METHODS FOR MAKING AN ELECTROACTIVE DEVICE FABRICATED WITH A NANOTUBE FILM ELECTRODE

Disclosed is a single wall carbon nanotube (SWCNT) film electrode (FE), all-organic electroactive device systems fabricated with the SWNT-FE, and methods for making same. The SWCNT can be replaced by other types of nanotubes. The SWCNT film can be obtained by filtering SWCNT solution onto the surface of an anodized alumina membrane. A freestanding flexible SWCNT film can be collected by breaking up this brittle membrane. The conductivity of this SWCNT film can advantageously be higher than 280 S/cm. An electroactive polymer (EAP) actuator layered with the SWNT-FE shows a higher electric field-induced strain than an EAP layered with metal electrodes because the flexible SWNT-FE relieves the restraint of the displacement of the polymeric active layer as compared to the metal electrode. In addition, if thin enough, the SWNT-FE is transparent in the visible light range, thus making it suitable for use in actuators used in optical devices.

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Fig. 1A

Fig. 1B
Fig. 3A

Dielectric Constant

Temperature (°C)

Fig. 3B

Dielectric Constant

Temperature (°C)
SWNT electrode (600 psi)
\(M_{33} = 3.86 \times 10^{-15} \text{ m}^2/\text{V}^2\)

SWNT electrode (3000 psi)
\(M_{33} = 2.80 \times 10^{-15} \text{ m}^2/\text{V}^2\)

SWNT electrode (6000 psi)
\(M_{33} = 1.93 \times 10^{-15} \text{ m}^2/\text{V}^2\)

Metal electrode
\(M_{33} = 1.58 \times 10^{-15} \text{ m}^2/\text{V}^2\)

Fig. 4
METHODS FOR MAKING AN ELECTROACTIVE DEVICE FABRICATED WITH A NANOTUBE FILM ELECTRODE

CROSS REFERENCE TO RELATED APPLICATION

This patent application is a divisional of pending U.S. patent application Ser. No. 13/938,622, filed Jul. 10, 2013, which claims the benefit of U.S. patent application Ser. No. 13/284,061, filed Oct. 28, 2011; which claims the benefit of U.S. patent application Ser. No. 11/937,155, filed Nov. 7, 2007, which claims the benefit of U.S. Provisional Application Nos. 60/857,531, filed Nov. 8, 2006, and 60/984,027 filed Oct. 31, 2007; the contents of each of the foregoing applications are hereby incorporated by reference in their entireties.

ORIGIN OF THE INVENTION

The invention described herein was made by an employee of the United States Government and may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment of any royalties thereon or therefor.

FIELD OF THE INVENTION

This invention relates generally to electroactive polymeric devices and compliant electrodes for these devices. More specifically, the invention relates to electroactive polymeric devices utilizing highly compliant nanotube film electrodes and methods for making same.

DESCRIPTION OF THE RELATED ART

As an interest in high performance polymeric electroactive devices increases, a request for new electrode materials has emerged. Known electroactive polymeric devices typically use metal electrodes, such as silver and gold, to provide electric fields. These metal electrodes often inhibit the displacement (elongation or contraction) of their electroactive layer because of less compliance (greater stiffness (modulus)) of the metal electrodes than the active polymer itself. Thus, the actual electric field-induced strain output of these devices with metal electrodes is always smaller than what they could intrinsically provide.

Conducting polymers have been used as alternative electrodes for electroactive polymeric devices. The conducting polymers relieved the restraint of movement in the polymeric active layer because their compliance is similar to that of the active polymeric layer, and exhibited higher strain than metal electrodes did. However, these conducting polymers have a disadvantage of low conductivity at high temperatures because of dehydration phenomena and dedoping, and therefore are unable to be used for applications which require high thermal stability. Therefore, a need existed for an alternative electrode with less stiffness than the conventional metallic electrodes and with good thermal stability.

SUMMARY OF THE INVENTION

In accordance with at least one embodiment of the present invention a novel freestanding flexible single-walled carbon nanotubes (SWCNT) film electrode (SWCNT-FE) is provided. This inventive electrode shows high conductivity and good thermal stability with comparable compliance to polymeric active layers. Additionally, in accordance with at least one embodiment of the present invention, a novel high performance all-organic electroactive device (or system) is provided, fabricated with the SWCNT-FE. Methods for the preparation of the electrode and device are also provided within the scope of the present invention. Features and advantages of the inventions will be apparent from the following detailed description taken in conjunction with the following figures.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1A is a schematic diagram depicting the preparation of an all-organic electroactive device system in accordance with at least one embodiment of the present invention;

FIG. 1B shows a photograph of a prototype of a transparent electroactive device fabricated with an EAP active layer and SWNT film electrodes, in accordance with at least one embodiment of the present invention;

FIG. 2A shows a cross-sectional SEM image of SWCNT-FE after pressing at 600 psi, in accordance with at least one embodiment of the present invention;

FIG. 2B shows a more detailed image of the pulled and porous networked SWCNTs shown in FIG. 2A;

FIG. 2C shows a cross sectional SEM image of SWCNT-FE after pressing at 6000 psi, in accordance with at least one embodiment of the present invention;

FIG. 3A is a graph depicting the dielectric constant of an inventive EAP layered with SWCNT-FE as a function of temperature and frequency;

FIG. 3B is a graph depicting the dielectric constant of an EAP layered with metal electrodes as a function of temperature and frequency;

FIG. 4 is a graph depicting the electric field-induced strain of an EAP layered with metal electrodes, and with an inventive SWCNT-FE;

FIGS. 5A and 5B are photographs of a freestanding flexible SWCNT-FE in accordance with at least one embodiment of the present invention, after it is removed from the membrane (shown in 5B), in accordance with the present invention.

DETAILED DESCRIPTION OF THE INVENTION

Shown in the drawings and described herein in detail are advantageous embodiments of the present invention. It should be understood that the present invention is susceptible of embodiments in many different forms and thus the present disclosure is to be considered as an exemplification of the principles of the invention and is not intended to limit the broad aspect of the invention to the embodiments described and illustrated herein.

Referring now to the drawings, FIG. 1A is a diagram depicting the preparation of an all-organic electroactive device system in accordance with at least one embodiment of the present invention (such as the device 10 shown in FIG. 1B). A SWCNT film can be prepared by a method similar to the method set forth in A. G. Rinzler and Z. Chen, U.S. Patent Application Publication 20040197546 (Oct. 7, 2004), the entire contents of which are hereby incorporated by reference. However, in accordance with the present invention, unlike U.S. Application Publication 20040197546, no surfactant is required to develop the SWNT film and no solvent is necessary to isolate the SWNT film from the filter membrane (by dissolving the membrane). Additionally, it
should be understood that while the described inventive embodiment utilizes SWCNTs, it is nevertheless within the scope of the present invention to replace the SWCNTs with multi-walled carbon nanotubes (MWCNT) or few wall carbon nanotubes (FWCNT). Additionally, other types of conductive nanotubes can be used in the instant invention, for example, boron nanotubes, boron carbon nitride nanotubes, and/or boron nitride nanotubes.

To explain, in accordance with one inventive method, the inventive electrode can be developed as follows. First, SWCNTs can be dispersed in an solvent, such as N,N-Dimethylacetamide (DMac), under sonication and filtered onto the surface of a brittle or breakable porous membrane, such as an anodized alumina membrane (pore size: 0.2 µm), to form a SWNT film on the membrane. Advantageous dispersion methods (not requiring surfactants or covalent bonds), and choices of appropriate solvents, which can be utilized in accordance with the present invention, can be found in co-pending U.S. patent applications, namely, application Ser. No. 10/288,797, entitled “Electrically Conductive, Optically Transparent Polymer Composites and Process for Preparation Thereof,” filed Nov. 1, 2002; application Ser. No. 11/452,201, entitled “Dispersions of Carbon Nanotubes in Polymer Matrices,” filed on May 11, 2006; and application Ser. No. 11/644,019, entitled “Nanocomposites from Stable Dispersions of Carbon Nanotubes in Polymeric Matrices Using Dispersion Interaction,” filed on Dec. 22, 2006. These three pending U.S. patent applications are incorporated herein by reference as set forth in their entirety.

After the formation of the SWCNT film on the membrane (for example, through the removal of the solvent in a known manner), a freestanding SWCNT film can then be easily delaminated by breaking the brittle (e.g. alumina) membrane. This breaking can be accomplished in a manner that would be known to one skilled in the art, the result of which is shown in FIG. 5B. In one advantageous embodiment, the delaminated SWCNT film will have the conductivity of about 280 S/cm. The thickness of the SWCNT film can be controlled from several tens of nanometers to several hundreds of micrometers by adjusting the concentration and quantity of SWCNT solution used. Adjusting the concentration and quantity of SWCNT solution used will also affect the final conductivity of the SWCNT film. Additionally, adjusting the thickness of the film will affect the transparency of the film. For example, it was found that a 2 µm thick SWCNT film was opaque (black), while a 300 nm thick SWCNT film was found to be optically transparent.

In accordance with at least one advantageous embodiment of the present invention, as shown in FIG. 1A, an inventive all-organic electroactive device (SWCNT-FE/EAP/SWCNT-FE) can be fabricated with an electroactive polymer (EAP) active layer 11 and the SWCNT films 12, 13 by pressing, for example, at 600, 3000 or 6000 psi, as shown in FIG. 1A. In accordance with one embodiment of the invention, the pressing temperature and time were 230° C. and 2 min., respectively. All of the sample specimens were preheated at 230° C. for 20 minutes prior to pressing. Silicone elastomer plates 14, 15 (e.g., 3 mm thick) can be used on the press plate surfaces for better contact adhesion between the SWCNT film and the actuating layer. This polymeric electroactive device layered with the SWCNT-FE can serve as a sensor. However, it should be understood that it is within the scope of the present invention that other devices (such as sensors, transducers, etc.) could also be fabricated utilizing the novel methods and inventions set forth herein. Additionally, the embodiment shown in FIG. 1A is merely illustrative of one possible device design. As is known in the art, depending upon the desired application and geometry, the device could be configured in many different ways, for example, with different numbers, sizes, shapes and locations of active layers and electrodes (e.g., round, interdigitated, etc.). Also, different types of active layers could be utilized, depending upon the application for which the particular device is designed. Examples of various active layers can be found in U.S. Pat. Nos. 5,891,581 and 5,909,905, as well as pending U.S. patent application Ser. No. 11/076,460, entitled “Sensing/Actuating Materials Made from Carbon Nanotube Polymer Composites and Methods for Making Same,” filed Mar. 3, 2005, and pending U.S. patent application Ser. No. 11/081,888, entitled, “Multilayer Electroactive Polymer Composite Material,” filed on Mar. 9, 2005. These patents and applications are hereby incorporated by reference as if set forth in their entirety herein.

FIGS. 2A and 2C show SEM images of cross-sections of inventive SWCNT-FEs 22, 23 after pressing at 600 psi and at 6000 psi, respectively. FIG. 2B shows a more detailed image of the pulled and porous networked SWCNTs shown in FIG. 2A. The cross-section of the SWCNT-FE 23 pressed under 6000 psi (FIG. 2C) was denser than that pressed under 600 psi (FIG. 2A).

The density (modulus or compliance) of the SWCNT-FE can be controlled by adjusting the fabrication pressure. As explained more fully below, it is anticipated that less dense (higher compliance) SWCNT-FE can present less constraint to the displacement by more closely matching the modulus of the polymeric active layers. Therefore, in at least one advantageous embodiment of the present invention, the fabrication pressure is adjusted to produce a SWCNT-FE with a compliance (and modulus) substantially matching the compliance of the device’s active layer. In this manner a device can be fabricated with substantially uniform compliance throughout, thereby potentially improving the performance of the device, for example, by maximizing the electric field-induced strain output of the device.

Most conducting polymers become unstable above 120° C., and lose their conductivity significantly. However, for many applications, the actuator system must be able to function at temperatures even up to 200° C. or higher. Therefore, it was necessary to examine if SWCNT-FE can present less constraint to the displacement by more closely matching the modulus of the polymeric active layers. Therefore, in at least one advantageous embodiment of the present invention, the SWCNT-FE can present less constraint to the displacement by more closely matching the modulus of the polymeric active layers. Therefore, in at least one advantageous embodiment of the present invention, the fabrication pressure is adjusted to produce a SWCNT-FE with a compliance (and modulus) substantially matching the compliance of the device’s active layer. In this manner a device can be fabricated with substantially uniform compliance throughout, thereby potentially improving the performance of the device, for example, by maximizing the electric field-induced strain output of the device.

The performance of the SWCNT film as an electrode was evaluated by measuring the dielectric properties of an Electroactive Polymer (EAP) layered with the SWCNT film as an electrode (SWCNT-FE) at a broad range of temperatures and frequencies. The performance of the SWCNT film as an electrode was evaluated by measuring the dielectric properties of an Electroactive Polymer (EAP) layered with the SWCNT film as an electrode (SWCNT-FE) at a broad range of temperatures (from 25° C. to 280° C.) and frequencies (from 1 kHz to 1 MHz). The temperature and frequency dependence of the dielectric constant for an EAP layered with SWCNT-FE is shown in FIG. 3A, which is almost the same as that of the dielectric properties of the same EAP layered with gold electrodes (FIG. 3B). The dielectric constant remained constant up to 220° C., and then increased. The increase of the dielectric constant at 220° C. is due to the glass transition temperature (T_g) of the EAP (β-CN)APB/ODPA polyimide, U.S. Pat. No. 5,891,581 Joyceelyn O. Simpson and Terry St. Clair, “Thermally stable, piezoelectric and pyroelectric polymeric substrates”). Above T_g, dipoles have a higher mobility and show a higher dielectric constant. Additionally, as frequency decreases, it is believed that these dipoles have enough time to orient themselves under an applied electric field, creating a higher dielectric constant. Thermally stable dielectric properties suggest that SWCNT-FE is suitable for high temperature applications at least up to 220° C. SWCNT usually do not oxidize below a temperature of about 400° C.,
Therefore, if a higher stability polymer was used a fabricated device could potentially function at a much higher temperature. Success in the use of known conducting polymer electrodes at high temperatures (above 100°C) has rarely been reported. Conducting polymers have a disadvantage of low conductivity at high temperatures because of dehydration phenomena and dedoping, and therefore are unable to be used for applications which require high thermal stability.

Electric field-induced strain values for EAP layered with metal electrodes and SWCNT-FE are shown in FIG. 4. The EAP actuator layered with the SWCNT-FE showed a higher electric field-induced strain than an EAP layered with metal electrodes under identical measurement conditions since the flexible, highly compliant SWCNT-FE relieves the restraint of the displacement of the polymeric active layer compared to the metal electrode. In addition, as explained above, when prepared thin enough, the SWCNT-FE can be transparent in the visible light range (see FIG. 1B). Actuators fabricated with the transparent SWCNT-FE can be used in optical devices such as optical switches and modulators.

As shown in FIG. 4, the out-of-plane strain (S_{33}) through the film thickness was plotted as a function of applied electric field strength. The strain (S_{33}) of EAP layered with silver electrodes increased quadratically with increasing applied electric field, indicating that the strain is mainly electrostrictively originated. The electrostrictive coefficient (M_{33}) vs. EAP layered with silver electrodes, calculated from a slope in a plot of strain (S_{33}) vs. the square of electric field strength (E), S_{33} = M_{33}E^2, was 1.58E-15 m^2/V^2. The strain of EAP layered with SWCNT-FE after pressing at 600 psi increased more rapidly than that layered with silver electrodes. The electrostrictive coefficient (M_{33}) of this SWCNT-FE system (600 psi) was 3.8E-15 m^2/V^2, more than 2 times higher than those of EAP layered with silver electrodes. This significant increase in strain indicates that the modulus of the SWCNT-FE prepared at 6000 psi was close to that of silver electrodes at the interface.

Additionally, all-organic electroactive device systems fabricated with single wall carbon nanotube (SWCNT) films used as electrodes have shown enhanced electroactive performance in comparison with conventional electroactive device system fabricated with metal electrodes. SWCNT can be replaced by multi wall carbon nanotubes (MWNT) or few wall carbon nanotubes (FWCNT). Further, SWCNT film electrodes (SWCNT-FE) have shown reliable capability as an electrode in an electrical device at high temperatures suitable for aerospace applications. Additionally, other types of conductive nanotubes may also be used in these applications, such as boron nanotubes, boron carbon nitride nanotubes, and/or boron-nitride nanotubes.

As explained above, certain mechanical properties of SWCNT-FE (e.g. Young’s modulus) can be controlled by adjusting the magnitude of the fabrication pressure, to form resultant electrodes with mechanical properties substantially matching with those of employed active layers. Additionally, in accordance with at least one embodiment of the invention, higher mechanical properties (e.g. Young’s modulus, strength, elongation at break, durability, robustness, etc.) of SWCNT-FE can be achieved by using acid-treated SWNTs (which are commercially available) and post-sintering at above 350°C temperature. A freestanding flexible SWCNT-FE with high conductivity has been developed. One such inventive freestanding flexible SWCNT-FE 52 is shown in FIGS. 5A and 5B, after delamination by breaking the brittle membrane 53. FIG. 5D shows the freestanding flexible SWCNT-FE 52 sitting on the broken membrane 53. As explained above, a freestanding SWCNT-FE can be pressed during the fabrication of a device, or, in the alternative, it could be independently pressed in order to achieve a desired thickness, conductivity, compliance, transparency, etc.

As explained above, the thickness of the SWCNT film is easily controlled by the concentration and quantity of SWCNT solution, and it can range from about several tens of nanometers to about several hundreds of micrometers. The SWCNT film which was thinner than several hundreds of nanometer was found to be transparent. Therefore, the freestanding transparent SWCNT film electrodes (SWCNT-FE) enables the inventive all-organic electroactive devices to be used in optical devices such as optical switches and modulators.

Potential applications for an all-organic electroactive device fabricated with carbon nanotubes, e.g., single wall carbon nanotube (SWCNT) film electrodes (SWCNT-FE), include electromechanical energy conversion devices such as electromechanical sensors and actuators, transducers, sonars, medical devices, prosthetics, artificial muscles, and materials for vibration and noise control. The high performance inventive all-organic electroactive devices possess many advantages over piezoceramic and shape-memory alloys owing to their light weight, conformability, high toughness, and tailorable properties needed in these applications. In addition, the transparency of the novel all-organic electroactive devices fabricated with SWNT-FE enables them to be used in optical devices such as optical switches and modulators. The freestanding flexible SWCNT-FE can provide a great degree of freedom to fabricate a variety of complex electroactive devices.

Although only a few exemplary embodiments of this invention have been described in detail above, those skilled in the art will readily appreciate that many modifications are possible in the exemplary embodiments without materially departing from the novel teachings and advantages of this invention. Accordingly, all such modifications are intended to be included within the scope of this invention as defined in the following claims. Additionally, it should be understood that the use of the term “invention” herein should not be limited to the singular, but rather, where applicable, it is meant to include the plural “inventions” as well. Further, in the claims, means-plus-function and step-plus-function clauses are intended to cover the structures or acts described herein as performing the recited function and not only structural equivalents, but also equivalent structures.

What is claimed as new and desired to be secured by Letters Patent of the United States is:

1. A method for making an electroactive device having a nanotube film electrode, comprising the steps of:
   providing at least one nanotube film electrode;
   providing at least one active layer;
   placing said at least one nanotube film electrode in contact with said at least one active layer;
   applying sufficient pressure to said at least one nanotube film electrode and said at least one active layer so as to produce an electroactive device having a substantially uniform compliance throughout, wherein said step of applying sufficient pressure comprises controlling a density of said at least one nanotube film electrode by
said sufficient pressure to control a compliance of said at least one nanotube film electrode.

2. The method of claim 1, comprising the step of heating said at least one nanotube film electrode and said at least one active layer.

3. The method of claim 1, wherein said sufficient pressure ranges between about 600 to about 6000 psi.

4. The method of claim 1, wherein said step of applying sufficient pressure comprises utilizing silicone elastomer plates on press plates.

5. The method of claim 1, where said active layer comprises an electroactive polymer.

6. The method of claim 1, wherein the nanotube film electrode consists essentially of at least one or more of:
   - single-walled carbon nanotubes;
   - multi-walled carbon nanotubes;
   - few walled carbon nanotubes;
   - boron nanotubes;
   - boron carbon nitride nanotubes, and
   - boron nitride nanotubes.

7. The method of claim 1, wherein the nanotube film electrode is prepared by a process comprising the steps of:
   - dispersing conductive nanotubes in a surfactant-free solvent under sonication to form a solution;
   - providing a breakable porous membrane;
   - filtering the solution onto the membrane; and
   - delaminating the nanotube film electrode from the membrane by physically breaking the membrane.