

Single Wall Carbon Nanotube–Nafion Composite Actuators

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ABSTRACT

Single wall carbon nanotube (SWNT)–Nafion composite actuators have been demonstrated for 0.1–18% w/w doping of purified SWNTs within the polymer matrix. The high purity SWNTs, >95% w/w, were homogeneously dispersed into the polymer through a series of homogenization and high shear mixing techniques. The efficient distribution of the high aspect ratio, conductive SWNT materials allowed for the actuation of the Nafion membrane to be reached at SWNT doping levels as low as 0.5% w/w. Utilizing a two-electrode bimorph cantilever actuator immersed into an aqueous lithium chloride solution, tip deflections up to 4.5 mm were observed.

There is currently considerable interest in actuator systems that convert electrochemical energy into mechanical energy for applications ranging from microswitches to artificial muscles. Polymer actuators based on ion-exchange membranes have been shown to have large displacements (i.e., 1–10 mm) and rapid response based on a reasonably applied voltage, i.e., 1–5 V. Specifically, Nafion, a perfluorinated sulfonated ionomer that has been doped with ~30% w/w metal has been shown to curl up to 5 mm¹ because of differential swelling in aqueous electrolyte solutions.^{2–6} This response is caused by an electroosmotic effect whereby the solvated cations enrich the water content at the cathode, which causes the swelling of the membrane.⁶ However, a limitation is associated with Nafion-based actuators because they tend to relax when the excitation potential is held constant because of the diffusion of the excess “free” water out of the hydrophilic cluster within the membrane.⁶ In this work our goal is to achieve efficient polymer actuation through the doping of Nafion with purified single wall carbon nanotubes (SWNTs).

The unique physiochemical properties of SWNTs have made them the subject of special interest since their discovery by Iijima et al. in 1993.^{7,8} The unique nature of the electronic and mechanical properties of SWNTs is exemplified by their electrochemical actuation properties. Preliminary studies have shown that SWNT electrochemical actuator systems could be potentially used for the efficient and direct conversion of electrical energy to mechanical energy.⁹ In this letter we

report the successful dispersion of purified SWNTs into Nafion with the subsequent demonstration of the efficient actuation behavior of the SWNT-doped composites.

The SWNTs used in this study were purchased from Carbon Nanotechnologies, Inc., i.e., HiPco or h-SWNTs. The h-SWNTs were purified according to the procedure established by Chiang et al.¹⁰ The purity of the final SWNT samples was determined quantitatively using thermogravimetric analysis (TGA) in conjunction with inductively coupled plasma spectroscopy,¹¹ and qualitatively by field emission scanning electron microscopy (FESEM), UV–vis–NIR spectroscopy, Raman spectroscopy, and transmission electron microscopy. The end result was a purified material that consistently contained at least 95% w/w single wall carbon nanotubes. Electron micrographs and thermogravimetric analyses representative of the raw and purified SWNT materials are shown in Figure 1.

Composites of Nafion and nanotube materials were prepared by the dispersion of the SWNTs in a 5% w/w Nafion-1100 2-propanol solution (Aldrich). The appropriate amounts of purified h-SWNTs were added to the Nafion-2-propanol solutions in order to achieve between 0.1 and 18% w/w nanotube loadings within the final polymer membrane. The SWNT–Nafion solutions were first homogenized for five 10-minute intervals until a highly homogeneous solution resulted. The solutions were then exposed to high shear stirring at room temperature for 72 h. After 72 h, the solutions were centrifuged to remove any nondispersed materials. After centrifugation, the mass of any residue was determined and the percent by weight was adjusted accordingly. Using traditional solution-casting techniques, thin film membranes

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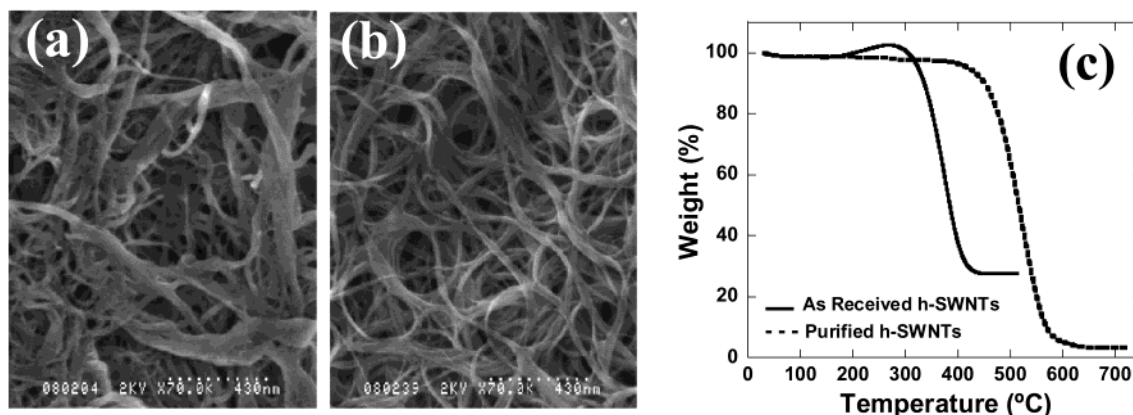


Figure 1. Analysis of h-SWNTs: (a) Hitachi model S-900 FESEM image of as-received material from Carbon Nanotechnologies Inc., the carbonaceous coating is clearly evident; (b) FESEM image of high purity, >95% w/w, h-SWNTs after purification; (c) TA Instruments model 2950 thermogram overlay displaying the decomposition of as-received and purified h-SWNT samples, 5 °C/min under 60 sccm flowing air atmosphere.

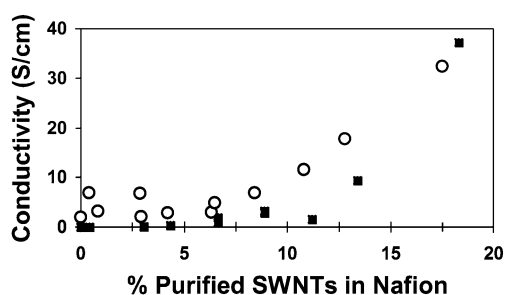


Figure 2. Conductivity for various percent by weight h-SWNT–Nafion composites are shown. The filled boxes represent the as-cast SWNT–composite membranes and the open circles the platinized SWNT–Nafion composite membranes. Measurements were conducted using a standard four-point resistivity probe.

of 25 μm thickness were cast onto a Bytac substrate. After stabilizing for 24 h in air, the membranes were dried in vacuo (100 mTorr) at 70 °C for 30 min. The resultant membranes were then easily removed from the casting plate. The relationship between SWNT doping level and composite conductivity is shown in Figure 2. Interestingly, FESEM analyses indicate a factor of 5 reduction in bundle size for a 10% w/w SWNT–Nafion composite, correlating to a factor of 25 reduction in number of SWNTs per bundle as shown in Figure 3. In a random sampling of 25 different bundles within a single image, the average bundle size for the purified material was $56 \text{ nm} \pm 13$, while the average bundle size of the SWNTs within the polymer matrix was $11 \text{ nm} \pm 1$. This “debundling” will be advantageous for an increased homogeneous distribution of the SWNTs throughout the Nafion matrix. The extent of bundle size reduction will directly improve the membrane conductivity for the same mass dopings. Interestingly, Figure 4 illustrates the effect that polymer encapsulation also has on the optical spectroscopy response of the SWNTs. It is quite clear that the intensity of the first van Hove singularity is drastically reduced. Whether this is a debundling, polymer encapsulation, and/or charge transfer effect is not clear at this time. We expect that it is an extremely complex interaction which warrants further study but is beyond the scope of this letter.

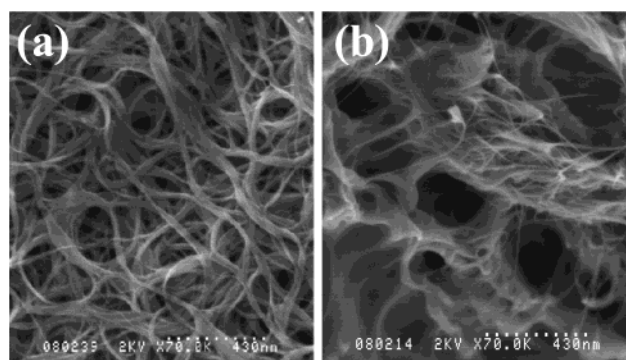


Figure 3. FESEM images depicting a 5-fold reduction in h-SWNT bundle diameter from (a) high purity, compared to (b) 10% w/w dispersion in Nafion.

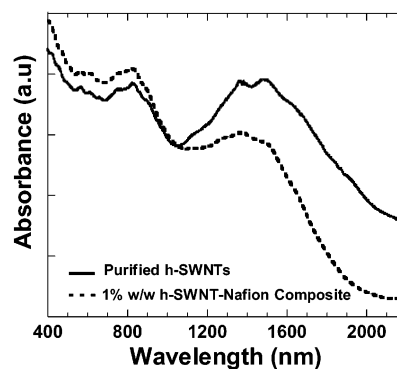


Figure 4. Overlay of the optical spectroscopy spectra for purified h-SWNTs and 1% w/w h-SWNT–Nafion composite with a Perkin-Elmer lambda 900 UV–vis–NIR spectrometer. Spectra were normalized at 1025 nm. A quench of the first van Hove singularity absorption intensity for the semiconducting SWNTs within the composite is evident at $\sim 1450 \text{ nm}$.

The analysis of the actuation properties of the SWNT–Nafion composite samples was accomplished utilizing a bimorph cantilever actuator apparatus.⁹ First, the composite membranes were cut to appropriate size strips of $25 \text{ mm} \times 4 \text{ mm} \times 25 \mu\text{m}$. To achieve a reproducible electrical contact to the membrane surface, the previously reported chemical reduction of platinum ions on the surface of the Nafion

membrane was utilized.^{3,6} Since high doping levels of metal ions can cause actuation in Nafion membranes,⁶ the platinization levels in this study were experimentally controlled to keep the platinum concentrations at 2–3% w/w, well below the doping levels (>30% w/w) necessary to cause independent Nafion actuation.⁶ The thin films were then immobilized on the parallel sides of an insulating 5 mm × 35 mm Kapton tape. After sealing the electrical contacts, the assembled electrodes were immersed into an aqueous 1 M LiCl solution. Lithium ions were chosen as the electrolyte cation because of the enhanced permeability of Nafion to the lithium as compared to other monovalent cations.⁶ A square wave excitation voltage ranging from ± 0.1 to ± 2.0 V was then applied to the electrodes with a stepping frequency from 1 to 50 Hz. The magnitude of actuation of the bimorph cantilever tip was determined with optical deflection analysis.⁹

The platinization of the composite films was achieved by first immersing the composite membrane into a 4 mM tetraamine Pt(II)Cl₂ solution.¹² The membrane was removed, washed, and reimmersed into a 0.1 M NaBH₄ 3:1 (distilled water/methanol) solution to reduce the Pt(II) to Pt(0). The anionic nature of the composite membrane and the kinetic control of the experiment limited the depth of penetration of the borohydride anion. After chemical reduction of Pt(II) to Pt(0), the membrane was thrice immersed for 1 h in 0.3 M HClO₄ acid solution. These washes removed residual Pt(II) ions and reconverted the Nafion membrane to the protonated form. This platinization process reproducibly resulted in a platinum penetration depth into the membrane on the order of ~0.1 microns as determined by FESEM. The resistivity of the films was a consistent 0.1 ohm·cm for platinized Nafion composites. Even though the nanotube-doped membranes with >5% w/w SWNTs resulted in films with high conductivity, they were platinized in order to maintain consistency in the experimental measurements.

Pure SWNT, SWNT–Nafion, platinized Nafion, and platinized SWNT–Nafion, as well as a series of control experiments with graphite–Nafion composite membranes, were all evaluated for their actuation properties. In the control experiments that included pure Nafion, platinized Nafion, graphite–Nafion, and platinized graphite–Nafion membranes, no actuation was observed. In the case of the graphite-doped Nafion systems, the maximum loading was the same as for the SWNT systems, 18% w/w. Another series of controls with various 5% w/w SWNT–polymer systems, prepared in a manner similar to that for the SWNT–Nafion composites, consisted of polyacrylonitrile, polyvinylbutryal, Eastman AQ-55, AQ-29, poly(4-vinylpyridine), poly(2-acrylamido-2-methyl-propane sulfonic acid), and polystyrene-*block*-poly(ethylene-*ran*-butylene)-*block*-polystyrene-sulfonate were also evaluated for actuation properties. None of these 5% w/w SWNT-doped polymer composites exhibited actuation properties in either aqueous or nonaqueous lithium electrolyte solutions. So it is clear from the observation that actuation occurs only for the SWNT–Nafion composites for which the increased conductivity necessary for the deformation of the polymer is caused by the efficient percolation of

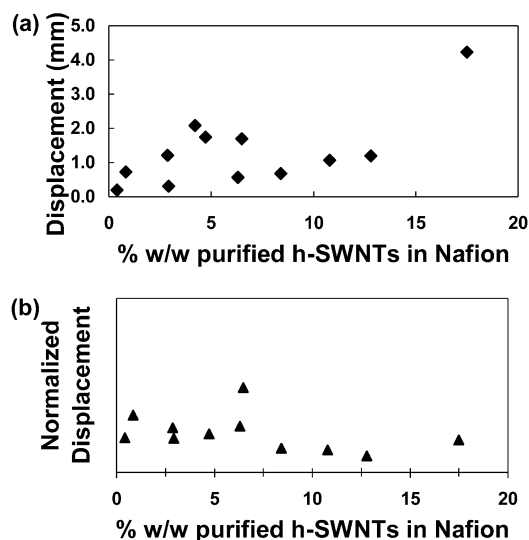


Figure 5. Actuation properties of the platinized h-SWNT–Nafion composite series. The magnitude of actuation of the bimorph cantilever tip was determined with optical deflection analysis: (a) cantilever tip displacement observed from a square-wave excitation voltage of ± 2V at a frequency of 1 Hz, (b) the displacement data in (a) normalized to the respective composite conductivity.

the nanotubes through the polymer matrix. It is also clear that it is possible to reach the actuation threshold at considerably lower doping levels when the SWNTs are used instead of metalization, 1% versus 30% w/w, respectively.

The actuation response for this complete range of h-SWNT doped polymer composites is illustrated in Figure 5a. For this series of h-SWNT weight percent doping levels, the deflection at the cantilever tip ranged from 0.2 to 4.5 mm for the 0.5–18% w/w composite at a ± 2.0 V bias, 1 Hz excitation, respectively. Unlike the metal-doped polymers, no relaxation of the cantilever tip was observed for the SWNT–Nafion composite actuators with SWNT doping levels greater than 1% w/w.⁶ When the cantilever tip deflection data for the h-SWNT–Nafion composite actuators was normalized to the composite membrane's conductivity, Figure 5b, it can be seen that the actuation response of the membranes was directly dependent on the doping level of SWNTs and conductivity of the Nafion matrix. As shown earlier, the electrical conductivity of SWNT–Nafion composite membranes is related to the SWNT doping level. This behavior illustrates the efficient percolation ability of the high aspect ratio SWNTs, which results in the actuation of the composite membrane. Most importantly, with SWNT dopants, the amount of dopant necessary to achieve the electrical conductivity threshold for Nafion actuation can be reached at extremely low weight percent levels as compared to metal dopings. Also, at the increased weight percent levels, the SWNTs dramatically enhance the membrane conductivities, corresponding to a markedly enhanced actuator deflection. Moreover, deflection values (1–2 mm) for the less than 5% w/w SWNT–Nafion platinized composites are comparable to reported metal-doped, 30% w/w Nafion actuators while the higher SWNT dopant level, 18% w/w, induces a significantly larger deflection, 4.5 mm.⁶

For comparison, Nafion composite membranes were also prepared using purified laser-generated single wall carbon nanotubes, 1-SWNTs. The material was produced and purified according to our previously reported procedures.^{11,13} The platinized 1-SWNT composite electrodes were constructed at 1 and 5% w/w doping. The membrane conductivities and cantilever tip deflections observed for these actuator systems were the same, within experimental error, as the measurements made of the platinized h-SWNT–Nafion composites.

To conclude, successful dispersion of high purity single wall carbon nanotubes (laser and HiPco) was achieved in the Nafion polymer at doping levels between 0.1 and 18% w/w. Apparent interactions between the SWNTs and Nafion matrix led to debundling of the purified SWNTs, enhancing dispersion of the tubes throughout the membrane. Due to the electrical conductivity of high aspect ratio SWNTs and the resulting efficient percolation pathways within the polymer composites, they exhibit superior performance as actuators when compared to metal-doped Nafion films. These SWNT composites should enable the production of high performance microactuators used potentially as MEM switches or artificial muscle fibers.

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