Carbon nanostructures (21) are surface modified by adding pendant alcohol groups (25) capable of chemical reaction. Poly(vinyl alcohol) (23) is disposed on the surface of the carbon such that it renders the carbon nanostructure capable of forming a substantially uniform stable dispersion in water.
FIG. 1

FIG. 2
SURFACE FUNCTIONALIZED CARBON NANOSTRUCTURED ARTICLES AND PROCESS THEREOF

FIELD OF THE INVENTION

[0001] This invention relates in general to carbon nanostructured articles and more particularly to surface functionalization techniques in carbon nanostructured articles.

BACKGROUND OF THE INVENTION

[0002] Carbon nanotubes are cylindrical structures based on the hexagonal lattice of carbon atoms that forms crystalline graphite, possessing remarkable electronic and mechanical properties. Their exotic electronic properties and very high strength has sparked interest in potential applications, for example, in nanometer-sized electronics or to strengthen polymer materials. An ideal nanotube can be thought of as a hexagonal network of carbon atoms that has been rolled up to make a seamless cylinder, although they cannot really be made that way. Depending on the direction that the tubes appear to have been rolled (quantified by the ‘chiral vector’), they are known to act as conductors or semiconductors. Three types of nanotubes are possible, called armchair, zigzag and chiral nanotubes, depending on how the two-dimensional graphite sheet is ‘rolled up’. Just a nanometer across, the cylinder can be tens of microns long, and each end is ‘capped’ with half of a fullerene molecule. Fullerene, also known as C60 molecules or buckminsterfullerene, is a molecule made up of 60 carbon atoms arranged in a series of interlocking hexagons and pentagons, forming a structure that looks similar to a soccer ball. C60 is a truncated icosahedron, consisting of 12 pentagons and 20 hexagons. Single-wall nanotubes can be thought of as the fundamental cylindrical structure, and these form the building blocks of both multi-wall nanotubes and the ordered arrays of single-wall nanotubes called ropes.

[0003] The unique properties of carbon nanotubes and fullerene has focused considerable effort on using these special materials in polymer composites and biomedical applications. All try to utilize the high mechanical and electrical properties of the carbon nanostructured articles, but the inertness of carbon is a barrier to creating useful structures for commercialization. Thus far, putting nanotubes in polymers has proven quite difficult, and biomedical applications require dissolution in water. Homogeneous distribution in both polymers and water is prevented mainly by the high van der Waals attraction between the tubes, causing aggregation and clumping. Some have attempted to solve this problem by the use of aqueous surfactants such as sodium dodecyl sulfate to temporarily modify the surface of the carbon structures. Although this has increased the solubility of nanotubes in water, it does not address the problems of polymer composites, and does not permit further chemical modification. Successful surface functionalization of these carbon nanostructures would be a significant addition to the art.

BRIEF DESCRIPTION OF THE DRAWINGS

[0004] The accompanying figures, where like reference numerals refer to identical or functionally similar elements throughout the separate views and which together with the detailed description below are incorporated in and form part of the specification, serve to further illustrate various embodiments and to explain various principles and advantages all in accordance with the present invention.

DETAILED DESCRIPTION OF THE INVENTION

[0005] FIG. 1 is a flow chart depicting the process of surface modifying carbon nanostructured articles in accordance with the present invention.

[0006] FIG. 2 is a schematic depiction of surface functionalized carbon nanostructured articles in accordance with the present invention.

[0007] As required, detailed embodiments of the present invention are disclosed herein; however, it is to be understood that the disclosed embodiments are merely exemplary of the invention, which can be embodied in various forms. Therefore, specific structural and functional details disclosed herein are not to be interpreted as limiting, but merely as a basis for the claims and as a representative basis for teaching one skilled in the art to variously employ the present invention in virtually any appropriately detailed structure. Further, the terms and phrases used herein are not intended to be limiting; but rather, to provide an understandable description of the invention. The terms a or an, as used herein, are defined as one or more than one. The term plurality, as used herein, is defined as two or more than two. The term another, as used herein, is defined as at least a second or more. The terms including and/or having, as used herein, are defined as comprising (i.e., open language). The terms coupled and disposed, as used herein, are defined as connected, although not necessarily directly, and not necessarily mechanically.

[0008] Carbon nanostructures can be surface modified by adding pendant alcohol groups capable of chemical reaction. Poly(vinyl alcohol) is non-covalently bonded on the surface of the carbon such that it renders the carbon nanostructure capable of forming a substantially uniform stable dispersion in water. The invention utilizes wet-chemistry processes to effectively functionalize carbon nanostructures, unlike other prior art functionalization techniques. The surface energetics of the carbon microstructure or carbon nanostructure is modified. Carbon microstructures or nanostructures include, but are not limited to, carbon black, activated carbon, carbon nanofibers, graphite, fullerenes, and carbon nanotubes (both multi-wall and single-wall). The invention is created by taking advantage of the hydrophobic nature of the carbon nanostructures and the ability of poly(vinyl alcohol) to crystallize onto hydrophobic surfaces. We postulate that the resultant carbon nanostructure has crystalline poly(vinyl alcohol) moieties attached to the surface of the now-modified carbon nanostructure and/or poly(vinyl alcohol) adsorbed on the surface. This allows the surface functionalized carbon nanostructure to have chemically versatile alcohol groups for further reaction to achieve improved strength, thermal properties, and electrical properties.

[0009] Referring now to FIG. 1, the process of creating surface modified carbon nanostructured articles is explained. Poly(vinyl alcohol) (PVA) is added (12) to very high purity water. Poly(vinyl alcohol) is a white or cream colored powder or pellet prepared from polyvinyl acetate by replacement of the acetate groups with hydroxyl groups. It softens
with decomposition at about 200°C and is soluble in hot or cold water. Poly(vinyl alcohol) has a generic structure of:

\[ \text{CH}_2-\text{CH(OH)} \text{CH}_2-\text{CH(OH)} \]

[0010] The water/PVA mixture is stirred with heating (14) until the PVA dissolves. The carbon nanostructure articles (nanofibers, fullerene, nanotubes, carbon black, activated carbon, etc.) are then added (16) to the heated solution and stirred further. After a period of time, the stirring and heating are terminated and the admixture is then cooled to room temperature (18). We have found that the cooling rate affects the end properties of the surface modified nanostructure. We believe that faster cooling rates facilitate smaller crystals of PVA on the surface of the nanostructure. A properly created surface modified carbon nanostructure will appear to be completely soluble or miscible in the water, exhibiting this stability for a period in excess of six months. That is, the surface modified carbon nanostructure will form a substantially uniform stable dispersion in water (predominantly black for carbon nanotubes, although other colors may result for the carbon nanotube and fullerene solution depending on their purity, size, and concentration). This method of surface functionalization of the carbon nanostructures is sensitive to processing variables such as concentration, pH, molecular weight of the poly(vinyl alcohol), temperature, time, amount of carbon nanostructured articles and/or poly(vinyl alcohol) used, added salt or additives, and methods of agitation (e.g., inclusion of ultrasound during mixing between carbon nanostructured articles and poly(vinyl alcohol)) will all influence the effectiveness of the surface modification.

[0011] Having described our novel method of surface functionalization, we now offer our hypothesis of how the carbon nanostructure is modified. Carbon nanostructures are relatively inert, and any successful method must reckon with the substantial van der Waals attraction of the bare tubes, thus we have little reason to believe that the poly(vinyl alcohol) has chemically reacted with the carbon, ruling out covalent or ionic bonding. Carbon nanostructures are highly hydrophobic, and aggregate or clump easily, thus difficult to suspend in water. Poly(vinyl alcohol) is a polymer that possesses both hydrophobic and hydrophilic moieties. The carbon backbone and residual acetyl groups in the polymer chain provide hydrophobic properties, while the pendant hydroxyl groups provide hydrophilic properties. When the PVA is dissolved in hot water, a solution is formed that will accommodate the hydrophobic carbon nanostructures. As the carbon nanostructure becomes surface functionalized with the PVA, the pendant alcohol groups provide enough hydrophilicity to render the surface modified carbon nanostructure compatible with water. The exact mechanism of this aqueous compatibility is uncertain, but it appears that the surface functionalized carbon nanostructures are now miscible, soluble or otherwise capable of forming a uniform dispersion in or with the water. While we are not certain of the actual mechanism of bonding, we believe that the PVA becomes attached to or otherwise disposed on the surface of the carbon nanostructure by non-covalent bonding or other physical adsorption means. We further hypothesize that the PVA might also be crystallized onto the surface. FIG. 2 depicts a schematic representation of how poly(vinyl alcohol) may adsorb, crystallize, or otherwise be disposed onto the carbon nanostructure surface. The hydrophobic polymer backbone 21 of the PVA molecule 23 is attracted to the likewise hydrophobic surface of the high aspect ratio carbon nanotube 22. The hydrophilic pendant alcohol groups 25 provide compatibility with aqueous media, and thus the PVA surface modified nanostructures are miscible, soluble, or easily dispersed in water. Additionally, some adsorption of the poly(vinyl alcohol) onto the carbon nanostructure surfaces may exist due to the imperfections of the poly(vinyl alcohol) crystallization. This sometimes creates an effective stable emulsion system of incompatible (or immiscible) liquids.

[0012] By using our novel surface modification technique leveraging the hydrophobic nature of the crystallization of poly(vinyl alcohol) out of aqueous solutions, one can achieve carbon nanostructured articles that have pendant alcohol groups that offer chemical reactivity. Alcohol groups are one of the most versatile functional groups towards further chemical modification. We have, then, essentially created an intermediate that is susceptible of further reaction to create a wide variety of new materials, with applications in many different areas, such as (but not limited to) fuel cells, photovoltaics, or other next generation energy storage devices, biological monitoring or other biologically driven applications, microelectronics, fillers for composites, and displays. The pendant hydroxyl groups are reactive to a wide variety of chemicals, for example hydrogen halides, phosphorus trihalides, mineral acids, organic acids, sodium, potassium, magnesium, aluminum, thionyl chloride, octadeclamine, poly(propionyloctyl)amine-co-ethylamine), carboxylic group functionalization, alkane and fluorine functionalization, glucose amine and gum Arabic functionalization, functionalization via metal-containing complex coordination, silanes, hydrates, borates, epoxy activation (with chemicals such as epichlorohydrin or 1,4-butanediol diglycidyl ether), periodate oxidation, glutaraldehyde coupling, 1,1-carboxyldi-imidazole chemistry, 1,1-carboxyldi-imidazole chemistry, 2,2,2-trifluoroethanesulfon fluoride chloride (trespil chloride), 2,4,6-trichloro-1,3,5-triazine (cyanuric chloride) or p-sulphate-(ethyl sulphonide)-aniline (SESA), 4-dimethoxyethyl-N-(1-pyridinio)benzamide (DMPB), photo-crosslinking with photoacid generators (such as (2,4-dihydroxyphenyl)dimethylsulphonium triflate), phototcrosslinkers (such as inositol, sucrose, resorcinol, pyrogallol), and miscible and immiscible polymer blends and complexes. This permits one to create a wide variety of useful materials that are otherwise not possible to create, because of the hydrophobic nature of the carbon nanotubes.

[0013] Having described our invention, illustrative examples are now provided.

EXAMPLE 1

[0014] 1. Twenty (20) ml of ultra-pure water prepared by using reverse osmosis was placed in a clean vial and a magnetic stir bar added.

[0015] 2. Poly(vinyl alcohol) pellets purchased from Aldrich Chemical with a molecular weight of 89,000–98,000 were added to the water at a concentration of 0.01 mM (molar concentration based on the repeat unit of the poly(vinyl alcohol)) with continuous stirring.

[0016] 3. The solution was heated with stirring to dissolve the poly(vinyl alcohol). Solubilization of PVA in water is complete when the pellet disappears (solubilized), and the solution is clear. This occurred
when the solution temperature reached approximately 90 degrees Celsius. Continue stirring for five minutes after the PVA is dissolved in water.

[0017] 4. Five (5) mg of carbon nanofibers (ASI Pyrograf III PR-24-HT carbon nanofibers) were then added to the heated PVA solution with stirring.

[0018] 5. Continue heating while stirring for 30 minutes.

[0019] 6. The solution was then removed from the heat source, covered and allowed to naturally cool to room temperature with stirring in a normal laboratory environment.

[0020] After 24 hours, the covered vial was examined and the contents were found to exhibit the characteristics of a uniform solution/ dispersion, with no phase separation and no clumping or other aggregation of the carbon nanotubes.

**EXAMPLE 2**

[0021] 1. Twenty (20) ml of ultra-pure water prepared by using reverse osmosis was placed in a clean vial and a magnetic stir bar added.

[0022] 2. Poly(vinyl alcohol) pellets purchased from Aldrich Chemical with a molecular weight of 89,000–98,000 were added to the water at a concentration of 0.1 mM (molar concentration based on the repeat unit of the poly(vinyl alcohol)) with continuous stirring.

[0023] 3. The solution was heated with stirring to dissolve the poly(vinyl alcohol). Solubilization of PVA in water is complete when the pellets disappear (solubilized), and the solution is clear. This occurred when the solution temperature reached approximately 90 degrees Celsius. Continue stirring for five minutes after the PVA is dissolved in water.

[0024] 4. Five (5) mg of carbon nanofibers (ASI Pyrograf III PR-24-HT carbon nanofibers) were then added to the heated PVA solution with stirring.

[0025] 5. Continue heating while stirring for one hour.

[0026] 6. The solution was then removed from the heat source, covered and allowed to naturally cool to room temperature with stirring in a normal laboratory environment.

[0027] After 8 hours, the covered vial was examined and the contents were found to exhibit the characteristics of a uniform solution/ dispersion, with no phase separation and no clumping or other aggregation of the carbon nanotubes.

**EXAMPLE 3**

[0028] 1. Twenty (20) ml of ultra-pure water prepared by using reverse osmosis was placed in a clean vial and a magnetic stir bar added.

[0029] 2. Poly(vinyl alcohol) pellets purchased from Aldrich Chemical with a molecular weight of 89,000–98,000 were added to the water at a concentration of 0.5 mM (molar concentration based on the repeat unit of the poly(vinyl alcohol)) with continuous stirring.

[0030] 3. The solution was heated with stirring to dissolve the poly(vinyl alcohol). Solubilization of PVA in water is complete when the pellets disappear (solubilized), and the solution is clear. This occurred when the solution temperature reached approximately 85–95 degrees Celsius. Continue stirring for five minutes after the PVA is dissolved in water.

[0031] 4. Five (5) mg of carbon nanofibers (ASI Pyrograf III PR-24-HT carbon nanofibers) were then added to the heated PVA solution with stirring.

[0032] 5. Continue heating while stirring for one hour.

[0033] 6. The solution was then removed from the heat source, covered and allowed to naturally cool to room temperature with stirring in a normal laboratory environment.

[0034] After 8 hours, the covered vial was examined and the contents were found to exhibit the characteristics of a uniform solution/ dispersion, with no phase separation and no clumping or other aggregation of the carbon nanotubes. After six (6) months, the appearance of the solution/ dispersion had not changed, and still exhibited uniformity.

**EXAMPLE 4**

[0035] Two (2) lots of surface functionalized carbon nanotubes were prepared following the method described in Example 1. One lot of the surface functionalized carbon nanotubes was further reacted with an organic silane by adding an aqueous solution of 3-aminopropyltriethoxysilane (1 wt %). This solution was shaken and allowed to react at room temperature for one hour. A third control lot of carbon nanotubes in water (non-functionalized) was also prepared at a similar concentration. The three lots were as follows:

[0036] Lot 1 (Control): Carbon nanotubes in water (not miscible)

[0037] Lot 2: Surface functionalized carbon nanotubes (PVA) (miscible)

[0038] Lot 3: Surface functionalized carbon nanotubes (PVA) and 3-aminopropyltriethoxysilane (miscible)

[0039] After ample time for functionalization, a portion of three glass slides were coated with each of the three solutions and allowed to stand under normal laboratory environment until dry. A drop of water was then placed on each glass slide and the static contact angle was measured.

[0040] Lot 1 (Control): Carbon nanotubes in water—contact angle less than 3 degrees.

[0041] Lot 2: Surface functionalized carbon nanotubes (PVA)—contact angle less than 3 degrees.

[0042] Lot 3: Surface functionalized carbon nanotubes (PVA) and 3-aminopropyltriethoxysilane—contact angle 50 degrees.

[0043] After measurement of the contact angle, each of the glass slides were tilted to allow the deposited water drop to freely fall off vertically. The water drop on the control lot of non-functionalized carbon nanotubes fell off the slide, indicating a hydrophobic surface. The water drop on the PVA functionalized carbon nanotubes did not fall off the slide, but clung tenaciously, indicating a hydrophilic surface. The
A water drop on the amino silane reacted functionalized carbon nanotubes likewise did not fall off the slide, indicating a hydrophilic surface.

[0044] We conclude that the amino silane did indeed react with the pendant alcohol groups on the surface functionalized carbon nanotubes to form a new family of surface functionalized carbon nanotubes. In like manner, reactive materials can be reacted with the pendant alcohol groups on the surface functionalized carbon nanotubes to create a wide variety of new materials. In summary, without intending to limit the scope of the invention, surface functionalization of carbon nanostructures according to a method consistent with certain embodiments of the invention can be carried out by altering the surface of the nanostructures with PVA. By using our modification technique, one can effectively create modified carbon nanostructured articles for improved reliability in bulk, thermal and electrical properties that can be applied in the automotive, microelectronics, and biomedical industries. We have discovered an easier and a more cost-effective way of creating these structures by using water-soluble polymers. Those skilled in the art will recognize that the present invention has been described in terms of exemplary embodiments based upon a wet solution process by mixing the carbon nanostructured articles into an aqueous solution of poly(vinyl alcohol). However, the invention should not be so limited, since other variations will occur to those skilled in the art upon consideration of the teachings herein. Multiple processing methods can also be envisaged to modify the carbon nanostructured articles, such as (but not limited to) spraying the poly(vinyl alcohol) onto a carbon nanostructured article template surface for selective modification.

[0045] While the invention has been described in conjunction with specific embodiments, it is evident that many alternatives, modifications, permutations and variations will become apparent to those of ordinary skill in the art in light of the foregoing description. Accordingly, it is intended that the present invention embrace all such alternatives, modifications and variations as fall within the scope of the appended claims.

What is claimed is:

1. A surface functionalized carbon microstructure having pendant alcohol groups, comprising:

   a carbon microstructure, selected from the group consisting of carbon nanotubes, activated carbon, and fullerenes;

   a surface functionalized moiety disposed on the surface of the carbon microstructure sufficient to cause the surface functionalized carbon microstructure to be substantially soluble in water.

2. The surface functionalized carbon microstructure as described in claim 1, wherein said surface functionalized moiety is noncovalently bonded to the carbon microstructure.

3. The surface functionalized carbon microstructure as described in claim 1, wherein said surface functionalized moiety contains pendant alcohol groups capable of chemical reaction.

4. The surface functionalized carbon microstructure as described in claim 3, wherein said surface functionalized moiety is poly(vinyl alcohol).

5. The surface functionalized carbon microstructure as described in claim 1, wherein said noncovalently bonded poly(vinyl alcohol) is further reactive with one or more members selected from the group consisting of hydrogen halides, phosphorous trihalides, mineral acids, organic acids, sodium, potassium, magnesium, aluminum, thionyl chloride, octadecylamine, poly(propionyletherimine-co-ethylenimine), glucose amine, gum Arabic, metal-containing complexes, silanes, hydrates, borates, epichlorohydrin, 1,4-butandiol diglycidyl ether, periodates, glutaraldehyde, 1,1-carbonyldi-imidazole, 1,1-carbonyldi-imidazole, 2,2,2-trifluoroethanesulfonyl chloride, 2,4,6-trichloro-1,3,5-triazine, p-b-sulfate-(ethyl sulphonide)-aniline, 4-dimethoxymethyl-N-(1-pyridino)benzamide, 3-aminopropyltriethoxysilane, (2,4-dihydroxyphenyl)dimethylsulfoxonium triflate, inositol, sucrose, resorcinol, and pyrogallol.

6. A surface functionalized carbon nanostructure having pendant alcohol groups capable of chemical reaction, comprising:

   a carbon nanostructure, selected from the group consisting of carbon nanotubes, activated carbon, and fullerenes;

   poly(vinyl alcohol) noncovalently bonded to the carbon nanostructure;

   wherein said surface functionalized carbon nanostructure forms a substantially uniform stable dispersion in water.

7. The surface functionalized carbon nanostructure as described in claim 6, wherein said noncovalently bonded poly(vinyl alcohol) is further reactive with one or more members selected from the group consisting of hydrogen halides, phosphorous trihalides, mineral acids, organic acids, sodium, potassium, magnesium, aluminum, thionyl chloride, octadecylamine, poly(propionyletherimine-co-ethylenimine), glucose amine, gum Arabic, metal-containing complexes, silanes, hydrates, borates, epichlorohydrin, 1,4-butandiol diglycidyl ether, periodates, glutaraldehyde, 1,1-carbonyldi-imidazole, 1,1-carbonyldi-imidazole, 2,2,2-trifluoroethanesulfonyl chloride, 2,4,6-trichloro-1,3,5-triazine, p-b-sulfate-(ethyl sulphonide)-aniline, 4-dimethoxymethyl-N-(1-pyridino)benzamide, 3-aminopropyltriethoxysilane, (2,4-dihydroxyphenyl)dimethylsulfoxonium triflate, inositol, sucrose, resorcinol, and pyrogallol.

8. A surface functionalized carbon nanostructure intermediate, comprising:

   a carbon nanostructure having poly(vinyl alcohol) noncovalently bonded thereto to render said surface functionalized carbon nanostructure substantially miscible with water.

9. The surface functionalized carbon nanostructure as described in claim 8, wherein said carbon nanostructure is one or more carbon nanostructures selected from the group consisting of carbon nanotubes, activated carbon, and fullerenes.

10. The surface functionalized carbon nanostructure as described in claim 8, wherein said noncovalently bonded poly(vinyl alcohol) is reactive to form additional compounds with one or more members selected from the group consisting of hydrogen halides, phosphorous trihalides, mineral acids, organic acids, sodium, potassium, magnesium, alu-
minum, thionyl chloride, octadecylamine, poly(propionyl-ethylenimine-co-ethylenimine), glucose amine, gum Arabic, metal-containing complexes, silanes, hydrates, borates, epichlorohydrin, 1,4-butanediol diglycidyl ether, periodates, glutaraldehyde, 1,1-carbonyldi-imidazole, 1,1-carbonyldi-imidazole, 2,2,2-trifluethanesulphonyl chloride, 2,4,6-trichloro-1,3,5-triazine, p-b-sulphate-(ethyl sulphonide)-aniline, 4-dimethoxymethyl-N-(1-pyridinio)benzamide, 3-aminopropyltriethoxysilane, (2,4-dihydroxyphenyl)dimethylsulphonium triflate, inositol, sucrose, resorcinol, and pyrogallol.

11. A method of creating a surface functionalized carbon nanostructure, comprising dissolving poly(vinyl alcohol) in heated water to form a poly(vinyl alcohol) solution, and adding carbon nanostructure to the heated poly(vinyl alcohol) solution to form a surface functionalized carbon nanostructure that forms a substantially uniform stable dispersion in water.