Thus, this may be further developed to be a versatile alternative technique complementing other nanofiber preparation methods already available in the literature.

Acknowledgment

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NMR Detection of Single-Walled Carbon Nanotubes in Solution

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Abstract: The detection of nanotube carbons in solution by 13C NMR is reported. The highly soluble sample was from the functionalization of 13C-enriched single-walled carbon nanotubes (SWNTs) with diamine-terminated oligomeric polyethylene glycol (PES). The thermomagnetic impurities due to the residual metal catalysts were removed from the sample via repeated magnetic separation. The nanotube carbon signals are broad but partially resolved into two overlapping peaks, which are tentatively assigned to nanotube carbons on semiconducting (upfield) and metallic (downfield) SWNTs. The solid-state NMR signals of the same sample are similarly resolved. Mechanistic and practical implications of the results are discussed.

Introduction

There have been extensive recent investigations on the functionalization of single-walled carbon nanotubes (SWNTs).1,2 The functionalization typically renders solubilities of the nanotubes, enabling their characterization in homogeneous organic and/or aqueous solutions. NMR is obviously one of the most desirable instrumental methods for studying the structures and properties of functionalized carbon nanotubes. However, a number of technical difficulties have probably hindered a direct 13C NMR probing of the functionalized nanotube itself in solution, such as limited sample solubility and the presence of ferromagnetic impurities, among others. Thus, the available solution-phase NMR results are centered on the characterization of the functional groups. For example, Chen et al.1 reported the use of 1H NMR results to validate their proposed noncova lent x-stacking interaction for the functionalization of SWNTs with poly(oxyethylene) polymers.3 Holzinger et al.4 used 1H NMR to characterize the soluble SWNT samples functionalized by various substituted oxazolonyl nitrene compounds.4 The NMR signals from the functional groups on SWNTs are often broader than those from the free functionalization agent, with generally similar patterns but sometimes shifting to the upfield.4

Solid-state 13C NMR has been applied to the characterization of nanotube carbons in the functionalized SWNT samples.5-7


The signals of the nanotube sp2 carbons are generally broad, centered around 120-130 ppm, similar to those for unfunctionalized SWNTs.8,9 In a recent study of polymer-functionalized SWNTs, solid-state 2D 13C-1H heteronuclear correlation spectroscopy was employed for evidence on significant interactions of the functional groups with the nanotubes.10 For solid-state NMR, however, it is widely acknowledged that NMR measurements and results can be negatively affected by the presence of substantial ferromagnetic impurities from the residual metal catalysts used in the synthesized SWNT production.8,9,10

Despite the development of various purification methods,11 the catalyst residues can often survive some of the rather harsh chemical and thermal treatments of carbon nanotube samples. As a result, SWNTs produced by using catalysts of nonferromagnetic metals (Ru/Pd or Pd/Pt, for example) have been used in some recent NMR studies.11-13

Here, we report results from the first attempt of a solution-phase 13C NMR study of nanotube carbons in functionalized SWNTs. The nanotube sample was produced with 13C isotope enrichment. The high nanotube equivalent solubility was

achieved via the known functionalization of SWNTs with disulfide-terminated oligomeric poly(ethylene glycol). The ferromagnetic impurities due to the residual metal catalysts were effectively removed from the functionalized nanotube sample in solution via repeated magnetic separation. The solution-phase NMR results are compared with those from solid-state NMR measurements. The partially resolved nanotube carbon signals in the NMR spectra are discussed in terms of theoretically predicted differences in chemical shifts between semiconducting and metallic SWNTs.

**Experimental Section**

Materials. Anhydrous D$_2$O powder (99.99% carbon, 1H content >98%) and graphite powder (CP grade) were supplied by DSM Isotopes and Bucky Carbon, respectively. Carbon dioxide was obtained from Du Pont Industries. Powders Ni (2.3-6.0 μm, 90.0%) and Co (1-6 μm, 99.9%) were purchased from Alfa Aesar. A mixture of 1:1 [1500 (PEG)$_{1500}$] was obtained from Aldrich and deuterated solvents from Cambridge Isotope Laboratories. Cellulose ester dialysis tubing (with a molecular weight cutoff of 12 000) was supplied by Sigma.

The SWNT sample without 13C enrichment was purchased from Carbon Solution. For the purification, raw material (1.2 g) was heated in Na$_2$CO$_3$ (100 °C for 30 min), followed by filtration in INDO (2.6 M, 50 mL) for 24 h. The mixture was then cooled to room temperature and subjected to centrifugation (~4000 g, Fisher Scientific Centri-22 Centrifuge). The sediment was repeatedly washed with deionized water and dried under vacuum to yield a purified SWNT sample (60 mg).

Measurements. Raman spectra were obtained on a Renishaw InVia Raman spectrometer equipped with a 50 mW diode laser source for 785 nm excitation and a CCD detector. Thermogravimetric analysis (TGA) experiments were carried out on a Mettler Toledo TGA/SDTA851e system with a typical heating rate of 10 °C/min. Electron microscopy imaging was conducted on a Hitachi HD-2000 scanning transmission electron microscope (STEM) operated at 200 kV with digital imaging capability. The atomic absorption analysis was provided by Goldie and Associates (Santa Ana, California). Samples for the analysis were digested by using hot HNO$_3$/HCl/mixed acid in accordance with the EPA 200.2 method.

NMR measurements were performed on a Bruker Avance 500 NMR spectrometer equipped with a 4 mm magic angle spinning (MAS) probe head for solids and a 5 mm auto-tune probe head for solutions. For very broad signals, exponential multiplication with a line broadening up to 500 Hz was applied for each carbon ID (free induction decay), coupled with user-defined spline baseline correction in the data processing. The spin-lattice relaxation times of both solid and solution samples were measured with the inversion recovery pulse sequence. Since the solution and solid-state NMR experiments showed that the nanotube carbon signals were not affected by the proton decoupling, the reported NMR spectra were collected without the decoupling (to avoid overloading the sample and potential damage to the equipment in solid-state experiments).

13C-Enriched SWNTs. The laser ablation method was used for the synthesis of 13C-enriched SWNTs. The laser source was a Spectra Physics Quanta-Ray PRO-290 Q-switched Nd:YAG laser operated at 10 Hz (2 J pulse at 1064 nm and 9 mm beam diameter). In a typical experiment, the filament target was prepared by mixing powders 1H (60.8%), graphite (1.52 g, (3)H$_2$O (2.36 g), and Co (0.23 g) with graphite (2.40 g) for hot-pressing (130 °C) into a pellet (about 10 mm thick and 18 mm in diameter), followed by heating at 600 °C in an air, cooling at 810 °C for 2 h, and annealing at 1200 °C for 30 h in nitrogen flow (20 scm, atmospheric pressure). The furnace temperature was set at 1150 °C, with a steady nitrogen flow (62 scm, 75 kPa), in an inert atmosphere. The ribbon-like carbon soot from the laser ablation was characterized by Raman, and the results were consistent with the expected substantial presence of 13C-enriched SWNTs in the soot. According to the characteristic G-band shift, the atomic content of 13C in the nanotubes was estimated at 10%. The purification of the 13C-enriched SWNT sample was similar to that discussed above for the regular SWNT sample.

Functionalization and Magnetic Separation. In a typical experiment, a purified 13C-enriched SWNT sample (60 mg) was mixed with PEG$_{3000}$ (1.2 g), and the mixture was heated to 120 °C. After 3 days at that temperature, the mixture remained solid in ambient. After 1 week, the mixture was washed with deionized water for 3 days (removing free PEG$_{3000}$) to yield a colored aqueous solution of PEG$_{3000}$-functionalized 13C-enriched SWNTs (PEG$_{3000}$-$^{13}$C-SWNT).

The same procedure was applied to obtain a magnesium-purified PEG$_{3000}$-functionalized SWNT sample without 13C enrichment for the nanotubes.

**Results and Discussion**

The properties (appearance, solubility, nanotube content, etc.) of the PEG$_{3000}$-$^{13}$C-SWNT system are similar to those of their counterpart without 12C enrichment already reported in the literature. The high solubility of these functionalized nanotubes, coupled with the 12C enrichment, made it possible to probe nanotube carbons in solution-phase NMR measurements. As shown in Figure 1 for PEG$_{5000}$-$^{12}$C-SWNT in D$_2$O (solution concentration ~30 mg/mL, SWNT equivalent), the nanotube sp$^2$ carbons exhibited a broad signal centered at ~132 ppm (from the aromatic ~134 ppm, which is consistent with theoretical predictions and close to those observed in solid-state NMR). Obviously, nanotube carbons can be detected by NMR in solution.

The broadness in the signals reflects the chemical shift dispersion of nanotube carbons, which are likely inhomogeneous due to different nanotube chiralities, lengths, adjacent defects, etc. Interestingly, however, there are some distinctive features in the broad signals, which are thought to originate from the curve into underlying peaks (e.g., the Lorentzian peaks of similar line-widths (~20 ppm, Figure 1)). The ratio of area under the peak centered at 128 ppm to that at 144 ppm is ~1.8. A variation of relaxation delay from 3 to 0.4 and a little effect on the signal shape, with similar line-widths and chemical shifts. We tentatively assign the two peaks

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Fig. 1. The $^{13}$C NMR spectrum of PEG$_{1500}$–$^{13}$C–SWNT in D$_2$O solution (30 000 4000, 5 s relaxation delay, acquired in the CP-MAS probe but without spinning and decoupling). Shown in the inset is a deconvolution based on two Lorentzian peaks (hypothetical curve, ---). The 70 ppm signal is due to backbone-attached PEG functional groups.

...to semiconducting (upfield) and metallic (downfield) SWNTs.$^{11}$ In fact, the observed difference in their chemical shifts ($\approx$16 ppm) is in reasonable agreement with what has been predicted by recent theoretical calculations.$^{20}$ These calculations suggested that there should be an approximately $\approx$12 ppm upfield shift for the semiconducting nanotube carbons from their metallic counterparts due to the localized ring currents.$^{8}$

There was also suggestion that the broad solid-state NMR signals of nanotube carbons could be deconvoluted into two peaks corresponding to semiconducting and metallic SWNTs, despite the fact that those signals were not resolved at all.$^{8}$

The peak shoulder structure shown in Figure 1 represents the first experimental confirmation that there is indeed a pair of broad signals associated with the $sp^2$ carbons in SWNTs. The acquisition of the partially resolved $^{13}$C NMR benefited significantly from the effective removal of residual metal catalyst via repeated magnetic precipitation in solution. It is well-known that the ferromagnetic residues associated with the Ni–Co catalysts interfere with NMR measurements.$^{7}$ These residues are often encapsulated in carbon cages or structural cavities and are, thus, impossible to remove completely in the chemical purification.$^{11,20}$ The solubilization of the nanotube sample enabled the solution-phase magnetic separation. The separation was effective, as confirmed by STEM analysis of the separated samples (Figure 2) and by TGA analysis (negligible residue), and also was reflected in the NMR results (diminished spinning sidebands in the solid-state NMR spectrum, for example). According to the atomic absorption analysis...

Fig. 2. STEM images of the PEG$_{1500}$–$^{13}$C–SWNT sample (in secondary electron mode, up) and the precipitate from magnetic separation (in Z-contrast mode, below). The Z-contrast imaging of the PEG$_{1500}$–$^{13}$C–SWNT sample revealed no metal. Scale bars $= 300$ nm.

Fig. 3. The solid-state MAS $^{13}$C NMR spectrum of PEG$_{1500}$–$^{13}$C–SWNT (in a mixture with KCl, 11 000 90°, 2 s relaxation delay, 14 kHz spinning rate, single pulse sequence, no decoupling).

...of the PEG$_{1500}$–$^{13}$C–SWNT sample, the Ni content was $\approx$0.67 at % and the Co content was much lower (below the detection limit).

The solid-state $^{13}$C MAS NMR spectrum of the PEG$_{1500}$–$^{13}$C–SWNT sample was acquired for comparison with the solution-phase result. The nanotube carbons signals in the solid-state spectrum are equally broad, with two obvious overlapping peaks at $\approx$128 and $\approx$136 ppm (Figure 3). Similar to the solution-phase signals, these two peaks may also be assigned to semiconducting and metallic SWNTs. The relative intensities...
of the two peaks are somewhat different in solid state versus in solution. Additionally, the overall intensity of the nanotube carbon signals in reference to that of PEG$_{1000}$ functional groups is significantly higher in solid state than in solution. These two differences between solid-state and solution-phase NMR results may share the same cause. As in other soluble functionalized SWNTs, the PEG$_{1000}$-^{13}C-SWNT sample contains bundled nanotubes in solution. The tumbling of larger bundles may proceed too slow to eliminate such orientation-dependent contributions to the NMR line-width as chemical shift anisotropy and dipolar coupling. These species are essentially NMR "silent" in solution, corresponding to a lower effective nanotube carbon concentration to result in their relatively weaker overall signal intensity in the solution-phase NMR spectrum. The functionalized semiconducting SWNTs disperse better in solution, as made evident by recent experimental results. Therefore, their NMR signals relative to those of their metallic counterparts are stronger in solution (Figure 1) than in the solid state (Figure 3).

There are apparently significant interactions between the nanotube carbons and the PEG moieties in the solid state, with the latter serving as spin–lattice relaxation centers. The relaxation time ($T_1$) of the nanotube carbons was estimated by using the null-point approach based on the inversion recovery sequence. Both nanotube components effectively "disappeared" at the same point, $T_{null} \approx 0.16$ s, corresponding to $T_1 \approx 2$ s. Despite the absence of ferromagnetic impurities in the PEG$_{1000}$-^{13}C-SWNT sample, the estimated $T_1$ is up to 2 orders of magnitude shorter than those of similarly^{13}C-enriched SWNTs without functionalization. The interactions are also reflected in the NMR results of the PEG carbons. For PEG$_{1000}$-^{13}C-SWNT in D$_2$O solution, the spin–lattice relaxation time of PEG carbon signals (500 ms) is close to that in free PEG$_{1000}$ (710 ms). However, in solid state, the relaxation time of PEG carbons in the PEG$_{1000}$-^{13}C-SWNT sample is more than an order of magnitude shorter (37 ms) than that in free PEG$_{1000}$ (450 ms). It seems that the segmental mobility of PEG moieties in PEG$_{1000}$-^{13}C-SWNT in the solid state is low, presumably with the motion of PEG carbons restricted by their proximity to the nanotubes. Such significant differences in the relaxation times for the nanotube-bound functional groups in solution phase versus in solid state is interesting. It may be exploited for potential applications in the NMR characterization of nano-composite materials, such as probing interactions of carbon nanotubes with the polymeric matrix.

In summary, we demonstrated that the nanotube carbons in solution could readily be detected in $^{13}$C NMR by using highly soluble functionalized SWNTs. The ferromagnetic impurities in the sample for NMR measurements were effectively removed via repeated magnetic separation. The nanotube carbon signals are broad, but partially resolved into two adjacent features, probably corresponding to nanotube carbons in semiconducting (upfield) and metallic (downfield) SWNTs. The solid-state NMR signals of the same sample are similarly resolved. These results suggest that $^{13}$C NMR may be explored to serve as a useful tool in the characterization of SWNTs of different electronic structures.

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Supporting Information Available: Raman spectra of $^{13}$C-enriched SWNTs and SWNTs without enrichment. This material is available free of charge via the Internet at http://pubs.acs.org.

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The electronic and optical properties of single-walled carbon nanotubes (SWNTs) have been investigated by many research groups. It is now well-established that the electronic structures of semiconducting SWNTs are characterized by several pairs of van Hove singularities in the electronic density of states. Transitions associated with the first $S_1$ and second $S_2$ singularity pairs are widely observed in absorption spectra of SWNT samples produced by various methods and thus of different diameters and diameter distributions. It has also been reported that the doping of the SWNT surface could have a significant effect on the $S_1$ absorption band and more dramatically that the surface modification via chemical functionalization could effectively eliminate the $S_1$ and $S_2$ absorption bands. The latter was attributed to significant perturbations in the electronic structure by the surface modification and a disruption of the extended π-network of the nanotube. We report here that a similar significant effect on the van Hove singularity pairs can be achieved by non-covalent complexation of the nanotube with planar aromatic molecules such as pyrene in solution, resulting in the absence of $S_1$ and $S_2$ bands in the near-IR absorption spectrum. Since the complexation is reversible, the characteristic absorption bands can be turned on and off with the complexation in a reversible fashion. The attachment of pyrene and other aromatic species to the carbon nanotube surface via non-covalent interactions (π−π stacking) has already been reported in the literature. In this work, we synthesized a pyrene derivative with a long alkyl tail, 1-docosylanthrylpyrene (DapPy), for the solubilization of SWNTs via non-covalent interactions. Details on the synthesis and characterization of DapPy are provided in the Supporting Information.

In the solubilization of SWNTs with DapPy, a purified SWNT sample (150 mg) was added to a THF solution of DapPy (10 mg/mL, 30 mL). The mixture was sonicated (Fisher Scientific FS 20, 70 W, 42 kHz) for 24 h, followed by centrifuging at 3000 rpm for 20 min. The solid residue was used as the starting material to undergo another round of sonication-centrifuging under the same experimental conditions. The solution in THF thus obtained was centrifuged at a higher speed (Eppendorf Centrifuge 5417R, 25000 g) for 3 h. The supernatant contained an equivalent of about 22 mg of SWNTs, namely that the non-covalent SWNT–DapPy interactions are about 15% of the starting SWNT sample in solution without precipitation even in such a strong centrifuging field (25000 g).

The supernatant containing the solubilized SWNTs and the entire DapPy sample was used to prepare specimen for Raman spectroscopy (785 nm excitation) as well as scanning (STEM, Hitachi HD-2000) and high-resolution transmission electron microscopy (HR-TEM, Hitachi H-2000) characterizations. The Raman results are typical of SWNTs (after removal of DapPy), and the electron microscopy images exhibit composite-like morphology with clear evidence for the substantial presence of exfoliated SWNTs (Figure 1).

The THF solution of the DapPy-solubilized SWNTs in the presence of DapPy was used in absorption measurements. The nanotube equivalent concentration in the solution was 0.7 mg/mL, with the DapPy concentration of 0.8 mg/mL. While the nanotube equivalent concentration was relatively high, there were no $S_1$ and $S_2$ bands in the observed visible–IR absorption spectra (Figure 2A). The same solution was dropped onto a glass slide to evaportate off the solvent THF. The absorption spectrum of the sample (SWNTs with DapPy) in the solid state also exhibited no $S_1$ and $S_2$ bands (Figure 2B). On the other hand, the deposition of an equivalent amount of purified SWNT sample without DapPy on the same substrate allows ready observation of the characteristic $S_1$ and $S_2$ transitions at 1650 and 1630 nm, respectively.
The absence of the \(S_1\) and \(S_2\) absorption bands for SWNTs in the solution with \(D_{\text{DOMP}}\) may be attributed to effects associated with the complexation of the nanotube with \(D_{\text{DOMP}}\) species, which is responsible for the nanotube stabilization. Such complexation is likely based on the non-covalent attachment of the planar pyrene moiety in \(D_{\text{DOMP}}\) to the nanotube surface (Scheme 1).1,11 and thus reversible under different experimental conditions. In order to remove the attached \(D_{\text{DOMP}}\) species from the nanotube surface, the solution of SWNTs with \(D_{\text{DOMP}}\) was treated in two different ways. One was to transfer the solution into a polyvinylidene fluoride (PVDF) membrane tubing (cutoff molecular weight \(\sim 250,000\), Spectrum Laboratories) for dialysis against THF until the disappearance of the characteristic pyrene absorption peaks at \(336\)–\(350\) nm. As a result of the \(D_{\text{DOMP}}\) removal in the dialysis, most of the nanotubes precipitated out of the solution. The other way was to reflux the SWNT–\(D_{\text{DOMP}}\) sample with cyclohexane for 12 h, followed by repeated cycles of cyclohexane washing–vigorous centrifuging. The solid residue contained primarily the recovered nanotubes according to thermogravimetric analysis. Both treatments were purposely designed to be under relatively mild experimental conditions so as not to invoke any processes for decomplexing covalently attached species. The successful removal of \(D_{\text{DOMP}}\) from the nanotube in both treatments lends strong support to the conclusion that the complexation is non-covalent in nature.

As expected, the recovered SWNTs exhibit the characteristic \(S_1\) and \(S_2\) absorption bands (Figure 2). These results suggest that the dimethyl band gap transitions of semiconducting SWNTs are due to the non-covalent complexation and that the effect on the transitions is reversible in accordance with the reversibility of the complexation.

It is known in the literature that the doping of SWNT surface could have a significant effect on the \(S_2\) absorption band, resulting in a reduction or even elimination in absorptivity, but much less effect on the \(S_1\) absorption band because of the higher energy.2 So far, elimination of both \(S_1\) and \(S_2\) absorption bands can be achieved only via covalent chemical modification of the SWNT sidewalls.3,4 Thus, it is often suggested that the stabilization of SWNTs by non-covalent techniques, such as those based on interactions with aromatic species, better preserves the nanotube electronic structure. The results reported here represent the first experimental demonstration that the non-covalent complexation of a semiconducting SWNT with aromatic molecules can also affect the nanotube electronic structures and the associated optical transitions in a dramatic fashion.

While the mechanism for such an effect is not clear, we suspect that the SWNT–\(D_{\text{DOMP}}\) complexation via non-covalent interactions probably changes the nanotube’s electronic density of states. Conceptually, a complex in which a SWNT is non-covalently covered by a layer of planar aromatic moieties (Scheme 1) may be viewed as a highly defective double-walled carbon nanotube (DVWNT), so that the electronic density of states may be significantly different from that in the naked SWNT. In fact, theoretical calculations have shown that, in a DWNT of small enough diameter, the electronic structure of the inner (semiconducting) tube could be strongly perturbed by the external layer, with energy gaps diminishing as a result of the overlap of the conductance and valence bands.13 This is an interesting mechanistic issue for further experimental and theoretical investigations.

Recent reports based on calculations and transistor device measurements suggested the presence of charge-transfer effects in a SWNT adsorbed with small aromatic molecules.7–10 The results presented here demonstrate that the electronic properties of SWNTs are indeed vulnerable to effects of planar aromatic moieties in a relatively strong and noninvasive fashion. Thus, there might be opportunities to manipulate or even control such properties for specific applications.

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Supporting Information Available: Synthesis and absorption spectrum of \(D_{\text{DOMP}}\) and other characterization results of \(D_{\text{DOMP}}\)–SWNT. This material is available free of charge via the Internet at http://pubs.acs.org.

References

Polymide-Functionalized Carbon Nanotubes: Synthesis and Dispersion in Nanocomposite Films

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ABSTRACT: In the preparation of high-quality polymeric carbon nanocomposites, the full compatibility of carbon nanotubes as the filler with the matrix polymer is required. For such a purpose, an amino functionalized polyamide, specifically designed to be structurally identical to the matrix polymer, was synthesized and used in the functionalization of carbon nanotubes. The functionalized carbon nanotube samples were analyzed and studied by using a series of techniques, and the results are presented and discussed. These nanotube samples and the matrix polyamide are solvable in the same organic solvents, allowing their intimate mixing in solution and the subsequent fabrication of polyamide-carbon nanotube composite films via wet casting. According to results from the spectroscopic and electron microscopic characterizations, the carbon nanotubes are homogeneously dispersed in the nanocomposite films.

Introduction

The use of single-walled (SWNT) and multi-walled (MWNT) carbon nanotubes in polymeric composites to materialize their superior properties has been attracting much recent attention.1−6 These nanocomposite materials are explored to attain enhanced mechanical features for efficient load transfer and tear resistance and to achieve certain levels of electric conductivity through a percolation network for charge mitigation and electromagnetic shielding.1,3,6 However, since carbon nanotubes are generally insoluble and severely bundled, their homogeneous dispersion in desired polymer matrices represents a significant challenge. Several approaches have been proposed and experimented, including the direct suspension of carbon nanotubes in the polymer solution via sonication,7−9 the in situ polymerization in the presence of carbon nanotubes,10,11 and the chemical modification of carbon nanotubes for their solubilization.12−19 For example, several research groups have recently reported a functionalization of living polymer chains on the carbon nanotube surface or the living polymerization from nanotube-bound initiators, resulting in carbon nanotubes functionalized with polymers of various structures and molecular weights.20−24 In the dispersion of carbon nanotubes for high-quality polymeric carbon nanocomposites, an important issue is the selection of dispersion agents such as surfactants in the sonication-based methods and functionalities in the solubilization with chemical modifications. The most desirable way is obviously the use of polymers that are structurally and property-wise identical or close to the matrix polymer in the dispersion or solubilization of carbon nanotubes because it ensures compatibility of the dispersed carbon nanotubes with the polymer matrix to avoid “impurities” associated with the dispersion agents and any potential microscopic phase separation in the nanocomposites.20−25 For example, Zhu et al. used acid-etched and fluorinated SWNTs in the preparation of epoxy resin-based nanocomposites, where both nanotube-bound carboxylic acids and fluorines could react with the end groups of epoxy resin or the curing reagents under the curing conditions.26 This was equivalent to the dispersion of epoxy resin-functionalized SWNTs in the matrix of the same resin, and the improved nanotube—matrix compatibility resulted in enhanced composite performance. Sun and co-workers have also shown that polystyrene-copolymers with pendant hydroxy or amine moieties can be covalently attached to carbon nanotubes via the esterification or amidation of the nanotube-bound carboxylic acids and that the soluble functionalized carbon nanotubes can be homogeneously dispersed in polystyrene polymer thin films.27 More recently, they reported the preparation of poly(vinyl alcohol)—carbon nanocomposite films via solution-casting, in which the carbon nanotubes were functionalized with the matrix polymer for solubility and “impurity-free” dispersion.28 These nanocomposite films are of high optical quality and exhibit improved mechanical properties.

Aromatic polyimides are candidate polymers for a variety of applications due to their useful properties such as low color, flexibility, high glass transition temperature, excellent thermal stability, and radiation resistance.29−31 Here we report on the homogeneous dispersion of both SWNTs and MWNTs into polyimide matrix for high-quality nanocomposites. The carbon nanotubes were functionalized with a specially synthesized low-molecular-weight polyimide that is structurally identical to the matrix polymer. Results from the characterization of the soluble polyimide-functionalized carbon nanotubes and the fabrication of polyimide-carbon nanocomposite films are presented and discussed.

Experimental Section

Materials. 4,4′-Hexafluoroisopropylidenediphtalic anhydride (99%) was purchased from Aldrich, 1,3-bis(3-ami...
Scheme 1

Marzin Polylamide

nephronylin/benzenoe was from TCI, 1-ethyl-3-(dimethylamino)propylcarbodiimide hydrochloride (EDAC), 88% was purchased from Afa Assay, and bromobenzene, 4-dimethylaminopyridine (DMAP, 98%), and 1-methyl-2-pyrrolidinone (NMP) were from Acros. Toluene, dimethylformamide (DMF), and all solvents were obtained from Mallinkrodt. NMP and DMF were distilled over sodium hydride before use. Dehydrated solvents for NMR measurements were supplied by Cambridge Isotope Laboratories. The polylamide based on 4,4'-hexafluoroisopropylidene diphenylamine anhydride and 1,3-bis(3-amino)phenyl)benzene (also referred to as La2C2P-4, Scheme 1) was provided by SRS Inc. (4.7 ± 10 mmL and 7.4 mL 

Swnt and MWNT samples were produced by using the arc-discharge and chemical vapor deposition (CVD) methods. In a typical purification, a nanotube sample (1 g) was suspended in an aqueous HNO3 solution (2 M, 1.5 L) and refluxed for 48 h. Upon vigorous centrifuging, the supernatant was decanted, and the remaining solids were washed repeatedly with deionized water until neutral pH and then dried under vacuum.

Measurements. NMR measurements were performed on a JEOL E-500 NMR spectrometer. UV/Vis/near-IR absorption spectra were recorded on a Shimadzu UV1600 and Thermo Nicolet Nexus 670 FT-NIR spectrometer. Raman spectra were obtained on a Renishaw Raman spectrometer equipped with a 50 mW Cu laser source for 862 nm excitation and a CCD detector. Thermogravimetric analysis (TGA) was carried out on a Mettler TGA/SDTA851e system. Scanning electron microscopy (SEM) images were obtained on a Hitachi S-4100 field-emission SEM system. Transmission electron microscopy (TEM) analyses were conducted on a Hitachi H-2000 ETM and Hitachi HD-2000 TEM/STEM systems, both with the digital imaging capability.

Aniline-Terminated Polylamide (PI-NH2): 1,3-Bis(3-amino)phenyln boron (0.5 g, 1.6 mol) was dissolved in dry NMP (10 mL) in a round-bottom flask. After the solution was cooled in an ice bath for 15 min, 4,4'-hexafluoroisopropylidenediphenylamine anhydride (0.5 g, 1.47 mmol) was added with vigorous stirring. The ice bath was removed after 1 h, and the reaction mixture was maintained at room temperature for 24 h. After the addition of toluene (4 mL), the flask containing the reaction mixture was attached to a condenser with a teflon-filled Dean–Stark trap and then heated to 150 °C. When the amount of water removed by the anisotropic reached ~0.05 mL, the reaction mixture was cooled to room temperature. Upon the removal of toluene and some NMP on a rotary evaporator, the mixture was precipitated into a large amount of methanol (80 mL). The product as solid precipitate was collected and dried under vacuum at 60 °C (0.58 g, 90% yield). H-NMR (500 MHz, DMSO-d6): 8.14 (d, J = 6.9 Hz), 7.93 (d), 7.70 (s), 7.57–7.47 (m), 7.47–7.30 (m), 7.27–7.07 (m), 6.98 (s), J = 8 Hz), 6.94–6.92 (m), 6.33 (s), J = 8.6 Hz, 6.22 (d), 6.15 ppm (d, J = 7.8 Hz).

Nanotube Functionalization. In a typical reaction, EDAC (400 mg, 2.1 mmol) was dissolved in DMF (10 mL). To the solution was added purified SWNTs (8.1 mg), and the mixture was sonicated in an ultrasonic bath (VIVAX Aquasonic 100/37) for 2 h. To the mixture was added a solution of PI-NH2 in DMF (10 mmol, 5 mL), followed by sonication for another 48 h. The suspension was centrifuged at 3000 rpm to separate the dark-colored supernatant from the insoluble residue (unfunctionalized or underfunc- 

tionalized nanotubes). Upon solvent removal on a rotary evaporator, the crude product was redissolved in THF (10 mL) for dialysis in a PDVF membrane tubing (cut off molecular weight ~250 000 against THF) for 3 days. The removal of the solvent THF yielded PI-NH2-SWNT as a black solid.

The same procedure was applied to the functionalization of MWNTs with PI-NH2. The PI-NH2-MWNT sample is also a black solid.

Nanocomposite Films. In a typical experiment, the matrix polylamide (1 g) was dissolved in DMF (2 mL) to form a homogeneous solution. To the solution was added dropwise a DMF solution of PI-NH2-functionalized carbon nanotubes under constant stirring. The resulting solution was further stirred in a flowing nitrogen atmosphere to slowly evaporate the solvent DMF until the total volume reduced to ~3 mL. The viscous solution thus obtained was cast onto a glass substrate with an adjustable film applicator (Gardco). The films were kept in flowing nitrogen atmosphere in a drybox at room temperature for 24 h and then in a vacuum oven at 50 °C for 48 h. The film thickness was measured by using a digital height gauge (Nikon Digimatic Stand MS 10C with an MFC-101 digital display device).

Results and Discussion

Polylamide Functionalization of Carbon Nanotubes. The amine-terminated polylamide PI-NH2 was synthesized by controlling the reaction conditions in the condensation polymerization of 4,4’-hexafluoroisopro- pylidenediphenylamine and 1,3-bis(3-amino)phenyl)benzene. A dihydroxyamine molar ratio of 7:8 was used for PI-NH2 with targeted seven repeating units and a molecular weight of ~5200. According to the NMR end group analysis, the integrations of the ~14 NMR signals for terminal aniline rings at 0.98, 0.63, 0.62, and 0.15 ppm vs those of other aromatic protons, molecular weights of the several batches of PI- 

NH2 are in the range 5000 to 8000, consistent with the synthetic target. FT-IR results of the PI-NH2 exhibit the characteristic amide peaks at 1787, 1730, 1639, and 721 cm−1, and phenolic amino peaks at 3510 and 3490 cm−1.

The amine-terminated polylamide PI-NH2 was used to functionalize SWNTs and MWNTs in carboxylic acid activated reaction conditions. The PI-NH2 functionalized carbon nanotube samples are soluble in many polar solvents, such as THF, DMF, and DMSO, to form dark colored homogeneous solutions. Since PI-NH2 is nearly colorless, the dark solution color serves as a visual indicator for the presence of carbon nanotubes. Shown in Figure 1 is an optical absorption spectrum of the functionalized SWNT sample in DMF solvent. The spectrum features absorption bands at 1820 and 1040 nm, corresponding to electronic transitions associated with the van Hove singularity for semiconducting SWNTs (S1 and S2, respectively) and a weak band at ~700 nm for metallic SWNTs (M). These absorption features are typical of SWNT samples produced via the arc discharge method. Thus, the results seem to suggest that the nanotube electronic structures are largely preserved in the functionalization, consistent with the functionalization being targeted at the defect sites on nanotubes. The solution was also dropped onto a glass slide, followed by the evaporation of DMF, to form a dark-colored transparent thin film. The absorption spectrum of the film shows similarly the characteristic features [Figure 1].

The PI-NH2-SWNT and PI-NH2-MWNT samples were characterized by resonance Raman spectroscopy. However, the Raman spectra are subject to strong luminescence interference, similar to those found in other
Figure 1. Optical absorption spectra of PI-NH₂-SWNT in DMSO solution (-) and as a solid-state sample deposited on a glass substrate (---).

Figure 2. 1H NMR spectra (500 MHz, DMSO-d₆) of PI-NH₂ before (bottom) and after (top) the functionalization with SWNTs.

Figure 3. 13C NMR spectra of PI-NH₂ before (bottom) and after (top) the functionalization with SWNTs.

The effects of amide linkages and nanotube ring currents on carbon NMR signals of the terminal aniline units in PI-NH₂ are illustrated in Figure 3. The carbon NMR data also suggest significant changes in chemical environment and/or mobility for terminal aromatic fragments in PI-NH₂ resulting from interactions with the attached nanotubes. The 13C NMR spectra of PI-NH₂ before and after the amidation reaction are mostly similar, with the spectrum after the reaction being somewhat broader. However, the signals at 104.7, 106.8, and 151.0 ppm corresponding to the terminal aniline carbons in free PI-NH₂ are not observed at their original positions in the spectrum of PI-NH₂-SWNT. These signals could be either broadened beyond detection or shifted to other regions where their overlap with more intense signals from repeating aromatic units makes their identification impossible.

The nanotube dispersion in the solubilized samples was examined by TEM. The TEM specimen was prepared by depositing a drop of the sample solution onto a carbon- or copper-coated copper grid, followed by solvent evaporation. As shown in Figure 4, the TEM image of a PI-NH₂-MWNT suggests the presence of amorphous materials on the nanotube surface, which may be attributed to the polyimide functionalities. The functionalized MWNTs of different lengths and diameters are apparently well dispersed in the solubilized sample (Figure 4, inset). The nanotubes appear not significantly shortened despite the amidation reaction condition involving continuous sonication for an extended period of time.

The TEM imaging of functionalized SWNTs is intrinsically more difficult because of the poor contrast between the nanotube and the heavy coating of functional groups. Despite repeated attempts in the TEM analysis of PI-NH₂-SWNT, there was no success to achieve the kind of imaging quality comparable to that for PI-NH₂-MWNT. Instead, a typical TEM image of the
Nanocomposite Films. The polyaniline based on 4,4’-hexafluoropropiophenone diphthalic anhydride and 1,3-bis(3-aminophenoxy)benzene is a polymer of many desirable properties, such as high optical transparency, thermal stability, solubility in many common solvent systems for solution-processed processing, and especially the durability in the space environment.25,26 As discussed earlier, the PI-NH3 was designed to be structurally identical to this polyaniline and thus fully compatible with the polymer matrix of the nanocomposites. The common solubility of the PI-NH3-functionalized carbon nanotubes and the matrix polyaniline also makes the solution casting easier.

In the film fabrication, the use of carefully dried DMF and the maintenance of a dry environment throughout the experiment are critical because the polyaniline films are sensitive to any moisture contamination. The nanocomposite films obtained without moisture contamination in the fabrication appeared optically transparent (even with a dark color in film of a high nanotube loading) and stable under ambient conditions. The films of 25–100 μm in thickness were cut to 1 in. × 3 in. pieces for characterization and other measurements. Shown in Figure 6 is a picture of a series of polyimide-SWNT composite thin films with different nanotube contents.

The optical absorption spectra of the films are similar to those of the solutions with different nanotube concentrations, suggesting that there are no fundamental changes in the PI-NH3-functionalized carbon nanotubes.
upon their dispersion into the polyimide matrix. The spectra of the films are also featured by the characteristic S1 and S2 absorption bands, with the observed absorbance increases proportional to nanotube contents in the films (Figure 7).

Raman spectra of the polyimide–SWNT composite films, similar to that of the functionalized SWNT sample discussed earlier, contain strong luminescence contributions. The luminescence interference is consistent with the fact that the SWNTs are well dispersed in the polyimide matrix. After the correction for the luminescence background, the G-band and D-band characteristics of SWNTs can be observed in the Raman spectra.

The dispersion of carbon nanotubes in the polyimide matrix was evaluated more directly by TEM imaging. The specimen were prepared from the microtome of the nanocomposite films in the cross-sectional direction into slices of ~100 nm in thickness. Because of the difficulty with TEM imaging of SWNTs in the presence of polymer matrix, the analysis was concentrated on the polyimide–MWNT composite film. According to the TEM image of the microtomed specimen shown in Figure 8, the MWNTs are apparently well-dispersed at the individual nanotube level in the polyimide matrix.

The same polyimide–MWNT composite film was stretched to failure, and the fractured edges were investigated by SEM. The specimen for the SEM analysis was coated with a thin layer of Pd/Au to mitigate surface charging effect. As shown in Figure 9, there are abundant well-dispersed MWNTs protruding out of the polymer matrix near the edge. These protruded nanotubes appear well-wetted by the polyimide, which might be considered as evidence for efficient load transfer between the polymer matrix and filler nanotube in the stretching of the nanocomposite film.\[15\]

In summary, both SWNTs and MWNTs were solubilized by the functionalization with a specifically de-
signed amine-terminated polyamide. The solubilized carbon nanotubes were dispersed into the polyimide matrix via solution-phase mixing and then wet-casting by taking advantage of the common solubility of the functionalized carbon nanotubes and the polyimide in DMF. The design of the amine-terminated polyamide to share the same structural units with the polyimide polymer ensured the full compatibility between the functionalized carbon nanotubes and the polyimide matrix. According to the electron microscopy characterization, the carbon nanotubes are nanoscale-distributed in the polyimide matrix. As a result, the polyimide–carbon nanotube composite films thus obtained are of a high quality, optically transparent, and homogeneous. The reported work demonstrates that a rational design of polymeric functionalities in the solubilization of the nanotubes by polyimide is highly plausible for the fabrication of desirable polymeric carbon nanocomposites.

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References and Notes

Selective Interactions of Porphyrins with Semiconducting Single-Walled Carbon Nanotubes

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Single-walled carbon nanotube (SWNT) samples produced via various techniques are generally mixtures of metallic and semiconducting SWNTs, which correspond to different electrical conductivities and other related properties. These properties are important to a variety of technological applications of SWNTs including, for example, the electrical conductivity and charge dissipation in polymeric/carbon nanocomposites and thin films. The enrichment of metallic over semiconducting SWNTs or vice versa in a nanotube sample, toward a complete separation of the two different kinds of SWNTs, has attracted much recent attention. In this communication, we report on the selectivity of a derivatized porphyrin toward semiconducting SWNTs as preliminarily noncovalent interactions resulting in significantly enriched semiconducting SWNTs in the solubilized sample and predominantly metallic SWNTs in the residual solid sample according to Raman, near-IR absorption, and bulk conductivity characterizations.

The SWNT sample was produced in Professor A. M. Rao’s laboratory (Physics Department, Clemson University) by using the arc-discharge method. It was purified via oxidative acid treatment according to an established procedure. The solubilized sample (10 mg/mL, 20 mL) was added to the solution of THPP (10 mL) in chloroform (10 mg/mL, 20 mL), and the mixture was sonicated (Fisher Scientific, W5, 40 kHz) for 40 h. After the removal of chloroform on a rotary evaporator, the solid mixture was extracted repeatedly with hexanes, coupled with vigorous centrifuging (~3000 g) for 20 min, to remove free THPP. Then, THPP (10 mL) was added to the solid sample to dissolve the THPP-attached SWNTs. Upon vigorous centrifuging for 10 min, the solid residue was collected and used to go through the same noncovalent solubilization procedure again (note: the third repeat was tried, but no further solubilization was observed). The remaining SWNT sample largely free from the porphyrin was obtained as the final solid residue (9 mg, denoted as “free-SWNT” sample). The solubilized THPP–SWNT samples from the two repeated experiments were combined, followed by a complete evaporation of the solvent THF. The removal of THPP from the combined solubilized sample was accomplished via washing the sample with acetic acid, coupled with vigorous centrifuging, resulting in the recovery of insoluble SWNTs (denoted as “recovered-SWNT” sample). The results from scanning electron microscopy analyses show that the two samples are largely similar. To ensure a rigorous comparison between the free-SWNT and recovered-SWNT samples in subsequent spectroscopy and conductivity characterizations, both solid-state samples were thermally treated under the same experimental condition of 800 °C for 1 h in a nitrogen atmosphere.

The recovered-SWNT sample is enriched in semiconducting SWNTs, while the free-SWNT sample contains predominantly metallic SWNTs. Their Raman spectra obtained with 785 nm (1.58 eV) excitation exhibit different features (Figure 1a). According to the widely cited work of Dresselhaus and coworkers, while semiconducting and metallic SWNTs have different tangential mode G-bands, the difference is not expected to be obvious for the as-produced SWNTs used in this work with the 785 nm excitation. The recent results and analyses by Papakonstantinou and coworkers on laser ablation-produced SWNTs reaffirmed such a conclusion (Figure 4 in ref 5). As shown in Figure 1a, however, the G-band of the free-SWNT sample is broader and more unsymmetrical than that of the recovered-SWNT sample, indicative of substantial enrichment in metallic SWNTs (Breit–Wigner–Fano line shapes). The Raman features in the radial breathing mode region are also consistent with an enrichment of metallic SWNTs in the free-SWNT sample.

The significant separation of semiconducting nanotubes (in recovered-SWNT sample) from metallic nanotubes (in free-SWNT sample) is made more evident by a quantitative comparison of the near-IR absorption spectra. The spectra shown in Figure 1b were obtained by measuring (Thermo-Nicolet Nexus 670) the thermally treated solid-state samples of the same quantity under the same experimental conditions. No surfactant or other dispersion agents were used in the preparation of the specimens for measurements to avoid even the remote possibility of any dyeing effects. For the semiconducting recovered-SWNT sample, the near-IR absorption spectrum contains significant bands at ~5390 cm⁻¹ (1855 nm, 0.67 eV) and ~9710 cm⁻¹ (1030 nm, 1.19 eV), corresponding to transitions associated with the first (Σg) and second (Σu) pairs, respectively, of van Hove singularities in the electronic density of states for semiconducting SWNTs. On the other hand, the absorption of the metallic free-SWNT sample is negligible over the near-IR region. The results suggest that most of the semiconducting SWNTs in the starting sample ended up in the

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Figure 1. (a) Raman spectral feature (785 nm excitation) and (b) near-IR absorption spectra of the semiconducting recovered-SWNT (---) and metallic free-SWNT (----) samples after the same thermal treatment.

The bulk electrical conductivities of the free-SWNT and recovered-SWNT samples (thermally treated under the same conditions, as described above) were very different. In a comparative conductivity evaluation, the two samples were pressed separately into pellets of approximately 9 mm × 3 mm × 1 mm in dimension. Results from the classical four-probe conductivity measurements under ambient conditions show that the bulk conductivities of the two samples differ by more than two orders of magnitude: 1.1 Scm for the metallic-free SWNT vs 6.0.07 Scm for the semiconducting recovered-SWNT.

To examine the effects of the nanotube on the THF species on the surface, the soluble THF-SWNT sample in solution was characterized by 1H NMR (data not shown). The NMR signals of THF are significantly broadened upon the attachment to SWNTs, which is likely due largely to the significantly reduced mobility of the THF species. Consistent with the NMR results it seems that the porphyrin ring is probably bound to the SWNT surface, leaving long alkyl chains to migrate around in solution. Such a picture is supported by the high-resolution TEM results, which show soft materials on the surfaces of individual nanotubes (Figure 2).

Figure 2. High-resolution TEM image (scale bar = 5 nm) of the soluble THF-SWNT sample.

The interactions of THF with SWNT are apparently specific to the porphyrin base, hindered upon the condensation of a metal cation. For example, the Zn—THF was used in the place of THF under the same experimental conditions, but no interaction leading to the solubilization of SWNTs was observed. The negative results with the use of metalloporphyrins also suggest that the selectivity toward semiconducting SWNTs reported above is associated with THF, not fragments of decomposed THF, because porphyrins with and without the center-chelated metal share similar decomposition patterns.

In summary, the derivatized porphyrin THF selectively interacts with and solubilizes semiconducting SWNTs, resulting in the “extraction” of most of the semiconducting SWNTs from the starting purified nanotube sample. Mechanistically, we suspect that the semiconducting and metallic SWNTs have significantly different surface properties. A speculation is that a semiconducting SWNT is more like a conjugated nanocomposite with the nanotube surface properties conceptually similar to those found in radical ion pairs, thus amenable to interactions with the free-base porphyrin molecules. Since the porphyrin is readily prepared and largely recoverable from the extraction experiment, the reported procedure may become an effective and convenient method for the separation of semiconducting SWNTs from metallic SWNTs.

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Supporting Information Available: Additional figures (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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