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Performance of nanocomposites stacked with carbon nanotubes and Nafion films

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ABSTRACT

Nanocomposites stacked layer-by-layer with carbon nanotubes (CNTs), referred to as CNT–Nafion^{TM}, are prepared using a spray and reproducible spin-cast deposition methodology. The CNTs used for the nanocomposite film were cylindrical with diameters in the range of 10–15 nm and lengths of up to several micrometers. The CNTs had a high purity of more than 95%. CNT–Nafion^{TM} nanocomposites with uniformly spray-coated CNTs provide sufficiently high electrical conductivity throughout, and show enhanced mechanical strength due to laterally aligned CNTs between each interface of the spin-coated Nafion film. Our results indicate that such a layer-by-layer film composed of CNTs and Nafion^{TM} is suitable for potential transducer applications at the microscale.

1. Introduction

Since their discovery in 1991 by Iijima [1], in addition to their various electronic properties depending on the crystalline orientation, carbon nanotubes (CNTs) have exhibited interesting mechanical properties [2,3]. Experimental studies and theoretical analyses have demonstrated that CNTs have a high Young's modulus, high conductivity, and flexibility. The outstanding properties of CNTs help overcome current problems with semiconductor devices based on silicon, and offer good potential for the development of an advanced composite material for transducer applications [4,5]. CNT–polymer actuators based on ion exchange membranes have been shown to have large displacements and rapid response even a low voltage below 5 V [6]. The behavior of these composites depends on many factors including the types of nanotubes used, their geometrical characteristics, and the concentration of CNTs in the composite. Two approaches are used in the development of CNTs-based composites. One approach is only focused on the fabrication of composites to enhance mechanical behaviors [7,8]. The other approach is related to the development of functional composites that have one or more properties that can be significantly changed in a controlled fashion by external stimuli such as stress, temperature, moisture, pH, electric fields, and magnetic fields [9–12]. The functional composites are much useful than the conventional composites for diverse applications of the material.

Various processing techniques at bulk scales have been widely studied in the research for further improvement of CNT–polymer actuators and sensors [13,14]. Most of the studies on CNT–polymer composites presented in the literature have focused on the dispersion of single-wall nanotubes (SWNTs) or multi-wall nanotubes (MWNTs) in the polymer matrix. This is because well-dispersed CNTs are needed to fully transfer the unique CNT properties to the polymer matrix. However, bulk CNTs that are embedded in the polymeric matrix tend to form aggregates that adhere poorly to the matrix and concentrate stresses, thereby compromising the effect of using CNTs as reinforcements. García et al. manufactured CNT–polymer composites by using wetting to grow arrays of vertically aligned CNTs [15]. Their experimental results support the feasibility of using these CNT arrays in large-scale hybrid advanced composite architectures. On the other hand, laterally aligned CNTs within a composite matrix also offer significant potential to harness the properties of nanocomposites at bulk scales. Yoon et al. proposed an imprint technique to localize CNTs laterally on the surface of a polymer sheet [16]. However, this technique is not applicable in many industries at present because the method requires the solvent evaporation process.

In this work, we propose new CNT–Nafion nanocomposites that are manufactured using spray and spin-cast methods. The spray method not only preserves the alignment of CNTs in the lateral direction on the surface of the Nafion films, but also allows easy dispersion of the CNTs into Nafion-based nanocomposites for transducer applications. In addition, we present a direct characterization of the mechanical properties of nanocomposite structures. Our enhanced mechanical reinforcement results support the feasibility of using these CNT arrays in various applications at the microscale. Such nanocomposites will also benefit from enhancements of multifunctional properties (e.g., electrical conductivity) due to the lateral alignment of the CNTs.

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2. Experimental details

MWNTs (>95% purity) with an average diameter of about 15 nm were purchased (Iljin Nanotech Ltd., Korea). The reason for choosing MWNTs is that they easily conduct electricity and their dispersion is comparatively easy due to their much lower absorption energy compared to that of SWCNTs. Furthermore, the price of MWNTs was much lower than the price of SWCNTs even though the MWNTs had better purity. A stock solution (SS) containing 1% by weight of sodium dodecyl benzene sulfonate (SDBS, Sigma–Aldrich Ltd.) in deionized (DI) water was used to prevent the re-aggregation of CNTs through van der Waals forces. 50 mg of CNTs was added to 500 ml of the SS. The CNT solution was tip-sonicated (ULH-700s, Ulsso Hightech Ltd.) at 700 W and 20 kHz for 13 h at 80% power output. Then, the sample was serially diluted by a factor of two, down to 1×10^{-3} mg/ml. Thus, the surfactant concentration was kept constant while that of the CNTs was serially reduced. The tip-sonication process was repeated for further dispersion of the CNTs in the SS, while the other solution was used to generate the next concentration. The entire set of samples produced by the dilution process was then bath-sonicated for 12 h. After the tip sonication process, all the SSs were purified using high-speed centrifugation at 150,000 rpm (HM-150IV, HNK Scientific Centrifuge Ltd.) for 1 h. This process was very effective in removing metallic catalyst particles from the SS containing the CNTs. A porous anodic aluminum oxide (AAO) filter (Anodisc 47, Whatman International Ltd.) was used to collect CNTs from the SS. The obtained CNT films were immersed in a sodium hydroxide solution for 1 hr to dissolve the AAO filter; they were then rinsed with DI water for 30 min. The floating CNTs were dispersed again in DI water using the tip sonicator for 3 h. Fig. 1(a) shows a schematic of a representative three-dimensional (3-D) element with well-dispersed CNTs using a spray method. Both the spray (CNTs) and spin-coating (Nafion film) processes were repeated to form stacked nanocomposites.

Fig. 1(b) shows the process flow for the fabrication of CNT–Nafion nanocomposites. After a silicon wafer was cleaned using standard cleaning processes, an Al layer was deposited on the wafer surface using an electron beam evaporator. The Al layer was used as a sacrificial layer because Al is easily etched by a buffered HF solution. Nafion solution (20 wt.%) obtained from Sigma–Aldrich was spin-coated on the wafer at 1000 rpm and then baked on a hot plate for 15 min at 105 °C. The parameters associated with spin speeds and layer numbers were important in determining the thicknesses of the nanocomposites. The measured thicknesses and weights for the spin-coated Nafion films are shown in Fig. 2(a) and (b). After our primary experiments with the Nafion solution, the prepared CNT solution was directly sprayed on the spin-coated Nafion layer. To avoid the recombination of CNTs on the surface, the CNTs were sprayed at intervals of several seconds, and the distance between the sample and mini-compressor was about 200 mm. Fig. 2(c) shows scanning electron microscope (SEM) and atomic force microscope (AFM) images of CNTs with a surface roughness R_a of about 10 nm. The comparatively homogeneous dispersion of CNTs on the Nafion film can be clearly identified, and serious aggregation or bundling of CNTs due to van der Waals forces was absent. The spin-coating and spray processes were repeated under the same conditions until the desired thickness of the nanocomposite was obtained.

3. Results and discussion

The mechanical performance of the CNT–Nafion nanocomposites was evaluated by measuring the displacement and the maximum force. In this experiment, eight different samples were prepared as described in Table 1. The displacements of the nanocomposites were measured with respect to time under 3 V_{ac} at various frequencies. When the external voltage was applied to the nanocomposite actuator, bending occurred toward the anode at a level that increased as the voltage increased until reaching saturation. Under alternating current (AC) voltage, the actuator underwent a swing movement and the displacement level depended on both the voltage magnitude and the driving frequency. In general, actuation at lower frequencies induced higher

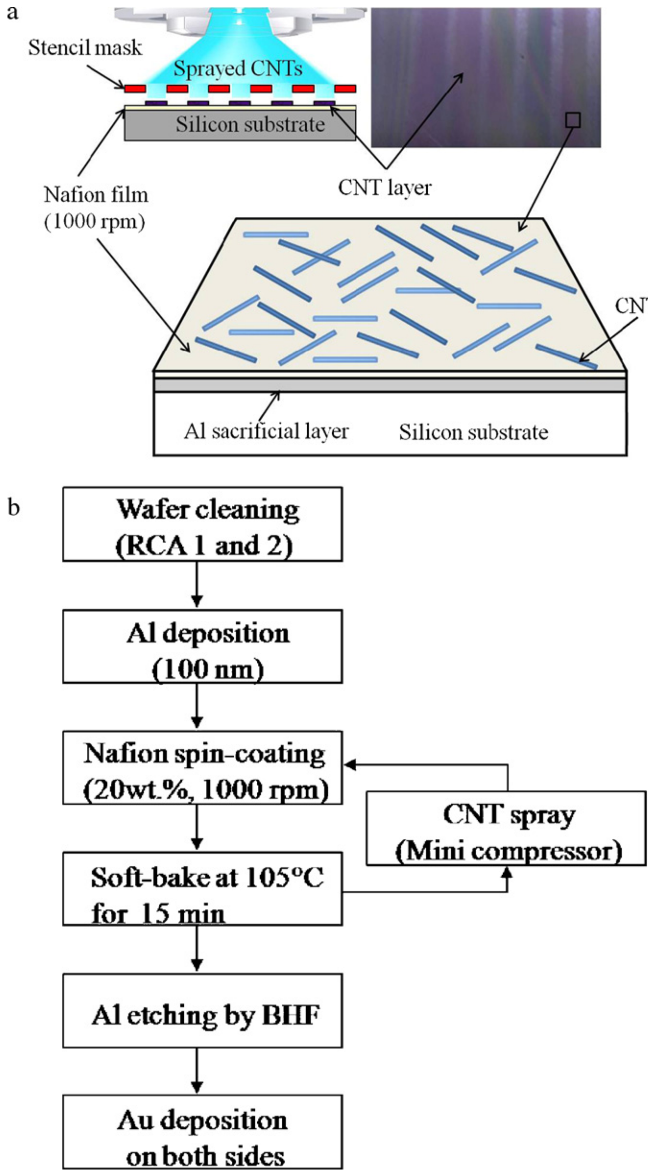

Fig. 1. (a) Schematic of a representative 3-D element with well-dispersed CNTs using the spray method. (b) Process flow for the fabrication of layer-by-layer CNT–Nafion nanocomposites.

Table 1
Processing conditions for various samples.

	wt.% of CNTs	Number of Nafion layers	Number of CNT layers
No. 1	0	4	3
No. 2	0.1	4	3
No. 3	0.5	4	3
No. 4	1	4	3
No. 5	2	4	3
No. 6	5	4	3
No. 7	1.5	4	2 (both surface layers)
No. 8	1.5	4	2 (interface layers)

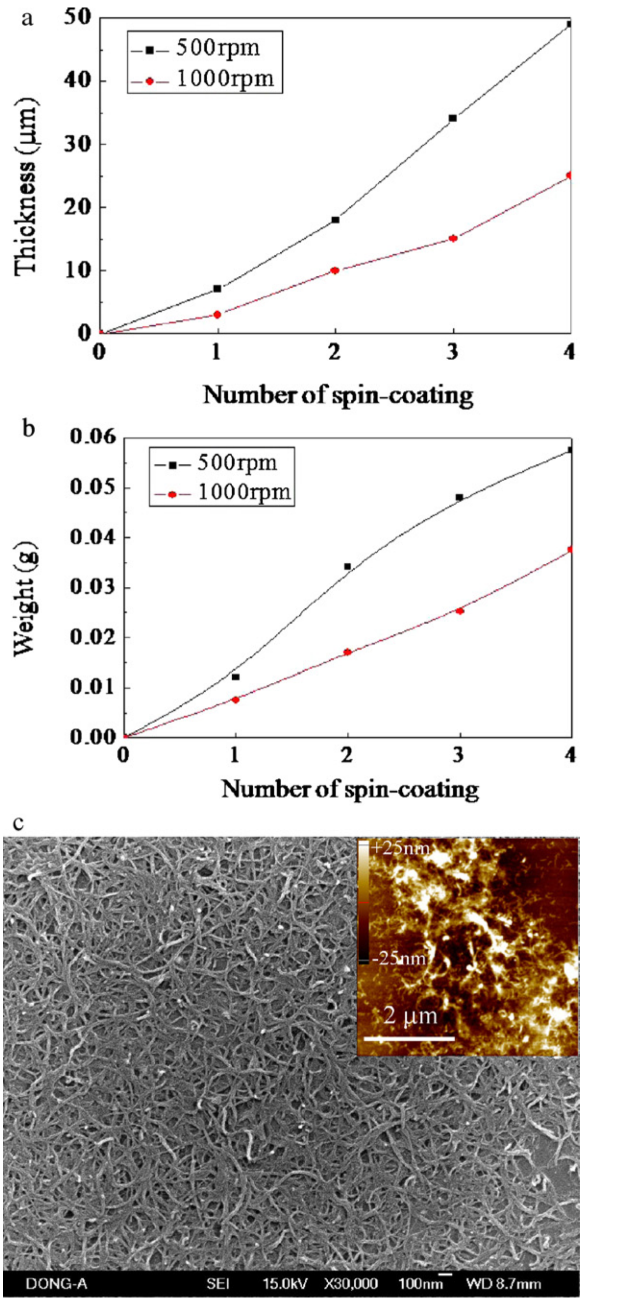

Fig. 2. Variations in (a) thickness and (b) weight as a function of spin speed and spin-coating number. (c) Scanning electron microscope image of well-distributed CNTs (inset: AFM image of CNTs with a surface roughness of about 10 nm).

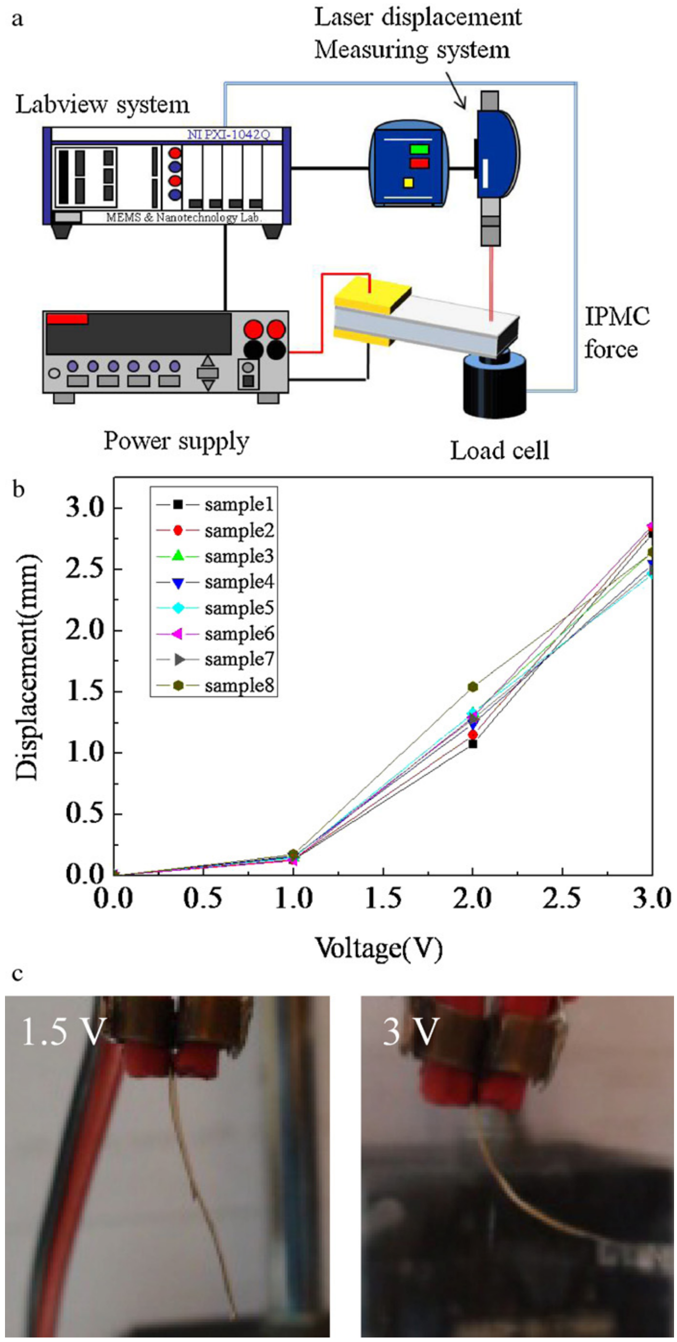

Fig. 3. (a) Experimental setup for the force measurement, (b) displacement of CNT–Nafion nanocomposites as a function of the driving voltage and (c) optical microscopic images of the actuating cantilever at various voltages.

displacement, and the displacement diminished as the frequency increased. A slight difference in displacement could be observed in the experiments, and the maximum displacement of the actuator was observed at the resonance frequency.

Fig. 3(a) shows our experimental setup for the precise measurement of actuator displacement. The composite actuators were vertically supported in air and were fixed at a length of 5 mm on both sides. The actuator displacement was defined as the maximum displacement when the actuators were under an electrical potential for a period of several seconds. As shown in Fig. 3(b) and (c), the deflection at the cantilever tip ranged from 0 mm to 3 mm for the various nanocomposites. These results show that the variation in the displacement of different nanocomposites with various CNT concentrations would be negligible for actuator applications at the microscale. The maximum force generated under DC voltage was measured using a small load cell. The tip force was defined as the maximum force value that occurred when a given electric potential was applied to the nanocomposite for several seconds. The total thickness of the CNTs layers used in the experiment was less than 300 nm, which is not compatible with the total thickness of the nanocomposites. Hence, there was no significant change in the total thickness that could be expected, even if we were to increase the CNT concentration. The lateral alignment was also clearly confirmed through all samples. Fig. 4(a) shows the tip forces of the CNT–Nafion nanocomposite with various structures when a DC voltage of 3 V was applied. The maximum force was slightly enhanced with an increase in the CNT concentration. These tip-force experiments clearly show that the generating force

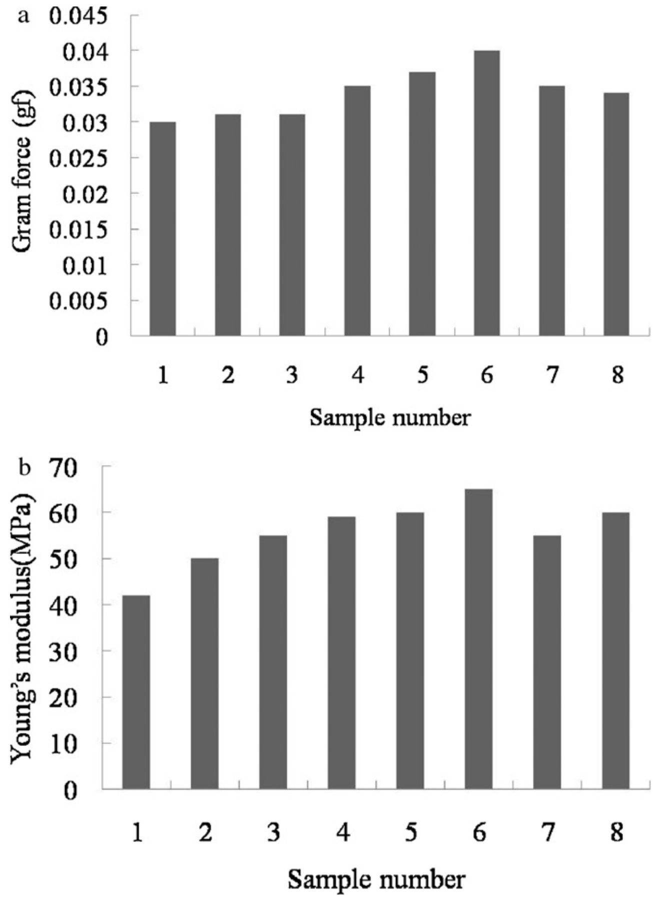

Fig. 4. (a) Young's modulus, and (b) maximum force for various CNT–Nafion nanocomposites.

was proportional to the number of stacked CNT layers. When the number of stacked CNTs increased, the bending stiffness was also enhanced, which was due to the effect of the lateral alignment of CNTs with high conductivity.

The aforementioned characteristics allow nanocomposites to be used for various actuator applications at the microscale. To calculate Young's modulus of the nanocomposites, one end of each nanocomposite with a cantilever structure was fixed, and an external load was applied to the other end using a load cell. The force applied to the cantilever (under no electrical potential) was obtained by bending the cantilever structure. We also determined the deflection of the cantilever based on the CNT–Nafion nanocomposite using a laser displacement system. Young's modulus of the nanocomposite is expressed as $(4FL^3)/(\delta bh^3)$ where F is the applied force, L is the length of the beam, b is the width, h is the thickness, and δ is the measured tip displacement of the nanocomposite actuator. This equation was based on the Roark's Formulas for Stress and Strain [17], which describes the relationship between the forces and displacements of cantilever structures. The measured Young's moduli of the nanocomposite actuators with various structures are shown in Fig. 4(b). As expected, Nafion film by itself had the lowest Young's modulus, and this value increased as the CNT concentration increased. In our original process for preparing CNT–Nafion nanocomposites, we pre-treated the CNTs in DI water using a sonication bath. However, we found that the effect of this step on the final electrical performance of the nanocomposites was not clear. Therefore, it appears to be possible to skip this process when evaluating the electrical properties. After the Au deposition process, the surfaces of the two sides of the specimens were covered with a silver paste layer to ensure good contact of the sample

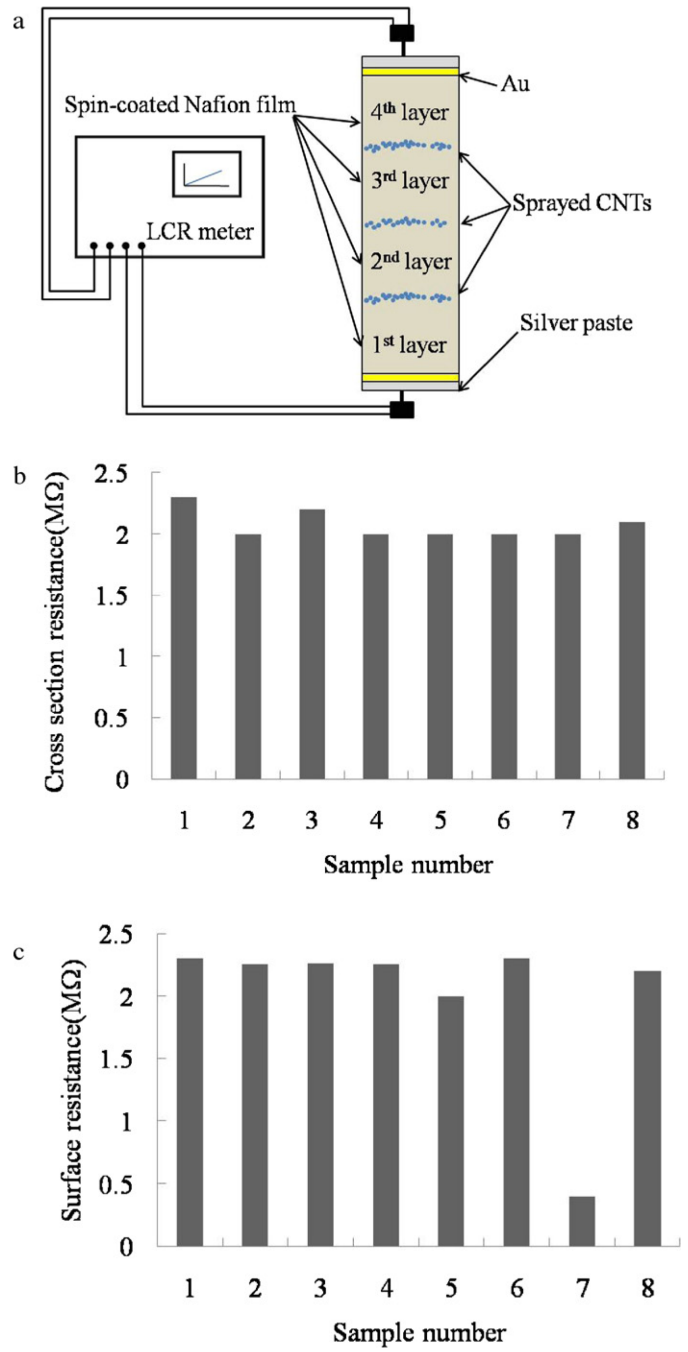

Fig. 5. (a) Schematic of samples for examining the distribution and anisotropy of electrical properties, (b) surface resistance, and (c) cross-sectional resistance of various nanocomposites.

surface with the Au electrodes. Copper wires of 100 μm diameter were used to make a good connection between the sample and the measurement systems. The conductivity of the composites was measured in dry air at the ambient temperature with a four-point resistance measurement method using an inductance, capacitance, and resistance (LCR) meter (SR720, Stanford Research Systems) as shown in Fig. 5(a). The four probes consisted of two outer current probes and two inner voltage probes; these were used to remove the contact resistance between the sample and the probes. The measured resistance R refers to the sample resistance between the inner probes. Our experimental results for the cross-sectional resistance and surface resistance of various nanocomposites are shown in Fig. 5(b) and (c), respectively. These results reveal that the electri-

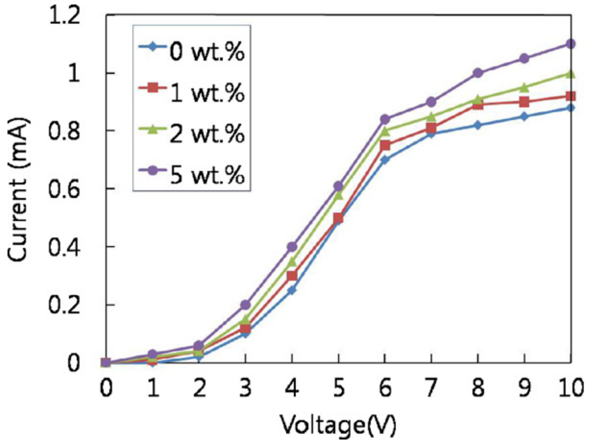

Fig. 6. Current vs. voltage characteristics of the fabricated nanocomposites.

cal conductivities along the two in-plane directions (i.e., the *x* and *y* directions) were identical and slightly higher than those along the thickness direction (i.e., the *z* direction). No significant change in the cross-sectional resistance was observed across all the samples. From these results, the isotropy and uniformity of the electrical properties of the nanocomposites can be nearly ensured.

The resistance distribution along the length of the nanocomposite was investigated in order to examine the induced gradient in the electric field. If the surface electrode has a large surface resistance, the cations and solvent molecules inside the nanocomposite will move toward the outer electrodes connected to the power supply due to the induced gradient in the electric field. As shown in Fig. 5c (Sample No. 7), the surface resistance was dramatically decreased due to the well-dispersed CNTs on the Nafion film. The maximum and minimum resistance values on the surface of the nanocomposite were within 5% of each other. This means that the electrical field over the entire surface of the nanocomposite was almost constant. Therefore, solvent molecules will mostly move up and down through the thickness. The relationship between the CNT doping level and current-to-voltage characteristics is shown in Fig. 6. The electrical resistance along the thickness direction of the nanocomposite was decreased slightly by increasing the CNT concentration.

4. Conclusion

The successful dispersion of high purity MWNTs was achieved in deionized water at doping levels between 0.1 and 5 wt.%. Well-dispersed CNTs were sprayed to localize CNTs at the interface of the spin-coated Nafion layer. The layer-by-layer nanocomposites stacked with CNT–Nafion generally consisted of more than seven layers. The nanocomposite was able to bend the curvature by moving ions through electrical conduction. The electrical and mechanical behaviors of the nanocomposites were successfully evaluated with four-point probes and a load-cell, respectively. Our results showed that the nanocomposites could be very suitable for actuator applications at the microscale. The biological compatibility of CNT–Nafion actuators coated with a thin parylene layer was also an advantage compared to that of silicon-based microactuators.

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Biographies

Suk-Min Cho received the MSc degree in mechanical engineering from Chonnam National University, South Korea with a focus on nanocomposites for biomedical applications. He is currently a Researcher at the MEMS and Nanotechnology Laboratory. His research interests include the design and performance characterization of micro/nano transducers, and applications of nano-materials based on functionalized devices.

Dong-Weon Lee has been a Professor of Mechanical Engineering at Chonnam National University, South Korea since March of 2004. Previously, he was with the IBM Zurich Research Laboratory in Switzerland, working mainly on microcantilever devices for chemical AFM applications. At CNU, his research interests include the evaluation of new materials and structures for MEMS, advanced high-sensitivity microsystems, and nanotransducers. He is a member of the technical program committee of IEEE Sensors and MNC (Microprocesses and Nanotechnology Conference) conferences.