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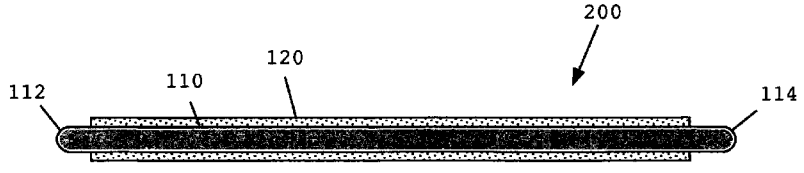
(54) Title: SHEATHED NANOTUBE FIBER AND METHOD OF FORMING SAME

FIG. 3



(57) Abstract: Embodiments of the invention provide a cellulose- sheathed carbon nanotube fiber. One aspect of the invention provides a sheathed nanotube fiber comprising: a carbon nanotube fiber; and a cellulose sheath extending co-axially along at least a first portion of a length of the carbon nanotube fiber. Another aspect of the invention provides a method of forming a sheathed carbon nanotube fiber, the method comprising: co-electrospinning a carbon nanotube fiber gel core within a cellulose solution sheath.

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SHEATHED NANOTUBE FIBER AND METHOD OF FORMING SAME

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims the benefit of US Provisional Patent Application No. 61/397,454, filed 11 June 2010, and co-pending US Patent Application No. 13/157,758, filed 10 June 2011, each of which is hereby incorporated herein.

TECHNICAL FIELD

Embodiments of the invention relate generally to conductive cable fibers and, more particularly, to conductive cable fibers with an insulating surface prepared by co-axial electrospinning of multi-walled nanotubes and cellulose.

BACKGROUND OF THE INVENTION

Carbon nanotubes (CNTs) have attracted significant interest for a wide variety of potential applications due to their strength, flexibility, and high electrical and thermal conductivities. The electrical properties of a polymer matrix have been enhanced by using shear mixing to introduce a very low loading of CNTs. However, the strong van der Waals interactions between CNTs make it difficult to achieve high CNT loadings, good dispersion, or alignment within polymer matrices. Therefore, the

preparation of structured CNT nanocomposites with desirable electrical, thermal, and strength properties remains challenging.

Electrospinning is a method of extruding fibers at high speed from a solution using electrostatic charging and has been used to prepare various types of hybrid nanofibers by incorporating nanomaterials into polymer solutions. It has been demonstrated that fibers can still be extracted from materials that normally cannot be electrospun through co-electrospinning, using a double needle spinneret.

SUMMARY OF THE INVENTION

Embodiments of the invention provide a cellulose-sheathed carbon nanotube fiber.

One aspect of the invention provides a sheathed nanotube fiber comprising: a carbon nanotube fiber; and a cellulose sheath extending co-axially along at least a first portion of a length of the carbon nanotube fiber.

Another aspect of the invention provides a method of forming a sheathed carbon nanotube fiber, the method comprising: co-electrospinning a carbon nanotube fiber gel core within a cellulose solution sheath.

The illustrative aspects of the present invention are designed to solve the problems herein described and other problems not discussed, which are discoverable by a

skilled artisan.

BRIEF DESCRIPTION OF THE DRAWINGS

These and other features of this invention will be more readily understood from the following detailed description of the various aspects of the invention taken in conjunction with the accompanying drawings that depict various embodiments of the invention, in which:

FIG. 1 shows a schematic view of the co-electrospinning of a carbon nanotube fiber gel core and a cellulose solution sheath to form a sheathed carbon nanotube fiber according to one embodiment of the invention.

FIG. 2 shows a schematic cross-sectional view of a sheathed carbon nanotube fiber according to an embodiment of the invention.

FIG. 3 shows the sheathed carbon nanotube fiber of FIG. 2 with portions of the carbon nanotube fiber core exposed.

FIGS. 4A-4D show scanning electron micrographs of fiber mats at various loadings of multi-walled nanotubes, according to embodiments of the invention.

FIG. 5 shows a chart of the conductivities of fiber mats at various loadings of multi-walled nanotubes, according to embodiments of the invention.

It is noted that the drawings of the invention are

not to scale. The drawings are intended to depict only typical aspects of the invention, and therefore should not be considered as limiting the scope of the invention. In the drawings, like numbering represents like elements among the drawings.

DETAILED DESCRIPTION OF THE INVENTION

Embodiments of the present invention provide co-axial core-sheath nanofibers with multi-wall carbon nanotubes (MWNTs) cores and cellulose sheathes. In some embodiments, such nanofibers may be produced using dry jet wet electrospinning using room temperature ionic liquid solvents.

According to one illustrative embodiment of the invention, MWNTs are mixed with an ionic liquid, such as 1-ethyl-3-methylimidazolium acetate. Other ionic liquids include, but are not limited to, 1-butyl-3-methylimidazolium chloride and 1-allyl-3-methylimidazolium chloride. Such mixing may be by mortar and pestle, for example, to form a homogenous gel. This core gel typically comprises between about 1% and about 10% MWNTs by weight, although lesser or greater MWNT concentrations may be used.

A sheath solution is prepared by dissolving cellulose in an ionic liquid, such as 1-ethyl-3-methylimidazolium acetate to a cellulose concentration of

about 1.5% by weight, although concentrations between about 1% and about 5% by weight may also be used. The sheath solution may be mixed using a magnetic stirrer or similar device to form a homogeneous solution. Solution formation may be aided by heating to about 80°C.

The core gel and sheath solution are then co-electrospun using a co-axial spinneret, such as those available from MECC (Fukuoka, Japan). FIG. 1 shows such a co-axial spinneret 100 having an inner, core needle 10 and an outer, sheath needle 20. The inner, core needle 10 has a diameter less than that of the outer, sheath needle 20. In one embodiment, a diameter of the inner, core needle 10 is about 0.94 mm and a diameter of the outer, sheath needle 20 is about 2.50 mm. Needles having other absolute and relative diameters may be employed, however, the diameters given here being merely for the purpose of describing one embodiment of the invention.

Flow rates of the inner core gel and the outer sheath solution are, according to some embodiments of the invention, between about 280 μL/minute and about 320 μL/minute. At those flow rates, a voltage between about 18 kV and 22 kV applied to the spinneret typically achieves good electrospinnability of both the inner core gel and the outer sheath solution.

The co-axial electrospun fibers 200 are collected in a coagulation bath 300, which typically includes a liquid

mixture capable of removing the ionic liquid. Suitable mixtures include, for example, a water/ethanol mixture. Once the ionic liquid is removed in the coagulation bath, the co-axial electrospun fibers 200 solidify to form a fiber mat. Upon removal from the coagulation bath 300, the fiber mat may then be washed with ethanol and dried under vacuum to remove residual water and ethanol.

FIG. 2 shows a schematic cross-sectional view of a co-axial electrospun fiber 200 according to an embodiment of the invention. As can be seen, co-axial electrospun fiber 200 includes a MWNT core 110 and a cellulose sheath 120. In FIG. 3, portions of the cellulose sheath 120 have been removed and portions 112, 114 of the MWNT core 110 exposed. The exposed portions 112, 114 of the MWNT core 110 may be used as electrical contacts.

Portions 112, 114 may be exposed using cellulase to digest areas of the cellulose sheath 120. In one embodiment, an aqueous cellulase solution may be applied to an absorbent material, such as hydrophilic poly(tetrafluoroethylene), which is then applied to an area of the cellulose sheath 120. The co-axial electrospun fiber 200 may then be washed to remove any digested cellulose and expose portions 112, 114 of the MWNT core 110.

FIGS. 4A, 4B, 4C, and 4D show scanning electron micrographs of MWNT-cellulose fiber mats at various MWNT

loadings. FIG. 4A shows a fiber mat at 45% MWNT, by weight. FIG. 4B shows a fiber mat at 40% MWNT, by weight. FIG. 4C shows a fiber mat at 30% MWNT, by weight. FIG. 4D shows a fiber mat at 40% MWNT, by weight.

Tensile Strength

The tensile strength of co-axial electrospun fiber mats according to embodiments of the invention are proportional to the cellulose:MWNT ratio of the fiber mats. A fiber mat of pure cellulose having dimensions of 15 mm x 15 mm x 50-80 μm was determined to have a tensile strength of 6.22 MPa. A co-axial electrospun fiber mat with a MWNT loading of 45% by weight exhibited a tensile strength of 2.54 MPa.

Tensile strength measurements were performed using Instron Materials Testing Machine (Norwood, MA) model 5543 equipped with a 10 N static load cell and hydraulic grips (Instron 2712-001). Specimens were tested at 0.25 mm/min tension speed with a 5 mm gauge length. Both load and grip-to-grip distance were measured. Tensile strength was calculated by dividing the peak load by the initial cross-sectional area of the sample.

Thermal Characteristics

Surprisingly, it was found that the temperature of

the onset of cellulose degradation increased with an increasing MWNT load. It is possible that either the cellulose crystallinity of the co-axial electrospun fiber is increased by MWNT loading or that MWNTs act as a heat sink or an antioxidant, protecting the cellulose from thermal degradation.

In evaluating the thermal characteristics of fiber mats of the invention, thermogravimetric analysis was performed using a computer-controlled TA Instruments (New Castle, DE) TGA Q50. Temperature was ramped up at 20 °C per minute up to 700 °C with the furnace open to allow air flow along with nitrogen purge gas.

Conductivity

Pristine fiber mats were found to be non-conductive, due to the substantially insulating effects of the cellulose sheath 120. Once portions 112, 114 (FIG. 3) of MWNT core 110 were exposed, however, the fiber mats were found to have conductive properties following Ohm's law. Where portions 112, 114 were separated by 1 cm, conductivity of the fiber mats was observed, confirming that MWNT core 110 was continuous for at least 1 cm.

In addition, it was found that the conductivities of the fibers increased with higher MWNT loading. In fact, a surprisingly large 2-order of magnitude increase in conductivity was obtained upon doubling the mass fraction

of the MWNTs. This may suggest that the continuity of the MWNT core 110 improves at higher MWNT loading and/or that the MWNTs in the MWNT core 110 form denser wire- or cable-like core structures. FIG. 5 shows a graph of conductivities obtained at MWNT loadings of 20%, 30%, 40%, and 45%. At 45% MWNT loading, conductivities as high as 10.7 S/m were obtained.

All of these conductivities are significantly higher than those reported with carbon nanotube-polymer fiber mats, which are typically around 3.7×10^{-2} S/m for poly(styrene)/single-wall nanotube fiber materials and 5.05×10^{-6} S/m for poly(ethyleneterephthalate)/MWNT fiber materials. The higher conductivities obtainable according to embodiments of the present invention may be due, at least in part, to the fact that the MWNT-cellulose fibers here consist of pure MWNTs free of a polymer matrix, which permits formation of a dense MWNT core that more effectively conducts an electrical current.

Conductivities of co-axial electrospun fiber mats according to the invention were measured by preparing two "sheath-off" areas, 1 cm apart, on a fiber mat between 50 μm and about 80 μm thick. The sheath-off areas were sandwiched by 20 μm thick aluminum foil and clamped at 0.7 MPa. Characteristic I-V curves were obtained at room temperature using a two-probe method using a Princeton

Applied Research (Oak Ridge, TN) model 273A electropotentiostat, with an applied voltage up to 1 V at a scan rate of 100 mV/second. Electrical conductivities were calculated according to the following equation:

$$\sigma = L / (R \cdot A),$$

in which σ is electrical conductivity in Siemens per meter (S/m), L is the distance between sheath-off areas, R is resistance, and A is a cross-sectional area of the fiber mat.

The co-axial electrospun fibers according to some embodiments of the invention may be employed in any number of applications. For example, the cellulose sheath serves as an effective nanoscale insulating layer, permitting two parallel co-axial electrospun fibers to be used in electrical double-layer supercapacitor devices. In such a device, the distance between the two electrodes would be double the sheath thickness, often on the scale of hundreds of nanometers, permitting very high specific capacitances.

Other applications of the co-axial electrospun fibers according to embodiments of the invention include, for example, their use as the separator of a biomorph actuator, based on the formation of an electrical double layer. The thin, flexible separator achievable using the co-axial electrospun fibers of the invention may improve

response properties of such an actuator.

The foregoing description of various aspects of the invention has been presented for purposes of illustration and description. It is not intended to be exhaustive or to limit the invention to the precise form disclosed, and obviously, many modifications and variations are possible. Such modifications and variations that may be apparent to a person skilled in the art are intended to be included within the scope of the invention as defined by the accompanying claims.

CLAIMS

What is claimed is:

1. A sheathed carbon nanotube fiber comprising:

a carbon nanotube fiber; and

a cellulose sheath extending co-axially along at least a first portion of a length of the carbon nanotube fiber.

2. The sheathed carbon nanotube fiber of claim 1, wherein the carbon nanotube fiber includes a multi-walled nanotube fiber.

3. The sheathed carbon nanotube fiber of claim 1, wherein the cellulose sheath does not extend along a second portion of the length of the carbon nanotube fiber.

4. The sheathed carbon nanotube fiber of claim 1, wherein the carbon nanotube fiber comprises at least about 20% of the sheathed carbon nanotube fiber by weight.

5. The sheathed carbon nanotube fiber of claim 4, wherein the carbon nanotube fiber comprises at least about 30% of the sheathed carbon nanotube fiber by

weight.

6. The sheathed carbon nanotube fiber of claim 5, wherein the carbon nanotube fiber comprises at least about 40% of the sheathed carbon nanotube fiber by weight.

7. The sheathed carbon nanotube fiber of claim 6, wherein the carbon nanotube fiber comprises at least about 45% of the sheathed carbon nanotube fiber by weight.

8. The sheathed carbon nanotube fiber of claim 1, wherein a fiber mat comprising the carbon nanotube fiber has a conductivity of at least about 1.0×10^{-1} S/m.

9. The sheathed carbon nanotube fiber of claim 8, wherein the fiber mat has a conductivity of at least about 1.0 S/m.

10. The sheathed carbon nanotube fiber of claim 9, wherein the fiber mat has a conductivity of at least about 10 S/m.

11. The sheathed carbon nanotube fiber of claim 1, wherein a tensile strength of a fiber mat comprising the

sheathed carbon nanotube fiber is between about 1.5 MPa and about 2.5 MPa.

12. A method of forming a sheathed carbon nanotube fiber, the method comprising:

co-electrospinning a carbon nanotube fiber gel core within a cellulose solution sheath.

13. The method of claim 12, wherein the carbon nanotube fiber gel includes between about 1% and about 10% multi-walled carbon nanotubes, by weight.

14. The method of claim 12, wherein each of the carbon nanotube fiber gel and the cellulose solution includes at least one ionic liquid.

15. The method of claim 14, wherein the at least one ionic liquid is, independently, selected from a group consisting of: 1-ethyl-3-methylimidazolium acetate, 1-butyl-3-methylimidazolium chloride, and 1-allyl-3-methylimidazolium chloride.

16. The method of claim 15, wherein the at least one ionic liquid includes 1-ethyl-3-methylimidazolium acetate.

17. The method of claim 14, further comprising:

removing the at least one ionic liquid from the co-electrospun carbon nanotube fiber gel and the cellulose solution to form a cellulose-sheathed carbon nanotube fiber.

18. The method of claim 17, further comprising:

removing the cellulose sheath from a portion of the carbon nanotube fiber.

19. The method of claim 18, wherein removing the cellulose sheath includes digesting the cellulose sheath with cellulase.

FIG. 1

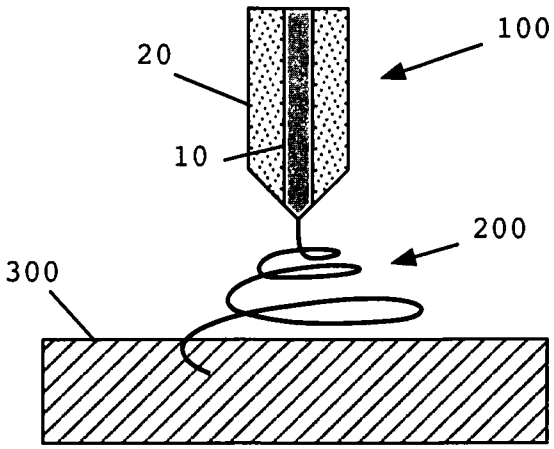


FIG. 2

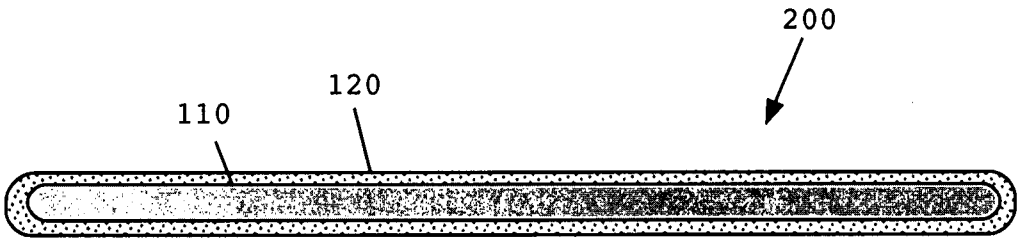


FIG. 3

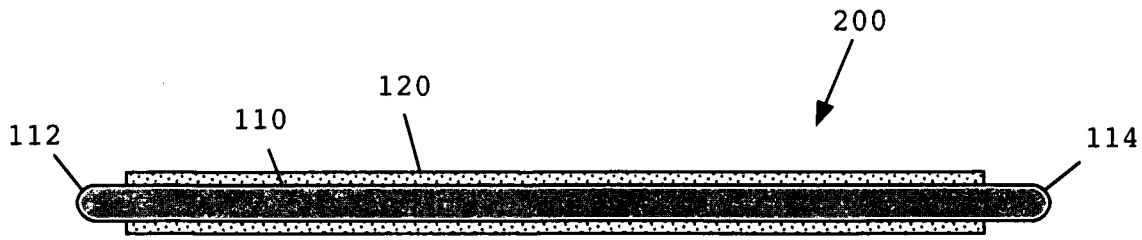


FIG. 4B

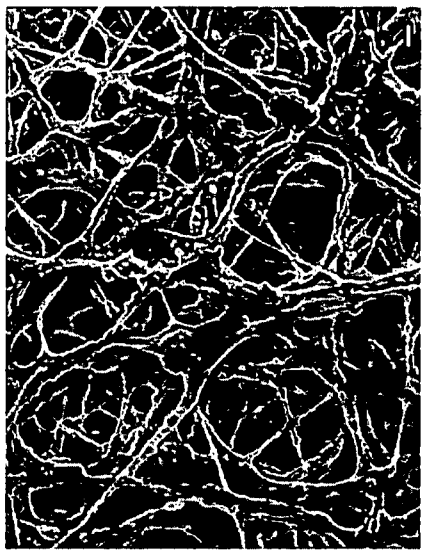


FIG. 4D

FIG. 4A

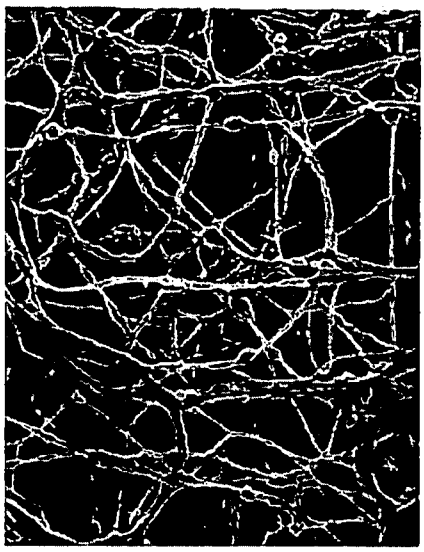
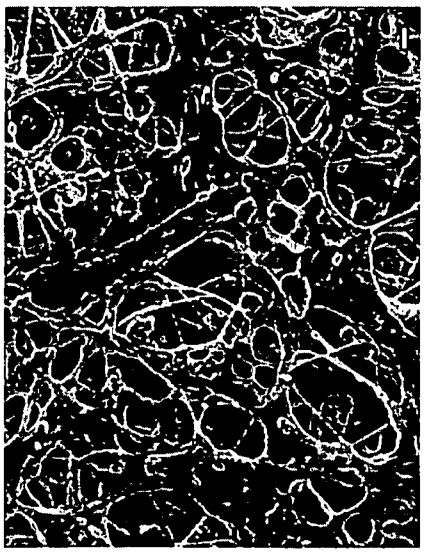


FIG. 4C



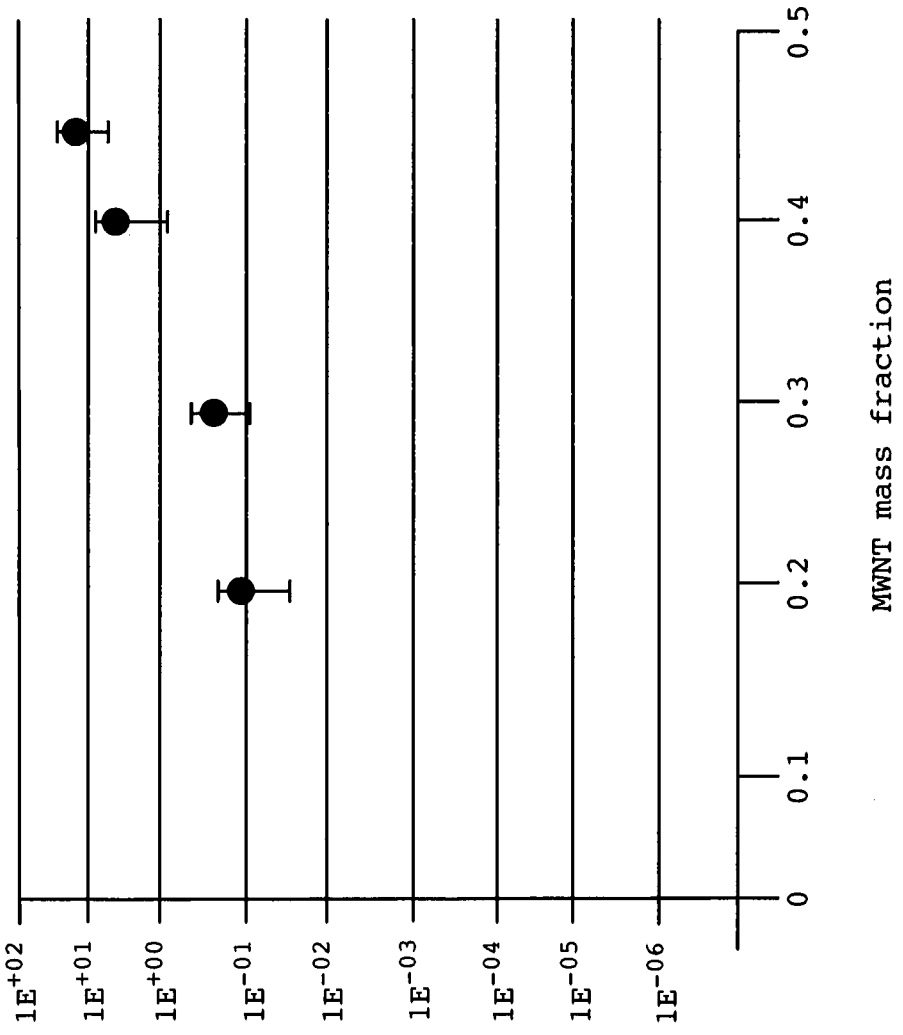

conductivity (S/m)
1E+02
1E+01
1E+00
1E-01
1E-02
1E-03
1E-04
1E-05
1E-06
0
0.1
0.2
0.3
0.4
0.5
MWNT mass fraction

FIG. 5