Title: IMPROVED OXIDATION OF CARBON NANOTUBES

Abstract: Methods of treating single walled and multiwalled carbon nanotubes with ozone are provided. The carbon nanotubes are treated by contacting the carbon nanotubes with ozone at a temperature range between 0°C and 100°C to yield functionalized nanotubes which are greater in weight than the untreated carbon nanotubes. The carbon nanotubes treated according to methods of the invention can be used to prepare complex structures such as three dimensional networks or rigid porous structures which can be utilized to form electrodes for fabrication of improved electrochemical capacitors. Useful catalyst supports are prepared by contacting carbon nanotube structures such as carbon nanotube aggregates, three dimensional network or rigid porous structures with ozone in the temperature range between 0°C and 100°C.
BACKGROUND OF THE INVENTION

Field of Invention

[0001] The invention relates to methods of treating the surface of single walled and multiwalled carbon nanotubes with ozone. The invention also encompasses methods of making aggregates of ozone-treated nanotubes, and methods of using the same. The invention further relates to methods of making complex structures such as three dimensional networks or rigid porous structures comprised of such ozone-treated carbon nanotubes linked to one another. The invention also includes methods of making a catalyst support from aggregates, three dimensional networks, or rigid porous structures that have been treated with ozone.

Description of the Related Art

Carbon Nanotubes

[0002] This invention lies in the field of submicron graphitic carbon fibrils, commonly referred to as nanotubes. Carbon fibrils are vermicular carbon deposits having diameters less than 1.0μ, preferably less than 0.5μ, and even more preferably less than 0.2μ. Carbon nanotubes can be either multi walled (i.e., have more than one graphite layer on the nanotube axis) or single walled (i.e., have only a single graphite layer on the nanotube axis). Other types of carbon nanotubes are also described below.

[0003] The carbon nanotubes which can be treated as taught in this application, are distinguishable from commercially available continuous carbon fibers. In contrast to these fibers which have aspect ratios (L/D) of at least 10^4 and often 10^6 or more, carbon fibrils have desirably large, but unavoidably finite, aspect ratios. The diameter of continuous fibers is also far larger than that of fibrils, being always >1.0 μ and typically 5 to 7 μ.
[0004] Carbon nanotubes differ physically and chemically from continuous carbon fibers which are commercially available as reinforcement materials, and from other forms of carbon such as standard graphite and carbon black. Standard graphite, because of its structure, can undergo oxidation to almost complete saturation. Moreover, carbon black is amorphous carbon generally in the form of spheroidal particles having a graphene structure, carbon layers around a disordered nucleus. The differences make graphite and carbon black poor predictors of carbon nanotube chemistry.

[0005] Carbon nanotubes exist in a variety of forms and have been prepared through the catalytic decomposition of various carbon-containing gases at metal surfaces. Such vermicular carbon deposits have been observed almost since the advent of electron microscopy. (Baker and Harris, Chemistry and Physics of Carbon, Walker and Thrower ed., Vol. 14, 1978, p. 83; Rodriguez, N., J. Mater. Research, Vol. 8, p. 3233 (1993)).

[0006] In 1976, Endo et al. (see Oberlin, A. and Endo, M., J. of Crystal Growth, Vol. 32 (1976), pp. 335-349), hereby incorporated by reference, elucidated the basic mechanism by which such carbon fibrils grow. They were seen to originate from a metal catalyst particle, which, in the presence of a hydrocarbon containing gas, becomes supersaturated in carbon. A cylindrical ordered graphitic core is extruded which immediately, according to Endo et al., becomes coated with an outer layer of pyrolytically deposited graphite. These fibrils with a pyrolytic overcoat typically have diameters in excess of 0.1 µm, more typically 0.2 to 0.5 µm.

[0007] In 1983, Tennent, U.S. Patent No. 4,663,230, hereby incorporated by reference, describes carbon fibrils that are free of a continuous thermal carbon overcoat and have multiple graphitic outer layers that are substantially parallel to the fibril axis. As such they may be characterized as having their c-axes, the axes which are perpendicular to the tangents of the curved layers of graphite, substantially perpendicular to their cylindrical axes. They generally have diameters no greater than 0.1 µm and length to diameter ratios of at least 5. Desirably they are substantially free of a continuous thermal carbon overcoat, i.e., pyrolytically deposited carbon resulting from thermal cracking of the gas feed used to prepare them. Thus, the Tennent invention provided access to smaller diameter fibrils, typically 35 to 700 Å (0.0035 to 0.070 µm) and to an ordered, "as grown" graphitic surface. Fibrillar carbons of less
perfect structure, but also without a pyrolytic carbon outer layer have also been
grown.

[0008] Tennent, et al., U.S. Patent No. 5,171,560, hereby incorporated by
reference, describes carbon fibrils free of thermal overcoat and having graphitic layers
substantially parallel to the fibril axes such that the projection of said layers on said
fibril axes extends for a distance of at least two fibril diameters. Typically, such
fibrils are substantially cylindrical, graphitic nanotubes of substantially constant
diameter and comprise cylindrical graphitic sheets whose c-axes are substantially
perpendicular to their cylindrical axis. They are substantially free of pyrolytically
deposited carbon, have a diameter less than 0.1μ and length to diameter ratio of
greater than 5. These fibrils can be oxidized by the methods of the invention.

[0009] When the projection of the graphitic layers on the nanotube axis
extends for a distance of less than two nanotube diameters, the carbon planes of the
graphitic nanotube, in cross section, take on a herring bone appearance. These are
termed fishbone fibrils. Geus, U.S. Patent No. 4,855,091, hereby incorporated by
reference, provides a procedure for preparation of fishbone fibrils substantially free of
a pyrolytic overcoat. These carbon nanotubes are also useful in the practice of the
invention.

[0010] Carbon nanotubes of a morphology similar to the catalytically grown
fibrils described above have been grown in a high temperature carbon arc (Iijima,
Nature 354, 56, 1991). It is now generally accepted (Weaver, Science 265, 1994; de
Heer, Walt A., “Nanotubes and the Pursuit of Applications,” MRS Bulletin, April,
2004, both incorporated by reference herein) that these arc-grown nanofibers have the
same morphology as the earlier catalytically grown fibrils of Tennent. Arc grown
carbon nanofibers often colloquially referred to as “bucky tubes”, are also useful in
the invention.

[0011] Useful single walled carbon nanotubes and process for making them
are disclosed, for example, in "Single-shell carbon nanotubes of 1-nm diameter", S
carbon nanotubes with single-atomic-layer walls," D S Bethune, C H Kiang, M S
articles of which are hereby incorporated by reference.

[0012] Single walled carbon nanotubes are also disclosed in U.S. Patent No.
6,221,330 to Moy et. al., the contents wherein of which are hereby incorporated by
reference. Moy disclosed a process for producing hollow, single-walled carbon nanotubes by catalytic decomposition of one or more gaseous carbon compounds by first forming a gas phase mixture carbon feedstock gas comprising one or more gaseous carbon compounds, each having one to six carbon atoms and only H, O, N, S or Cl as hetero atoms, optionally admixed with hydrogen, and a gas phase metal containing compound which is unstable under reaction conditions for said decomposition, and which forms a metal containing catalyst which acts as a decomposition catalyst under reaction conditions; and then conducting said decomposition reaction under decomposition reaction conditions, thereby producing said nanotubes. The invention relates to a gas phase reaction in which a gas phase metal containing compound is introduced into a reaction mixture also containing a gaseous carbon source. The carbon source is typically a C1 through C6 compound having as hetero atoms H, O, N, S or Cl, optionally mixed with hydrogen. Carbon monoxide or carbon monoxide and hydrogen is a preferred carbon feedstock.

Increased reaction zone temperatures of approximately 400°C to 1300°C and pressures of between about 0 and about 100 p.s.i.g., are believed to cause decomposition of the gas phase metal containing compound to a metal containing catalyst. Decomposition may be to the atomic metal or to a partially decomposed intermediate species. The metal containing catalysts (1) catalyze CO decomposition and (2) catalyze SWNT formation.

[0013] The invention of U.S. Patent No. 6,221,330 may in some embodiments employ an aerosol technique in which aerosols of metal containing catalysts are introduced into the reaction mixture. An advantage of an aerosol method for producing SWNT is that it will be possible to produce catalyst particles of uniform size and scale such a method for efficient and continuous commercial or industrial production. The previously discussed electric arc discharge and laser deposition methods cannot economically be scaled up for such commercial or industrial production. Examples of metal containing compounds useful in the invention include metal carbonyls, metal acetyl acetonates, and other materials which under decomposition conditions can be introduced as a vapor which decomposes to form an unsupported metal catalyst. Catalytically active metals include Fe, Co, Mn, Ni and Mo. Molybdenum carbonyls and iron carbonyls are the preferred metal containing compounds which can be decomposed under reaction conditions to form vapor phase catalyst. Solid forms of these metal carbonyls may be delivered to a pretreatment
zone where they are vaporized, thereby becoming the vapor phase precursor of the catalyst. It was found that two methods may be employed to form SWNT on unsupported catalysts.

[0014] The first method is the direct injection of volatile catalyst. The direct injection method is described is U.S. Patent No. 6,696,387, incorporated herein by reference. Direct injection of volatile catalyst precursors has been found to result in the formation of SWNT using molybdenum hexacarboxyl [Mo(CO)₆] and dicobalt octacarbonyl [CO₂ (CO)₈] catalysts. Both materials are solids at room temperature, but sublime at ambient or near-ambient temperatures--the molybdenum compound is thermally stable to at least 150°C, the cobalt compound sublimes with decomposition "Organic Syntheses via Metal Carboxyls," Vol. 1, I. Wender and P. Pino, eds., Interscience Publishers, New York, 1968, p. 40).

[0015] The second method described in U.S. Patent No. 6,221,330 uses a vaporizer to introduce the metal containing compound (see FIG. 1 in U.S. Patent No. 6,221,330). In one preferred embodiment of the invention, the vaporizer 10, shown at FIG. 2 of U.S. Patent No. 6,221,330, comprises a quartz thermowell 20 having a seal 24 about 1" from its bottom to form a second compartment. This compartment has two 1/4" holes 26 which are open and exposed to the reactant gases. The catalyst is placed into this compartment, and then vaporized at any desired temperature using a vaporizer furnace 32. This furnace is controlled using a first thermocouple 22. A metal containing compound, preferably a metal carbonyl, is vaporized at a temperature below its decomposition point, reactant gases CO or CO/H₂ sweep the precursor into the reaction zone 34, which is controlled separately by a reaction zone furnace 38 and second thermocouple 42. Although applicants do not wish to be limited to a particular theory of operability, it is believed that at the reactor temperature, the metal containing compound is decomposed either partially to an intermediate species or completely to metal atoms. These intermediate species and/or metal atoms coalesce to larger aggregate particles which are the actual catalyst. The particle then grows to the correct size to both catalyze the decomposition of CO and promote SWNT growth. In the apparatus of FIG. 1 of U.S. Patent No. 6,221,330, the catalyst particles and the resultant carbon forms are collected on the quartz wool plug 36. Rate of growth of the particles depends on the concentration of the gas phase metal containing intermediate species. This concentration is determined by the vapor pressure (and therefore the temperature) in the vaporizer. If the concentration is too
high, particle growth is too rapid, and structures other than SWNT are grown (e.g., MWNT, amorphous carbon, onions, etc.) All of the contents of U.S. Patent No. 6,221,330, including the Examples described therein, are hereby incorporated by reference.

[0016] U.S. Pat. No. 5,424,054 to Bethune et al., hereby incorporated by reference, describes a process for producing single-walled carbon nanotubes by contacting carbon vapor with cobalt catalyst. The carbon vapor is produced by electric arc heating of solid carbon, which can be amorphous carbon, graphite, activated or decolorizing carbon or mixtures thereof. Other techniques of carbon heating are discussed, for instance laser heating, electron beam heating and RF induction heating.


[0020] U.S. Patent No. 6,761,870 (also WO 00/26138) to Smalley, et. al, hereby incorporated by reference, discloses a process of supplying high pressure (e.g., 30 atmospheres) CO that has been preheated (e.g., to about 1000°C) and a catalyst precursor gas (e.g., Fe(CO)₅) in CO that is kept below the catalyst precursor decomposition temperature to a mixing zone. In this mixing zone, the catalyst precursor is rapidly heated to a temperature that is reported to result in (1) precursor
decomposition, (2) formation of active catalyst metal atom clusters of the appropriate size, and (3) favorable growth of SWNTs on the catalyst clusters.


**Aggregates of Carbon Nanotubes and Assemblages**

[0022] As produced, carbon nanotubes may be in the form of discrete nanotubes, aggregates of nanotubes or both.

[0023] Nanotubes are prepared as aggregates having various morphologies (as determined by scanning electron microscopy) in which they are randomly entangled with each other to form entangled balls of nanotubes resembling bird nests ("BN"); or as aggregates consisting of bundles of straight to slightly bent or kinked carbon nanotubes having substantially the same relative orientation, and having the appearance of combed yarn ("CY") e.g., the longitudinal axis of each nanotube (despite individual bends or kinks) extends in the same direction as that of the surrounding nanotubes in the bundles; or, as, aggregates consisting of straight to slightly bent or kinked nanotubes which are loosely entangled with each other to form an "open net" ("ON") structure. In open net structures the extent of nanotube entanglement is greater than observed in the combed yarn aggregates (in which the individual nanotubes have substantially the same relative orientation) but less than that of bird nest. Other useful aggregate structures include the cotton candy ("CC") structure.

[0024] The morphology of the aggregate is controlled by the choice of catalyst support. Spherical supports grow nanotubes in all directions leading to the formation of bird nest aggregates. Combed yarn and open nest aggregates are prepared using supports having one or more readily cleavable planar surfaces, e.g., an iron or iron-containing metal catalyst particle deposited on a support material having one or more readily cleavable surfaces and a surface area of at least 1 square meters per gram.

U.S. Patent No. 6,143,689 to Moy et al., entitled "Improved Methods and Catalysts for the Manufacture of Carbon Fibrils", filed June 6, 1995, hereby incorporated by
reference, describes nanotubes prepared as aggregates having various morphologies (as determined by scanning electron microscopy).


Nanotube mats or assemblages have been prepared by dispersing carbon nanotubes in aqueous or organic mediums and then filtering the nanotubes to form a mat or assemblage. The mats have also been prepared by forming a gel or paste of nanotubes in a fluid, e.g. an organic solvent such as propane and then heating the gel or paste to a temperature above the critical temperature of the medium, removing the supercritical fluid and finally removing the resultant porous mat or plug from the vessel in which the process has been carried out. See, U.S. Patent Application Number 08/428,496 entitled “Three-Dimensional Macroscopic Assemblages of Randomly Oriented Carbon Fibrils and Composites Containing Same” by Tennent et al, which has issued as U.S. Patent No. 5,691,054 on November 25, 1997, hereby incorporated by reference.

**Oxidation Of Carbon Nanotubes**

While many uses have been found for carbon nanotubes and aggregates of carbon nanotubes, as described in the patents and patent applications referred to above, it had been previously discovered that many different and important uses may still be developed if the nanotubes surfaces are functionalized with oxygen containing moieties. One method used to functionalizing the carbon nanotubes is through oxidation reactions with liquid oxidizing agents such as nitric acid or hydrogen peroxide. Oxidation can permit interaction of the functionalized nanotubes with various substrates to form unique compositions of matter with unique properties.
and permit structures of carbon nanotubes to be created based on linkages between the functional sites on the surfaces of the carbon nanotubes.

[0028] However, a common unwanted side effect is the simultaneous destruction of the carbon nanotubes or carbon nanotube structures themselves. And thus, not only is the strength and integrity of the carbon nanotube or carbon nanotube structure compromised, but there is also a restricted limit as to how much oxygen containing moieties can be deposited onto the carbon nanotube or carbon nanotube structure. As such, there is a need for an improved method for functionalizing carbon nanotubes which will result in less destruction to the carbon nanotube or carbon nanotube structure while at the same time yielding a higher concentration of oxygen containing moieties on the carbon nanotube surface.

SUMMARY OF THE INVENTION

[0029] The present invention provides methods of treating single walled or multiwalled carbon nanotubes with ozone at a temperature range of from 0°C to 100°C under conditions sufficient to form functionalized nanotubes which are greater in weight than the original carbon nanotubes. Preferably, the nanotubes are contacted with ozone at or about room temperature. More preferably, the nanotubes are contacted with ozone at a temperature range between 0°C and 60°C and most preferably between 20°C and 50°C.

[0030] The ozone may be contacted with the carbon nanotubes via a gaseous or liquid medium. The carbon nanotubes to be treated may be in individual form or in the form of carbon nanotube structures such as aggregates having a macromorphology resembling the shape of a cotton candy, bird nest, combed yarn or open net. Other carbon nanotube structures include mats, assemblages, three dimensional networks, rigid porous structures, etc. Preferred multiwalled carbon nanotubes have diameters no greater than 1 micron and preferred single walled carbon nanotubes have diameters less than 5 nm.

[0031] The ozone treated carbon nanotubes can be further subjected to a secondary treatment step whereby the oxygen containing moieties of the ozone treated nanotubes react with suitable reactants to add at least a secondary group onto the surface of the treated nanotubes.
The ozone treated carbon nanotubes are also useful in preparing a network of carbon nanotubes, a rigid porous structure or as starting material for electrodes utilized in electrochemical capacitors.

Catalyst supports are preferably prepared by contacting or treating carbon nanotube aggregates, three dimensional networks or rigid porous structures with ozone at a temperature range of from 0°C to 100°C. Preferably, the aggregates, three dimensional networks or rigid porous structures are contacted with ozone at or about room temperature. More preferably, the aggregates, three dimensional networks or rigid porous structures are contacted with ozone at a temperature range between 0°C and 60°C and most preferably between 20°C and 50°C. Catalyst support structures functionalized using ozone exhibit higher acid titer, thus enabling higher catalyst loading and better retention of their original support structure and integrity.

Electrochemical capacitors assembled from electrodes made from the ozone treated carbon nanotubes of the invention exhibit enhanced electrochemical characteristics, such as specific capacitance.

In summary, the present invention includes a carbon nanotube structure comprising a multiplicity of carbon nanotubes entangled with one another, said structure exhibiting upon titration an acid titer from 1 to 2 meq/g. The carbon nanotube structure may be in the form of aggregate of carbon nanotubes having a macromorphology resembling a shape selected from the group consisting of cotton candy, bird nests, combed yarn and open net aggregates. The carbon nanotube structure may also be a three dimensional network, a carbon nanotube mat or assemblage, a rigid porous structure, or any other carbon nanotube structure.

The present invention further includes carbon nanotubes which exhibit upon titration an acid titer between 1.6 and 2.2 meq/g, or greater than 2 meq/g, or between 2.5 to 3.5 meq/g. Additionally, the present invention includes ozone treated carbon nanotubes which exhibit upon titration an acid titer increase of at least 1.5 meq/g, or of at least 2 meq/g, or between 1.5 meq/g and 3 meq/g, when compared to the acid titer of the non-ozone treated carbon nanotubes.

Other improvements which the present invention provides over the prior art will be identified as a result of the following description which sets forth the preferred embodiments of the present invention. The description is not in any way intended to limit the scope of the present invention, but rather only to provide a
working example of the present preferred embodiments. The scope of the present invention will be pointed out in the appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

5 [0038] Figure 1 is a plot of fibril weight as a function of reaction time during ozone treatment based on the results of Example 2.
[0039] Figure 2 displays several oxygen 1s spectra of the various fibril samples in accordance with Example 5.
[0040] Figure 3 illustrates electron micrographs of ozone treated fibrils in accordance with Example 6.
[0041] Figures 4A and 4B are TEM micrographs illustrating fibrils before and after treatment with ozone.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Definitions

[0042] The terms “nanotube”, “nanofiber” and “fibril” are used interchangeably to refer to single walled or multiwalled carbon nanotubes. Each refers to an elongated structure preferably having a cross section (e.g., angular fibers having edges) or a diameter (e.g., rounded) less than 1 micron (for multiwalled nanotubes) or less than 5 nm (for single walled nanotubes). The term “nanotube” also includes “buckytubes”, and fishbone fibrils.

[0043] “Multiwalled nanotubes” as used herein refers to carbon nanotubes which are substantially cylindrical, graphitic nanotubes of substantially constant diameter and comprise cylindrical graphitic sheets or layers whose c-axes are substantially perpendicular to the cylindrical axis, such as those described, e.g., in U.S. Patent No. 5,171,560 to Tennent, et al.

[0044] “Single walled nanotubes” as used herein refers to carbon nanotubes which are substantially cylindrical, graphitic nanotubes of substantially constant diameter and comprise a single cylindrical graphitic sheet or layer whose c-axis is substantially perpendicular to their cylindrical axis, such as those described, e.g., in U.S. Patent No. 6,221,330 to Moy, et al.
[0045] The term “functional group” refers to groups of atoms that give the compound or substance to which they are linked characteristic chemical and physical properties.

[0046] A “functionalized” surface refers to a carbon surface on which chemical groups are adsorbed or chemically attached.

[0047] “Graphenic” carbon is a form of carbon whose carbon atoms are each linked to three other carbon atoms in an essentially planar layer forming hexagonal fused rings. The layers are platelets only a few rings in diameter or they may be ribbons, many rings long but only a few rings wide.

[0048] “Graphitic” carbon consists of graphenic layers which are essentially parallel to one another and no more than 3.6 angstroms apart.

[0049] The term “aggregate” refers to a dense, microscopic particulate structure comprising entangled carbon nanotubes.

[0050] The term “micropore” refers to a pore which has a diameter of less than 2 nanometers.

[0051] The term “mesopore” refers to pores having a cross section greater than 2 nanometers and less than 50 nanometers.

[0052] The term “surface area” refers to the total surface area of a substance measurable by the BET technique.

[0053] The term “accessible surface area” refers to that surface area not attributed to micropores (i.e., pores having diameters or cross-sections less than 2 nm).

[0054] The term “isotropic” means that all measurements of a physical property within a plane or volume of the structure, independent of the direction of the measurement, are of a constant value. It is understood that measurements of such non-solid compositions must be taken on a representative sample of the structure so that the average value of the void spaces is taken into account.

[0055] The term “untreated” when used in comparison to “ozone treated” carbon nanotubes, aggregates or any other carbon nanotube structures mean that the carbon nanotubes, aggregates, or structures have not been specifically treated with ozone. It does not preclude carbon nanotubes, aggregates, or structures which have been subjected to other non-ozone treatments before the treatment with ozone.
Methods Of Treating Carbon Nanotubes With Ozone

[0056] In the present invention, the surface properties and characteristics of carbon nanotubes are modified by subjecting them to treatments with ozone in accordance with the preferred embodiment. One desirable result of treating the fibrils in accordance with the preferred embodiment is that the surface of the fibrils become functionalized with oxygen containing moieties.

[0057] Additionally, the resulting ozone treated nanotubes can be easily dispersed in both organic and inorganic solvents, and especially in water. The ozone treated nanotubes can be placed in matrices of other materials, such as plastics, or made into structures useful in catalysis, chromatography, filtration systems, electrodes, capacitors and the like. Furthermore, the ozone treated nanotubes can also be used to form other useful carbon nanotube structures as discussed in the subsequent sections.

[0058] In the preferred embodiment, the carbon nanotubes are substantially cylindrical, graphitic carbon fibrils of substantially constant diameter and are substantially free of pyrolytically deposited carbon. The nanotubes include those having a length to diameter ratio of greater than 5 with the projection of the graphite layers on the nanotubes extending for a distance of at least two nanotube diameters.

[0059] The single walled and multiwalled carbon nanotubes useful for the methods of the present invention have been more specifically described under the previous heading “Carbon Nanotubes.” In a preferred embodiment, the multiwalled nanotubes are prepared according to Patent No. 5,171,560 to Tennent, et al. or U.S. Patent No. 6,696,387 to Moy, et. al, both of which are incorporated herein by reference. The multiwalled carbon nanotubes preferably have diameters no greater than one micron, more preferably no greater than 0.2 micron. Even more preferred are multiwalled carbon nanotubes having diameters between 2 and 100 nanometers, inclusive; most preferably between 3.5 and 75 nanometers.

[0060] Alternatively, preferred single walled carbon nanotubes are prepared as disclosed in U.S. Patent No. 6,211,330 to Moy, et. al, incorporated herein by reference. The single walled carbon nanotubes preferably have diameters no greater than 5 nanometers, more preferably between 0.6 and 5 nanometers.

[0061] Ozone used to treat the carbon nanotubes may be delivered in the form of gaseous ozone, liquid ozone, or ozone dissolved in aqueous solvent such as water.
Ozone containing gas may be optionally diluted with gases such as oxygen, air, nitrogen, noble gases and mixtures thereof. Any conventionally or commercially available ozone generator may be used to produce the ozone or ozone containing gas. The ozone generator may be fed with gases such as air or pure oxygen in order to generate the ozone or ozone containing gas. The use of air as the feed gas will often yield an ozone containing gas which also contains oxides of nitrogen that may react with a medium such as water to create nitric acid. This extra oxides of nitrogen or nitric acid byproduct in the ozone containing gas may affect the desired functionalization of the carbon nanotube. On the other hand, the use of pure oxygen as the feed gas will yield a purer ozone containing gas, without any or with much smaller amounts of extra byproducts such as oxides of nitrogen which may affect the desired functionalization of the carbon nanotubes.

[0062] In one embodiment, ozone may be introduced to the carbon nanotubes at a rate of 250 mg/hr. Preferably, ozone is introduced to the carbon nanotubes at a rate of 200 to 300 mg/hr. One skilled in the art will understand that the actual flow rate of the ozone containing gas will depend on the amount of ozone in the gas and the quantity of carbon nanotubes to treat.

[0063] The ozone may be introduced to the carbon nanotubes using any known conventional reactors, processes or methods, including through vertical reactors such as through the use of a vertical tube reactor, packed bed, fluidized bed, etc. Non-vertical or horizontal reactors may also be utilized. For example, ozone may be fed through a sparger into a tumbling reactor or rotating drum reactor wherein the vessel housing the carbon nanotubes is rotated to more evenly distribute the carbon nanotube’s exposure to the ozone and result in more even functionalization of the carbon nanotubes.

[0064] In the preferred embodiment, carbon nanotubes are treated with ozone at temperatures ranging from 0°C to 100°C. Preferably, the nanotubes are contacted with ozone at or about room temperature. More preferably, the nanotubes are contacted with ozone at a temperature range between 0°C and 60°C and most preferably between 20°C and 50°C.

[0065] In the exemplary embodiment, this ozonolysis process at the preferred temperatures may be carried on for over 24 hours. Preferably, the reaction is permitted to continue between 3 to 8 hours, or 10 to 45 hours, and more preferably between 15 to 25 hours. One skilled in the art will understand that the run time of this
process depend on factors such as the size and temperature of the reactor, the amount of carbon fibrils needed for treatment, the rate of ozone being introduced to the fibrils, the manner by which ozone is introduced to the fibrils (i.e., in a gaseous or liquid medium), the desired acidity, etc.

Carbon nanotubes treated in accordance with this preferred embodiment result in a number of unexpected benefits.

It has been unexpectedly found that the ozone treated carbon nanotubes of the preferred embodiment experience a weight gain instead of a weight loss which is what would have been expected when treating carbon nanotubes with oxidizing agents. The increase in weight may be greater than 1%, and preferably greater than 5%. In one embodiment, the ozone treated carbon nanotubes of the preferred embodiment exhibit a 5 to 20% weight gain, more preferably a 10 to 15% weight gain.

Without being bound to any theory, it is believed this overall weight gain can be attributed to the ozone at the recited temperature ranges preferentially engaging in surface treatment of the carbon nanotube surface (thereby resulting in the attachment, formation, substitution or deposition of functional groups onto the surface of the carbon nanotubes and aggregates) as opposed to engaging in uncapping, stripping or shortening reactions (thereby resulting in either minimal or no measurable or visual loss of carbon mass) that are more typical with other oxidizing agents at higher temperatures (for example nitric acid - degrades aggregates to form weathered rope structures). On a more atomic level, ozone treatment at moderate temperatures in accordance with the preferred embodiment is believed to proceed via an addition reaction by which ozone forms a five membered "ozonide" ring with the double bonded surface carbon atoms which then decomposes into COOH and C=O. This result is surprising since ozone is a strong oxidant at higher temperatures, and thus would have been expected to aggressively uncap, strip or shorten the carbon nanotubes as with other strong oxidants such as nitric acid. The mechanisms of ozonolysis is described in Murray, Robert W., "The Mechanism of Ozonolysis," Accounts of Chemical Research, Volume 1, pp. 313-320 (October, 1968), herein incorporated by reference.

Consistent with the weight gain, it has also been unexpectedly found that treatment of carbon nanotubes with ozone in accordance with the preferred embodiment yields carbon nanotubes with higher amounts of functional groups.
(especially acidic groups) on the nanotube surface than treatments using other oxidizing agents. (As a result, in the specification and claims, the term “functionalized” nanotubes may be used interchangeably with “ozone treated carbon nanotubes” where the nanotubes were treated with ozone). Specifically, carbon nanotubes treated with ozone can reach a higher acid titer (i.e., have more acidic groups) than those treated with other oxidizing agents such as nitric acid and hydrogen peroxide. Acid titer can be measured using the methods described in the application, such as the method described under the heading entitled “Method of Measuring Titer” in the Examples section.

[0070] Ozone treated carbon nanotubes of the preferred embodiment can reach an acid titer greater than 2 meq/g, preferably in the range of 1.6 to 2.2 meq/g. Alternatively, ozone treated carbon nanotubes can reach an acid titer in the range of 0.0040-0.0080 meq/m². As acid titer measurements are an indication of the quantity of acid reacting oxygen containing moieties such as COOH, phenolic OH, lactone, etc. which have been deposited onto the carbon nanotubes, the exceedingly high acid titer reached confirms that the ozone in the method of the preferred embodiment is reacting with the surface side walls of the carbon nanotubes and not just the end caps.

[0071] It has also been found that ozone can be used in accordance with the preferred embodiment to further treat carbon nanotubes which have already been oxidized or functionalized by other oxidizing agents. For example, a single or multi walled carbon nanotube mixture which contain amorphous carbon can first be oxidized with nitric acid using conventional methods to, inter alia, purify the mixture (i.e., to remove the amorphous carbon via oxidation). These oxidized carbon nanotubes will be consequently functionalized with some oxygen containing moieties, and thus will yield a low acid titer upon titration. When further treating these oxidized carbon nanotubes with ozone in accordance with the preferred embodiment, the ozone treated carbon nanotubes was discovered to exhibit upon titration an increase in acid titer by at least 1.5 meq/g and preferably greater than 2 meq/g. For example, the increase in acid titer may be between 1.5 meq/g to 3 meq/g, or between 2 meq/g to 2.5 meq/g. (These acid titer increases may also apply to ozone treated carbon nanotubes when comparing to as made carbon nanotubes which have not previously been treated with oxidizing agents). The final ozone treated carbon nanotubes may themselves exhibit upon a titration an acid titer greater than 2.5 meq/g or between 2.5 meq/g to 3.5 meq/g.
Additionally, the use of ozone to treat carbon nanotubes at the recited temperature range also results in a more efficient generation (higher percentage) of surface acidic groups compared to carbon nanotubes which have been oxidized with nitric acid or hydrogen peroxide. Carbon nanotubes treated with ozone at the recited temperature range have higher oxygen content than those oxidized with nitric acid or hydrogen peroxide. The surface of the ozone treated carbon nanotubes of the preferred embodiment can have an oxygen content greater than 4 percent (e.g., 4-10%), preferably greater than 6 percent (e.g., 6-10%). Preferred functional groups resulting from the ozone treatment include carboxyl, anhydride and ketone.

It has been further discovered that ozone treatment of carbon nanotubes in accordance with the preferred embodiment also results in less destruction to the carbon nanotube itself as compared to other oxidizing agents. Experimental data and scanning electronic micrographs such as those shown in Figures 4A and B reveal minimal or otherwise no measurable or visible loss of carbon mass from the ozone treated carbon nanotube itself.

In addition to the surface and structural benefits on the carbon nanotube itself (i.e., more functional groups, less carbon destruction), a further benefit in using the preferred ozone treatment is the energy and cost savings imparted as a result of being able to carry out the ozone oxidation treatment at a lower temperature range such as at room temperature. Thus, compared other oxidation processes, additional heating equipment is not necessarily required.

**Ozone Treated Carbon Nanotube Structures - General Summary**

All of these benefits were also discovered to apply when treating any carbon nanotube structure (e.g., fibril aggregates, mats, assemblages, three dimensional networks, rigid porous structures, etc.) with ozone. The ozone treated structures remained intact despite high degree of surface oxidation and all of the above recited weight gain, oxygen content and acid titer characteristics apply as well.

Furthermore, as explained in the subsequent sections, similar benefits are also conferred upon carbon nanotube structures which are made from these ozone oxidized carbon nanotubes.

Carbon nanotube structures include, but are not limited to the following groups: aggregates, assemblages, networks and rigid porous structures.
a. Aggregates are dense microscope particulate structures of entangled carbon nanotubes and may resemble the morphology of birds nest, cotton candy, combed yard or open net.

b. Assemblages are carbon nanotube structures which have relatively uniform properties in along one, preferably two and most desirably three dimensional axis of the three dimensional assemblage. (E.g., U.S. Patent No. 5,691,054 hereby incorporated by reference). Generally, assemblages are formed by de-aggregating the carbon nanotube aggregate structure, and then reassembling them to form assemblages.

c. Networks are formed by linking individual functionalized carbon nanotubes together by using a linking molecule between the functionalized groups located on the surface of the carbon nanotubes. (E.g., PCT/US97/03553 or WO 97/32571, hereby incorporated by reference).

d. Rigid porous structures are formed by either linking the individual functionalized carbon nanotubes together without the use of a linking molecule, or by gluing carbon nanotube aggregate structures together with a gluing agent. (E.g., U.S. Patent No. 6,099,965, hereby incorporated by reference).

[0078] In the preferred embodiment, ozone treated carbon nanotube structures may be made by forming the respective structure first and then subjecting that structure to ozone treatment as described above in “Methods Of Treating Carbon Nanotubes With Ozone.” Alternatively, ozone treated carbon nanotube structures may be formed from the ozone treated carbon nanotubes themselves.

**Methods Of Treating Aggregates Of Carbon Nanotubes With Ozone**

[0079] It has also been discovered that improved aggregates of carbon nanotubes can be formed by treatment with ozone in accordance with the preferred embodiment. As defined previously, aggregates are dense microscopic particulate structures of entangled carbon nanotubes and can be made using any of the procedures previously described or incorporated by reference in the section entitled “Aggregates of Carbon Nanotubes and Assemblages.” Preferred aggregates have diameters less than 50 microns.

[0080] Consistent with the non-destructive treatment of carbon nanotubes discussed above, it has been further discovered that improved aggregates of carbon nanotubes may be formed from the ozone treated carbon nanotubes described. Alternatively, improved aggregates of carbon nanotubes may formed by subjecting
the untreated aggregates to ozone treatment in accordance with the preferred embodiment.

[0081] When forming aggregates of carbon nanotubes from ozone treated carbon nanotubes, the individual carbon nanotubes are first subjected to ozone treatment as disclosed in the previous section “Method Of Treating Carbon Nanotubes With Ozone” to form ozone treated carbon nanotubes. The ozone treated carbon nanotubes are then formed into ozone treated aggregates of carbon nanotubes using any method disclosed in the references incorporated by reference in the previous section entitled “Aggregates Of Carbon Nanotubes And Assemblages.”

[0082] Alternatively, if aggregates of untreated carbon nanotubes have already been formed, then those untreated aggregates may be subject to ozone treatment in the same manner and conditions described in the previous section “Method Of Treating Carbon Nanotubes With Ozone.”

[0083] In either embodiment, ozone treated aggregates of carbon nanotubes were discovered to have a number of similar benefits as ozone treated carbon nanotubes. For example, the ozone treated aggregates exhibit an unexpected weight gain compared to untreated aggregates of carbon nanotubes. The increase in weight of the ozone treated aggregates of carbon nanotubes may be greater than 1%, and preferably greater than 5%, by comparison to the untreated aggregates of carbon nanotubes. In one embodiment, the ozone treated carbon nanotube aggregates of the preferred embodiment exhibit a 5 to 20% weight gain, more preferably a 10 to 15% weight gain.

[0084] Moreover, it has also been unexpectedly found that the ozone treatment in accordance with the preferred embodiment yields aggregates of carbon nanotubes with higher amounts of functional groups (especially acidic groups) on the nanotube surface than treatments using other oxidizing agents. Specifically, ozone treated aggregates of carbon nanotubes can reach a higher acid titer (i.e., have more acidic groups) than those treated with other oxidizing agents such as nitric acid and hydrogen peroxide. Ozone treated aggregates of carbon nanotubes can reach an acid titer between 1 meq/g to 2 meq/g.

[0085] Even more surprising is the discovery that the ozone treated aggregates of carbon nanotubes substantially retain the structure of the original untreated aggregates while reaching acid titers between 1 meq/g to 2 meq/g. This substantial retention of structure again confirms the non-destructive effect of ozone when used in...
accordance with the preferred embodiment. Aggregates of carbon nanotubes which have been subjected to treatment with other oxidizing agents such as nitric acid are unable to reach such a high acid titer since those oxidizing agents will engage in uncapping, stripping and shortening reactions on the carbon nanotubes and thereby cause the aggregate structure to unravel and come apart.

[0086] Experiments further confirm that the use of ozone to treat aggregates of carbon nanotubes at the recited temperature range results in a more efficient generation (higher percentage) of surface acidic groups compared to carbon nanotubes which have been oxidized with nitric acid or hydrogen peroxide. Ozone treated aggregates of carbon nanotubes have higher oxygen content than those oxidized with nitric acid or hydrogen peroxide. The surface of the ozone treated aggregates of carbon nanotubes can have a oxygen content greater than 4 percent (e.g., 4-10%), preferably greater than 6 percent (e.g., 6-10%). Experiments also showed that preferred functional groups resulting from the ozone treatment were carboxyl, anhydride and ketone.

Methods Of Treating Other Carbon Nanotube Structures With Ozone

[0087] Consistent with the previous section entitled “Methods Of Treating Aggregates Of Carbon Nanotubes With Ozone,” other improved carbon nanotube structures may be formed from the ozone treated carbon nanotubes. Alternatively, the untreated carbon nanotube structure may be subjected to ozone treatment in accordance with the preferred embodiment. Ozone treatment may be performed in gaseous or liquid phase.

[0088] Ozone treated carbon nanotubes can also be used to functionalize high quality extrudates which can be formed by using a small amount of water soluble binder. In the preparation of extrudates, the functionalized surface of the nanotubes allows for improved binder dispersion during the mixing stage and minimizes the segregation of binder in the subsequent heating step.

[0089] Methods for producing a network of carbon nanotubes comprising treating carbon nanotubes with ozone for a period of time sufficient to functionalize the surface of the carbon nanotubes, contacting the ozone treated carbon nanotubes with a reactant suitable for adding a secondary functional group to the surface of the carbon nanotube, and further contacting the secondarily treated nanotubes with a cross-linking agent effective for producing a network of carbon nanotubes. A
preferred cross-linking agent is a polyl, polyamine or polycarboxylic acid. A useful polyl is a diol and a useful polyamine is a diamine.

[0090] In one aspect of the invention a network of carbon nanotubes is obtained by first oxidizing the as-produced carbon nanotubes with ozone (alternatively, liquid phase ozone may be used), followed by subjecting the ozone treated nanotubes to conditions which foster crosslinking. For example, heating the ozone treated nanotubes in a temperature range from 180°C to 650°C results in crosslinking the ozone treated nanotubes together with elimination of the oxygen containing moieties of the ozone treated nanotubes.

[0091] The invention also includes three-dimensional networks formed by linking the ozone treated nanotubes of the preferred embodiment. These complexes include at least two surface-modified nanotubes linked by one or more linkers comprising a direct bond or chemical moiety. These networks comprise porous media of remarkably uniform equivalent pore size. They are useful as adsorbents, catalyst supports and separation media.

[0092] Stable, porous 3-dimensional networks or structures with meso- and macropores (pores >2 nm) are very useful as catalysts or chromatography supports. Since nanotubes can be dispersed on an individualized basis, a well-dispersed sample which is stabilized by cross-links allows one to construct such a support. Ozone treated nanotubes are ideal for this application since they are easily dispersed in aqueous or polar media and the oxygen-containing moieties present on the oxidized nanotubes provide cross-link points. Additionally, the oxygen containing moieties also provide points to support the catalytic or chromatographic sites. The end result is a rigid, 3-dimensional structure with its total surface area accessible with secondary group sites on which to support the active agent.

[0093] Although the interstices between these nanotubes are irregular in both size and shape, they can be thought of as pores and characterized by the methods used to characterize porous media. The size of the interstices in such networks can be controlled by the concentration and level of dispersion of nanotubes, and the concentration and chain lengths of the cross-linking agents. Such materials can act as structured catalyst supports and may be tailored to exclude or include molecules of a certain size. Aside from conventional industrial catalysis, they have special applications as large pore supports for biocatalysts.
[0094] Typical applications for these supports in catalysis include their use as a highly porous support for metal catalysts laid down by impregnation, e.g., precious metal hydrogenation catalysts. Moreover, the ability to anchor molecular catalysts by tether to the support via the secondary groups combined with the very high porosity of the structure allows one to carry out homogeneous reactions in a heterogeneous manner. The tethered molecular catalyst is essentially dangling in a continuous liquid phase, similar to a homogeneous reactor, in which it can make use of the advantages in selectivities and rates that go along with homogeneous reactions. However, being tethered to the solid support allows easy separation and recovery of the active, and in many cases, very expensive catalyst.

[0095] These stable, rigid structures also permits carrying out heretofore very difficult reactions, such as asymmetric syntheses or affinity chromatography by attaching a suitable enantiomeric catalyst or selective substrate to the support. The rigid networks can also serve as the backbone in biomimetic systems for molecular recognition. Such systems have been described in US Patent No. 5,110,833 and International Patent Publication No. WO93/19844. The appropriate choices for cross-linkers and complexing agents allow for stabilization of specific molecular frameworks.

Methods of Preparing Ozone Treated Rigid Porous Structures

[0096] Rigid porous structures are prepared by first preparing ozone treated nanotubes as described above, dispersing them in a medium to form a suspension, separating the medium from the suspension to form a porous structure, wherein the ozone treated nanotubes are further interconnected to form a rigid porous structure, all in accordance with methods more particularly described in U.S. Patent No. 6,099,965 entitled “Rigid Porous Carbon Structures, Methods of Making, Methods of Using and Products Containing Same” filed on May 15, 1997, hereby incorporated by reference.

[0097] The hard, high porosity structures can be formed from carbon nanotubes or nanotube aggregates. In order to increase the stability of the nanotube structures, it is also possible to deposit polymer at the intersections of the structure. This may be achieved by infiltrating the assemblage with a dilute solution of low molecular weight polymer cement (i.e., less than about 1,000 MW) and allowing the solvent to evaporate. Capillary forces will concentrate the polymer at nanotube intersections. It is understood that in order to substantially improve the stiffness and
integrity of the structure, only a small fraction of the nanotube intersections need be cemented.

[0098] The nanotubes may be uniformly and evenly distributed throughout the structure or in the form of aggregate particles interconnected to form the structure.

5 When the former is desired, the nanotubes are dispersed thoroughly in the medium to form a dispersion of individual nanotubes. When the latter is desired, nanotube aggregates are dispersed in the medium to form a slurry and said aggregate particles are connected together with a gluing agent to form said structure.

[0099] The medium used may be selected from the group consisting of water and organic solvents. Preferably, the medium comprises a dispersant selected from the group consisting of alcohols, glycerin, surfactants, polyethylene glycol, polyethylene imines and polypropylene glycol.

[00100] The medium should be selected which: (1) allows for fine dispersion of the gluing agent in the aggregates; and (2) also acts as a templating agent to keep the internal structure of the aggregates from collapsing as the mix dries down.

[00101] One preferred embodiment employs a combination of polyethylene glycol (PEG) and glycerol dissolved in water or alcohol as the dispersing medium, and a carbonizable material such as low MW phenol-formaldehyde resins or other carbonizable polymers or carbohydrates (starch or sugar). Once the rigid porous structure has been prepared, it can then be treated with ozone in accordance with the preferred embodiment in preparation for use in electrochemical capacitors, for example.

[00102] In other words, a preferred embodiment includes a method for forming a catalyst support comprising the steps of: forming a rigid porous structure comprising carbon nanotubes, and contacting said rigid porous structure with ozone at a temperature range between 0°C to 100°C under conditions sufficient to form a functionalized rigid porous structure which is greater in weight than said rigid porous structure.

[00103] In another embodiment, if ozone treated carbon nanotubes or aggregates are employed to form the rigid porous structure, the nanotubes are treated with ozone in accordance with the preferred embodiment prior to dispersing in the medium and are self-adhering forming the rigid structure by binding at the nanotube intersections. The structure may be subsequently pyrolyzed to remove oxygen. A
useful pyrolysis temperature range is from about 200°C to about 2000°C and preferably from about 200°C to about 900°C.

[00104] According to another embodiment, the nanotubes are dispersed in said suspension with gluing agents and the gluing agents bond said nanotubes to form said rigid structure. Preferably, the gluing agent comprises carbon, even more preferably the gluing agent is selected from a material that, when pyrolized, leaves only carbon. Accordingly, the structure formed with such a gluing may be subsequently pyrolized to convert the gluing agent to carbon. Additional methods and details for forming rigid porous structures are found in U.S. Patent No. 6,099,965, hereby incorporated by reference.

[00105] Preferably, the gluing agents are selected from the group consisting of acrylic polymers, carboxylic polymers, cellulose, carbohydrates, polyethylene, polystyrene, nylon, polyurethane, polyester, polyamides, polyvinyl acetate/alcohol emulsions or resins, amino resins, epoxy resins and phenolic resins.

[00106] According to further embodiments of the invention, the step of separating comprises filtering the suspension or evaporating the medium from said suspension.

[00107] According to yet another embodiment, the suspension is a gel or paste comprising the nanotubes in a fluid and the separating comprises the steps of:

(a) heating the gel or paste in a pressure vessel to a temperature above the critical temperature of the fluid;

(b) removing supercritical fluid from the pressure vessel;

and

(c) removing the structure from the pressure vessel.

[00108] Isotropic slurry dispersions of nanotube aggregates in solvent/dispersant mixtures containing gluing agent can be accomplished using a Waring blender or a kneader without disrupting the aggregates. The nanotube aggregates trap the resin particles and keep them distributed.

[00109] These mixtures can be used as is, or can be filtered to remove sufficient solvent to obtain cakes with high nanotube contents (5-20 % dry weight basis). The cake can be molded, extruded or pelletized. The molded shapes are sufficiently stable so that further drying occurs without collapse of the form. On
removing solvent, disperant molecules, along with particles of gluing agent are concentrated and will collect at nanotube crossing points both within the nanotube aggregates, and at the outer edges of the aggregates. As the mixture is further dried down and eventually carbonized, nanotube strands within the aggregates and the aggregates themselves are glued together at contact points. Since the aggregate structures do not collapse, a relatively hard, very porous, low density particle is formed. The resulting rigid porous structure can then be subjected to ozone treatment under the same manner and conditions described in the “Method Of Treating Carbon Nanotubes With Ozone.”

[00110] As set forth above, the rigid, porous structures may also be formed using ozone treated nanotubes with or without a gluing agent. Carbon nanotubes become self-adhering after being oxidized by ozone. Very hard, dense mats are foamed by highly dispersing the oxidized nanotubes (as individualized strands), filtering and drying. The dried mats have densities between 1-1.2 g/cc, depending on oxygen content, and are hard enough to be ground and sized by sieving. Measured surface areas are about 275 m²/g.

[00111] The ozone treated nanotubes may also be used in conjunction with a gluing agent. Ozone treated nanotubes are good starting materials since they have attachment points to stick both gluing agents and templating agents. The latter serve to retain the internal structure of the particles or mats as they dry, thus preserving the high porosity and low density of the original nanotube aggregates. Good dispersions are obtained by slurrying ozone treated nanotubes with materials such as polyethyleneimine cellulose (PEI Cell), where the basic imine functions form strong electrostatic interactions with carboxylic acid functionalized fibrils. The mix is filtered to form mats. Pyroizing the mats at temperatures greater than 650°C in an inert atmosphere converts the PEI Cell to carbon which acts to fuse the nanotube aggregates together into hard structures. The result is a rigid, substantially pure carbon structure, which can then be further treated again with ozone if desired.

[00112] Solid ingredients can also be incorporated within the structure by mixing the additives with the nanotube dispersion prior to formation of the structure. The content of other solids in the dry structure may be made as high as fifty parts solids per part of nanotubes.

[00113] According to one preferred embodiment, nanotubes are dispersed at high shear in a highshear mixer, e.g., a Waring Blender. The dispersion may contain
broadly from 0.01 to 10% nanotubes in water, ethanol, mineral spirits, etc. This procedure adequately opens nanotube bundles, i.e. tightly wound bundles of nanotubes, and disperses the nanotubes to form self-supporting mats after filtration and drying. The application of high shear mixing may take up to several hours. Mats prepared by this method, however, are not free of aggregates.

If the high shear procedure is followed by ultrasonication, dispersion is improved. Dilution to 0.1% or less aids ultrasonication. Thus, 200 cc of 0.1% fibrils, for example, may be sonified by a Bronson Sonifier Probe (450 watt power supply) for 5 minutes or more to further improve the dispersion.

To achieve the highest degrees of dispersion, i.e., a dispersion which is free or virtually free of nanotube aggregates, sonication must take place either at very low concentration in a compatible liquid, e.g., at 0.001% to 0.01% concentration in ethanol or at higher concentration e.g., 0.1% in water to which a surfactant, e.g., Triton X-100, has been added in a concentration of about 0.5%. The mat which is subsequently formed may be rinsed free or substantially free of surfactant by sequential additions of water followed by vacuum filtration. The mat thus formed can then be treated with ozone in accordance with the preferred embodiment.

Particulate solids such as MnO₂ (for batteries) and Al₂O₃ (for high temperature gaskets) may be added to the ozone treated nanotube dispersion prior to mat formation at up to 50 parts added solids per part of nanotubes.

Reinforcing webs and scrims may be incorporated on or in the mats during formation. Examples are polypropylene mesh and expanded nickel screen.

Catalyst Supports

Carbon nanotube structures such as carbon nanotube aggregates, three dimensional networks or rigid porous structures can be used as catalyst supports, including but not limited to catalyst supports for catalysts which catalyze the formation of carbon nanotubes. Of these choices, rigid porous structures offer the preferred combination of size, strength and surface area as catalyst supports.

Thus, the preferred embodiments include forming catalyst supports by functionalizing carbon nanotube structures such as aggregates, rigid porous structures or three dimensional networks via treatment with ozone. Aggregates may be prepared by any methods discussed previously, including those disclosed in U.S. Patent No. 5,165,909 to Tennent; U.S. Patent No. 5,456,897 to Moy et al.; Snyder et al., U.S.
Rigid porous structures may be made using any methods discussed previously, including those disclosed in U.S. Patent No. 6,432,866 to Tennent et al., hereby incorporated by reference. In summary, rigid porous structures such as those described above or in U.S. Patent No. 6,432,866, are typically prepared by oxidizing the nanotubes and then heating them to cause cross-linking between the nanotubes or are prepared by mixing nanotubes with a gluing agent and heating to carbonize the gluing agent. Three dimensional networks may be made using any methods disclosed in U.S. Patent No. 5,968,650 to Tennent et al., hereby incorporated by reference.

One important aspect of a catalyst support is that the support must be able to hold onto the catalyst during the course of the catalytic reaction, whether via chemical bonding, adhesion, or any other forces which permit the catalyst to remain on the support itself. To promote stable and sufficient bonding between the catalyst and the support, it is preferred that the support itself contain a number of functional groups on its surface which the catalyst will bind to or react with so as to establish the desired bonding between the catalyst and the support.

Another important aspect of a catalyst support is that the support be able to maintain its structure during the course of a reaction instead of deteriorating or breaking apart.

In the preferred embodiment, catalyst supports are created by treating or contacting the carbon nanotube structure such as carbon nanotube aggregates, three dimensional networks or rigid porous structures with ozone at a temperature range between 0°C to 100°C, preferably between 0°C to 60°C, most preferably between 20°C to 50°C or at about room temperature. Ozone is especially preferred since it has been discovered to add functional groups onto the carbon nanotube structures without weakening or destroying the crosslinking, glue or other forces or bonds which hold those structures together (i.e., no observable change in structure).
[00124] Other strong oxidizing agents such as nitric acid can also be used to add functional groups onto the surface of these structures, however, it has been discovered that nitric acid is more likely to hydrolyze crosslinked bonds or dissolve the glue bonds or diminish other bonds so as to either weaken the integrity of the original support structure. Conversely, weak oxidizing agents such as hydrogen peroxide, while they may not weaken the integrity of the support structure, do not result in enough functional groups being added to the support surface (i.e., low acid titers) to be of commercially practical use.

[00125] Thus, to obtain catalyst support structures with sufficient structural integrity and sufficient functional groups, it is preferred to prepare catalyst support structures by contacting the carbon nanotube structures such as carbon nanotube aggregates, three dimensional networks or rigid porous structures with ozone as the preferred oxidizing agent, since that will result in catalyst supports with higher concentration functional groups (i.e., higher acid titers, and thus better retention of the catalyst) and stronger structural integrity as compared to treating those structures with other oxidizing agents.

[00126] Preferred catalyst supports comprise ozone treated carbon nanotube structures which exhibit upon titration an acid titer greater than 1 meq/g such as from 1 to 2 meq/g. These ozone treated carbon nanotube structures further exhibit no observable change in structure in comparison to the original untreated carbon nanotube structures. The ozone treated carbon nanotube structure can also exhibit a weight gain of greater than 1%, preferably 5 to 20% weight gain, more preferably a 10 to 15% weight gain. Other acid titer, oxygen contents, and weight gain characteristics as described earlier apply to the functionalized structures used as catalyst supports as well.

**Electrochemical Capacitors**

[00127] Carbon nanotubes are electrically conductive. Electrodes and their use in electrochemical capacitors comprising carbon nanotubes and/or functionalized carbon nanotubes have been described in U.S. Patent No. 6,031,711 entitled “Graphitic Nanofibers in Electrochemical Capacitors,” filed on May 15, 1997 and is incorporated herein by reference.

[00128] Further details about electrochemical capacitors based on catalytically grown carbon nanotubes are disclosed in Chumming Niu et al., “High Power

[00129] The quality of sheet electrode depends on the microstructure of the electrode, the density of the electrode, the functionality of the electrode surface and mechanical integrity of the electrode structure.

[00130] The microstructures of the electrode, namely, pore size and size distribution determines the ionic resistance of electrolyte in the electrode. The surface area residing in micropores (pore diameter < 2 nm) is considered inaccessible for the formation of a double layer (2). On the other hand, distributed pore sizes, multiple-pore geometries (dead end pores, slit pores, cylindrical pores, etc.) and surface properties usually give rise to a distributed time constant. The energy stored in an electrode with a distributed time constant can be accessed only with different rates. The rapid discharge needed for pulsed power is not feasible with such an electrode.

[00131] The density of the electrode determines its volumetric capacitance. An electrode with density less than 0.4 g/cc is not practical for real devices. Simply, the low-density electrode will take up too much electrolyte, which will decrease both volumetric and gravimetric capacitance of the device.

[00132] The surface of the carbon nanotubes is related to the wetting properties of electrodes towards electrolytes. The surface of as-produced, catalytically grown carbon nanotubes is hydrophobic. The hydrophobic surface properties of the as produced carbon nanotubes can be changed to hydrophilic by treatment of the as produced carbon nanotubes or aggregates of carbon nanotubes with ozone in accordance with the preferred embodiment. Furthermore, the capacitance can be increased by further attaching redox groups on the surface of the carbon nanotubes.

[00133] Finally, the structural integrity of the electrodes is critical to reproducibility and long term stability of the device. Mechanical strength of electrodes incorporating carbon nanotubes is determined by the degree of entanglement of the carbon nanotube and bonding between carbon nanotubes in the electrode. A high degree of entanglement and carbon nanotube bonding can also improve the conductivity, which is critical to the power performance of an electrode. The specific capacitance (D.C. capacitance) of the electrodes made from gas-phase treated fibrils was about 40 F/g.
[00134] One aspect of the present invention relates to preparing electrodes and electrochemical capacitors from ozone treated carbon nanotubes. Broadly, as prepared carbon nanotubes have been treated with ozone in accordance with the preferred embodiment to provide surface oxidized, single walled or multiwalled carbon nanotubes which can be used to prepare the electrodes of the invention.

[00135] In another aspect of the invention, the ozone treated nanotubes can be further treated with a reactant suitable to react with moieties present on the oxidized nanotubes to form nanotubes having secondary groups on its surface which are also useful in preparing the electrodes of the present invention.

[00136] Electrodes are assembled by simple filtration of slurries of the ozone treated nanotubes. Thickness is controlled by the quantity of material used and the geometry, assuming the density has been anticipated based on experience. It may be necessary to adjust thickness to get selfsupporting felts.

[00137] The electrodes are advantageously characterized by cyclic voltammetry, conductivity and DC capacitance measurement.

EXAMPLES

[00138] The following examples serve to provide further appreciation of the invention but are not meant in any way to restrict the effective scope of the invention.

Method Of Measuring Titer

[00139] As an initial matter, measuring an acid titer can be effected in a number of ways. In one embodiment, 0.10 g of fibrils are transferred to a Waring Laboratory Blender containing 350-400 CC of D.I. water. The fibrils are blended at slow speed for 10-15 minutes until all fibrils in the water phase appeared to be homogenously black. 10 CC of standard 0.10 N sodium hydroxide solution is added to the blender containing fine fibrils slurry and again blended for 4-5 minutes. The slurry is then transferred to a beaker containing a stirring rod and a pH electrode. A solution of hydrochloric acid of known strength is then added gradually to neutralize the fibrils slurry at pH 7.0. The volume of hydrochloric acid used to neutralize fibrils slurry is noted and used in calculation of meq/g of fibrils. The results of titer measurement may be expressed in either milliequivalence per nanotube weight (i.e., meq/g) or milliequivalence per nanotube surface area (i.e., meq/m²).
Example 1

[00140] Ozone was generated via an air purifier made by Del Industry, San Luis Obispo, CA, which can generate ozone at a rate of 250 mg/hr. A mixture of ozone and air (0.29% ozone) at a flow rate of 1200 mL/min was then passed through a 1-inch (OD) reactor tube packed with dry as-made fibrils. The weight of fibrils before and after ozone treatment were recorded. The reaction was allowed to proceed for a period of 3 to 45 hours at room temperature.

[00141] In a separate experiment, 20 grams of as-made fibrils were placed in a flask containing 500 mL 30% or 60% nitric acid. The reaction flask was then heated to reflux temperature of 95-120°C for 4-6 hours. After the reaction was stopped, the fibrils were cooled to room temperature, filtered, and washed with water until neutral. In another separate experiment, 20 grams of as-made fibrils were placed in a flask containing 376.2 grams of 30% H₂O₂ in molar ratio of 1:2. The temperature was set to be in the vicinity of 35°C, but it rose to reflux temperature quickly. A water bath was applied to maintain the reaction temperature at 30°C. After 2-hour reaction, the slurry was filtered and washed until all the residual H₂O₂ was removed.

[00142] The results are reported below:

Table 2  Weight changes during fibril oxidation

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Oxidant</th>
<th>Weight (g)</th>
<th>Run Time (hr)</th>
<th>Weight Change (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>O₃/air</td>
<td>3</td>
<td>20</td>
<td>+13.9</td>
</tr>
<tr>
<td>2</td>
<td>O₃/air</td>
<td>3</td>
<td>20</td>
<td>+8.0</td>
</tr>
<tr>
<td>3</td>
<td>O₃/air</td>
<td>10</td>
<td>45</td>
<td>+10.4</td>
</tr>
<tr>
<td>4</td>
<td>O₃/air</td>
<td>9</td>
<td>45</td>
<td>+10.2</td>
</tr>
<tr>
<td>5</td>
<td>O₃/air</td>
<td>3</td>
<td>25</td>
<td>+12.1</td>
</tr>
<tr>
<td>6</td>
<td>30% HNO₃</td>
<td>20</td>
<td>6</td>
<td>-6.4</td>
</tr>
<tr>
<td>7</td>
<td>60% HNO₃</td>
<td>20</td>
<td>4</td>
<td>-15.3</td>
</tr>
<tr>
<td>8</td>
<td>30% H₂O₂</td>
<td>20</td>
<td>2</td>
<td>-1.7</td>
</tr>
</tbody>
</table>

[00143] Experimental data confirmed that oxidation of carbon nanotubes using ozone at room temperature as compared to other oxidizing agents such as nitric acid or hydrogen peroxide resulted in a surprising difference in weight of the final product. Namely, carbon nanotubes subjected to ozone treatment at room temperature posted a
significant weight gain instead of weight loss as compared to carbon nanotubes which have been subjected to other oxidation treatment. This is surprising given that ozone is a strong oxidant.

[00144] With respect to using nitric acid as the oxidizing agent, the nitric acid strength and reaction condition affected the degree of weight loss. The weight loss is attributed to the oxidation of carbon to form CO or CO₂, which evolve from the reactor system.

**Example 2**

[00145] 3 grams of dry fibrils was placed in a vertical reactor and ozone-containing air was passed through them at room temperature. The reactor was shut off periodically at every hour and the total weight of fibrils plus the reactor tube were measured on an electric balance. The weight gain of fibrils against reaction time was then obtained after tarring off the reactor weight.

[00146] The results of this measurement are displayed in Figure 7, which shows that the sample’s weight increased over the course of reaction and leveled off after approximately 15 hours of reaction time.

**Example 3**

[00147] Various oxidized fibrils prepared according to the methods in Example 1 such as Samples 1-3 and 5-7 were measured to determine their relative amount of acidic groups through titration. 0.25 gram of each sample was placed into a flask containing 300 mL D.I. water and the slurry was titrated with 0.1N NaOH. The consumption of NaOH was translated into the quantity of total surface acidic groups as meq/g.

**Table 3 Measurement of surface acidic groups through titration.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sample weight (g)</th>
<th>Oxidant</th>
<th>Weight change (%)</th>
<th>Titer (meq/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3</td>
<td>O₃/air</td>
<td>13.95</td>
<td>1.45</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>O₃/air</td>
<td>8.0</td>
<td>1.07</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>O₃/air</td>
<td>10.40</td>
<td>1.57</td>
</tr>
<tr>
<td>5</td>
<td>3</td>
<td>O₃/air</td>
<td>12.12</td>
<td>1.16</td>
</tr>
<tr>
<td>8</td>
<td>20</td>
<td>60% HNO₃</td>
<td>-15.28</td>
<td>1.20</td>
</tr>
<tr>
<td>Sample</td>
<td>As-made (surface area)</td>
<td>Ozone treated (surface area)</td>
<td>60% Nitric acid treated (surface area)</td>
<td>Titer (meq/m²) surface area</td>
</tr>
<tr>
<td>--------</td>
<td>------------------------</td>
<td>-----------------------------</td>
<td>----------------------------------------</td>
<td>-----------------------------</td>
</tr>
<tr>
<td>9</td>
<td>240 m²/g</td>
<td>247 m²/g</td>
<td></td>
<td>0.0055</td>
</tr>
<tr>
<td>10</td>
<td>240 m²/g</td>
<td>323 m²/g</td>
<td></td>
<td>0.0029</td>
</tr>
<tr>
<td>11</td>
<td>240 m²/g</td>
<td>404 m²/g</td>
<td></td>
<td>0.0028</td>
</tr>
</tbody>
</table>

As shown in Table 3, more acidic groups can be deposited onto the surface of carbon nanotubes when oxidized with ozone at room temperature than with other oxidizing agents such as nitric acid or hydrogen peroxide. In other words, treatment of carbon nanotubes with ozone at room temperature will yield nanotubes with a higher titer (i.e., an indicator of acidic groups) than nanotubes resulting from treatment with other oxidizing agents.

Additionally, even though carbon nanotubes treated with nitric acid was able to reach a titer within the range of the lowest titer yielded by ozone treatment, such nitric acid treated nanotubes may be unsuitable for certain applications due to the significant weight loss that accompany such titer range.

Table 3 further confirms that ozone treatment at room temperature yields carbon nanotubes which are significantly more acidic than those by weak acids such as hydrogen peroxide or diluted nitric acid.

Example 4

To compare the degree of damage done to the carbon nanotube surface by the oxidation treatments, the surface area of the treated fibrils was measured using an Autosorb-1 instrument. For the room temperature ozone oxidized fibrils, the average BET surface area at −196°C were all in the range of 240-250 m²/g, which is very close to as-made untreated fibrils. On the other hand, the average BET surface area (measured at 196°C) of oxidized fibrils treated with nitric acid increased from 250 m²/g to 341 m²/g.
Such increase in surface area is believed to be caused by the stripping of layers or uncapping of nanotubes. Therefore, minimal or no measurable damage was generated on the surface of carbon nanotubes during ozone treatment at room temperature.

**Example 5**

XPS (X-ray Photoelectron Spectroscopy) was applied to characterize the fibril surface of fibril aggregates treated using nitric acid, hydrogen peroxide, gaseous ozone, (all as described earlier) and liquid ozone (as described later) as compared to plain untreated fibril aggregates.

Three sets of characteristics were measured: the atomic concentration of surface oxygen; carbon functionality and oxygen functionality.

**Table 4** A and B Surface composition and carbon functionality of different fibrils

(Table 4A)

<table>
<thead>
<tr>
<th>Fibril Sample</th>
<th>C (%)</th>
<th>O (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plain CC</td>
<td>98.0</td>
<td>2.0</td>
</tr>
<tr>
<td>Nitric acid CC</td>
<td>96.4</td>
<td>3.6</td>
</tr>
<tr>
<td>H₂O₂ CC</td>
<td>96.3</td>
<td>3.7</td>
</tr>
<tr>
<td>O₃ (gas phase) CC</td>
<td>93.1</td>
<td>6.9</td>
</tr>
<tr>
<td>O₃ (liquid phase) CC</td>
<td>95.8</td>
<td>4.2</td>
</tr>
</tbody>
</table>

(Table 4B)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Graphitic C (%)</th>
<th>-C-OH (%)</th>
<th>-C=O (%)</th>
<th>-CO₂H (%)</th>
<th>-CO₃ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plain CC</td>
<td>80.0</td>
<td>11.4</td>
<td>3.4</td>
<td>2.3</td>
<td>2.9</td>
</tr>
<tr>
<td>Nitric Acid CC</td>
<td>73.2</td>
<td>12.7</td>
<td>6.0</td>
<td>3.4</td>
<td>4.6</td>
</tr>
<tr>
<td>H₂O₂ CC</td>
<td>77.6</td>
<td>12.4</td>
<td>3.4</td>
<td>3.0</td>
<td>3.6</td>
</tr>
<tr>
<td>O₃ (gas) CC</td>
<td>71.8</td>
<td>14.3</td>
<td>6.3</td>
<td>4.0</td>
<td>3.6</td>
</tr>
<tr>
<td>O₃ (liquid) CC</td>
<td>74.7</td>
<td>12.2</td>
<td>5.5</td>
<td>3.1</td>
<td>4.4</td>
</tr>
</tbody>
</table>

As expected, plain fibril had the least amount of oxygen on the surface, which is generally created upon exposure to air after production. Table 4A further confirms that oxidation yields more oxygenated groups onto the fibril surface as the
oxygen content was increased for all fibrils treated with oxidizing agents. Table 4A and 4B both confirm that the highest oxygen content was exhibited in gaseous ozone treated carbon nanotubes at room temperature.

Table 4B further displays the breakdown of those oxygenated contents on the fibril surfaces and confirms that different oxidizing agents yield different quantities of different functional groups. For example, carbon nanotubes treated with H$_2$O$_2$ treatment created more –OH groups while nitric acid generated more –COOH as a percentage increase of the total functional groups generated. The fibrils treated with gaseous ozone at room temperature yielded the greatest -COOH increase.

Further analysis on the oxygen content so as to determine more information on the surface functional groups of the fibrils are shown in Table 4C and Figure 8. Figure 8 showed the oxygen spectra at the 1s region. The raw data are represented by the plotted dots while the fitted data and deconvoluted signals are represented by the solid lines. The peaks at 531 eV, 533 eV and 535 eV are assigned to the C-O, C=O and H$_2$O configuration. The data in Figure 8 was summed up in Table 4C below:

<table>
<thead>
<tr>
<th>Sample</th>
<th>O-(C) (%)</th>
<th>O=(C) (%)</th>
<th>H$_2$O (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plain CC</td>
<td>77.2</td>
<td>16.8</td>
<td>6.0</td>
</tr>
<tr>
<td>CC-H$_2$O$_2$</td>
<td>66.5</td>
<td>25.0</td>
<td>8.6</td>
</tr>
<tr>
<td>CC-nitric acid</td>
<td>38.5</td>
<td>51.3</td>
<td>10.2</td>
</tr>
<tr>
<td>CC-O$_3$ (Gas phase)</td>
<td>37.3</td>
<td>59.1</td>
<td>3.6</td>
</tr>
</tbody>
</table>

As shown in Table 4C, the oxygen groups of plain fibril generally are in a single bond “O-” conformation. Fibrils subjected to H$_2$O$_2$ oxidization yielded more oxygen groups in the form of –OH and C=O. However, since the single bond -O conformation still dominated, this may explain the lower titer results of nanotubes treated with hydrogen peroxide.

On the other hand, nitric acid or ozone oxidation yielded carbon nanotubes in which the surface oxygen group was switched from being predominately single bond –O conformation to predominately double bond =O conformation. Furthermore, fibrils subjected to gas phase ozone treatment resulted in less moisture content as well.
Example 6

[00160] Ozone treated fibrils at room temperature were examined using SEM. Analysis of the fibril aggregate structure under the scanning electron microscope as shown in Figure 9 confirmed that the fibril aggregates structure remained intact after the ozone treatment at room temperature.

Example 7

[00161] Differences between untreated fibril aggregates, fibril aggregates oxidized with nitric acid and fibril aggregates oxidized with ozone were demonstrated by the following test. Three sets of fibril aggregates were prepared in the same manner. The first fibril aggregates were left untreated after preparation. The second fibril aggregates were subsequently treated with nitric acid at room temperature. The third fibril aggregates were subsequently treated with ozone at room temperature. The three sets of fibril aggregates were dispersed in water and the following differences were observed:

<table>
<thead>
<tr>
<th>Fibril Aggregate</th>
<th>Hydrophobic vs. Hydrophilic</th>
<th>Wetting Characteristic</th>
<th>Structural Retention</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>hydrophobic</td>
<td>non-wetting</td>
<td>retains structure</td>
</tr>
<tr>
<td>Oxidized with Nitric Acid</td>
<td>hydrophillic</td>
<td>wetting</td>
<td>breaks apart</td>
</tr>
<tr>
<td>Oxidized with Ozone</td>
<td>hydrophillic</td>
<td>wetting</td>
<td>retains structure</td>
</tr>
</tbody>
</table>

Thus, fibril aggregates treated with ozone have different characteristics from untreated fibril aggregates (i.e., hydrophobic and non wetting v. hydrophillic and wetting) as well as from fibril aggregates treated with strong oxidants such as nitric acid (i.e., retains structure v. breaks apart).

Example 8

[00162] The following experiments were performed using the procedure described in Example 1, except a heating device such as heating tape was applied to the 1-inch reactor tube. Ozone treatment of dry fibril aggregates was carried out at room and slightly elevated temperatures. The following data was obtained.
<table>
<thead>
<tr>
<th>Sample weight (g)</th>
<th>Temperature (°C)</th>
<th>Reaction time (h)</th>
<th>Weight change (%)</th>
<th>Titer (meq/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>25</td>
<td>1</td>
<td>0.52</td>
<td>0.3</td>
</tr>
<tr>
<td>1</td>
<td>50</td>
<td>1</td>
<td>1.38</td>
<td>0.5</td>
</tr>
<tr>
<td>1</td>
<td>50</td>
<td>3</td>
<td>2.55</td>
<td>0.9</td>
</tr>
<tr>
<td>1</td>
<td>100</td>
<td>1</td>
<td>0</td>
<td>0.1</td>
</tr>
<tr>
<td>1</td>
<td>100</td>
<td>8</td>
<td>-4.9</td>
<td>0.2</td>
</tr>
</tbody>
</table>

[00163] These experiments confirm that conditions such as temperature and reaction time can affect the resulting ozone treatment on the carbon nanotubes. Reactions carried out at temperatures between 0°C to 100°C result in the efficient generation of abundant surface functional groups without the resultant destruction of fibril aggregate mass. Experiments carried out at 100°C or greater for extended periods of time can lead to more substantial reactions between ozone with carbon to form CO and CO₂ resulting in loss of fibril aggregate mass.

**Example 9**

[00164] 1 gram of nitric acid treated fibrils exhibiting a titer of 0.93 meq/g was subject to ozone treatment at room temperature for a period of five hours. The treatment followed the same procedure as described in Example 1. The resulting materials exhibited a weight gain of 10.6% and its titer was improved to 1.84 meq/g. This titer level is unexpected and surprising since it could not be achieved with the nitric acid oxidation without substantially damaging and disassembling the carbon nanotube structures.

**Example 10**

[00165] An impure mixture of single wall carbon nanotubes and amorphous carbon was subjected to selective oxidation treatment with nitric acid to reduce soot and amorphous carbon. The resulting oxidized mixture as analyzed by electron micrograph was approximately 20-50% impure and exhibited upon titration an acid titer of 0.9 meq/g. Using the procedure described in Example 1, the oxidized mixture was subjected to ozone treatment at room temperature for approximately 5 hours. The ozone treated mixture exhibited upon titration an acid titer of 2.86 meq/g.

**Example 11**
[00166] The ozone treated fibrils were further blended with water to form a slurry with solid content of 15–25% and then subject to extrusion through a 1/8 inch die. Cylindrical extrudates of oxidized fibrils were obtained and dried at 180°C for 12 hours. The extrudates appeared to be very strong similar to those generated with nitric acid oxidized fibrils. It is believed that the abundant surface functional groups may cross-link to self-assemble a rigid porous structure. As-made fibrils cannot form this type of structures without proper binding materials.

**Example 12**

[00167] 20 grams of as-made CC nanotubes were placed in a Waring blender. 60 grams gluing agent containing 10% polymer, e.g. polyacrylic acid (MW=15000), in aqueous solution, was added into the carbon nanotubes and the mixture was blended till uniform. The resulting material was then push through a 1/8” tie via a Brabender extruder followed by drying and calcination at temperatures between 300 and 600°C in argon. The resulted extrudates were then treated with ozone for 20 hours using the procedure described in Example 1. After ozone treatment, the extrudates exhibited an acid titer of 0.79–0.93.

**Example 13**

[00168] 10 grams of as-made fibrils were placed in cyclohexane in a reaction flask. Ozone containing gas was then passed through the slurry with vigorous agitation. The reaction was allowed to proceed for 8-10 hours under ambient conditions. After reaction, fibrils was filtered, washed and dried. Suitable liquid media could, but not limited to be, water, saturated alcohol, saturated hydrocarbon or cyclic hydrocarbons, etc. The reaction can also be carried out at elevated temperatures and pressures up to supercritical conditions.

**Example 14**

[00169] 1/16 inch carbon nanotube extrudates were placed into rotating drum reactors. Ozone containing gas generated from the feed of pure oxygen gas into an ozone generator was introduced via a sparger into the rotating drum reactors at rates of 1 L/min and 2.5 L/min. Two samples were titrated from each reactor at selected times to compare the functionalization uniformity. The following results were obtained:
<table>
<thead>
<tr>
<th>Run Time (hr)</th>
<th>Ozone Flow Rate (L/min)</th>
<th>Titer – Sample 1 (meq/g)</th>
<th>Titer – Sample 2 (meq/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>1</td>
<td>0.23</td>
<td>0.19</td>
</tr>
<tr>
<td>8</td>
<td>1</td>
<td>0.29</td>
<td>0.26</td>
</tr>
<tr>
<td>24</td>
<td>1</td>
<td>0.44</td>
<td>0.49</td>
</tr>
<tr>
<td>48</td>
<td>1</td>
<td>0.69</td>
<td>0.63</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Run Time (hr)</th>
<th>Ozone Flow Rate (L/min)</th>
<th>Titer – Sample 1 (meq/g)</th>
<th>Titer – Sample 2 (meq/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>2.5</td>
<td>0.08</td>
<td>0.18</td>
</tr>
<tr>
<td>8</td>
<td>2.5</td>
<td>0.21</td>
<td>0.29</td>
</tr>
<tr>
<td>24</td>
<td>2.5</td>
<td>0.40</td>
<td>0.41</td>
</tr>
</tbody>
</table>

[00170] The terms and expressions which have been employed are used as terms of description and not of limitations, and there is no intention in the use of such terms or expressions of excluding any equivalents of the features shown and described as portions thereof, it being recognized that various modifications are possible within the scope of the invention.
We claim:

1. A method of functionalizing carbon nanotubes comprising the step of:
   contacting carbon nanotubes with ozone at a temperature range
   between 0°C to 100°C under conditions sufficient to form functionalized nanotubes
   which are greater in weight than said carbon nanotubes.

2. The method of claim 1, wherein said temperature range is between 0°C to 60°C.

3. The method of claim 1, wherein said temperature range is between 20°C to 50°C.

4. The method of claim 1, wherein said carbon nanotubes are multiwalled
   carbon nanotubes having a diameter of less than 0.1 micron.

5. The method of claim 1, wherein said carbon nanotubes are single
   walled nanotubes having a diameter less than 5 nanometer.

6. The method of claim 1, wherein the surface of said functionalized
   nanotubes have an oxygen content greater than 4 percent.

7. The method of claim 1, wherein the surface of said functionalized
   nanotubes have an oxygen content greater than 6 percent.

8. The method of claim 1, wherein said functionalized nanotubes exhibit
   upon titration an acid titer greater than 2 meq/g.

9. The method of claim 1, wherein said functionalized nanotubes exhibit
   upon titration an acid titer from 1.6 to 2.2 meq/g.

10. The method of claim 1, wherein said functionalized nanotubes exhibit
    upon titration an acid titer from 2.5 to 3.5 meq/g.

11. The method of claim 1, wherein said functionalized nanotubes exhibit
    upon titration an acid titer which is at least 1.5 meq/g greater than the acid titer of said
    carbon nanotubes.

12. The method of claim 1, wherein said functionalized nanotubes exhibit
    upon titration an acid titer which is at least 2 meq/g greater than the acid titer of said
    carbon nanotubes.

13. The method of claim 1, wherein said functionalized nanotubes exhibit
    upon titration an acid titer which is 1.5 meq/g to 3 meq/g greater than said carbon
    nanotubes.
14. The method of claim 1, wherein said functionalized carbon nanotubes exhibit a weight gain greater than 5% by comparison to said carbon nanotubes.

15. The method of claim 1, wherein said functionalized carbon nanotubes exhibit a weight gain from 5% to 20% by comparison with said carbon nanotube.

16. The method of claim 1, wherein said functionalized carbon nanotubes exhibit a weight gain from 10% to 15% by comparison with said carbon nanotube.

17. The method of claim 1, further comprising treating said functionalized carbon nanotubes with a reactant suitable to react with moieties of said functionalized carbon nanotubes thereby adding at least a secondary group onto the surface of said functionalized nanotubes.

18. The method of claim 17, wherein said additional secondary group is selected from the group consisting of an alkyl or aryl silane wherein said alkyl has C₁ to C₁₈, said aryl has C₁ to C₁₈, an alkyl of C₁ to C₁₈ or an aralkyl group of C₁ to C₁₈, a hydroxyl group of C₁ to C₁₈ and an amine group of C₁ to C₁₈.

19. The method of claim 17, wherein said additional secondary group is a fluorocarbon.

20. The method of claim 1 further comprising dispersing said functionalized carbon nanotubes into a liquid medium to form a mixture;

filtering said medium to collect a residue of functionalized carbon nanotubes; and

drying said residue to form a mat.

21. The method of claim 20, further comprising heating said mat to a temperature range of 200°C to 900°C.

22. The method of claim 20, further comprising forming said mat into an electrode.

23. The method of claim 1, wherein said carbon nanotubes are in the form of aggregates having a macromorphology resembling a shape selected from the group consisting of cotton candy, bird nests, combed yarn and open net aggregates.

24. The method of claim 23, wherein said aggregates have an average diameter of less than 50 microns.

25. A method for producing a network of carbon nanotubes comprising the steps of:
(a) contacting carbon nanotubes with ozone at a temperature range between 0°C to 100°C under conditions sufficient to form functionalized nanotubes which are greater in weight than said carbon nanotubes;

(b) subjecting said functionalized nanotubes to conditions sufficient to cause crosslinking.

26. The method of claim 25, wherein said temperature range is between 0°C to 60°C.

27. The method of claim 25, wherein said temperature range is between 20°C to 50°C.

28. The method of claim 25, wherein said conditions sufficient to cause crosslinking include heating said functionalized nanotubes in air in a temperature range from 200°C to 600°C.

29. The method of claim 25, wherein said conditions sufficient to cause crosslinking include heating said functionalized nanotubes in an inert atmosphere in a temperature range from 200°C to 2000°C.

30. A method for producing a network of functionalized carbon nanotubes comprising the steps of

(a) contacting carbon nanotubes with ozone at a temperature range between 0°C to 100°C under conditions sufficient to form functionalized nanotubes which are greater in weight than said carbon nanotubes;

(b) treating said functionalized nanotubes with a reactant suitable to react with moieties of said functionalized nanotubes thereby adding at least a secondary group onto the surface of said functionalized nanotubes;

(c) further contacting said nanotubes bearing secondary groups with an effective amount of crosslinking agent.

31. The method of claim 30, wherein said temperature range is between 0°C to 60°C.

32. The method of claim 30, wherein said temperature range is between 20°C to 50°C.

33. The method of claim 30, wherein said crosslinking agent is selected from the group consisting of a polyol or polyamine.

34. The method of claim 30, wherein said polyol is a diol and said polyamine is a diamine.
35. A method for preparing a rigid porous structure comprising the steps of:
   (a) contacting carbon nanotubes with ozone at a temperature range between 0°C to 100°C under conditions sufficient to form functionalized nanotubes which are greater in weight than said carbon nanotubes;
   (b) dispersing said functionalized nanotubes in a medium to form a suspension; and
   (c) separating said medium from said suspension to form a porous structure of entangled functionalized nanotubes wherein said nanotubes are interconnected to form a rigid porous structure.

36. The method of claim 35, wherein said temperature range is between 0°C to 60°C.

37. The method of claim 35, wherein said temperature range is between 20°C to 50°C.

38. The method of claim 35, wherein said carbon nanotubes are in the form of aggregates having a macromorphology resembling a shape selected from the group consisting of cotton candy, bird nests, combed yarn and open net aggregates.

39. The method of claim 35, further comprising heating said suspension in air to a temperature in a range from about 200°C to about 600°C thereby forming said rigid porous structure.

40. The method of claim 35, further comprising heating said suspension in an inert gas to a temperature in a range from about 200°C to about 2000°C thereby forming said rigid porous structure.

41. The method of claim 35, wherein said medium is water or organic solvents.

42. The method of claim 35, wherein said medium comprises a dispersant selected from the group consisting of alcohols, glycerin, surfactants, polyethylene glycol, polyethylene imines and polypropylene glycol.

43. The method of claim 35, wherein said suspension further comprises gluing agents selected from the group consisting of cellulose, carbohydrate, polyethylene, polystyrene, nylon, polyurethane, polyester, polyamides and phenolic resins.

44. The method of claim 35, further comprising the steps of:
(a) forming said rigid porous structure into a mat;
    and
(b) forming said mat into an electrode.

45. An electrochemical capacitor having at least one electrode comprising
    the functionalized carbon nanotubes prepared by the method of claim 1.

46. An electrochemical capacitor having at least one electrode prepared by
    a method which comprises the following steps:
    (a) contacting aggregates of carbon nanotubes with ozone at a
    temperature range between 0°C to 100°C under conditions sufficient to form
    aggregates of functionalized nanotubes which are greater in weight than said carbon
    nanotubes;
    (b) dispersing said aggregates of functionalized nanotubes prepared in
    step (a) in a liquid medium to form a slurry;
    (c) filtering and drying said slurry to form a mat of functionalized
    carbon nanotubes; and
    (d) subjecting said mat to conditions sufficient to cause the
    crosslinking of said functionalized carbon nanotubes.

47. The method of claim 46, wherein said temperature range in step (a) is
    between 0°C to 60°C.

48. The method of claim 46, wherein said temperature range in step (a) is
    between 20°C to 50°C.

49. The electrochemical capacitor of claim 46, wherein said conditions of
    step (d) include heating said mat to a temperature in the range of from 180°C to 350°C.

50. An electrochemical capacitor having at least one electrode formed by a
    method comprising the following steps:
    (a) dispersing aggregates of carbon nanotubes in a liquid medium to
    form a slurry;
    (b) filtering and drying said slurry to form a mat of carbon nanotubes;
    (c) treating said mat with ozone at a temperature range between 0°C to
    100°C under conditions sufficient to form a mat of functionalized carbon nanotubes
    which are greater in weight than said mat of carbon nanotubes.

51. Ozone treated carbon nanotubes which exhibit upon titration an acid
    titer greater than 2 meq/g.
52. Ozone treated carbon nanotubes which exhibit upon titration an acid titer between 1.6 and 2.2 meq/g.

53. Ozone treated carbon nanotubes which exhibit upon titration an acid titer between 2.5 and 3.5 meq/g.

54. An ozone treated carbon nanotube structure which exhibits upon titration an acid titer greater than 1 meq/g, said ozone treated carbon nanotube structure comprising a multiplicity of carbon nanotubes entangled with one another.

55. The ozone treated carbon nanotube structure of claim 54, wherein said structure is in the form of aggregate of carbon nanotubes having a macromorphology resembling a shape selected from the group from the group consisting of cotton candy, bird nests, combed yarn and open net aggregates.

56. The ozone treated carbon nanotube structure of claim 54 which substantially retains the original untreated carbon nanotube structure.

57. The ozone treated carbon nanotube structure of claim 54 which exhibits upon titration an acid titer between 1 and 2 meq/g.

58. A method for forming catalyst support comprising the steps of:

forming an aggregate of carbon nanotubes, and

contacting said aggregate with ozone at a temperature range between 0°C to 100°C under conditions sufficient to form a functionalized aggregate which is greater in weight than said aggregate.

59. The method of claim 58, wherein said temperature range is between 0°C to 60°C.

60. The method of claim 58, wherein said temperature range is between 20°C to 50°C.

61. The method of claim 58, wherein said carbon nanotubes are multiwalled carbon nanotubes having a diameter of less than 0.1 micron.

62. The method of claim 58, wherein said carbon nanotubes are single walled nanotubes having a diameter less than 5 nanometer.

63. The method of claim 58, wherein the surface of said functionalized aggregate have an oxygen content greater than 4 percent.

64. The method of claim 58, wherein the surface of said functionalized aggregate have an oxygen content greater than 6 percent.
65. The method of claim 58, wherein said functionalized aggregate exhibits upon titration an acid titer from 1 to 2 meq/g and retains the structure of said aggregate.

66. The method of claim 58, wherein said functionalized aggregate exhibits upon titration an acid titer from 1 to 2 meq/g.

67. The method of claim 58, wherein said functionalized aggregate exhibits a weight gain greater than 5% by comparison to said aggregate.

68. The method of claim 58, wherein said functionalized aggregate exhibits a weight gain from 5% to 20% by comparison with said aggregate.

69. The method of claim 58, wherein said functionalized aggregate exhibits a weight gain from 10% to 15% by comparison with said aggregate.

70. A catalyst support formed by the method of claim 58.

71. A catalyst support formed by the method of claim 58 wherein the functionalized aggregate exhibits upon titration an acid titer between 1 to 2 meq/g.

72. A catalyst support formed by the method of claim 58 wherein the functionalized aggregate exhibits upon titration an acid titer greater than 1 meq/g and retains the structure of said aggregate.

73. A method for forming a catalyst support comprising the steps of: forming a network of carbon nanotubes, and contacting said network with ozone at a temperature range between 0°C to 100°C under conditions sufficient to form a functionalized network which is greater in weight than said network.

74. The method of claim 73, wherein said temperature range is between 0°C to 60°C.

75. The method of claim 73, wherein said temperature range is between 20°C to 50°C.

76. The method of claim 73, wherein said carbon nanotubes are multiwalled carbon nanotubes having a diameter of less than 0.1 micron.

77. The method of claim 73, wherein said carbon nanotubes are single walled nanotubes having a diameter less than 5 nanometer.

78. The method of claim 73, wherein the surface of said functionalized network have an oxygen content greater than 4 percent.

79. The method of claim 73, wherein the surface of said functionalized network have an oxygen content greater than 6 percent.
80. The method of claim 73, wherein said functionalized network exhibits upon titration an acid titer greater than 1 meq/g and retains the structure of said network.

81. The method of claim 73, wherein said functionalized network exhibits upon titration an acid titer from 1 to 2 meq/g.

82. The method of claim 73, wherein said functionalized network exhibits a weight gain greater than 5% by comparison to said network.

83. The method of claim 73, wherein said functionalized network exhibits a weight gain from 5% to 20% by comparison with said network.

84. The method of claim 73, wherein said functionalized network exhibits a weight gain from 10% to 15% by comparison with said network.

85. A catalyst support formed by the method of claim 73.

86. A catalyst support formed by the method of claim 73 wherein the functionalized network exhibits upon titration an acid titer between 1 to 2 meq/g.

87. A catalyst support formed by the method of claim 73 wherein the functionalized network exhibits upon titration an acid titer greater than 1 meq/g and retains the structure of said network.

88. A method for forming a catalyst support comprising the steps of: forming a rigid porous structure comprising carbon nanotubes, and contacting said rigid porous structure with ozone at a temperature range between 0°C to 100°C under conditions sufficient to form a functionalized rigid porous structure which is greater in weight than said rigid porous structure.

89. The method of claim 88, wherein said temperature range is between 0°C to 60°C.

90. The method of claim 88, wherein said temperature range is between 20°C to 50°C.

91. The method of claim 88, wherein said carbon nanotubes are multiwalled carbon nanotubes having a diameter of less than 0.1 micron.

92. The method of claim 88, wherein said carbon nanotubes are single walled nanotubes having a diameter less than 5 nanometer.

93. The method of claim 88, wherein the surface of said functionalized rigid porous structure have an oxygen content greater than 4 percent.

94. The method of claim 88, wherein the surface of said functionalized rigid porous structure have an oxygen content greater than 6 percent.
95. The method of claim 88, wherein said functionalized rigid porous structure exhibits upon titration an acid titer greater than 1 meq/g and retains the structure of said rigid porous structure.

96. The method of claim 88, wherein said functionalized rigid porous structure exhibit upon titration an acid titer from 1 to 2 meq/g.

97. The method of claim 88, wherein said functionalized rigid porous structure exhibit a weight gain greater than 5% by comparison to said rigid porous structure.

98. The method of claim 88, wherein said functionalized rigid porous structure exhibit a weight gain from 5% to 20% by comparison with said rigid porous structure.

99. The method of claim 88, wherein said functionalized rigid porous structure exhibit a weight gain from 10% to 15% by comparison with said rigid porous structure.

100. A catalyst support formed by the method of claim 88.

101. A catalyst support formed by the method of claim 88 wherein the functionalized rigid porous structure exhibit upon titration an acid titer between 1 to 2 meq/g.

102. A catalyst support formed by the method of claim 88 wherein the functionalized rigid porous structure exhibits upon titration an acid titer greater than 1 meq/g and retains the structure of said rigid porous structure.
FIG. 1