The present invention is directed towards processes for covalently attaching molecular wires and molecular electronic devices to carbon nanotubes and compositions thereof. Such processes utilize diazonium chemistry to bring about this marriage of wire-like nanotubes with molecular wires and molecular electronic devices.

11 Claims, 12 Drawing Sheets
OTHER PUBLICATIONS


* cited by examiner
Figure 1

1. \text{Br-} \text{N}_2^+ \text{BF}_4^- \quad 2. \text{Cl-} \text{N}_2^+ \text{BF}_4^- \\
3. \text{F-} \text{N}_2^+ \text{BF}_4^- \quad 4. \text{O}_2\text{N-} \text{N}_2^+ \text{BF}_4^- \\
5. \text{O}_2\text{N-} \text{N}_2^+ \text{BF}_4^- \quad 6. \text{H}_3\text{CO}_2\text{C-} \text{N}_2^+ \text{BF}_4^- \\
7. \text{C}_{12} \quad 8. \text{N}_2^+ \text{BF}_4^- \\
9. \text{O-} \text{O-} \text{O-} \text{O-} \text{N}_2^+ \text{BF}_4^- \\
10. \text{S-} \text{N}_2^+ \text{BF}_4^- \\
11. \text{HOO-} \text{N}_2^+ \text{BF}_4^- \\
12. \text{HOOC-} \text{N}_2^+ \text{BF}_4^-
Figure 2

\[
\begin{align*}
\text{a) } & \text{TosCl, } H_2O, \text{THF} & \text{b) } 4\text{-nitrophenol, } \\
& \text{DMF, } K_2CO_3 & \text{c) } H_2, \text{Pd/C} & \text{d) } NOBF_4, \\
& \text{CH}_3\text{CN} &
\end{align*}
\]
Figure 6

Intensities vs. Shift (cm\(^{-1}\))

Figure 7

Transmittance vs. Wavenumber (cm\(^{-1}\))
Figure 12

\[ \text{SWNT} + \begin{array}{c} \text{R} \\ \text{N}^2 \end{array} \overset{1,2\text{-dichlorobenzene}}{\longrightarrow} \begin{array}{c} \text{CH}_3\text{CN, 2:1} \\ 60^\circ\text{C, 12 h} \end{array} \]

16, \( R = \text{Cl} \)
17, \( R = \text{tert-butyl} \)
18, \( R = \text{CO}_2\text{CH}_3 \)
19, \( R = \text{NO}_2 \)
20, \( R = \text{COOH} \)
21, \( R = \text{OH} \)

Figure 13

Absorbance

Wavelength (nm)
Figure 14

![Graph showing intensity vs. shift (cm⁻¹)]

Figure 15

\[ \text{N}_2^+\text{BF}_4^- + \text{1,2-dichlorobenzene + SWNTs} \overset{\text{UV light}}{\longrightarrow} \text{SWNTs} \text{Cl} \text{Cl} \} \text{n} \]
Figure 16

\[ A \]

\[ R = H_2C-C=CH_2 \]

\[ \text{heat} \]

cured epoxy (thermoset) resin

Figure 17

phenol derivatized nanotubes

thiophenol derivatized nanotubes

aniline derivatized nanotubes

aliphatic alcohol derivatized nanotubes
1,2-dichlorobenzene or dimethylformamide
or
heating at or near 175 °C
Cured thermoset resin in which the derivatized nanotubes act as a crosslinking agent by chemical reaction with the polymer matrix.
PROCESS FOR ATTACHING MOLECULAR WIRES AND DEVICES TO CARBON NANOTUBES AND COMPOSITIONS THEREOF

FIELD OF INVENTION

The present invention relates broadly to carbon nanotubes. More specifically, the invention relates to derivatization of carbon nanotubes with diazonium compounds and to uses for the derivatized carbon nanotubes.

BACKGROUND OF THE INVENTION


Since 1991, there has been a great deal of interest in derivatization of carbon nanotubes, and more, particularly, single-wall carbon nanotubes, to facilitate their manipulation, to enhance the solubility of such nanotubes, and to make the nanotubes more amenable to composite formation. This is because single-wall carbon nanotubes are one of the more striking discoveries in the chemistry and materials genre in recent years. Nanotubes possess tremendous strength, an extreme aspect ratio, and are excellent thermal and electrical conductors. A plethora of potential applications for nanotubes have been hypothesized, and some progress is being made towards commercial applications. Accordingly, chemical modification of single-wall carbon nanotubes, as well as multi-wall carbon nanotubes, will be necessary for some applications. For instance, such applications may require grafting of moieties to the nanotubes: to allow assembly of modified nanotubes, such as single-wall carbon nanotubes, onto surfaces for electronics applications; to allow reaction with host matrices in composites; and to allow the presence of a variety of functional groups bound to the nanotubes, such as single-wall carbon nanotubes, for sensing applications.

While there have been many reports and review articles on the production and physical properties of carbon nanotubes, reports on chemical manipulation of nanotubes have been slow to emerge. There have been reports of functionalizing carbon nanotubes ends with carboxylic groups (Rao et al., Chem. Commun., 1996, 1525-1526; Wong et al., Nature, 1998, 394:52-55), and then further manipulation to tether them to gold particles via thiol linkages (Liu et al., Science, 1998, 280:1253-1256). Haddon and co-workers (Chen et al., Science, 1998, 282:95-98) have reported solvating single-wall carbon nanotubes by adding octadecylamine groups on the ends of the tubes and then adding dichloro-carbenes to the nanotube sidewall, albeit in relatively low quantities (~2%). Success at covalent sidewall derivatization of single-wall carbon nanotubes has been limited in scope, and the reactivity of the sidewalls has been compared to the reactivity of the basal plane of graphite. Aihara, J. J. Phys. Chem., 1994, 98, 9773-9776. A viable route to direct sidewall functionalization of single-wall carbon nanotubes has been fluorination at elevated temperatures, which process was disclosed in a co-pending application commonly assigned to the assignee of the application, U.S. patent application Ser. No. 09/010,390, “Chemical Derivatization Of Single-Wall Carbon Nanotubes To Facilitate Solvation Thereof; And Use Of Derivatized Nanotubes To Form Catalyst-Containing Seed Materials For Use In Making Carbon Fibers,” to Margraves et al., filed Mar. 16, 2001. These functionalized nanotubes may either be de-fluorinated by treatment with hydrazine or allowed to react with strong nucleophiles, such as alkyllithium reagents. Although fluorinated nanotubes may well provide access to a variety of functionalized materials, the two-step protocol and functional group intolerance to organolithium reagents may render such processes incompatible with certain, ultimate uses of the carbon nanotubes. Other attempts at sidewall modification have been hampered by the presence of significant graphitic or amorphous carbon contaminants. Chen, Y. et al., J. Mater Res. 1998 13, 2423-2431.

It would thus be desirable to develop a direct approach to high degree of functionalization of nanotubes that would be accommodating (i.e. a one step approach and one that is compatible with certain, ultimate uses of the nanotubes). Such uses include applications to utilize the tremendous strength, extreme aspect ratios, and excellent thermal and electrical conductive properties of the nanotubes. Accordingly, it is an object of this invention to provide a method for derivatizing carbon nanotubes, especially the sidewalls and end-caps of single-wall carbon nanotubes, utilizing chemistries that are direct, accommodating, and compatible with the ultimate uses and applications of the nanotubes.

SUMMARY OF THE INVENTION

The invention incorporates new processes for the chemical modification of carbon nanotubes. Such processes involve direct modification of the end-caps and sidewalls of carbon nanotubes, including small diameter (ca. 0.7 nm) single-wall carbon nanotubes, with diazonium species. The method allows the chemical attachment of functional groups to the surface of carbon nanotubes.
compounds to the side and ends of carbon nanotubes. These chemically modified nanotubes have applications in polymer composites, molecular electronic applications, and sensor devices. The methods of derivatization include electrochemical induced reactions, thermally induced reactions (via in-situ generation of diazonium compounds or via pre-formed diazonium compounds), and photochemically induced reactions. The derivatization causes significant changes in the spectroscopic properties of the nanotubes. The estimated degree of functionality is ca. 1 out of every 20 to 30 carbons in a nanotube bearing a functionality moiety.

The electrochemical induced processes include procedures utilizing an assembly of nanotubes, such as a piece of “bucky paper” or mat, which can be held with a silver paste covered alligator clip and immersed in an acetonitrile solution of a diazonium salt and a supporting electrolyte salt, while applying a potential (typically a negative potential) to the assembly of nanotubes. By such a process, a molecular wire (such as an oligo(phenylene ethynylene) molecular wire) and also a molecular electronic device have been covalently attached to a nanotube. This represents the marriage of wire-like nanotubes with molecular wires and with molecular electronic devices.

Such electrochemical processes can be adapted to apply site-selective chemical functionalization of nanotubes. Moreover, it allows for the controlled attachment of two or more different chemical functionalities to different locations on the nanotubes.

The thermally induced processes include procedures in which a dispersion of carbon nanotubes in an organic solvent mixture is treated with a precursor to a reactive diazonium species. This precursor is then transformed in-situ to the reactive species, and its thermal decomposition leads to chemical attachment to the carbon nanotubes. It is believed that such a process has the advantage of scalability and avoids the necessity of isolating and storing potentially unstable diazonium compounds, i.e., the species that reacts with the carbon nanotubes.

Moreover, the thermal induced processes also include procedures utilizing pre-formed diazonium species. The reactive species can be prepared beforehand, isolated, and added to the mixture. Additional variations include variations in the temperature of the process (ambient temperature and higher and lower temperatures), ratio of reactants, and a variety of organic solvents.

The photochemical induced processes are similar to the thermal induced reaction except that a photochemical process (not a thermal process) is utilized to cause the decomposition of the diazonium species that leads to the chemical attachment of the moieties to the carbon nanotubes.

When modified with suitable chemical groups, the nanotubes are chemically compatible with a polymer matrix, allowing transfer of the properties of the nanotubes (such as mechanical strength) to the properties of the composite material as a whole. To achieve this, the modified carbon nanotubes can be thoroughly mixed (physically blended) with the polymeric material, and/or, if desired, allowed to react at ambient or elevated temperature. These methods can be utilized to append functionalities to the nanotubes that will further covalently bond to the host polymer matrix, or directly between two tubes themselves.

There is a multitude of variations in the chemical structure of the polymer matrix, i.e., polyethylene, various epoxy resins, polypropylene, polycarbonate etc. In general, possible composite materials could be made with chemically modified nanotubes and thermoplastics, thermosets, elastomers, and others. There is also a host of variations possible in the chemical groups that can be attached to the nanotubes. The specific group will be chosen to enhance compatibility with the particular polymer matrix desired and, if desired, to cause chemical bonding to the host material.

Furthermore, when modified with suitable chemical groups, the nanotubes can be used as a generator of polymer growth. i.e., the nanotubes would be derivatized with a functional group that could be an active part of a polymerization process, which would also result in a composite material in which the carbon nanotubes are chemically involved.

**BRIEF DESCRIPTION OF THE DRAWINGS**

FIG. 1 shows the structure of certain aryl diazonium salts used to derivatize single-wall carbon nanotubes.

FIG. 2 shows the scheme utilized to prepare Compounds 9 and 11 as reflected in FIG. 1.

FIG. 3 shows the absorption spectra in dimethylforma- mide for (A) SWNT-p and (B) SWNT-1.

FIG. 4 shows the absorption spectra in dimethylforma- mide for (A) SWNT-p and (B) SWNT-8.

FIG. 5 shows the Raman spectra from solid samples, with excitation at 782 nm, for (A) SWNT-1 and (B) SWNT-2.

FIG. 6 shows the Raman spectra in the radial breathing mode region for (A) SWNT-4 and (B) SWNT-p.

FIG. 7 shows the infrared spectra (attenuated total reflectance) of derivatized nanotubes for (A) SWNT-4 and (B) SWNT-6.

FIG. 8 shows the thermogravimetric analysis data in argon for SWNT-10.

FIG. 9 shows the Raman spectra for (A) SWNT-p, (B) SWNT-2, and (C) SWNT-2 after TGA.

FIG. 10 shows the high-resolution TEM images for (A) SWNT-p and (B) SWNT-4. The scale bar applies to both images.

FIG. 11 shows electrochemical grafting of an aryl diazo- nium salt onto a carbon surface.

FIG. 12 shows the reaction sequence for derivatization of single-wall carbon nanotubes by in-situ generation of the diazonium species, and examples of functionalized phenyl moieties employed in reactions.

FIG. 13 shows the absorption spectra in dimethylforma- mide for (A) SWNT-p and (B) 18. The spectra for 16, 17, and 19 are similar, with little or no visible structure. The spectrum of the material from the sequence to produce 20 was essentially equivalent to that shown for SWNT-p.

FIG. 14 shows the Raman spectra from solid samples, with excitation at 782 nm, for (A) SWNT-p and (B) 17. The Raman spectra of 16, 18, and 19 are similar, but with differing ratios of the peak intensities. In all these cases, the relative intensity of the disorder mode is increased. The spectrum of the material from the sequence to produce 20 was essentially equivalent to that shown for SWNT-p.

FIG. 15 shows the reaction sequence for photochemical derivatization of a single-wall carbon nanotube.

FIG. 16 shows an example of the portions comprising an epoxy resin.

FIG. 17 shows examples of nanotubes that are chemically modified with groups compatible with the curing agent portion, and reactive with the epoxy portion of a thermosetting resin.

FIG. 18 shows a schematic depiction of carbon nanotube containing composite material where the freehand lines represent the polymer matrix that is cross-linked by the chemically modified carbon nanotubes, creating a thermosetting composite material.
FIG. 19 shows a depiction of chemically modified carbon nanotubes cross-linked via disulfide linkages.

FIG. 20 shows the preparation of nanotubes chemically modified with thiophenol moieties.

FIG. 21 shows the preparation of carbon nanotubes chemically modified with pendant epoxy groups that are compatible with the epoxy portion of a resin and reactive with the curing agent portion of a thermosetting resin, as reflected in FIG. 16.

FIG. 22 shows an example of a composite material based on poly(methylmethacrylate) and chemically modified carbon nanotubes, based on a hydrogen bonding motif (indicated by the dashed lines).

FIG. 23 shows an example of chemically modified nanotubes being used in a polymerization process to grow the polymer from the nanotubes.

DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS

Electrochemical Derivatization of Carbon Nanotubes with Diazonium Species

Aryl diazonium salts are known to react with electron deficient olefins, as known in the Meerwein reaction. Obushak, M. D., et al., Tett. Lett. 1998, 39, 9567-9570. In such solution phase reactions, diazonium salt decomposition is typically catalyzed by a metal salt such as copper(I) chloride, giving a reactive aryl radical. In some cases, the reaction is believed to proceed through an aryl cation. This type of chemistry has been successfully applied to the modification of carbon surfaces via grafting of electrochemically reduced aryl diazonium salts. Delamar, M., et al., Carbon 1997, 35, 801-807; Allongue, P., et al., J. Am. Chem. Soc. 1997, 119, 201-207; Ortiz, B., et al., J. Electro. Chem. 1998, 455, 75-81; Saby, C., et al., Langmuir 1997, 13, 6805-6813; Delamar, M., et al., J. Am. Chem. Soc. 1992, 114, 5883-5884. Reduction may give an aryl radical that covalently attaches to the carbon surface. This technique has been applied to both highly ordered pyrolytic graphite (HOPG) and glassy carbon (GC) electrodes.

Methylene chloride and acetonitrile were distilled from calcium hydride. Dimethylformamide was distilled and stored over molecular sieves. Tetrahydrofuran was distilled from sodium/benzophenone ketyl. All other reagents were obtained commercially and used without further purification.

Carbon Nanotubes. A method for producing small diameter (ca. 0.7 nm) single-wall carbon nanotubes has been developed by Smalley, et al. Nikolaev, P., et al., Chem. Phys. Lett. 1999, 313, 91-97. This method is disclosed in a co-pending application commonly assigned to the assignees of the application. U.S. patent application Ser. No. 09/830, 642 “Gas-Phase Nucleation and Growth of Single-Wall Carbon Nanotubes from High Pressure CO,” to Smalley et al., filed Apr. 27, 2001, which is incorporated herein by reference. This material is now commercially available (Carbon Nanotechnologies Inc., HiPco material). As the diameter of these nanotubes is approximately the same as that of C_{60}, these nanotubes are understood to display enhanced reactivity relative to the larger diameter tubes typically produced by laser oven methods, since the reactivity of C_{60} has been attributed in part to curvature strain. While the present invention is also pertinent to multi-wall carbon nanotubes and larger diameter single-wall carbon nanotubes, these small diameter nanotubes were primarily utilized during the examples demonstrating the present process. A variety of diazonium salts have been used, including those that provide moieties conducive to further elaboration after attachment of the nanotubes. Also, an oligo (phenylene ethynylene) molecular device similar to the one that has been shown to exhibit memory and room temperature negative resistance (Chen, J., et al., App. Phys. Lett. 2000, 77, 1224-1226) has been attached to the nanotubes.

The following examples, as well as, the other examples described herein, are presented to further illustrate the invention and, are not to be construed as unduly limiting the scope of this invention.

A. EXAMPLE NOS. 1-11

For the electrochemical derivatization experiments, a piece of bucky paper, formed by filtration of a suspension, was used as the working electrode in a three-electrode cell and immersed in an acetonitrile solution containing the diazonium salt and an electrolyte. The diazonium salts were probably reduced to aryl radicals at the surface of the bucky paper, and subsequently become covalently attached to the nanotubes. The conductivity of single-wall carbon nanotubes has been well documented. In general, aryl diazonium salts are easily prepared under conditions that tolerate a variety of functional groups. Consequently, the method described herein allows functionalization of nanotubes with a wide variety of diazonium salts, including those that provide chemical handles for additional elaboration after attachment to nanotubes.

The purified single-wall nanotubes (hereafter, SWNT-p) used in this investigation contained little amorphous or other extraneous carbon contaminants. The purification technique for the nanotubes is discussed in more detail below. The fact the SWNT-p contained little amorphous or other extraneous carbon contaminants is significant, as the presence of such material may have hindered the ability to determine whether previous derivatization efforts were successful. (While the lack of impurities was an issue in the initial demonstrations respecting the operability of the reactions, it should be noted that these reactions will work on raw, impurified multi- and single-wall carbon nanotubes, i.e. the reactions will work even in the absence of a purification process.) In addition, the residual iron content (catalyst from the gas-phase growth technique) was <1 atomic % by electron microprobe analysis (EMPA) (ca. 0.3 atomic %). The diazonium salts used to derivatize SWNT-p are shown in FIG. 1. Compounds 1-7 and 11 were prepared from the corresponding aniline derivatives by known methods (Kosynkin, D.; Tour, J. M. Org. Lett. 2000), using nitrosonium tetrafluoroborate as the diazonization reagent. Compound 8 was prepared using the process reported in Kosynkin, D., et al., Org. Lett. 2003, 3, 993-995. Compound 9 and 10 were prepared according to the scheme reflected in FIG. 2. Characterization of these compounds is further discussed below. Reaction of these compounds with SWNT-p generated SWNT-x, where x=1-9 and 11-12, respectively.

The small diameter single-wall carbon nanotubes used in this investigation were produced by a gas-phase catalytic technique, using carbon monoxide as the feedstock and iron carbonyl as the catalyst. Nikolaev, P., et al., Chem. Phys. Lett. 1999, 313, 91-97; U.S. patent application Ser. No. 09/830,642. (These carbon nanotubes are now commercially available; Carbon Nanotechnologies Inc., HiPco material). The raw production material was purified by air oxidation at 150°C for a period of 12 hours, followed by annealing in argon at 800°C for 6 hours. This material was sonicated in concentrated hydrochloric acid (ca. 50 mg in 60 mL),
filtered, washed extensively with water and 2-propanol, and dried under vacuum. The purity of these samples was verified by SEM, TEM, and EMPA.

Bucky Paper. The use of bucky paper as a working electrode for the derivatization raises several unique issues. Electrical contact between the source and the bucky paper during the electrophoresis process is an issue. This situation can be improved by application of colloidal silver paste to the alligator clip used to hold the bucky paper. It is also believed that the success of the reaction is at least partially dependent on the quality of the bucky paper employed as the working electrode. Accordingly, it was helpful to achieve a suspension that contained little or no visible particulate prior to filtration to form the bucky paper.

General procedure for diazotization of aniline derivatives. A portion of nitrosotetrafluoroborate (1.2 molar equivalents) was weighed out in a glove box and sealed. After removal from the glove box, acetonitrile was added (3 mL/mmol of aniline), and the solution was cooled to −30°C. A solution of the aniline derivative (1 molar equivalent) in acetonitrile (ca. 1 mL/mmol) was added dropwise while stirring (vide infra).; In some cases, dry methylene chloride was used as a co-solvent for the aniline derivative. After complete addition, stirring was continued for 30 minutes, at which time the cold bath was removed. After stirring for a total of 1 hour, the solution was diluted with a 2× volume of ether and stirred. The precipitate was collected by filtration.

4-Bromobenzenediazonium tetrafluoroborate (1). Yield: 85%. MP 138°C. 1H NMR (400 MHz, CD3CN) δ 8.22 (ABq, J=9.1 Hz, Δv=102.1 Hz, 4H).

Chlorobenzenediazonium tetrafluoroborate (2). Yield: 78%. MP 134°C. 1H NMR (400 MHz, CD3CN) δ 8.24 (ABq, J=9.2 Hz, Δv=214.2 Hz, 4H).

Fluorobenzenediazonium tetrafluoroborate (3). Yield: 79%. MP 160°C. 1H NMR (400 MHz, CD3CN) δ 8.64 (dd, J=9.4 Hz, 9.5 Hz, 2H), 7.69 (dd, J=9.4 Hz, 9.5 Hz, 2H).

Tert-Butylbenzenediazonium tetrafluoroborate (4). The tert-butylaniline was dissolved in a 1:1 mixture of acetonitrile and dry methylene chloride prior to addition to the nitrosotetrafluoroborate. Yield: 78%. MP 91°C. IR (KBr) 3364.8, 3107.3, 2968.6, 2277.2, 1579.2, 1482.0, 1418.0, 1373.5, 1269.8, 1056.9, 841.1, 544.6, 621.4 cm−1. 1H NMR (400 MHz, CD3CN) δ 8.16 (ABq, J=9.0 Hz, Δv=298.7 Hz, 4H), 1.30 (s, 12H).

4-Chlorobenzenediazonium tetrafluoroborate (5). Yield: 87%. MP 142°C. 1H NMR (400 MHz, CD3CN) δ 8.72 (ABq, J=9.4 Hz, Δv=65.4 Hz, 4H).

4-{2-[2-(2-Methoxyethoxy)ethoxy]ethyl}nitrobenzene (14). A portion of 13 (9.0 g, 28.3 mmol) was dissolved in 50 mL of dimethylformamide. Potassium carbonate (11.75 g, 85.0 mmol) and 4-nitrophenol (3.82 g, 27.5 mmol) were added. The solution was removed by distillation at reduced pressure. Chromatography (silica, hexane:ethyl acetate, 1:2) was employed to isolate the product (5.71 g, 73% yield). IR (neat) 3093.2, 2919.5, 2289.6, 1577.8, 1473.7, 1078.0, 1024.8, 844.5, 813.8, 761.9, 541.0, 510.2 cm−1. 1H NMR (CDCl3) δ 8.07 (d, J=9.3 Hz, 2H), 6.88 (d, J=9.3 Hz, 2H), 4.12 (app t, 2H), 3.79 (app t, 2H), 3.62 (m, 2H), 3.58 to 3.53 (m, 3H), 3.44 to 3.42 (m, 2H), 3.26 (s, 3H); 13C NMR (100 MHz, CDCl3) δ 164.29, 141.93, 126.24, 114.99, 72.29, 71.29, 71.03, 70.98, 69.77, 68.60, 59.44.

4-[2-(2-Methoxyethoxy)ethoxyl]aniline (15). A portion of 14 (5.77 g, 20.2 mmol) was dissolved in 40 mL of acidic ethanol, and a catalytic amount of 10% palladium on carbon was added. The mixture was hydrogenated on a Parr apparatus (60 psi, 70°C) for 3 hours. The mixture was then filtered over Celite, washing with ethanol. Solid sodium bicarbonate was added, and the mixture was stirred for 2 hours, and then filtered. The solvent was removed by distillation at reduced pressure, leaving a brown oil (5.0 g, 98% yield). IR (neat) 3441.82, 3360.64, 2983.88, 2283.41, 1634.41, 1516.56, 1449.79, 1324.71, 1101.56, 906.97, 722.62 cm−1. 1H NMR (400 MHz, CDCl3) δ 6.65 (ABq, J=8.7 Hz, Δv=51.5 Hz, 4H), 4.01 (t, J=5.4 Hz, 2H), 3.77 (t, J=4.6 Hz, 2H), 3.69 (app t, J=5.6 Hz, 2H), 3.65 to 3.59 (m, 4H), 3.51 (app t, J=4.9 Hz, 2H), 3.34 (s, 3H), 3.0 (brs, 2H).

13C NMR (100 MHz, CDCl3) δ 152.30, 140.58, 116.75, 116.24, 72.31, 71.14, 71.02, 70.93, 70.30, 68.49, 59.44.

4-[2-(2-Methoxyethoxy)ethoxy]ethyl benzenediazonium tetrafluoroborate (9). Compound 15 was subjected to the procedure described above for diazotization. The product was not crystalline, but rather a dark red, sticky material that was difficult to manipulate. The residue was mixed three times with ether, decanting the solvent. This material was sufficiently pure by 1H NMR, and was used without further purification or characterization.
was added a solution of t-butylnitrite (5.59 mL, 103.12 mmol) in 20 mL of THF. The solution was stirred and was calibrated, and data were taken from several different reference electrode and platinum wire counter electrode. A 45 s position in semiconducting nanotubes. The width of these functionalization rather than simple adsorption to the invention. Additionally, parameters such as added potential, the duration of the applied potential, the solvent, and the supporting electrolyte can be varied. Furthermore, alkyl, alkenyl and alkyl derivatives could be used for the process of the invention.

B. Characterization

Scanning electron microscopy (SEM) experiments were performed on a Phillips ESEM XL-30, at an accelerating voltage of 50,000 V. This instrument was equipped with an EDAX detector. Samples for TEM imaging were drop dried from THF onto a 200 mesh lacey carbon grid on a copper support. The accelerating voltage was 100 K.V. Raman spectra were collected on a Renishaw Ramascope, on solid samples, with excitation at 782 nm. UV/Vis/NIR absorption spectra were collected on a Shimadzu UVPC-3101, in double beam mode, with solvent reference. FT-IR spectra were collected using an attenuated total reflectance (ATR) accessory. TGA data were collected in argon, on a TA Instruments SDT-2960. AFM experiments were performed in tapping mode on a Digital Multi-mode SPM. Samples for these experiments were dispersed by sonication and spin coated on a freshly cleaved mica substrate. EMMA experiments were performed on a Cameca SX-50. The instrument was calibrated, and data were taken from several different points on each sample. The average of these points is reported below. NMR data were collected on a Bruker Avance 400. Chemical shifts are reported in ppm downfield from TMS, and referenced to solvent. Melting points are not corrected.

Electronic Structure and Optical Properties. The electronic structure and optical properties of single-wall carbon nanotubes have been well investigated. Liang, W. Z., et al., J. Am. Chem. Soc. 2000, 122, 11129-11137; Jost, O., et al., Phys. Rev. Lett. 1999, 83, 1861-1864; Wu, J., et al., App. Phys. Lett. 2000, 77, 2554-2556. The UV/Vis/NIR absorption spectrum of SWNT-p and SWNT-1 is shown in FIG. 3. The features (van Hove bands) in the spectrum of SWNT-p are due to singularities in the density of states (DOS), and, in this spectral region, are attributed to the band gap transitions in semiconducting nanotubes. The width of these features is due to the overlap of features from tubes of different diameters and chiral indices. These transitions are no longer visible for SWNT-1, and the spectrum is essentially featureless. The absorption spectra of SWNT-2-SWNT-7 and SWNT-11-SWNT-12 are similar, with no apparent features. The spectra of SWNT-8 (FIG. 4) and SWNT-9 retained some visible features, but these were significantly reduced relative to SWNT-p. The loss of structure in the absorption spectra is indicative of significant electronic perturbation of the nanotubes and disruption of the extended π network. This effect is most consistent with covalent functionalization rather than simple adsorption to nanotube walls or end caps.

to the distribution of tube diameters in the sample. The weaker band centered at ca. 1290 cm⁻¹ (ω₀₂) is attributed to disorder or sp³-hybridized carbons in the hexagonal framework of the nanotube walls. The minor band at 850 cm⁻¹ is also characteristic of these small diameter nanotubes, although its molecular origin is not certain. The spectrum of SWNT-1 (FIG. 5B) is quite different. Notably, the relative intensity of the disorder mode is much greater. This is a result of the introduction of covalently bound moieties to the nanotube framework, wherein significant amounts of the sp³ carbons have been converted to sp³-hybridization. The Raman spectra of the other functionalized materials display similar modifications, relative to SWNT-p, but to different degrees. The frequency of the disorder mode and the relative intensities of the three major bands are shown in Table 1.

### Table 1

<table>
<thead>
<tr>
<th>Compound</th>
<th>ω₀₁</th>
<th>ω₀₂</th>
<th>ω₀₃</th>
<th>Int. Ratio (ω₀₁:ω₀₂:ω₀₃)</th>
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<td>SWNT-p</td>
<td>1291</td>
<td>1.00:2.7:3.7</td>
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<td></td>
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<td>SWNT-1</td>
<td>1295</td>
<td>1.00:2.0:3.0</td>
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<tr>
<td>SWNT-2</td>
<td>1294</td>
<td>1.00:2.2:2.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SWNT-3</td>
<td>1295</td>
<td>1.00:2.0:4.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SWNT-4</td>
<td>1200</td>
<td>1.00:1.4:3.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SWNT-5</td>
<td>1251</td>
<td>1.00:3.0:3.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SWNT-6</td>
<td>1252</td>
<td>1.00:3.5:3.5</td>
<td></td>
<td></td>
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<tr>
<td>SWNT-7</td>
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<td>1.00:3.3:8</td>
<td></td>
<td></td>
</tr>
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<td>SWNT-8</td>
<td>1252</td>
<td>1.00:7.3:0</td>
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<td></td>
</tr>
<tr>
<td>SWNT-9</td>
<td>1253</td>
<td>1.00:6.2:5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SWNT-11</td>
<td>1252</td>
<td>1.00:8.2:9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SWNT-12</td>
<td>1251</td>
<td>1.00:10:3.4</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*ω₀₁ = radial breathing mode, ω₀₂ = disorder mode, ω₀₃ = tangential mode. Intensity taken at 265 cm⁻¹; other intensities taken at maximum.

While there is no significant change in the frequency of the disorder mode, the intensity of this mode increased relative to the intensity of the other two modes in all cases. The intensity of the tangential mode is also increased relative to the radial breathing mode in most cases, and the overall intensity is lower. In some cases, Raman spectra collected after functionalization revealed changes in the relative intensities of the peaks within the radial breathing mode region. For example, the Raman spectra in this region is shown in FIG. 6 for SWNT-p and SWNT-4.

Infrared Spectroscopy. Infrared spectroscopy (FT-IR, ATR) was also used to characterize some of the derivatized materials. The spectrum of SWNT-4 (FIG. 7A) clearly shows significant C—H stretching from the tert-butyl moiety at ca. 2950 cm⁻¹. In the spectrum of SWNT-6 (FIG. 7B), the carbonyl (CO) stretch is apparent at 1731 cm⁻¹ (1723 cm⁻¹ in precursor diazonium salt), along with minor C—H stretching modes in the 2900 cm⁻¹ region.

Electron Microprobe Analysis. Electron microprobe analysis (EMPMA) experiments revealed 2.7 atomic % chlorine for SWNT-2 (average of four points), and 3.5 atomic % fluorine for SWNT-3 (average of five points). These percentages correspond to estimated stoichiometries of Cl₉₀₁₃₅₆ for SWNT-2, and Cl₈₀₋₉₃ for SWNT-3, where C is a carbon in the nanotube framework, and R is the functionalizing moiety. Accordingly, approximately one out of every 10-20 carbons in the nanotube bears a functional moiety.

Thermogravimetric Analysis. In thermogravimetric analysis (TGA) of SWNT-2 (FIG. 8), a total weight loss of ca. 25% was observed on heating to 600° C. under argon. After TGA of SWNT-2, the Raman spectrum is restored to approximately that of SWNT-p, as seen in FIG. 9. It is believed that this restoration indicates removal of the functional moieties, leaving the nanotubes intact. The stoichiometry estimated from the EMPA data predicts a weight loss of ca. 25% in the case of such a removal. Thus, these figures are in excellent agreement. The TGA and EMPA data for SWNT-3 are also in good agreement. SWNT-p suffers a ca. 5% weight loss following the same temperature profile. TGA data and estimated stoichiometries for the remaining materials (with the exception of SWNT-8, which was not performed) are shown in Table 2.

### Table 2

<table>
<thead>
<tr>
<th>Compound</th>
<th>Observed % weight loss</th>
<th>Stochiometry Ratio*</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWNT-p</td>
<td>5</td>
<td>NA</td>
</tr>
<tr>
<td>SWNT-1</td>
<td>35</td>
<td>1/25</td>
</tr>
<tr>
<td>SWNT-2</td>
<td>30</td>
<td>1/27</td>
</tr>
<tr>
<td>SWNT-3</td>
<td>26</td>
<td>1/20</td>
</tr>
<tr>
<td>SWNT-4</td>
<td>27</td>
<td>1/34</td>
</tr>
<tr>
<td>SWNT-5</td>
<td>26</td>
<td>1/31</td>
</tr>
<tr>
<td>SWNT-6</td>
<td>31</td>
<td>1/28</td>
</tr>
<tr>
<td>SWNT-7</td>
<td>39</td>
<td>1/36</td>
</tr>
<tr>
<td>SWNT-8</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>SWNT-9</td>
<td>36</td>
<td>1/40</td>
</tr>
<tr>
<td>SWNT-10</td>
<td>28</td>
<td>1/44</td>
</tr>
<tr>
<td>SWNT-11</td>
<td>24</td>
<td>1/32</td>
</tr>
</tbody>
</table>

*Nano tube carbons bearing a functionalized phenyl moiety. These values are compensated for weight loss at low temperatures due to solvent evaporation and degassing (ca. 2-4% in all cases).

Table 2 reflects that the degree of functionality for these compounds is at least about one moiety to forty carbon atoms, and typically at least about one moiety to thirty carbon atoms. The estimated degree of functionality is ca. out of every 20 to 30 carbons in the nanotube bearing a functionality moiety.

### Scanning and Transmission Electron Microscopy

Due to insufficient resolution, analysis of the reaction products by scanning electron microscopy (SEM) did not reveal any visible evidence of functionalization or significant change from SWNT-p. Transmission electron microscopy (TEM) imaging of SWNT-4 revealed significant changes due to the functionalization. In images of SWNT-p (FIG. 10A), the nanotube walls are essentially clean and uniform, and there is no overcoating of graphite carbon. Images of SWNT-4 (FIG. 10B) revealed the presence of bumps on the sidewalls of the tubes, on the order of 2-6 Å in dimension. These bumps are seen on almost all individual tubes and on the exterior of ropes, though the resolution is not sufficient to determine whether they are present on the walls of tubes buried within the ropes. These features are a result of functionalization.

### Solubility

Solubility. The solubility of single-wall carbon nanotubes is of significant interest to persons skilled in the art of the invention. The three solvents most applicable for the derivatized small-diameter nanotubes are dimethylformamide, chloroform, and 1,2-dichlorobenzene. SWNT-4 was the only material found to offer significantly improved solubility in organic solvents. SWNT-4 was even found to be somewhat soluble in tetrahydrofuran (THF), as opposed to a complete lack of solubility for SWNT-p in that solvent. After sonication for about 30 minutes, the THF solution was found to contain approximately 50 mg L⁻¹ of SWNT-4, with no visible particulate. After 36 hours, some visible particulate was present, but the solvent was still almost black. This dark color was retained for at least several weeks. Solubility
in dimethylformamide, chloroform, and 1,2-dichlorobenzene was also improved, with suspensions being formed much more rapidly than in the case of SWNT-p, and higher concentrations being achievable. It is believed that this improvement in solubility is likely due to the blocking effect of the bulky tert-butyl group, which could inhibit the close contact necessary for “roping” of the nanotubes. SWNT-5 and SWNT-8 were found to be more soluble in dimethylformamide, but solubility in other solvents (tetrahydrofuran, toluene, 2-propanol, carbon disulfide) was not improved. SWNT-9 was prepared in an effort to effect improved solubility in water and other hydrogen bonding solvents. This functionalization, however, had quite the opposite result. SWNT-9 was not dispersible in water or some cases, direct treatment with pre-formed diazonium salts is observed to be effective at moderate or even room temperature, and it is expected that reactions could be observed at temperatures below room temperature.

**A. EXAMPLES NOS. 12-17**

The nanotubes used in this investigation were again produced by a gas-phase catalytic process developed by Smalley et al., and are now commercially available (Carbon Nanotechnologies Inc., HiPco material). The production material was purified by oxidation in wet air at 250°C for 24 hours, then stirring in concentrated hydrochloric acid at room temperature for 24 hours. The resulting material was washed with copious amounts of water, then 10% aqueous sodium bicarbonate, and finally with additional water. After drying under vacuum, the material was used for the functionalization reactions.

The reaction sequence is depicted in FIG. 12. In a typical experiment, 8 mg of single-wall carbon nanotubes was sonicated for 10 minutes in 10 mL of 1,2-dichlorobenzene (ODCB). To this suspension was added a solution of the aniline derivative (2.6 mmol, ca. 4 equiv/mol of carbon) in 5 mL of acetonitrile. After transfer to a septum capped reaction tube (Ace Glass, 8648-03) and bubbling with nitrogen for 10 min, 4.0 mmol of isoamyl nitrite was quickly added. The septum was removed and replaced with a Teflon screw-cap, and the suspension was stirred at 60°C for approximately 15 hours. Due to the system utilized, considerable pressure was attained in the vessel due to the evolved nitrogen. This was alleviated by partially unscrewing the cap for venting every ~30 min for the first 3 hours.

After cooling to ~45°C, the suspension was diluted with 30 mL of dimethylformamide (DMF), filtered over a Teflon (0.45 μM) membrane, and washed extensively with DMF. Repeated sonication in, and further washing with DMF constituted purification of the material.

**B. Characterization**

Functionalized nanotube materials 16-19 and 21 displayed significantly altered spectroscopic properties, akin to those reported for materials derivatized via the electrochemical method described above. For example, the UV/vis/NIR absorption spectrum of 18 (FIG. 13) shows an almost complete loss of the van Hove singularities. This loss of structure is characteristic of the disrupted π-system, and again indicates covalent modification of the nanotubes. In the Raman spectra reflected in FIG. 14, the overall intensity of the scattered light is lower, and the relative intensities of the three main modes are altered.

Relative to the tangential mode at ca. 1590 cm⁻¹, the intensity of the radial breathing mode (ca. 250 cm⁻¹) is decreased, and the intensity of the disorder mode (1290 cm⁻¹) is significantly increased. The increase in the relative intensity of the disorder mode can be attributed to an increased number of sp²-hybridized carbons in the nanotube framework, and can be taken as a crude measure of the degree of functionalization. Additionally, as previously discussed, the functionalized phenyl moieties attached to the nanotubes can be removed by heating in an argon atmosphere, and that thermal gravimetric analysis (TGA) consequently provides a quantitative estimate of the degree of functionalization. Upon heating 16-19 to 600°C in an argon atmosphere, the observed weight loss values were as follows, with the value previously reported for the same materials prepared via the electrochemical technique in parenthesis: 16: 26% (30%), 17: 25% (27%), 18: 26% (31%), 19: 23% (26%) 21 (not prepared by the electrochemi,...
Derivatization with aryl diazonium species can also be induced photochemically. A photochemical reaction was performed utilizing 4-chlorobenzenediazonium tetrafluoroborate, which is the same diazonium species prepared and utilized in Example No. 2. Thus, a suspension of SWNT-p in 1,2-dichlorobenzene was created by sonication. To this suspension was added a portion of the diazonium salt dissolved in minimal acetonitrile. The resulting mixture was stirred while residing within the chamber of a photochemical reaction apparatus, with an excitation wavelength of ca. 254 nm (an ultraviolet light source). The light source for the photochemically induced reaction may be any wavelength, and typically is an ultraviolet or visible wavelength. This reaction is reflected in FIG. 15. The resultant material was similar in all respects to SWNT-2 that was prepared by the electrochemical technique of the present invention.

The thermal technique is then comparable in its effectiveness to the electrochemical method to that obtained by the electrochemical processes of the present invention. Experiment Nos. 13-18 were performed with a large excess of the aniline derivative, i.e. sufficient to provide the diazonium species in amounts equivalent to the amount of diazonium tetrafluoroborate salts used in the previously discussed reported electrochemical examples. Hence, these Examples Nos. 13-18 are comparable in this fashion.

For material 16, straightforward comparison is available through electron microprobe analysis. This analysis gave a value of 2.2 atomic % chlorine, relative to 97 atomic % carbon. Similar material prepared by the electrochemical technique was analyzed to have 2.7 atomic % chlorine, relative to 96 atomic % carbon (vide supra).

The TGA data also give additional insight into the relative efficiency of the thermal method. For example, the mass loss for 19 corresponds to an estimated 1 in 37 carbons in the nanotubes being functionalized, versus the 1 in 34 ratio achieved by the electrochemical method. It is believed that the thermal technique is then comparable in its effectiveness to the electrochemical method for the equivalent material (SWNT-5). It is believed that optimization of the conditions could provide a higher degree of functionalization. The observed efficacy is sufficient to significantly alter the properties of the single-wall carbon nanotubes, and will likely be satisfactory for numerous applications, such as cross-linked materials and composite formation as discussed below.

The thermal reaction of the present invention was found to be nearly as efficacious as the electrochemical process of the present invention, although, in certain respects, this thermal reaction is simpler to execute and more adaptable for scalability.

It is again noted that the chemical derivatization of nanotubes can also be successfully performed using preformed diazonium species. The diazonium species can be prepared beforehand, isolated, and added to the mixture. The derivatization can then be induced thermally. Additional variations include variations in the temperature of the process (ambient temperature and higher and lower temperatures), ratio of reactants, and a variety of organic solvents.

Photochemical Derivatization of Carbon Nanotubes with Diazonium Species

EXAMPLE NO. 18

Derivatization with aryl diazonium species can also be induced photochemically. A photochemical reaction was performed utilizing 4-chlorobenzenediazonium tetrafluoroborate, which is the same diazonium species prepared and utilized in Example No. 2. Thus, a suspension of SWNT-p in 1,2-dichlorobenzene was created by sonication. To this suspension was added a portion of the diazonium salt dissolved in minimal acetonitrile. The resulting mixture was stirred while residing within the chamber of a photochemical reaction apparatus, with an excitation wavelength of ca. 254 nm (an ultraviolet light source). The light source for the photochemically induced reaction may be any wavelength, and typically is an ultraviolet or visible wavelength. This reaction is reflected in FIG. 15. The resultant material was similar in all respects to SWNT-2 that was prepared by the electrochemical technique of the present invention.

This experiment further confirmed that reaction of the diazonium salt leads to covalent attachment to the nanotube. Controlled, Site-Specific Functionalization of Carbon Nanotubes with Diazonium Species

By utilizing the electrochemically induced reaction of the present invention, control can be exerted to derivatize the nanotubes at specific sites. Existing technologies (M. S. Fuhrer, et al., “Crossed Nanotube Junctions” Science, 288, 21 Apr. 2000, page 494; Yu Huang, et al., “Directed Assembly of One-Dimensional Nanostructures into Functional Networks” Science, 291, 26 Jan. 2001, page 630; Yi Cui, et al., “Functional Nanoscale Electronics Devices Assembled Using Silicon Nanowire Building Blocks” Science, 291, 2 Feb. 2001, p 851) can be used to prepare a crossbar architecture of nanotubes, wherein one nanotube is fixed to a substrate and a second nanotube is suspended a finite distance above. Both nanotubes can be individually addressed electrically. Application of opposite potentials to the two tubes causes the top tube to deform and essentially come into contact with the lower tube. “Contact” as used herein means both actual physical contact, but also proximity of the entities within an infinitesimally small distance (referred to as van der Walls contact), in which the entities may influence each other on a molecular and electronic scale.

This deformation results in two features of significance. First, the top tube is physically deformed, leading to a potentially higher chemical reactivity at the point of deformation, based on current understanding of the effects of curvature strain on reactivity. This feature would allow selective functionalization at the junction via the electrochemical technique of reaction with diazonium salts. Secondly, higher potential is achieved at the point of “cross” between the tubes.

In the present invention, directed functionalization of the crossed-nanotube junctions can be performed by applying a potential to the ends of the nanotubes (as is known in the art) in the presence of o,o-bis(diazeniun) salts or mono-diazenium salts with an interacting group at the opposite end of the tube. Application of potentials to the ends of the nanotubes would permit control of the functionalization at the cross point domain.

Any cross bar array of nanotubes could be functionalized by such processes. For instance, a crossbar architecture of nanotubes will be prepared by fluid flow over a patterned substrate, or by direct tube growth between posts, or by some other method. Furthermore, the diazonium salt assembly described here could occur in a diazonium solution, with voltages on orthogonal tubes, regardless of the assembly method for the tube arrays. Application of potentials to the nanotubes in the presence of diazonium salts would permit functionalization at the cross point domain.

The diazonium species are directed by the potential existing at the junction to react with the surface of the nanotube, thus placing functional molecular devices at the junctions. Site-specific functionalization could enable the use of nanotubes in molecular electronic applications since device functionality is critical at the cross points. The crossed nanotubes therefore provide a method of directly addressing the functionalized molecules, including molecules that function as molecular switches, molecular wires, and in other capacities and uses as is generally known in the art.
attachment of two or more different chemical functionalities to different locations on nanotubes. This would be performed by applying a potential at a specified set of positions while in a solution of a first diazonium salt, then moving to a solution of a second diazonium salt and applying a potential at other positions, etc. In addition, site specific functionalization will allow individual molecules or groups of molecules to be electrically addressed by metallic contact pads or other contact means as are known in the art. Just such a molecule of electronic interest is incorporated into SWNT-8.

Application of Chemically Modified Carbon Nanotubes in Polymer Composite Materials

Polymer and polymer/composite materials are widely used for structural materials and a variety of other applications. The derivatized carbon nanotubes made using the processes disclosed herein can be used in combination with existing polymer matrices to create new polymer/composite materials. In general, possible composite materials could be made with chemically modified nanotubes and thermoplastics, thermostets, elastomers, and others. There are a multitude of variations in the chemical structure of the polymer matrix, i.e. polyethylene, various epoxy resins, polypropylene, polycarbonate etc. There is also a host of variations possible in the chemical groups that can be attached to the nanotubes. According, it is possible to select a specific polymer and specific moiety to enhance the properties of the particular polymer/composite material desired.

Thus, the polymer/composite material will have significantly enhanced properties, such as, for example, enhanced strength and/or conductivity. And, when modified with suitable chemical groups, the nanotubes will be chemically compatible with the polymer matrix, allowing transfer of the properties of the nanotubes (especially mechanical strength) to the properties of the composite material as a whole. Typically, to achieve this, the modified carbon nanotubes can be thoroughly mixed (physically blended) with the polymeric material, and allowed to react at ambient or elevated temperature.

Thermosets. It may be desired to form a polymer/composite material in which the carbon nanotubes are chemically bound at multiple points to the polymer (thermosets). For example, this can be done, for example, utilizing an epoxy resin. Epoxy resins are typically composed of two portions that are mixed in a certain ratio. The resulting mixture then hardens, or “cures,” over a period of time into an adhesive or structural material. The two parts are the epoxy portion (labeled “A” in FIG. 16, in this case derived from the reaction of bisphenol-A with epichlorohydrin) and the curing agent (labeled “B” in FIG. 16). The curing agent contains chemical groups that react with a repeatedly occurring chemical group in the epoxy portion. I.e., the cured or cross-linked resin results from the reaction of A (specifically, the terminal epoxy functionalities) with B (specifically, the terminal amine functionalities). Because both the epoxy portion and the curing agent contain numerous reactive groups, a “cross-linked” material is created, with numerous chemical bonds that impart strength to the cured material (labeled “C” in FIG. 16). The result of the reaction is a highly cross-linked thermoset material.

A wide variety of commercially available epoxy components exist, where the chemical structure of both parts A and B can vary greatly. For example, curing agents may be based on diamines, polymeric amines, phenol containing materials, etc., and may be polymeric. The addition of chemically modified carbon nanotubes to this type of system will greatly increase the strength of the resulting material, due to the strength of the nanotubes themselves. The nanotubes can be chemically modified with groups that are compatible with either the epoxy portion or the curing agent portion. For example, modified nanotubes can be prepared as shown in FIG. 17. (In the figures, the shaded cylinder represents the carbon nanotubes.

Carbon nanotubes thus modified will be thoroughly mixed with either the curing agent portion or the epoxy portion. The resulting material will then be thoroughly mixed with the second portion and allowed to react, or cure at either ambient or elevated temperature, depending on the particular system. The resulting composite material will then be cross-linked not only by the curing agent, but also by the modified carbon nanotubes, via, for example, aryl-thioether linkages, as shown in FIG. 18, where the freehand lines schematically represent the polymer matrix.

These types of materials can be prepared using a variety of modified carbon nanotubes, exemplified by the examples in FIG. 17. Thus, the linkages between the polymer matrix and the nanotubes could be either, thiourea, amine, salt bridge (such as SWNT-11 in an amine containing host polymer) or other linkages. It is understood that the direct chemical bond between the nanotubes and the surrounding polymer matrix will enable the transference of the strength properties of the nanotubes to the composite material itself. It is also noted that enhancement of the material properties by the nanotubes may be caused by factors other than such direct chemical bonding; for example, improved dispersion of the nanotubes within the polymer matrix, enabled by the functionalization, may allow enhancement.

In addition to the chemical bond between the nanotubes and the surrounding polymer matrix, in the case of thiophenol derivatized nanotubes, there will be a chemical interaction between the nanotubes themselves. The formation of disulfide linkages between nanotubes, as shown in FIG. 19, will serve to further strengthen the material. The disulfide linkages can be further reduced (chemically, for instance) to once again provide the non-crosslinked tubes. Hence, this is a stealth-like crosslinking. In fact, such cross-linked nanotubes will represent an enhanced strength material in their own right for some applications.

Another possibility is modification of carbon nanotubes with chemical groups that are compatible with the epoxy portion rather than the curing agent portion, such as, for example, shown in FIG. 21. The material resulting from the incorporation of nanotubes derivatized in this manner would again be a chemically bound, three-dimensional network, cross-linked by both the curing agent and the chemically modified nanotubes.

Other specific chemical interactions between modified carbon nanotubes and a polymer matrix are also possible. For example, a system based on a hydrogen bonding interaction is shown in FIG. 22. This type of interaction would be in an extended three-dimensional network, again imparting the strength of the nanotubes to the composite material.

Utilizing the electrochemical process described in this invention, the derivatized nanotubes reflected in FIG. 20 were prepared. From this, what is believed to be a step of deprotection of the thiol was performed by treatment with trifluoroacetic acid in 1,2-dichlorobenzene (acid hydrolysis). Alternatively, this step could be performed by treatment with trifluoroacetic acid in dimethylformamide, or by thermolysis at or about 175°C. Again, the functionalized nanotubes formed as reflected in FIG. 20 would chemically react with, for example an epoxy resin, with the free thiol group (SH) acting as a crosslinking agent.
Thermoplastics. In addition to thermosets, derivatized nanotubes can be utilized for thermoplastics. As in the case of thermosets, the derivatized nanotubes may or may not be chemically bound to the polymer matrix. It is understood that a modest degree of chemical attachment between the derivatized nanotubes and the polymer matrix could be tolerated, while retaining the thermoplastic properties (specifically, the ability to heat and reform the material without significant degradation). As noted above, physical blending of the carbon nanotubes with the polymer can be enhanced by the derivatization process (specifically by making the nanotubes more compatible with, or more soluble in, the host polymer).

For instance, a polymer/composite material containing pure (and underivatized) single-wall carbon nanotubes may be desired so that the polymer would have certain enhanced conductive properties; however, the pure and underivatized carbon nanotubes may not sufficiently disperse in the polymer. By derivatizing the nanotubes with a particular moiety, the derivatized nanotubes could then be dispersed adequately. Because the derivatization of the nanotube may likely have affected the conductivity of the nanotube (and will thus effect the conductivity of the polymer/composite), it may be desirable to reverse the derivatization process to remove the functional groups from the nanotubes after dispersal. In this manner, the conductivity of the material can be recovered. This can be done by any process that reverses the derivatization, such as raising the temperature of the polymer/composite material to a temperature at which the functional group disassociates. Typically, this temperature appears to be at least about 250°C.

A. EXAMPLE NOS. 19-25

Moreover, the thermoplastic may also be formed utilizing the derivatized carbon nanotube. The functional groups, while not necessarily chemically bond to the polymer, would be physical extensions from the tube (like branches from a tree) that will afford additional strength to the polymer/composite materials. This enhancement may be due to a roughening effect on the nanotube surface, increasing friction and reducing sliding of the polymer matrix along the nanotube length. As is understood in the art, such an effect would further enable transference of the desirable nanotube properties to the composite material.

Utilizing processes discussed above the following functionalized single-wall carbon nanotubes where prepared where n=1 in 20 to 1 in 40 functional groups per nanotube carbons):

This derivatized material (17) was dispersed in High-Impact-Polystyrene (HIPS) at various concentrations. Tensile strength, tensile modulus, and % strain to failure data of the resulting composite material were then gathered. The results of these examples are reflected in Table 3.

<table>
<thead>
<tr>
<th>Material</th>
<th>Tensile Strength (MPa)</th>
<th>Tensile Modulus (MPa)</th>
<th>% Strain to Failure</th>
</tr>
</thead>
<tbody>
<tr>
<td>HIPS (pure)</td>
<td>18.1</td>
<td>454.5</td>
<td>56.4</td>
</tr>
<tr>
<td>1 wt % 17</td>
<td>32.5</td>
<td>729.3</td>
<td>4.6</td>
</tr>
<tr>
<td>3 wt % 17</td>
<td>17.8</td>
<td>821.3</td>
<td>2.2</td>
</tr>
<tr>
<td>3 wt % pristine*</td>
<td>22.8</td>
<td>560.0</td>
<td>11.0</td>
</tr>
<tr>
<td>5 wt % 17</td>
<td>26.3</td>
<td>736.5</td>
<td>3.9</td>
</tr>
<tr>
<td>7 wt % 17</td>
<td>22.0</td>
<td>724.4</td>
<td>3.1</td>
</tr>
</tbody>
</table>

*3 wt %, unfunctionalized nanotubes (SWNT-p), for direct comparison

On the whole, there is a substantial improvement in the tensile properties of the polymer/composite materials with the functionalized nanotubes. There is improvement over both the pristine HIPS polymer, and over the composite of HIPS and unfunctionalized nanotubes.

Polymerization. Furthermore, a polymer that includes carbon nanotubes can be formed by derivatizing the carbon nanotubes with a functional group that is capable of polymerizing or initiating a polymerization. Once the functional group is attached, standard polymerization techniques can then be employed to grow the polymer from the functional group in situ, i.e., the functional group attached to the nanotube could be used as a generator of polymer growth. Such standard polymerization techniques could be any of the standard known types, such as radical, cationic, anionic, condensation, ring-opening, methathesis, or ring-opening-metathesis (ROMP) polymerizations, when appropriate groups are bound to the nanotubes. For instance, FIG. 23 reflects an example of a carbon nanotube that has been derivatized with a functional group 4-aminophenyl that is subsequently polymerized with styrene to grow the polymer from the functional group. Accordingly, the functional group attached to the nanotube would be a chemically active part of the polymerization, which would result in a composite material in which the nanotubes are chemically involved.

All of the compositions and methods disclosed and claimed herein can be made and executed without undue experimentation in light of the present disclosure. While the compositions and methods of this invention have been described in terms of preferred embodiments, it will be apparent to those of skill in the art that variations may be applied to the compositions and methods and in the steps or in the sequence of steps of the method described herein without departing from the concept, spirit and scope of the invention. More specifically, it will be apparent that certain agents which are both chemically and physiologically related may be substituted for the agents described herein while the same or similar results would be achieved. All such similar substitutes and modifications apparent to those skilled in the art are deemed to be within the spirit, scope and concept of the invention as defined by the appended claims.

What is claimed is:

1. A process comprising:
   (a) derivatizing a carbon nanotube with a diazonium specie; and
   (b) covalently attaching a molecular wire to the derivatized carbon nanotube.

2. The process of claim 1, wherein the carbon nanotube is a single-wall carbon nanotube.

3. The process of claim 2 further comprising connecting a molecular electronic device to the molecular wire.

4. The process of claim 2, wherein the molecular wire comprises an oligo(phenylene ethynylene) molecular wire.
5. The process of claim 1 further comprising connecting a molecular electronic device to the molecular wire.

6. The process of claim 1, wherein the molecular wire comprises an oligo(phenylene ethynylene) molecular wire.

7. A process comprising:
   (a) derivatizing a carbon nanotube with a diazonium specie; and
   (b) covalently attaching a molecular switch to the derivatized carbon nanotube.

8. The process of claims 7, wherein the carbon nanotube is a single-wall carbon nanotube.

9. A method for derivatizing carbon nanotubes comprising:
   (a) preparing an assembly, wherein
      (i) the assembly comprises a first plurality of carbon nanotubes and a second plurality of carbon nanotubes; and
      (ii) wherein the carbon nanotubes in the first plurality and the carbon nanotubes in the second plurality can be individually addressed electronically;
   (b) immersing the assembly in a diazonium specie; and
   (c) applying a negative potential to the assembly to cause the first plurality to essentially come in contact with the second plurality; wherein
      applying said negative potential facilitates an electrochemical reaction of the assembly with the diazonium specie so as to derivatize at least one of the first plurality and second plurality of nanotubes.

10. The method of claim 9, wherein the diazonium specie comprise molecules that function in a capacity selected from the group consisting of molecular switches and molecular wires.

11. The method of claim 9, wherein the electrochemical reaction of said diazonium specie occurs at a junction between said first plurality of nanotubes and said second plurality of nanotubes.