A method for functionalizing the wall of single-wall or multi-wall carbon nanotubes involves the use of acyl peroxides to generate carbon-centered free radicals. The method allows for the chemical attachment of a variety of functional groups to the wall or end cap of carbon nanotubes through covalent carbon bonds without destroying the wall or endcap structure of the nanotube. Carbon-centered radicals generated from acyl peroxides can have terminal functional groups that provide sites for further reaction with other compounds. Organic groups with terminal carboxylic acid functionality can be converted to an acyl chloride and further reacted with an amine to form an amide or with a diamine to form an amide with terminal amine. The reactive functional groups attached to the nanotubes provide improved solvent dispersibility and provide reaction sites for monomers for incorporation in polymer structures. The nanotubes can also be functionalized by generating free radicals from organic sulfoxides.
U.S. PATENT DOCUMENTS

FOREIGN PATENT DOCUMENTS
WO WO 00/17101 3/2000
WO WO 02/16257 2/2002
WO WO 02/64868 8/2002
WO WO 02/64869 8/2002

OTHER PUBLICATIONS


* cited by examiner
Figure 1

Ph-C=O-O-C-Ph $\xrightarrow{-2\text{CO}_2}$ 2Ph• $\xrightarrow{\text{SWNT}}$ 2

Ph
Figure 2

4a. \( R = -(\text{CH}_2)_{17}\text{CH}_3 \)

4b. \( R = -(\text{CH}_2)_3\text{CH}_3 \)

4c. \( R = -\text{CH(CH}_3\text{)CH}_2\text{CH}_3 \)

4d. \( R = -\text{CH}_2\text{CONH}_2 \)

4e. \( R = -(\text{CH}_2)_3\text{Cl} \)

4f. \( R = -\text{CH}_2\text{CN} \)

4g. \( R = -(\text{CH}_2)_3\text{-O-THP} \)

4h. \( R = -\text{CH}_2\text{COOCH}_2\text{CH}_3 \)

4i. \( R = -(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \quad (n \approx 3) \)

4j. \( R = -\text{CH}_2\text{C(\text{CH}_3)}_3 \)
**Figure 3**

\[
\begin{align*}
\text{Fe}^{+2} + \text{H}_2\text{O}_2 & \rightarrow \text{HO}\cdot + \text{HO}^- + \text{Fe}^{+3} \\
\text{H}_3\text{C} = \text{S} - \text{CH}_3 & \xrightarrow{\text{HO}\cdot} \text{H}_3\text{C} - \text{S} - \text{CH}_3 \xrightarrow{\text{HO}^\cdot} \text{H}_3\text{C} - \text{S} - \text{CH}_3 \\
\cdot\text{CH}_3 & \xrightarrow{\text{SWNT}} \text{CH}_3 \\
\end{align*}
\]

**Figure 4**

\[
\begin{align*}
\text{H}_3\text{C} - \text{S} - \text{CH}_3 & \xrightarrow{\text{Fe}^{+2} \text{H}_2\text{O}_2} \cdot\text{CH}_3 \\
\cdot\text{CH}_3 & \xrightarrow{\text{RI}} \text{CH}_3\text{I} + \text{R}
\end{align*}
\]
Figure 5

\[
\text{R-S-R'} \xrightarrow{\text{Fe}^{+2} / \text{H}_2\text{O}_2} \text{.R} + \text{.R'}
\]

\[
\text{.R} + \text{.R'} \xrightarrow{\text{SWNT}} \text{R R'}
\]

5a. R, R' = -CH₃
5b. R, R' = -CH₂CH₂CH₃
5c. R, R' = -CH(CH₃)₂
5d. R, R' = -CH₂CH₂CH₂CH₃
5e. R, R' = -CH(CH₃)CH₂CH₃
5f. R, R' = -Ph
Figure 6

\[
\text{HOC(CH_2)_nCOOC(CH_2)_nCOH} \xrightarrow{\text{Heat} - \text{CO}_2} \text{(CH_2)_nCOH} \xrightarrow{\text{SWNT}} \{(\text{CH}_2)_n\text{COH}\}_x
\]

6a, n=2
6b, n=3

Figure 7

\[
\text{SWNT-(CH}_2\text{CH}_2\text{COOH)}_x \xrightarrow{\text{SOCl}_2} \text{SWNT-(CH}_2\text{CH}_2\text{COCl)}_x \xrightarrow{\text{Ethylene diamine}} \text{SWNT-(CH}_2\text{CH}_2\text{CONHCH}_2\text{CH}_2\text{NH}_2)_x
\]

7a, n=2
7b, n=3

8
Figure 8

\[
\text{SWNT-} \text{(CH}_2\text{CH}_2\text{CH}_2\text{COOH})_x \xrightarrow{\text{SOCl}_2} \text{SWNT-} \text{(CH}_2\text{CH}_2\text{CH}_2\text{COCl})_x \xrightarrow{4,4'-\text{methylenebis(cyclohexylamine)}}
\]

7b
Figure 9

$$\text{SWNT-CH}_2\text{CH}_2\text{CH}_2\text{COOH} \xrightarrow{\text{SOCl}_2} \text{SWNT-CH}_2\text{CH}_2\text{CH}_2\text{COCl} \xrightarrow{120^\circ\text{C}, \text{diethyltoluenediamine}}$$

$$\text{SWNT-} \big(\text{CH}_2\text{CH}_2\text{CH}_2\text{CONH}\big)_{\text{x}}$$
Figure 10

\[
\begin{align*}
\text{CH}_2\text{COOH}_x & \xrightarrow{2\text{M NaOH}} \text{CH}_2\text{COOH}_x \\
\text{CH}_2\text{COCl}_x & \xrightarrow{\text{SOCl}_2} \text{CH}_2\text{COCl}_x \\
\text{CH}_2\text{COCl}_x & \xrightarrow{\text{CH}_3(\text{CH}_2)_{17}\text{NH}_2} \text{CH}_2\text{CONH}(\text{CH}_2)_{17}\text{CH}_3_x
\end{align*}
\]
Figure 11

Intensity vs. Wavenumbers (cm\(^{-1}\))

- 11A: Peaks at 230, 265, 1594
- 11B: Peaks at 208, 268, 1591
- 11C: Peaks at 208, 1296, 1596
- 11D: Peaks at 208, 1299, 1592

Wavenumbers (cm\(^{-1}\))

500, 1000, 1500
Figure 12

![Graph showing absorbance spectra with wavenumbers in cm^{-1}.]
**Figure 13**

Mass
- a: 29
- b: 44
- c: 45
- d: 73
- e: 72

Time (minute)
Figure 14

Chemical Shift (ppm)
METHOD FOR FUNCTIONALIZING CARBON NANOTUBES UTILIZING PEROXIDES

CROSS-REFERENCE TO RELATED APPLICATIONS

The present application claims priority to the following U.S. Provisional Patent Applications: Ser. No. 60/426,784, filed Nov. 15, 2002, and Ser. No. 60/483,817, filed Jun. 30, 2003, both of which are incorporated herein by reference.

This invention was made with support from the Robert A. Welch Foundation (Grant Nos. C-0109), the Texas Higher Education Coordinating Board's Advanced Technology Program (Grant Nos. 003604-00026-2001), and the National Science Foundation. Government may have certain rights.

FIELD OF THE INVENTION

This invention relates generally to carbon nanotubes, particularly the functionalization of carbon nanotubes, and more particularly to a method for functionalizing the wall of carbon nanotubes utilizing peroxides.

BACKGROUND OF THE INVENTION

Since their discovery in 1993, single-walled carbon nanotubes (SWNT) have become an area of wide-reaching research and development activity due to their exceptional chemical and physical properties, including high strength, stiffness, and thermal and electrical conductivity. SWNT are hollow, tubular fullerene molecules consisting essentially of sp²-hybridized carbon atoms typically arranged in hexagons and pentagons. Single-wall carbon nanotubes typically have diameters in the range of about 0.5 nanometers (nm) and about 3.5 nm, and lengths usually greater than about 50 nm.

Multi-wall carbon nanotubes are nested single-wall carbon cylinders and possess some properties similar to single-wall carbon nanotubes. However, since single-wall carbon nanotubes have fewer defects than multi-wall carbon nanotubes, single-wall carbon nanotubes are generally stronger and more conductive.

There is considerable interest in the chemical modification of single-wall carbon nanotubes to take advantage of single-wall carbon nanotubes’ remarkable tubular framework structure in various applications, particularly, in the engineering of multi-functional materials. SWNT derivatized with organic functional groups can provide a high binding affinity and selectivity through formation of either hydrogen or covalent bonds. Through functionalization, SWNT can exhibit improved solubility in common organic solvents, as well as improved material properties and processability of composites, including fibers and nanotube-reinforced composite materials, such as those based on organic and inorganic polymers. SWNT that have been chemically derivatized with hydrophilic substituents, such as those containing terminal hydroxyl or carboxylic acid groups, are particularly attractive for medical and biological applications.

Exoehal SWNT functionalization can generally be classified into three main categories: 1) non-covalently bonded, supramolecular complexation, wrapping and coating with detergents and polymers, such as given in International Patent Publication, “Polymer-wrapped Single-wall Carbon Nanotubes” WO 02/016257 published Feb. 28, 2002, incorporated herein by reference in its entirety; 2) generation and functionalization of open and closed tube ends, such as given in International Patent Publication, “Carbon Fibers formed from Single-wall Carbon Nanotubes” WO 98/39250 published Sep. 11, 1998, incorporated herein by reference in its entirety; and 3) direct chemical functionalization of the nanotube sidewalls using addition reactions, such as given in “Chemical Derivatization of Single-Wall Carbon Nanotubes to Facilitate Solvation Thereof, and Use of Derivatized Nanotubes,” WO 00/17101 published Mar. 30, 2000, incorporated herein by reference in its entirety.

Of the two chemically-bonded functionalization categories, the functionalization referred to as “end-derivatization,” or “end-functionalized” will be defined herein to include bonds on edges and open tube ends. “Sidewall derivatization” or “sidewall functionalization” will be defined herein to include bonds made to the wall that keep the carbon-carbon bonds of the wall intact. “End-cap derivatization” or “end-cap functionalization” will be defined herein to include bonds made to the end cap that keep the carbon-carbon bonds of the end cap intact. Regardless of whether the single-wall carbon nanotubes are derivatized on their ends, sides, end caps, or combination thereof, the SWNT will be referred to as derivatized SWNT for convenience and clarity.

End-functionalization of single-wall carbon nanotubes often proceeds through oxidation routes to form shortened nanotubes with carboxylic acid groups at the tube ends which can be further derivatized by reactions with a chlorinating agent, such as thionyl chloride, and long-chain alcohols or esterification. Carboxylic acid functionality can also be created on SWNT edges and defects on partially etched (“unzipped”) side walls by oxidative treatment with various oxidants.


One method of functionalizing fullerenes with moieties having terminal carboxylic acid groups has been demonstrated with C₆₀ using a two-step process (Bingel 2+1 cycloaddition reaction followed by deesterification) yielding carboxylated methanofullerene structures. (see Kini, V. U.; Khabashesku, V. N.; Margrave, J. L.; Rice Quantum Institute Sixteenth Annual Summer Research Colloquium, Aug. 9,
Sidewall functionalization of single-wall carbon nanotubes with aryl radicals has been reported when aryl diazonium salts were reduced electrochemically using single-wall carbon nanotube buckypaper as electrodes (see Bahir). Functionalization has also been reported using dizonium compounds generated in situ (see J. L. Bahir, et al., Chem. Mater. 2001, 13, 3823–3824). Radical addition of perfluoroalkyl groups generated by photolysis of corresponding species possessing a carbon-iodine bond has also been reported by Holzinger. Other examples of sidewall functionalization include electrochemical reductive and oxidative coupling by substituted phenylated derivatives (see S. E. Kooi, et al., Angew. Chem. Int. Ed. 2002, 41, 1353–1355) and electrophilic addition of chloroform followed by hydrolysis and esterification (see N. Tagmatarchis, et al., Chem. Commun. 2002, 2010–2011.). Dissolved lithium metal in liquid ammonia (Birch reduction) was used to hydrogenate SWNT. (see S. Pekker, et al., J. Phys. Chem. B., 2001, 105, 7938–7943.)

There remains, however, a need for a convenient and efficient method for non-destructively functionalizing single-wall carbon nanotubes with a variety of functional groups, especially organic groups which can be used for further reactions, so as to be bound or otherwise associated with polymers, biomedical species, and other materials for a particular end-use application.

SUMMARY OF THE INVENTION

In one embodiment, the present invention involves a convenient, economical method for non-destructively functionalizing the sidewall of single-wall carbon nanotubes (SWNT) or fluorinated single-wall carbon nanotubes utilizing peroxides. In one embodiment, the method for sidewall functionalizing a single-wall carbon nanotube comprises decomposing a diacyl peroxide in the presence of carbon nanotubes wherein the decomposition generates carbon-centered free radicals that react and form covalently bonds with carbon in the single-wall carbon nanotube wall to form a single-wall carbon nanotube sidewall functionalized with at least one organic group through a carbon bond to the nanotube. An acyl peroxide, also known as a diacyl peroxide, is a compound with a structure of the type RCOOCHR', where R and R' groups can be either alkyl or aryl. In one embodiment, the acyl peroxide is an acryl peroxide wherein the R or R' group comprises an aromatic component. In another embodiment, the acyl peroxide is an acryl peroxide and comprises benzoyl peroxide, which, upon decomposition, liberates carbon dioxide and generates phenyl radicals that attach to the sidewalls of the nanotubes to form sidewall phenylated single-wall carbon nanotubes.

In an embodiment of the present invention, the acyl peroxide is a peroxyxycarbonate. A peroxyxycarbonate is an acyl peroxide wherein the R and R' groups can be either alkyl or aryl. In another embodiment, the acyl peroxide is an acryl peroxide with terminal carboxylic acid groups. Examples of acyl peroxides with terminal carboxylic acid groups include, but are not limited to, succinic acid peroxide and glutaric acid peroxide. In this embodiment, the peroxide decomposes, liberating carbon dioxide and forming carbon-centered free radicals that attach to the sidewalls of the nanotubes and provide organic groups with terminal carboxylic acid functionality that are then available for further reaction. An example of further reactions with a carboxylic acid functional group include, but are not limited to, reaction with a chlorinating agent (such as thionyl chloride) to form an acetylene and further reaction of the acetylene with an amine to form an amide or a diamine to form a amide linkage with a terminal amine group.

Suitable peroxides for use with this invention include, but are not limited to, acyl peroxides, wherein the R and R' groups can be the same or different. When the R and R' groups are the same, the acyl peroxide is a symmetrical peroxide. When the R and R' groups are different, the acyl peroxide is an asymmetrical peroxide. The R and R' organic groups of the acyl peroxide can comprise R and R' groups of the form including, but not limited to, alkyl, cyclic, aryl and combinations thereof.

In one embodiment, the method involves generating a phenyl radical, such as through the decomposition of the acyl peroxide, benzoyl peroxide, and reacting the phenyl radical with an organic iodide to generate a carbon-centered radical from the organic group that was bonded to the iodine. The organic group can be alkyl or aryl. When the organic group is an alkyl, the alkyl radical reacts with the single-wall carbon nanotube to form a covalent bond with the sidewall of the single-wall carbon nanotube to form a sidewall-fluorinated single-wall carbon nanotube. The alkyl iodide can comprise various alkyl groups, including, but not limited to, a hydrocarbon alkyl group, an alkyl amide, an alkyl amine, alkyl halide, an alkyl cyanide, an alkyl ether, an alkyl thioether, a trialkyl phosphine, an alkyl carboxylic acid, an alkyl carboxylate and combinations thereof. Generally, the number of carbons in the alkyl group of the alkyl iodide is in the range of 1 to about 30. All radicals attach by a carbon linkage to the carbon nanotube.

In another embodiment, carbon-centered free radicals can be generated from hydroxyl radicals and organic sulfoxides. In this embodiment, hydroxyl radicals are formed from Fenton's reagent, wherein hydrogen peroxide and divalent iron react. The hydroxyl radicals further react with an organic sulfoxide of the form R–SO–R' to form R and R' carbon-centered free radicals. The R and R' free radicals then react with single-wall carbon nanotubes and bond to the sidewall to form single-wall carbon nanotubes with R and R' groups attached to their sidewall. R and R' can be the same or different. The R and R' groups can also be aryl groups, such as, but not limited to phenyl groups and other aromatic groups. The reaction generates carbon-centered free radicals from an organic sulfoxide and will be referred to as a "Minisci" or "Minisci-type" reaction. The carbon-centered free radicals can be generated from the organic sulfoxide using Fenton's reagent, which generates hydroxyl radicals from the reaction of hydrogen peroxide and an Fe(II) catalyst, such as FeSO₄. The method of this invention applies to both single-wall and multi-wall carbon nanotubes to functionalize the exterior wall of the carbon nanotube without destroying the carbon wall structure. Besides pristine, underivatized nanotubes, sidewall-fluorinated carbon nanotubes can also be used as the initial nanotubes for further sidewall derivatization. Although not meant to be bound by theory, the presence of sidewall fluorine groups appears to make the nanotubes more reactive to sidewall derivatization.

Certain properties of the nanotubes can be imparted to other materials more effectively when the nanotubes have sidewall functionality. The sidewall-functionalized nanotubes can be made more compatible and dispersible in other materials. In one embodiment, the non-destructive sidewall functionalization of single-wall carbon nanotubes enables...
the incorporation of the nanotubes into composite materials by reacting with an appropriate functionality attached to the sidewall of the single-wall carbon nanotube. In another embodiment, the sidewall functionalization of single-wall carbon nanotubes with aromatic groups or long chain alkyl groups, oligomers, or polymers can make the single-wall carbon nanotubes more compatible with various materials, such as, but not limited to, polymers and other organic materials, and enable composites with high dispersability and enhancement of the materials’ properties. Because the structure of the nanotubes is still intact after the sidewall functionalization, the mechanical properties of the nanotubes can contribute to the strength and modulus of the composite materials.

**BRIEF DESCRIPTION OF THE DRAWINGS**

FIG. 1 shows a reaction of one embodiment of the present invention wherein benzyl peroxide 1 is used to functionalize the sidewall of a single-wall carbon nanotube (SWNT) and form sidewall-phenylated-SWNT 2.

FIG. 2 shows a reaction scheme of one embodiment of the present invention wherein a phenyl radical, such as from benzyl peroxide 1 reacts with R 3, where examples of R  are given in the list of 4a though 4j, to form an R carbon-centered free radical, which attaches to the SWNT sidewall to form sidewall-derivatized R-SWNT 4.

FIG. 3 shows a reaction scheme of one embodiment of the present invention wherein hydrogen peroxide in the presence of Fe2+ forms a hydroxyl free radical. The radical is further reacted with dimethyl sulfoxide to form a methyl radical. The methyl radical attaches to the SWNT sidewall to form sidewall-methylated-SWNT 5a.

FIG. 4 shows a reaction scheme of one embodiment of the present invention wherein dimethyl sulfoxide in the presence of Fe2+ and hydrogen peroxide generates a methyl radical. The methyl radical in the presence of an iodo-R compound R1 generates iodomethane and an .R carbon-centered free radical.

FIG. 5 shows a reaction scheme of one embodiment of the present invention wherein an organic sulfoxide (R-S(O)—R') in the presence of Fe2+ and hydrogen peroxide generates .R and .R' radicals, which further react with SWNT to form R- and R'-sidewall functionalized SWNT.

FIG. 6 shows a reaction scheme of one embodiment of the present invention wherein in a dicarboxylic acid acyl peroxide such as 6a or 6b, in the presence of heat, liberates CO2, and generates a carbon-centered free radical which bonds to the sidewall of a single-wall carbon nanotube to form sidewall derivatized SWNT with organic groups having terminal carboxylic acid groups, such as 7a or 7b.

FIG. 7 shows a reaction scheme of one embodiment of the present invention wherein a single-wall carbon nanotube side-wall functionalized with alkyl having a terminal carboxylic acid group 7a is reacted with thionyl chloride to form an alkyl acyl chloride side-wall-functionalized SWNT which is further reacted with ethylene diamine to form a sidewall alkyl amide functionalized SWNT 9, wherein the alkyl side-wall functional group has a terminal amine. The subscript “x” indicates a variable number of sidegroup attachments.

FIG. 9 shows a reaction scheme of one embodiment of the present invention wherein a single-wall carbon nanotube side-wall functionalized with an alkyl having a terminal carboxylic acid group 7b is reacted with thionyl chloride to form a terminal acyl chloride side-wall-functionalized SWNT which is further reacted with diethyltoluenediamine to form an aryl side-wall functionalized SWNT 10, wherein the aryl side-wall function has an amide linkage and a terminal amine. The subscript “x” indicates a variable number of sidegroup attachments.

FIG. 10 shows a reaction scheme wherein single-wall carbon nanotubes that have been sidewall functionalized with an ester are saponified with sodium hydroxide and neutralized with hydrochloric acid to form single-wall carbon nanotubes that have alkyl groups with terminal carboxylic acid functionality, which are further chlorinated with thionyl chloride to form an acyl chloride, which is further reacted with octadecyl amine to form an alkyl amide group that is bonded to the single-wall carbon nanotube sidewall, where the subscript "x" indicates a variable number of sidegroup attachments.

FIG. 11 shows Raman spectra for certain embodiments of the present invention, including spectra for the following pristine and sidewall-derivatized SWNT, wherein the subscript “x” indicates a number of sidegroup attachments which is variable depending on the sidegroup and conditions of preparation:

- FIG. 11A for pristine SWNT;
- FIG. 11B for SWNT-(CH2CH2COOH)x;
- FIG. 11C for SWNT-(CH2CH2COOH)2;
- FIG. 11D for SWNT-(CH2CH2COOH)x after heating to 800° C. in argon per TGA.

FIG. 12 shows FTIR spectra for certain embodiments of the present invention including spectra for the following sidewall-derivatized SWNT, wherein the subscript “x” indicates a number of sidegroup attachments which is variable depending on the sidegroup and conditions of preparation:

- FIG. 12A for SWNT-(CH2CH2COOH)x;
- FIG. 12B for SWNT-(CH2CH2CONHCH2CH2NH2)x;
- FIG. 12C for SWNT-(CH2CH2CONHC6H(C2H5)2CH2NH2)x and
- FIG. 12D for SWNT-(CH2CH2CONH(C6H4CH2CH2CH2CH2NH2)x.

FIG. 13 shows TGA/MS of SWNT-(CH2CH2COOH)x, with peak evolutions due to the following sidegroup fragments and associated atomic mass:

- a: —CH3CH3 (mass: 29),
- b: —COO— (mass: 44),
- c: —COOH (mass: 45),
- d: —CH3CH2COOH (mass: 73) and
e: —CH3CH2COO— (mass: 72).

FIG. 14 shows 13C NMR spectra for certain embodiments of the present invention including spectra for the following pristine and sidewall-derivatized SWNT, wherein the subscript “x” indicates a number of sidegroup attachments which is variable depending on the sidegroup and conditions of preparation:

- FIG. 14A for pristine H2PCO SWNT;
- FIG. 14B for SWNT-(CH2CH2CH2COOH)x;
- FIG. 14C for SWNT-(CH2CH2COOH)x and
- FIG. 14D for SWNT-(CH2CH2CONH(C6H4CH2CH2CH2NH2)x.
The carbon nanotubes, according to the present invention, can be made by any known method. Single-wall carbon nanotubes are generally made in high-temperature processes using a carbon source and a metallic catalyst, typically comprising Group VIb and/or Group VIIIb transition metals. Methods for synthesizing single-wall carbon nanotubes include DC arc processes; laser vaporization of graphite doped with transition metal atoms; high temperature, high pressure gas-phase syntheses involving a carbon-containing feedstock gas, such as carbon monoxide; and a volatile transition metal catalyst precursor, and chemical vapor deposition (CVD) processes in which single-wall carbon nanotubes are formed from a carbon-containing gas on a nanoparticle-scale metal catalyst particles, which can be supported on a substrate or catalyst support. The process type and operating conditions will produce single-wall carbon nanotubes having a particular distribution of diameters and lengths. Generally, the lengths of as-produced single-wall carbon nanotubes are in excess of about 50 nm, and more typically, greater than about 100 nm. Commonly, single-wall carbon nanotubes have lengths in the range of about 1 and 10 microns.

All known methods of synthesizing single-carbon nanotubes also produce a distribution of reaction products, including, but not limited to, single-wall carbon nanotubes, amorphous carbon, metallic catalyst residues, and, in some cases, multi-wall carbon nanotubes. The distribution of reaction products will vary depending on the process and the operating conditions used in the process.

The nanotubes can be optionally purified. In one embodiment, single-wall carbon nanotube powder is purified to remove non-nanotube carbon, such as amorphous carbon and metallic catalyst residues. Metals, such as Group VI and/or VIII are possible catalysts for the synthesis of single-wall carbon nanotubes, and the metallic residues after catalysis may be encapsulated in non-nanotube carbon, such as graphitic shells of carbon. The metallic impurities may also be oxidized through contact with air or by oxidation of the non-nanotube carbon during purification.

Purification can be done by any known means. Procedures for purification of carbon nanotubes are related in International Patent Publications “Process for Purifying Single-Wall Carbon Nanotubes and Compositions Thereof,” WO 02/064,869 published Aug. 22, 2002, and “Gas Phase Process for Purifying Single-Wall Carbon Nanotubes and Compositions Thereof,” WO 02/064,868 published Aug. 22, 2002, and incorporated by reference herein in their entirety. In an embodiment of the present invention, the nanotubes are purified by heating at 250°C in air saturated with water vapor. The heating is done for a length of time so as to oxidize at least some of the non-nanotube carbon, and, may, to some extent, oxidize the metal impurities. The oxidation temperature can be in the range of about 200°C to about 400°C, preferably about 200°C to about 300°C. The oxidation can be conducted in any gaseous oxidative environment, which can comprise such oxidative gases as such as oxygen, air, carbon dioxide, and combinations thereof. The concentration of the oxidative gases can be adjusted and controlled by blending with nitrogen, an inert gas, such as argon, or combinations thereof. The duration of the oxidation process can range from a few minutes to days, depending on the oxygen, its concentration, and the oxidation temperature.

After oxidatively heating the nanotubes, the nanotubes are treated with acid to remove metallic impurities and to form a slurry of nanotubes in the acid. The acid can be a mineral acid, an organic acid, or combinations thereof. Examples of acids that could be used to treat and slurry the nanotubes include, but are not limited to, hydrochloric acid, hydrofluoric acid, hydrobromic acid, hydroiodic acid, sulfuric acid, oleum, nitric acid, chloric acid, oxalic acid, chlorosulfonic acid, phosphoric acid, trifluoromethane sulfonic acid, glacial acetic acid, monobasic organic acids, dibasic organic acids, and combinations thereof. The acid used can be a pure acid or diluted with a liquid medium, such as an aqueous and/or organic solvent. Generally, an aqueous solvent is preferred. Concentrated aqueous hydrochloric acid is preferred for removing metallic impurities.

After the metallic impurities react with the acid, the nanotubes are filtered and washed to remove the acid from the nanotubes. Examples of washing media that could be used to wash the acid from the nanotubes include, but are not limited to, water, alcohols, aldehydes, ketones, dilute alkaline solutions, ammonium hydroxide, primary, secondary and tertiary amines, oxygenated hydrocarbons, hydroxylated hydrocarbons, organic aromatics and combinations thereof. After the nanotubes are washed, they can, optionally, be dried, such as in a vacuum oven or an inert environment, such as in nitrogen or an inert gas atmosphere, with or without heat.

Furthermore, the single-wall carbon nanotubes can, optionally, be sidewall fluorinated. Sidewall fluorinated single-wall carbon nanotubes are designated “F-SWNT” herein. F-SWNT can be prepared, preferably with purified single-wall carbon nanotubes, by direct fluorination using such procedures as given in Z. Gu, et al., Nano Lett., 2002, 2, 1009. The F-SWNT can be fluorinated to any level up to the theoretical limit of one fluorine to two carbon atoms on the SWNT and still have the wall structure intact. The stoichiometry of maximum SWNT fluorination is C2F.

Sidewall Functionalization of Carbon Nanotubes Utilizing Acyl and Aroyl Peroxides

In one embodiment of the present invention, the decomposition of acyl peroxides is used to generate carbon-centered free radicals, which non-destructively add organic groups through a carbon linkage to the sidewall and/or closed end cap of a carbon nanotube.

Acyl peroxides, or alternatively, diacyl peroxides, have the chemical formula. R—C(O)O—O(O)C—R’. The R—O—O bond is very weak and under suitable conditions, the R—O bond can readily undergo bond homolysis to form an intermediate carboxyl radical which decarboxylates to produce carbon dioxide and carbon-centered radicals, such as R, R’, or a combination thereof. The R and R’ groups can be the same or different. The R and R’ can be alkyl, aryl, or cyclic. In addition, the R and R’ groups can have terminal functional groups and contain heteroatoms, other than carbon and hydrogen. Acyl peroxides are conveniently and economically available, or can be synthesized, with a wide variety of R and R’ groups.

In one embodiment of the present invention, an alkyl group, such as an undecyl (C11H23) group can be bonded to the sidewalls of single-wall carbon nanotubes using undecyl groups generated by the decomposition of the acyl peroxide, also known as laurel peroxide (C11H23—C(O)OO(O)C—C11H23). Laurel peroxide is also known by other nomenclature, such as, but not limited to, dilauryl peroxide and dodecanoyl peroxide. The procedures for attaching alkyl groups to the sidewall of the nanotube comprise, making a suspension of nanotubes in a suitable solvent, such as benzene. Sonication, stirring and other means of agitation...
can be used to facilitate dispersion of the nanotubes. The acyl peroxide is then added to the SWNT suspension. The nanotubes and peroxide are heated to a temperature above the decomposition temperature of the acyl peroxide and mixed for a time effective to decompose the peroxide, generate free carbon-centered radicals and bond the free radicals to the sidewalls of the carbon nanotubes.

Examples of other suitable acyl peroxides of the form \( R--C(\text{O})\text{O}-O(O)C--R' \), wherein the \( R \) and \( R' \) are organic groups that can be the same or different and can include, but are not limited to, acetyl peroxide, n-butyryl peroxide, sec-butyryl peroxide, t-butyryl peroxide, t-pentyl peroxide, iso-valeryl peroxide, feruloyl peroxide, palmitoyl peroxide, decanoyl peroxide, laurowyl peroxide, disopropyl peroxycarbonate and butylperoxyisopropyl carbonate. The \( R \) or \( R' \) group can comprise a normal, branched or cyclic alkyl group wherein the number of carbons can range from one to about 30, and typically, in the range of about 8 and about 20. The \( R \) or \( R' \) group can contain one or more cyclic rings, examples of which are trans-t-butylocyclohexanoyl peroxide, trans-4-cyclohexanecarboxyl peroxide and cyclohexyl peroxide.

The degree of functionalization of the nanotube will depend on various factors, including, but not limited to, the type and structure of side group, steric factors, the desired functionalization of the nanotube (SWNT) and form sidewall-phenylated-SWNT. The \( R \) or \( R' \) group can have other substituents on one or more aromatic rings, such as in p-methylbenzoyl peroxide, p-methoxybenzoyl peroxide, and bis(2,4-dichlorobenzoyl)peroxide. The aryl peroxide can also have other substituents per one or more aromatic rings, such as in p-nitrobenzoyl peroxide, p-bromobenzoyl, p-chlorobenzoyl peroxide, and bis(2,4-dichlorobenzoyl)peroxide.

In another embodiment, organic iodides, herein denoted RI, can be used as a source of the R organic group for sidewall functionalization of the wall of the carbon nanotubes. The R group can be an alkyl, aryl group, cyclic group, or combination thereof. The R group can contain functional moieties, such as, but not limited to, carboxylic acid, carboxylates, cyanide groups, nitro groups, esters, ketones, amides, heteroatoms, such as nitrogen, oxygen, halogens, and combinations thereof. Generally, the number of carbons in the organic iodide is in the range of 1 to about 30. The R—I bond is a carbon-iodine bond, such that the free radical generated from RI is a carbon-centered free radical. In this embodiment, RI is mixed with a peroxide, such as benzylic peroxide. After the benzylic peroxide decomposes to phenyl radicals, a free radical displacement of iodide by the phenyl radical generates an .R carbon-centered free radical, which then bonds covalently to the carbon nanotube sidewall. In embodiments wherein the carbon nanotubes are single-wall carbon nanotubes, the result is a sidewall R-derivatized SWNT. FIG. 2 shows a reaction scheme wherein a phenyl radical (such as from benzoyl peroxide) undergoes a radical displacement of iodide from RI to generate an R carbon-centered free radical and wherein the .R free radical bonds to the SWNT sidewall and forms sidewall derivatized SWNT. Various organic R groups are shown in FIG. 2 as 4a through 4j. "THP" in 4g means "tetrahydropyran".

**Solid State and Liquid State Preparation Procedures**

In another embodiment of the present invention, the proportion of single-wall carbon nanotubes used is approximately one to two times that of the acyl peroxide on a weight basis. For solid state reactions, a mechanically-ground mixture of reactants is used in a sealed reactor, such as a stainless steel reactor. The temperature of the reactor is heated above the decomposition temperature of the peroxide, such as a temperature of about 200°C. for a time sufficient to carry out the reaction to the desired state of completion. The reaction time will vary depending on the acyl peroxide used. A typical reaction time can be about 12 hours. Solid state reactions can be done with solid peroxides and carbon nanotubes. The method is convenient and no solvent dispersion or solvent removal is required.

For solution phase reactions, the single-wall carbon nanotubes are dispersed in a suitable solvent, such as, for example, benzene, o-dichlorobenzene, or nitrobenzene.

Dispensing the nanotubes in solvent can be facilitated by sonication or ultrasonication. The time required to disperse the nanotubes is dependent on the solvent and the amount and type of nanotubes being dispersed. Generally, the nanotubes can be dispersed in about 30 minutes to about 2 hours.
although longer mixing times may be required, depending on the dispersing apparatus, among other factors. After dispersing the nanotubes in solvent, the acyl peroxide is added and the mixture is refluxed under an environment of nitrogen or an inert gas, such as argon. The solvent is also selected such that the refluxing is done above the decomposition temperature of the selected peroxide. For example, when using o-dichlorobenzene as a solvent and either benzoyl peroxide or lauroyl peroxide, the reflux conditions are in a temperature range of about 80°C to about 100°C for a time in a range of about 3 hours to about 120 hours effective for the decomposition of the acyl peroxide to form carbon-centered radicals. For example, in one embodiment, purified single-wall carbon nanotubes are sonicated for 30 minutes to suspend the nanotubes in benzyl alcohol. The suspension is then heated in the presence of benzyl alcohol to 75°C and held at temperature for 24 hrs under an argon atmosphere to bond phenyl groups to the single-wall carbon nanotube sidewalls.

After the sidewall functionalization reaction is complete, the sidewall functionalized single-wall carbon nanotubes can be isolated from unreacted peroxides and by-products by washing with solvent. For example, sidewall-functionalized SWNT can be filtered from the unreacted products and by-products, and washed with a solvent, such as chloroform. The nanotubes can then be dried, such as in a vacuum oven at about 100°C overnight.

Preparation of SWNT Sidewall Functionalized with Alkyl Radicals from Organic Iodides

In another embodiment, the acyl peroxide, benzoyl peroxide, is used with R-iodide (RІ) to attach organic R groups other than phenyl to the carbon nanotube sidewall. In this embodiment, benzoyl peroxide is decomposed to carbon dioxide and phenyl radicals. The phenyl radicals react with the R-iodide via an iodide displacement to form .R radicals. The .R radicals bond to the nanotubes to form carbon nanotubes with R groups bonded to the sidewall of the nanotubes. The chemical reaction scheme for this method of preparing sidewall functionalized SWNT is shown in FIG. 2a, wherein 3 is RI and 4 represents sidewall functionalized R-SWNT. Examples of R groups are also shown in FIG. 2a as 4a through 4i. The groups represented are n-octadecyl 4a, n-propyl 4b, sec-butyl 4c, ethyl amide 4d, n-propyl chloride 4e, acetonitrile 4f, and n-propyl tetrahydropryran ether 4g, ethyl acetate 4h, poly(ethylene glycol)-n-buty ether 4i, and neopentyl 4j. Examples of other R groups that may be attached to the sidewall of single-wall carbon nanotubes in this manner, include, but are not limited to, linear, cyclic and/or heteroatoms, such as halides, nitro groups, amino groups, and combinations thereof.

Preparation of SWNT Sidewall Functionalized with Methyl Groups

Methyl radicals can be generated from dimethyl sulfoxide and hydroxyl radicals can bond to the carbon nanotube wall to form methylated carbon nanotubes. One embodiment for methylating the sidewall of single-wall carbon nanotubes is diagrammed in FIG. 3. As shown in FIG. 3, hydrogen peroxide, in the presence of Fe²⁺, forms a hydroxyl free radical. The radical is further reacted with a dimethyl sulfoxide to form a methyl radical. The methyl radical attaches to the SWNT sidewall to form a sidewall-methylated-SWNT 5a. Although the methyl radicals effectively bond to the sidewall of the SWNT, the resulting methylated SWNT has less solubility in most organic solvents than SWNT alkylated with groups comprising more carbon atoms or larger functional groups.

Preparation of Methyl Radicals Using the Minisci Route and the Formation of Other Organic Radicals Using Radical Displacement of Iodine

Because the methyl radical is the least stable alkyl radical, it can be used to selectively generate other alkyl radicals. The methyl radicals generated using the Minisci method can also be used to generate other alkyl radicals using organic iodides (RI) as the source of other alkyl or aryl groups. This process, diagrammed in FIG. 4, offers another route to other free radicals and another embodiment for adding functional groups to the carbon nanotube sidewall. FIG. 4 shows a reaction scheme wherein dimethyl sulfoxide, in the presence of Fe²⁺ and hydrogen peroxide, generates a methyl radical. The methyl radical in the presence of an iodo-R compound RI generates isomethane and an R radical, which can be bonded to the carbon nanotube sidewall.

Preparation of SWNT Sidewall Functionalized with Various Organic R Groups Using the Minisci Method of Generating Free Radicals

Alkyl and aryl radicals can be generated using the Minisci method using sulfoxides with various alkyl and/or aryl groups. In this embodiment, other alkyl groups can be attached to the SWNT sidewall without the iodide displacement reaction. In this embodiment, sulfoxides, which have the form R-S(O)-R', where -R and -R' can be the same or different, can also be used to generate various carbon radicals without the use organic iodides. The R groups can be alkyl or aromatic or a combination thereof. This process, diagrammed in FIG. 5, offers another route to other free radicals and another embodiment for adding functional groups to the carbon nanotube sidewall. FIG. 5 shows a reaction scheme wherein an organic sulfoxide (R-S(O)-R'), in the presence of Fe²⁺ and hydrogen peroxide, generates .R and .R' radicals, which further react with SWNT to form R- and R'-sidewall functionalized SWNT. Examples of R groups shown in FIG. 5 include methyl groups 5a, n-propyl groups 5b, isopropyl groups 5c, n-butyl groups 5d, sec-butyl groups 5e, and phenyl groups 5f. The R or R' group generally can comprise a number of carbons in the range of 1 and about 30.

Preparation of SWNT Sidewall Functionalized Organic Moieties with Terminal Carboxylic Acid Groups

In another embodiment, alkyl groups terminated with the carboxylic acid functionality are attached to the sidewalls of the single-wall carbon nanotubes. FIG. 6 shows an embodiment wherein a dicarboxylic acid acyl peroxide such as 6a or 6b, in the presence of heat, liberates CO₂ and generates a carbon-centered free radical which bonds to the sidewall of a single-wall carbon nanotube to form sidewall derivatized SWNT with organic groups having terminal carboxylic acid.
groups, such as 7a or 7b. In one embodiment diagrammed in FIG. 6, organic acyl peroxides of dicarboxylic acids, such as

\[ \text{HO(O)}(\text{C})_{\text{n}}\text{O} \text{(C})_{\text{n}}\text{O} \text{OH} \text{ (where n=2, is succinic acid peroxide; and n=3, is glutaric acid peroxide; are used to functionalize the sidewall of single-wall carbon nanotubes with functional groups of the form HO(O)(CH)_{n} = \text{HO(O)}(\text{CH})_{n} \text{O} \text{OH} \text{ (where the sidewall functionalized SWNT for n=2 using 6a is represented by 7a and for n=3 using 6b is represented by 7b. In another embodiment, phthalic acid peroxide is decomposed to an organic radical, wherein the radical bonds, with wall of the carbon nanotube and the resulting organic sidegroup has a terminal carboxylic acid group.}

Acyl peroxides have the form, RC(O)OO(O)OCR, where R can be aliphatic, aromatic or another group, and readily decompose to release carbon dioxide and form free radicals R upon mild heating. Succinic acid peroxide, 6a, decomposes to form 3-carboxyl-propionyl-oxyl radicals, which can subsequently release CO\text{2} to yield another radical, 2-carboxyl-ethyl. Glutaric acid peroxide, 6b, yields a 3-carboxyl-propyl radical via a similar route. These carboxyl-alkyl radicals, generated in situ from corresponding peroxides 6a and 6b, react with single-wall carbon nanotubes to produce sidewall-acid-functionalized SWNT-derivatives 7a and 7b, as diagrammed in FIG. 6. The subscript “x” in the functionalized SWNT derivatives indicates the attachment of a variable number of sidegroups to the nanotube.

Reactions of Carboxylic Acid Sidewall Functionalized SWNT with Amines and Diamines

Single-wall carbon nanotubes with sidewall alkyl groups having terminal carboxylic acid functionality, such as 7a and 7b, shown in FIG. 6, can further be reacted to yield nanotubes with other reactive functionality. For example, amide derivatives can be made by reacting the carboxylic acid functionality with a chlorinating agent, such as thionyl chloride, and subsequently with an amine compound. Other possible chlorinating agents, include, but are not limited to phosphorous trichloride, phosphorous pentachloride, and oxalyl chloride (C\text{2}O\text{2}Cl\text{2}). To give the SWNT side group a carboxyl-alkyl linkage and a terminal amine, the subscript “x” in 9 indicates a variable number of sidegroups on the nanotube.

In another embodiment, diagrammed in FIG. 8, a diamine having a cyclic ring, 4,4’-methylenebis(cyclohexylamine), is used to give a terminal amine functionality to group on the SWNT sidewall. FIG. 8 shows a reaction scheme wherein a single-wall carbon nanotube sidewall functionalized with an alkyl having a terminal carboxylic acid group 7b is reacted with thionyl chloride to form an alkyl acyl chloride sidewall-functionalized SWNT which is further reacted with 4,4’-methylenebis(cyclohexylamine) to form a sidewall alkyl amide functionalized SWNT 9, wherein the sidewall organic group has a terminal amine. The subscript “x” in 9 indicates a variable number of sidegroups on the nanotube.

In another embodiment, an aryl diamine, diethyltoluenediamine, is used in the reaction scheme diagrammed in FIG. 9. FIG. 9 shows a reaction scheme wherein a single-wall carbon nanotube sidewall functionalized with an alkyl having a terminal carboxylic acid group 7b is reacted with thionyl chloride to form a terminal acyl chloride sidewall-functionalized SWNT which is further reacted with diethyltoluenediamine to form an aryl sidewall functionalized SWNT 10, wherein the aryl sidewall function an amide linkage and a terminal amine. The subscript “x” in 10 indicates a variable number of sidegroups on the nanotube.

The method of this invention is also generally applicable to multi-wall carbon nanotubes. In the case of multi-wall carbon nanotubes, the outer sidewall can be functionalized in the same manner as that of the single wall of a single-wall carbon nanotube.

The following examples are included to demonstrate preferred embodiments of the invention. It should be appreciated by those of skill in the art that the techniques disclosed in the examples which follow represent techniques discovered by the inventors to function well in the practice of the invention, and thus can be considered to constitute preferred modes for its practice. However, those of skill in the art should, in light of the present disclosure, appreciate that many changes can be made in the specific embodiments which are disclosed and still obtain a like or similar result without departing from the spirit and scope of the invention.

**EXAMPLE 1**

This example describes the procurement, preparation and purification of the single-wall carbon nanotubes. HIPCO® single-wall carbon nanotubes, having an average diameter of about 1 nm, were obtained from Rice University (HIPCO is a trademark registered to Carbon Nanotechnologies, Inc., Houston, Tex.) To remove iron, used as a catalyst, the nanotubes were purified using a gaseous wet air oxidation followed by an aqueous hydrochloric acid rinse according to the procedures of Chiang, I. et al. *J. Phys. Chem. B*, 2001, 105, 8297–8301 (“Chiang”). Following the purification, the nanotubes were annealed at 800° C. for 2 hours in argon.

**EXAMPLE 2**

This example demonstrates a procedure for functionalizing the sidewalls of single-wall carbon nanotubes using the acyl peroxide, benzoyl peroxide.

Purified SWNT (50 mg) was sonicated in benzene (65 ml) for 2 hours to form a SWNT suspension. 6.7 g benzoyl peroxide, which decomposes under mild conditions (75–80° C.) to form carbon dioxide and phenyl radicals, as shown in FIG. 1, was added to the SWNT suspension. The heterogeneous mixture was stirred under argon at 70–80° C. overnight to decompose the benzoyl peroxide and form sidewall-phenylated-SWNT (Ph-SWNT). During the heating, the benzoyl peroxide decomposed to phenyl radicals and carbon dioxide, and the phenyl radicals attached to the sidewalls of the SWNT to form sidewall-derivatized phenyl-SWNT (Ph-SWNT). 50 ml ethanol was then added to precipitate the dissolved Ph-SWNT. The mixture was then filtered through a 0.2 μm PTFE (polytetrafluoroethylene) filter and washed with ethanol. The nanotubes that were collected from the filter were washed by suspending the nanotubes in 100 ml ethanol, sonicating the mixture for 20 min and filtering again. The ethanol-washing procedure was repeated twice, except that hot ethanol was used in the last washing. The ethanol-washed Ph-SWNT was dried under vacuum for 4 hours at 70° C.
The degree of phenyl-group functionalization was estimated by TGA (thermal gravimetric analysis) to be about one phenyl group for about 14 carbon atoms in the nanotube framework. (See FIG. 1 which gives a diagram of the chemical reaction. See also Example 3 in Table 1 below.) Increasing the peroxide concentration did not substantially increase the degree of phenyl functionalization, suggesting that steric effects may be a limiting factor in the degree of phenyl-group functionalization.

The phenyl-functionalization caused the nanotubes to exhibit remarkably improved solubility and/or dispersibility in CHCl₃, CH₂Cl₂, DMSO (dimethylsulfoxide), DMF (dimethylformamide) and 1,2-dichlorobenzene solvents. Although the solubility of the phenylated nanotubes also was higher than pristine nanotubes in benzene, toluene and THF (tetrahydrofuran), the increase in solubility was not as pronounced in CHCl₃, CH₂Cl₂, DMSO, DMF and 1,2-dichlorobenzene. The phenylated nanotubes were insoluble in n-hexane and ether.

EXAMPLE 3

This example demonstrates a general method for functionalizing the sidewalls of single-wall carbon nanotubes with R groups other than phenyl groups using benzoyl peroxide as an initial source of free radicals that react with R-iodides. To attach R groups other than phenyl to the SWNT sidewall, R-iodide, (RI) (2.5 equivalents per mole of benzoyl peroxide) was used with benzoyl peroxide. The R groups used in this example are given in Table 1, shown below. The corresponding R-iodide compounds were obtained from Aldrich, except for the iodo derivative of poly(ethylene glycol)-n-butyl ether (See 4f in Table 1), which was prepared as follows according to procedures adapted from S. Arndt, et al., Chem. Eur. J. 2001, 7, 993–1005. To a solution of imidazole (3.3843 g, 49.71 mmol) and PPh₃ (5.214 g, 19.88 mmol) in 110 ml CHCl₃ at 0°C, iodine (5.467 g, 21.54 mmol) was added. The solution was stirred for 5 min, and poly(ethylene glycol)-n-butyl ether HO(CH₂CH₂O)m(CH₂)₃CH₃ (3.4135 g, 16.57 mmol, average MW about 206, m=3) dissolved in 20 ml CH₂Cl₂, was then added slowly. The mixture was stirred for 4 hrs with exclusion of light. The reaction was then quenched by adding 20 ml saturated aqueous solution of sodium sulfite Na₂SO₃. The aqueous layer was extracted with ethyl ether and the extract dried over MgSO₄. The solvents were removed by rotary evaporator. The crude iodo derivative of poly(ethylene glycol)-n-butyl ether was purified by column chromatography (3.403 g, 10.77 mmol, yield 65%).

The reaction scheme for the preparation of sidewall functionalized R-SWNT is shown in FIG. 2. The benzoyl peroxide is decomposed to phenyl radicals, which, in tum, bond to the sidewall of the single-wall carbon nanotube. The general procedures, which follow, were used with different RI compounds.

20 mg purified single-wall carbon nanotubes (1.6 mmol carbon) were suspended in 30 ml benzene and sonicated for 30 min. in a bath sonicator (Cole Parmer) to form a SWNT-benzene suspension. R-iodide (4.0 mmol) and 403 mg benzoyl peroxide (1.6 mmol) were added to the SWNT-benzene suspension. The resulting mixture was heated under argon at 75°C for 24 hours with stirring. After the heating, the mixture was diluted with 100 ml benzene and filtered through a 0.2 μm PTFE (polytetrafluoroethylene) membrane. The sidewall-functionalized R-SWNT was caught on the filter and washed with copious amounts of benzene. The washing procedure (filtering and washing) was repeated twice with benzene and once each with acetone and methanol. The washed R-SWNT was finally removed from the filter and dried under vacuum at 80°C for 12 hours. Even though benzoyl peroxide was used as the initial radical source, no evidence of phenyl groups was evident on the various sidewall-functionalized R-SWNT. The R groups shown are shown in Table 1, along with the TGA (thermogravimetric analysis) of the sidewall R-functionalized SWNT. TGA was used to determine the weight loss due to the evolution of the particular R group and the associated estimate of the ratio of carbons associated with SWNT to the number of R groups bonded to the SWNT sidewalls. The TGA/MS (thermogravimetric analysis/mass spectroscopy) for sidewall phenylated SWNT indicate the phenyl groups detach at about 400°C.

**TABLE 1**

<table>
<thead>
<tr>
<th>Example Number</th>
<th>R group on SWNT sidewall</th>
<th>Weight loss (wt%)* from TGA</th>
<th>Ratio of SWNT carbons to each R group</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>-Phenyl</td>
<td>3.6</td>
<td>NA</td>
</tr>
<tr>
<td>4</td>
<td>-(CH₂)₄CH₃</td>
<td>31</td>
<td>14</td>
</tr>
<tr>
<td>4a</td>
<td>-(CH₂)₂CH₃</td>
<td>31</td>
<td>14</td>
</tr>
<tr>
<td>4b</td>
<td>-(CH₂)₃CH₃</td>
<td>40</td>
<td>31</td>
</tr>
<tr>
<td>4c</td>
<td>-(CH₂)₂(CH₂)₃CH₃</td>
<td>46</td>
<td>5</td>
</tr>
<tr>
<td>4d</td>
<td>-(CH₂)₂CONH₂</td>
<td>48</td>
<td>5</td>
</tr>
<tr>
<td>4e</td>
<td>-(CH₂)₃Cl</td>
<td>44</td>
<td>8</td>
</tr>
<tr>
<td>4f</td>
<td>-(CH₂)₂CN</td>
<td>30</td>
<td>8</td>
</tr>
<tr>
<td>4g</td>
<td>-(CH₂)₃-O-THPb</td>
<td>41</td>
<td>17</td>
</tr>
<tr>
<td>4h</td>
<td>-(CH₂)₃COO(CH₂)₃CH₃</td>
<td>35</td>
<td>13</td>
</tr>
<tr>
<td>4i</td>
<td>-(CH₂)₄O₅₇(CH₂)₂(CH₂)₃</td>
<td>26</td>
<td>45</td>
</tr>
</tbody>
</table>

*All values were compensated for weight loss of about 2–3% due to degrading at low temperature.

**EXAMPLE 4**

This example demonstrates further reactions of SWNT having sidewall-functional groups. SWNT sidewall-derivatized with ethyl acetate (See 4h in Table 1) was made according to procedures given in Example 3. 38.6 mg SWNT-sidewall derivatized with ethyl acetate was sonicated in 50 ml 2M NaOH for 30 min. Alkaline hydrolysis was conducted at 100°C for 24 hours, followed by acidification with 2 M HCl at 100°C. For 24 hours to convert the ethyl ester group to an acetic acid group. To further functionalize the nanotubes to an amide by reaction with an amine, the nanotubes sidewall derivatized with acetic acid groups were dried under vacuum and then sonicated in 1 ml of anhydrous DMF to form a dispersion in DMF. The dispersion was immediately added to 10 ml thionyl chloride (SOCl₂) and heated at 70°C for 24 hours to convert the terminal carboxylic acid group to a terminal acyl chloride. The single-wall nanotubes with sidewall-functionality having terminal acyl chloride were filtered onto the filter and dried under vacuum at 80°C for 12 hours. Even though benzoyl peroxide was used as the initial radical source, no evidence of phenyl groups was evident on the various sidewall-functionalized R-SWNT. The R groups shown are shown in Table 1, along with the TGA (thermogravimetric analysis) of the sidewall R-functionalized SWNT. TGA was used to determine the weight loss due to the evolution of the particular R group and the associated estimate of the ratio of carbons associated with SWNT to the number of R groups bonded to the SWNT sidewalls. The TGA/MS (thermogravimetric analysis/mass spectroscopy) for sidewall phenylated SWNT indicate the phenyl groups detach at about 400°C.
for 96 hours. The reaction of the acyl chloride with the ODA formed a SWNT having an alkyl amide sidegroup.

The reaction scheme for the preparation of SWNT with a sidewall-functionalized amide from the SWNT having a sidewall-functionalized alkyl ester is shown in FIG. 10. FIG. 10 shows a reaction scheme wherein single-wall carbon nanotubes that have been sidewall functionalized with an ester are saponified with sodium hydroxide and neutralized with hydrochloric acid to form single-wall carbon nanotubes that have alkyl groups with terminal carboxylic acid functionality, which are further chlorinated with thionyl chloride to form an acyl chloride, which is further reacted with octadecyl amine to form an alkyl amide group that is bonded to the single-wall carbon nanotube sidewall. The subscript “x” indicates a variable number of sidegroups on the nanotube. After the heating, the reaction mixture was cooled to room temperature and excess ODA was removed by collecting the sidewall-functionalized nanotubes on a filter and washing with copious amounts of ethanol and chloroform.

The single-wall carbon nanotubes sidewall-functionalized with the alkyl amine were dried in the form of a thick paper by suspending the nanotubes in water, sonicating for 15 min, degassing at low temperature. The resulting sidewall-functionalized SWNT was subjected to TGA analysis to determine the weight loss due to the evolution of the particular R group and to estimate the ratio of carbons associated with SWNT to the number of R groups bonded to the SWNT sidewall. The results are tabulated in Table 2 below.

**TABLE 2**

<table>
<thead>
<tr>
<th>Example Number</th>
<th>Figure Number</th>
<th>R group on SWNT sidewall</th>
<th>Weight loss (%)</th>
<th>Ratio of SWNT carbons to each R group</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>None (pristine SWNT)</td>
<td>CH₃</td>
<td>3.6</td>
<td>NA</td>
</tr>
<tr>
<td>5</td>
<td>5a</td>
<td>CH₃</td>
<td>15</td>
<td>7</td>
</tr>
<tr>
<td>5</td>
<td>5b</td>
<td>CH₃(CH₂)CH₃</td>
<td>18</td>
<td>16</td>
</tr>
<tr>
<td>5</td>
<td>5c</td>
<td>CH(CH₂)₂</td>
<td>15</td>
<td>18</td>
</tr>
<tr>
<td>5</td>
<td>5d</td>
<td>CH₃(CH₂)CH₃</td>
<td>17</td>
<td>22</td>
</tr>
<tr>
<td>5</td>
<td>5e</td>
<td>CH₃(CH₂)CH₂CH₃</td>
<td>12</td>
<td>32</td>
</tr>
<tr>
<td>5</td>
<td>5f</td>
<td>Phenyl</td>
<td>13</td>
<td>40</td>
</tr>
</tbody>
</table>

*All values were compensated for weight loss of about 2-3% due to degassing at low temperature.

**EXAMPLE 6**

This example demonstrates the use of acyl peroxides for the preparation of sidewall-derivatized single-wall carbon nanotubes having sidegroups terminated with carboxylic acid and amine terminated groups. The carbon-centered free radicals terminated with carboxylic acid groups were generated from the decomposition of the diacyl peroxides having terminal carboxylic acid groups. Examples of such peroxides include, but are not limited to, succinic acid peroxide and glutaric acid peroxide, derived from succinic anhydride and glutaric anhydride, respectively. The diamines used were ethylene diamine, 4,4'-methylenebis(cyclohexylamine), and diethylthiouaemadiene.

HIPCO single-wall carbon nanotubes were obtained, purified and prepared according to Example 1.
Preparation of Succinic (6a) and Glutaric Acidperoxides (6b)

Succinic acid peroxide (6a) and glutaric acid peroxide (6b) were synthesized using the one-step procedure of Clover, et al. Am. Chem. J. 1903, 42, 43–60. 10 g finely powdered succinic or glutaric anhydride (each obtained from Aldrich) were added to 20 ml ice cold 8% hydrogen peroxide and stirred for 60 minutes until all the powder dissolved and a white gel-like solution formed. The solution was filtered through a 1-μm pore size PTFE (polytetrafluoroethylene) membrane (Cole Palmer). The filtrate was washed with small amount of water and air-dried for 10 minutes. White peroxide product was collected from the membrane, put into a glass vial and vacuum dried for 24 hours at room temperature. Approximately 6.5 g of each peroxide, 6a and 6b, were obtained using this procedure.

The peroxides 6a and 6b were analyzed by ATR-FTIR (Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy) using a Thermo Nicolet Nexus 870 FTIR system equipped with ATR capability and solid state 13C NMR (Nuclear Magnetic Resonance) to confirm the synthesis. ATR-FTIR spectra of both peroxides 6a and 6b showed similar features: a broad band in the 3000–3500 cm−1 range due to the carboxylic O–H stretches, peaks of the C–H stretchings in the 2850–3000 cm−1 range, absorptions near 1700 cm−1 characteristic of the acid carbonyl groups, and pairs of peaks at 1812 and 1779 cm−1 assigned to the peroxide carbonyls. CP MAS (Cross Polarized Magic Angle Spinning) spectra of acid peroxides 6a and 6b were obtained with a Bruker (50.3 MHz 13C, 200.1 MHz 1H) NMR spectrometer using 5 kHz MAS, a 1-ms contact time, 32.9-ms FID (free induction decay), and 5-s relaxation delay. The solid state 13C NMR spectra of 6a showed three methylene peaks at 28.4, 28.8, and 24.7 ppm and three carbonyl carbon peaks at 181.1, 177.9, and 168.7 ppm, and of 6b three methylene peaks at 33.0, 28.4, and 19.0 ppm and two carbonyl peaks at 182.2 and 170.3 ppm.

Preparation of Sidewall-functionalized Succinic acid-SWNT (7a) and Glutaric acid-SWNT (7b)

Sidewall-functionalized succinic acid-SWNT (7a) and glutaric acid-SWNT (7b) were prepared by the following procedure. 50 mg purified single-wall carbon nanotubes were placed into a 250-ml flask filled with 50 ml dry o-dichlorobenzene and sonicated (17 W/55 kHz, Cole Palmer bath) for 30 minutes to form a SWNT suspension. The SWNT suspension was heated at 80–90°C for 10 days while adding 0.5 g of peroxide 6a or 6b each day. The carboxyl-alkyl radicals were thermally produced from the dicarboxylic acyl peroxides 6a and 6b (FIG. 6) which have half-lives on the order of one hour at 90°C. (according to Atotina Chemicals, Inc. as related at website www.atotinachemicals.com). Due to the stabilizing inductive effect of the carboxylic group, the reactivity of the carboxylic-alkyl radicals with SWNT was somewhat reduced compared to undecyl and phenyl radicals. Therefore, a larger excess of peroxide precursor over SWNT (~10:1 weight ratio) was used to promote the addition reaction (FIG. 7) by a concentration effect.

After the reaction was complete, the suspension was cooled and poured into a 500-ml Erlenmeyer flask containing a large amount of tetrahydrofuran and sonicated for 15 minutes to form a solution. After sonication, the solution was filtered using a 0.2 μm pore size PTFE (Cole Palmer) membrane. Functionalized SWNT (7a or 7b) that collected on the membrane was placed into 100 ml of ethanol, sonicated for 20 minutes and the resulting suspension was refiltered. During filtration, ethanol, in copious amounts, was used to completely wash unreacted peroxides and reaction byproducts from the functionalized SWNT. After the ethanol washing, the functionalized SWNT 7a or 7b was vacuum dried overnight at 70°C.

Characterization of SWNT Derivatives by Optical Spectroscopy

Raman: Raman spectra of purified and functionalized SWNT were collected with a Renishaw 1000 micro-Raman system using a 780-nm laser source. FIG. 11 shows a Raman spectra for pristine SWNT and certain embodiments of the present invention, wherein the subscript “x” indicates a variable number of sidegroup attachments that is variable depending on the sidegroup and conditions of preparation:

1) pristine SWNT (FIG. 11A);
2) SWNT-(CH2CH2COOH)x (FIG. 11B);
3) SWNT-(CH2CH2CH2COOH)x (FIG. 11C); and
4) SWNT-(CH2CH2COOH)x after heating to 800°C in argon per TGA (FIG. 11D).

FIG. 12 shows FTIR spectra for certain embodiments of the present invention, wherein the subscript “x” indicates a variable number of sidegroup attachments that is variable depending on the sidegroup and conditions of preparation:

1) SWNT-(CH2CH2COOH)x (FIG. 12A);
2) SWNT-(CH2CH2CONHC6H(C2H5)2CH3NH2)x (FIG. 12B); and
3) SWNT-(CH2CH2CONHC6H(C2H5)2CH3NH2)x (FIG. 12C).

Raman spectra of purified SWNT, given in FIG. 11A, shows a tangential mode shift at 1594 cm−1 and radial breathing mode shifts at 212, 225 and 265 cm−1, indicative of SWNT nanotube diameters in the range of about 0.7 nm and about 1.2 nm.

Raman (FIGS. 11B and 11C) and IR (FIG. 12A) spectra of sidewall functionalized SWNT indicated the presence of aliphatic functionality. When organic groups were attached to the SWNT sidewall, such as in the case of SWNT-(CH2CH2COOH)x, (7a), a prominent Raman peak appearing at ~1296 cm−1 (see FIG. 11B) indicates a disruption in the aromatic π-electron system of the sp2 carbon hybridization (i.e., sp2 hybridization is occurring at the points of reaction). The breathing mode peaks were weaker in the sidewall functionalized spectrum versus pristine SWNT. Raman spectrum of SWNT-(CH2CH2COOH)x (7b), shown in FIG. 11C, is similar to that of 7a (FIG. 11B) except that the sp2 mode peak at ~1296 cm−1 showed a slightly lower intensity which was attributed to a somewhat lower number of organic groups attached to the nanotube sidewall surface for 7b compared to 7a.

No van Hove band structure was observed for sidewall functionalized SWNT 7a and 7b by UV-Vis-NIR. The van Hove band structure is typically observed with pristine SWNT.

The sidewall functionalized groups were removed by heating sidewall functionalized SWNT 7a and 7b in argon up to a temperature of 800°C at 10°C/min in a TGA system. The defunctionalization of the sidewall derivatized SWNT was evidenced by both weight loss and Raman spectra analyses. The Raman spectra of the nanotube material collected after the pyrolysis showed a dramatic reduction of the sp2 carbon mode intensity, (see FIG. 11D) which is indicative of defunctionalization.

Although IR spectra of pristine SWNT are featureless, ATR-FTIR spectroscopy of sidewall-functionalized SWNT
showed features, such as in IR spectrum of the SWNT-derivative 7a shown in FIG. 12A. The peaks in the 2800-3050 cm⁻¹ region indicate C==H stretches and a broad shoulder band in the 3100-3600 cm⁻¹ range indicate acidic O==H stretches. The dominant peak at 1708 cm⁻¹ is attributed to the acid carbonyl stretching mode. The broad band at 1384 cm⁻¹ is attributed to C==H bending and a broad peak at 1149 cm⁻¹ to the C==O stretching modes. The IR spectrum for sidewall-functionalized 7b was similar.

EXAMPLE 7

This example demonstrates the preparation of amine terminated sidewall-derivatized single-wall carbon nanotubes from sidewall-functionalized, carboxylic acid-terminated SWNT made using acyl peroxides.

Preparation of Sidewall-functionalized Amide-SWNT 8

Sidewall-functionalized amide-SWNT 8 was prepared using acid-functionalized SWNT 7a according to the reaction scheme diagrammed in FIG. 7. 20 mg acid-functionalized SWNT 7a was placed into a dry 100-ml flask to which 20 ml thionyl chloride was added and the mixture stirred for 12 hours. The reaction mixture was then filtered through a 0.2 µm pore size membrane. A solid precipitate that collected on the membrane was flushed with copious amounts of dry acetone and then dried in air. The air-dried precipitate was then placed into a 100-ml flask containing 20 ml ethylenediamine (Aldrich), and stirred for 12 hours at room temperature. The stirred mixture was then filtered through a 0.2 µm pore size membrane and the precipitate flushed with copious amounts of ethanol. The precipitate, amide-functionalized SWNT 8, was collected on a membrane and dried overnight in a vacuum oven at 70°C.

Preparation of Sidewall-functionalized Amide-SWNT 9

A similar procedure was applied for preparation of amide-functionalized SWNT 9, according to the reaction scheme diagrammed in FIG. 8, by using acid-functionalized SWNT 7b with SOCl₂ and 4,4'-methylenebis(cyclohexylamine) (Aldrich).

Preparation of Sidewall-amide-functionalized SWNT 10

A similar procedure was applied for preparation of amide-functionalized SWNT 10, according to the reaction scheme diagrammed in FIG. 9, by using acid-functionalized SWNT 7b with SOCl₁ and diethytolenediamine (Aldrich). Unlike the reactions with ethylene diamine, given in FIG. 7, and 4,4'-ethylenebis(cyclohexylamine), given in FIG. 8, which proceeded at room temperature, the synthesis of amide-functionalized SWNT 10 from 7b required heating at 120°C for 12 hours during the reaction with diethytolenediamine.

Analysis of Sidewall-amide-functionalized SWNT 8, 9 and 10

IR: A Thermo Nicolet Nexus 870 FTIR system with ATR capability was used to obtain ATR-FTIR spectra. UV-Vis-NIR spectra were obtained using a Shimadzu 3101 PC UV/Vis/NIR spectrometer. The FTIR spectrum (FIG. 12B) of SWNT-(CH₂CH₂CONHCH₂CH₂NH₂)ₓ 8 (See FIG. 7) shows an intense peak at 3284 cm⁻¹ which was assigned to the N-H stretching mode of the amide moiety. The carbonyl peak in 8 downshifts to 1691 cm⁻¹ with respect to 7a as a result of the C==O-NH linkage formation. The latter is also characterized by the in-plane amide NH deformation mode observed at 1542 cm⁻¹. The prominent peak at 1639 cm⁻¹ was assigned to the NH₂ scissoring mode in 8. The C==H stretches in 8 are only slightly enhanced as compared to 7a, the spectrum of which is given in FIG. 12A.

The SWNT-derivative 7b was readily converted into an amide derivative 9 by SOCl₁ and 4,4'-methylenebis(cyclohexylamine) at room temperature in accordance with the reaction in FIG. 8. In the IR spectrum of 9, shown on FIG. 12C, the features of the methylene C==H stretches at 2915 and 2848 cm⁻¹ are greatly enhanced. The peak at 1711 cm⁻¹ and the broad band at ~3400 cm⁻¹ were assigned to the C==O and N==H stretching modes, respectively. The NH₂ scissor motion was associated with the peak at 1626 cm⁻¹. The amidation reaction, shown in FIG. 9, of diethyltoluenediamine with 7b was negligible at room temperature, but proceeded upon heating at 120°C to yield the sidewall-wall functionalized SWNT 10, whose IR spectrum is shown on FIG. 12D. The bands at 2950 and 2867 cm⁻¹, as well as those at 2916 and 2837 cm⁻¹ were assigned to CH stretches of the CH₃ and CH₂ groups, respectively. The carbonyl stretching peaks at 1711 cm⁻¹ and the NH stretching at ~3400 cm⁻¹ were weak. The bands at 1621, 1451 and 1375 cm⁻¹ were assigned to the NH₂ scissor, CH deformation and phenyl ring modes, respectively.

TGA/MS: Identification and quantification of thermal degradation and volatile products were performed with a TGA/MS instrument equipped with a Q500 Thermal Graviometric Analyzer coupled with a Pfeiffer Thermal Star mass spectrometer. TGA-MS (Thermal Gravimetric Analysis-Mass Spectroscopy) provided evidence for covalent attachment of alkyl-carboxyl sidewall functionalized SWNT 7a and 7b. TGA was conducted over a range of 50-800°C, using 15 mg of 7a or 7b placed into a TGA pan and heated at 10°C/min up to 800°C under an argon flow. FIG. 13 presents ion current versus time curves for molecular and fragment ions originating from the evolution products detaching from the 7a sidegroups. FIG. 13 shows TGA/MS of SWNT-(CH₂CH₂COOH)ₓ, with peak evolutions due to the following sidegroup fragments and associated atomic mass: a: -CH₃CH₂ (mass: 29); b: -COO- (mass: 44); c: -COOH (mass: 45); d: -CH₃CH₃COOH (mass: 73); and e: -CH₃CH₂COO— (mass: 72). The evolution curves were obtained for the parent ion (m/z 73) of the detaching CH₃CH₂COOH radical, and fragment ions with the m/z 72 [CH₃CH₂COO], m/z 45 [COOH], m/z 44 [COO], and m/z 29 [CH₃CH₂]. That all curves for the fragment ions have the same evolution temperature indicates that the fragments originated from the same parent molecular ion.

For 7a SWNT-(CH₂CH₂COOH)ₓ, fragment evolutions started at about 170°C which is comparable to that of methylated, butylated and hexylated SWNT (~160°C) and relatively lower than phenylated SWNT (~250°C). Assuming that all weight loss was due to sidegroup detachment, the number of sidewall functional groups was estimated to be one functional group for every 24 nanotube carbons for 7a.

Solid State NMR: Solid state MAS (Magic Angle Spinning) NMR spectra were obtained with a Bruker (50.3 MHz ¹³C, 200.1 MHz ¹H) NMR spectrometer. MAS spectra were obtained by packing each sample in a 4-mm OD (outer diameter) rotor and spinning at 7.5 kHz in the case of pristine SWNT and at 11.0 kHz for functionalized SWNT. The spinning sidebands appeared well outside the sp² and sp³ centerband regions of interest (149 ppm upfield or downfield from the centerband in case of SWNT and 219 ppm upfield or downfield from a centerband for functionalized SWNT). Each spectrum was obtained with a 4.5-μs 90° pulse and a 32.9-μs, proton-decoupled FID, followed by a 180° relaxation delay for pristine SWNT or a 45-s relax-
A method for functionalizing a carbon nanotube, comprising:

(a) providing phenyl radicals in the presence of an organic iodide, wherein the phenyl radicals react with the organic iodide to form carbon-centered free radicals; and

(b) reacting the carbon-centered free radicals with a carbon nanotube to form a functionalized carbon nanotube.

2. The method of claim 1, wherein the functionalized carbon nanotube is a sidewall-functionalized carbon nanotube.

3. The method of claim 1, wherein (a) the organic iodide comprises an organic group R; (b) the carbon-centered free radicals comprise R carbon-centered free radicals; and (c) the functionalized carbon nanotube comprises the organic group R bonded to a sidewall of the carbon nanotube.

4. The method of claim 3, wherein (a) the organic iodide has a form R1; and (b) a carbon atom in the organic group R is bonded to iodine.

5. The method of claim 1, wherein the carbon nanotube is selected from the group consisting of a single-wall carbon nanotube, a multi-wall carbon nanotube and a combination thereof.

6. The method of claim 5, wherein the carbon nanotube is a sidewall-fluorinated carbon nanotube.

7. The method of claim 1, wherein the phenyl radicals are provided by decomposition of benzoyl peroxide.

8. The method of 1, wherein the organic iodide comprises an organic group selected from the group consisting of an alkyl group, an aryl group, a cyclic group, and combinations thereof.

9. The method of claim 1, wherein the organic iodide is an alkyl iodide.

10. The method of claim 9, wherein the alkyl iodide comprises an alkyl group selected from the group consisting of a hydrocarbon alkyl group, an alkyl amide, an alkyl amine, alkyl halide, alkyl cyanide, a nitro alkyl, alkyl ether, an alkyl ester, an alkyl ether, an alkyl ketone, an alkyl carboxylic acid, an alkyl carboxylate and combinations thereof.

11. The method of claim 9, wherein the alkyl iodide comprises an alkyl group comprising heterotons selected from the group consisting of nitrogen, oxygen, halogens, and combinations thereof.

12. The method of claim 10, wherein the alkyl group has a number of carbon atoms in the range of 1 and about 30.

13. The method of claim 11, wherein the alkyl group has a number of carbon atoms in the range of 1 and about 30.

14. The method of claim 3, wherein the organic group is a polymeric group.

15. The method of claim 14, wherein the polymeric group comprises poly(ethylene glycol).

16. The method of claim 14, wherein the polymeric group is selected from the group consisting of a polyolefin, a polyester, a polyurethane, and combinations thereof.