DNA-coated MWNT microfibers for electrochemical actuator

Su Ryon Shin[a], Chang Kee Lee[a], Tae Won Eom[a], Sung-Ho Lee[a], Cheong Hoon Kwon[a], Insuk So[b,*], Seon Jeong Kim[a,**]

[a] Center for Bio-Artificial Muscle and Department of Biomedical Engineering, Hanyang University, Seoul 133-791, Republic of Korea
[b] Department of Physiology, Seoul National University, Seoul 110-744, Republic of Korea

ARTICLE INFO

ABSTRACT

The deoxyribonucleic acid (DNA)-coated multi-walled carbon nanotube (MWNT) hybrid fibers were fabricated by wet-spinning method. The fibers were made up with entangled nanowire networks of DNA-coated MWNTs, and it shows a strain of ~0.15% as electrochemical actuators under low potential cycling between 0 and −0.9 V versus Ag/AgCl in 2 M NaCl solution. The fibers also show good electric conductivity (~60 S/cm) and capacitance (50 ± 5 F/g) behaviors. Based on the appropriation of its electro-chemo-mechanical systems, the DNA/MWNT fiber can be one of the new intelligent materials for biomedical application.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Biomolecules are combined with several nanostructures, and these materials can be possible to form multifunctional hybrid materials. DNA is considered as one of the representative hybrid materials with carbon nanotube (CNT) in material science and technology because there is strong affinity between DNA and CNT [1,2]. This DNA–CNT system offers unique properties such as good electrical conductivity, and it is applicable to several electrochemical actuators, especially in biomedical fields.

The multi-walled carbon nanotube (MWNT) can offer a greater choice for electro-chemo-mechanical systems design because it observes high purity, is not subject to the chirality-related restrictions on electrical properties, is generally amenable to more aggressive processing, and is significantly cheaper than single-walled carbon nanotubes (SWNTs) [3,4]. However, bare MWNTs have a high surface energy and strongly attractive van der Waals forces, and tend to aggregate or sinter in solution. This aggregation can be prevented by protecting nanocomposites via steric/electrostatic stabilization by biomolecules such as DNA on a nanotube surface [5]. The biomolecules coating layer also makes MWNTs softer and more deformable as a surfactant, allowing their assembly to be manipulated. This structure can generate useful electrical and mechanical properties by combining two distinct inherent properties of DNA and MWNT. Herein we describe a method for preparing nanowire networks composed of DNA-coated MWNTs, and the observation of a simultaneous electrochemical actuator and capacitor.

2. Experimental

2.1. Materials

The thin MWNT (CMP-310F, 3–5 nm diameter, 10–20 μm length) were purchased from Hanwha Nanotech (Korea). The DNA (double strand, salmon sperm, 10,000 bps), ethanol, NaCl, and HNO$_3$ used were purchased from Sigma Chemicals (USA).

2.2. Fiber preparation

To prepare the spinning solution, DNA (0.3 wt%) was dissolved in deionized water for 30 min. MWNTs (0.7 wt%) were then added to this solution, which was sonicated for 1 h to obtain a black ink-like solution. The DNA/MWNT fibers were prepared by the wet spinning method. A narrow jet of spinning solution was injected through a 16-gauge diameter needle at a feed rate of 650 μl/min into a coagulation bath containing 0.3 M HNO$_3$/ethanol (volume ratio = 9:1), which was rotated at 15 rpm. The coagulation time was about 30 min. The coagulated fibers were finally washed several times in deionized water and ethanol alternately.

2.3. Characterization

The structure of the DNA/MWNT fibers was examined with an SEM (Hitachi Model S4700, Japan) and an HRTEM (Philips CN30,

* Corresponding author. Tel.: +82 2 740 8228; fax: +82 2 763 9667.
** Corresponding author. Tel.: +82 2 2220 2321; fax: +82 2 2291 2320.
E-mail addresses: insuk@plaza.snu.ac.kr (I. So), sjk@hanyang.ac.kr (S.J. Kim).

USA). All CD spectra were recorded on a Jasco-810 spectropolarimeter equipped with a programmable temperature control unit. The conductivity of the fibers was determined using a homemade four-probe conductivity cell operated at constant humidity (50%) and temperature (20 °C). The electrodes were circular pins with 0.2 cm separation, and the fibers were connected to the pins using silver paint. A constant current was applied between the two outer electrodes using a potentiostat/galvanostat (EDAQ). The potential difference between the inner electrodes was recorded using a digital multimeter (Agilent 34401A). A three-electrode electrochemical cell coupled to a CHI 600B potentiostat (USA) was used for the cyclic voltammetry and actuator tests. A hybrid fiber was used as the working electrode with a Ag/AgCl reference electrode and a Pt mesh counter electrode.

For actuator testing, the sample was held vertically in the electrochemical cell with the bottom end of the fiber firmly clamped and the top end connected to the lever arm of a dual mode force sensor/controller (Aurora Scientific) with an AD Instruments MacLab interface. The fibers were allowed to equilibrate for several hours under a desired tensile load in a 2 M NaCl solution. The specific capacitance, C_{mass}, was derived from the current plateau (at +0.6 V), I, at a given scan rate, ν, and the weight of the DNA/MWNT fiber, m (where $C_{mass} = I/(\nu \times m)$). The mechanical tests were performed with the fibers submerged in a 2 M NaCl electrolyte using a dual mode force sensor/controller.

3. Results and discussion

As we reported in our previous work, a double-stranded DNA (dsDNA) is a good ion-conducting binder for improved electrical conductivity and mechanical stability for electrochemical devices with SWNTs [1]. DNA is known to effectively coat, separate, and solubilize SWNTs better than other surfactants because of the large surface area of its phosphate backbone, which interacts with water, and because there are many bases in dsDNA that can bind to SWNTs [6]. In the present study, we used the B-form duplex dsDNA structure with a positive band near 275 nm, a negative band at 247 nm, and a crossover at 260 nm (Fig. 1(c)) [7]. The dsDNA bound to the MWNT sidewall still showed distinct characteristics of the B-form duplex structure, more like the circular dichroism (CD) spectrum of neat dsDNA. An assembly of dsDNA molecules in water probably has a spongy spherical structure [8], and such agglomerated dsDNA molecules gradually disentangle into individual dsDNA molecules and adhere onto the surface of MWNTs. The state of the MWNT (Fig. 1(a)) and the monodispersed DNA-coated MWNTs were observed by high-resolution transmission electron microscope (HRTEM) (Fig. 1(b)). The diameter was ~15 nm, which is expected for an individual thin MWNT (diameter: 3–5 nm) efficiently coated with several DNA strands (the diameter of double-stranded DNA was 2.3 nm) through π-stacking on the surface of the nanotubes. Such thin-layered DNA assemblies will effectively interact with the MWNT, and therefore DNA molecules probably modify the surface electronic states of the MWNTs.

The DNA-coated MWNT dispersion was readily obtained as a black-ink solution was stable, without any observable aggregation. DNA can prevent aggregation of MWNTs by steric or electrostatic stabilization that can be used in aqueous solutions where MWNTs become charged and/or surrounded by a hydration layer, which again prevents their coalescence. As in the previous work [9], the randomly entangled network of dsDNA was denatured and condensed without dissolving by protonation in the acid conditions (pH < 2). The acid medium is known to effectively decrease its solubility for randomly entangled networks of dsDNA. Therefore, the DNA-coated MWNTs exhibited solidification in the acid coagulation bath (pH < 1), where the water molecules were repelled from most of the phosphate groups in the DNA because of excess
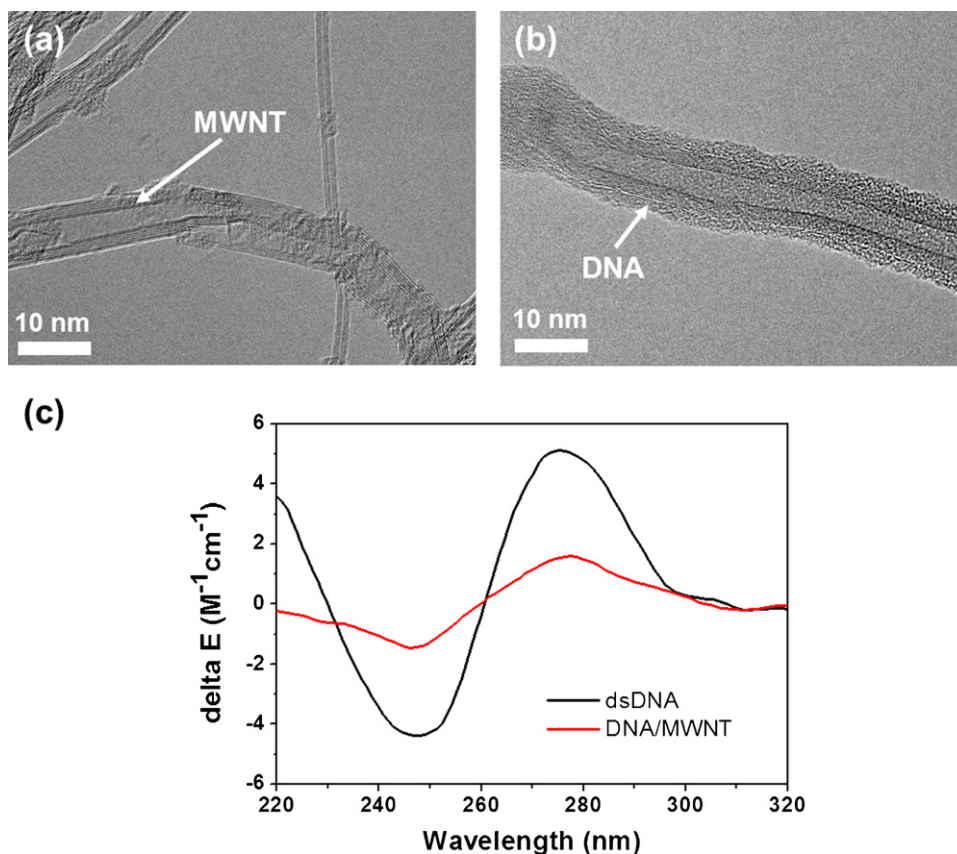

Fig. 1. HRTEM image of MWNT (a) and individual DNA-coated MWNT. (b) Comparison of CD spectra for double-stranded DNA (dsDNA) and DNA-coated MWNT.
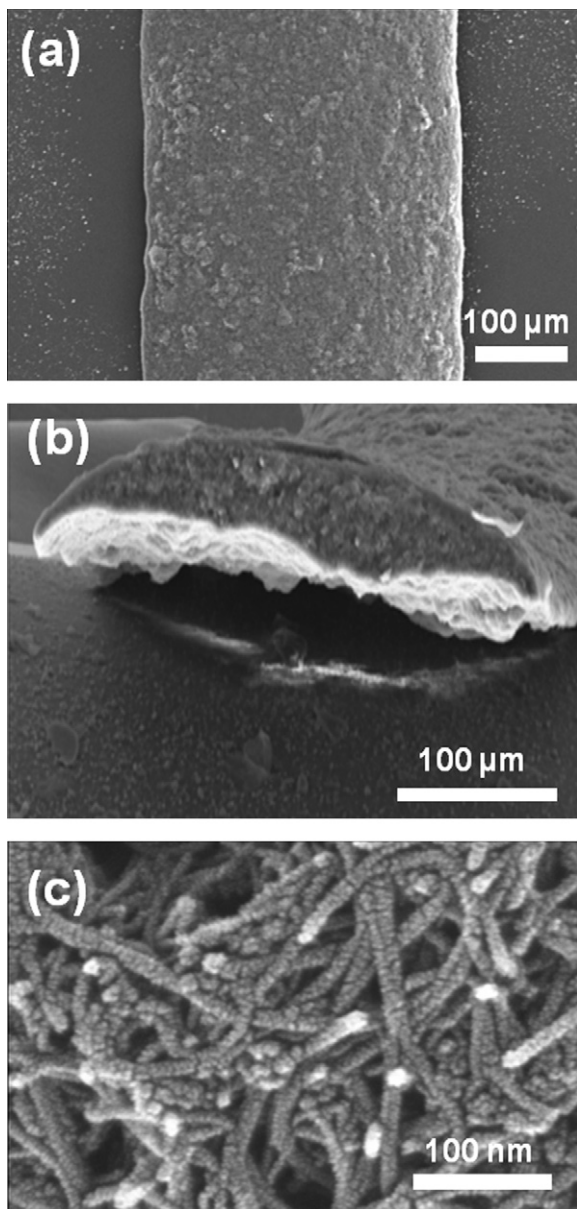
Fig. 2. (a) SEM images of DNA/MWNT microfibers coagulated in HNO$_3$/ethanol. (b) The cross section of the DNA/MWNT fiber. (c) Surface morphology of DNA/MWNT fiber.
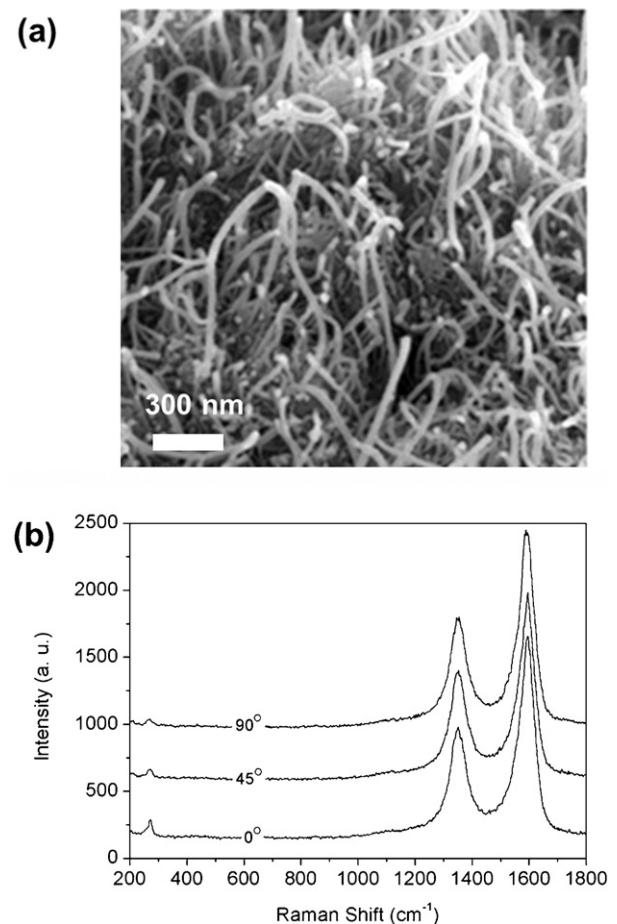

Fig. 3. (a) Orientation of DNA-coated MWNTs shown in the cross section. (b) Polarized Raman spectra of a randomly oriented DNA/MWNT fiber with the fiber axis at 0°, 45°, and 90° with respect to the excitation polarization direction.

protonation (phosphate group pK$_a$ = 1.2)[10]. The excess protonation was destroyed of electrostatic stabilization generated by the loss of charge and/or being surrounded by a hydration layer. Consequently, the dispersed solution of DNA-coated MWNTs was injected in a coagulation bath of 0.3 M nitric acid and ethanol. The fiber formed by consisting of an entangled nanowires network, which showed porous structure with a density of ∼0.81 g/cm^3. The free-standing DNA/MWNT fiber was shown ellipse shape to be typically (350 μm, semimajor axis length and 100 μm semiminor axis length) in Fig. 2(b), and exhibited flexibility (Fig. 2(a)). The morphology of the DNA/MWNT fiber surface was shown in (Fig. 2(c)), and DNA and MWNTs composites are well-aligned each other with a diameter of ∼20 nm.

To confirm the degree of orientation of the MWNTs within the DNA/MWNT fibers, we used polarized Raman spectroscopy (Fig. 3(b)). These generally exhibit three groups of peaks: the inner diameter of MWNTs from their radial breathing modes just near 271 cm^{-1}, the disorder-induced D-band centered at 1352 cm^{-1},

and the tangential G-band modes with peak at 1595 cm^{-1}. Note that the intensities of all three features exhibit the same orientation dependence. Because the MWNTs in the fibers exhibited anisotropic polarization, the ratio of the intensity of the G-band (excitation and detection in the same polarization plane) provides a useful probe of the relative degree of alignment, and decreases continuously as the angle between the nanotube axis and the direction of polarization increases. However, Fig. 3(b) shows almost the same G-band intensity as the angle on the fibers. Consequently, this result indicated that the MWNTs in the hybrid fibers were randomly oriented to the fiber axis. A closer view on the cross section of the fiber (Fig. 3(a)) showed a well-resolved network of DNA-coated MWNT nanocomposites. The mechanically entangled DNA-coated MWNTs nanocomposites were preferentially oriented in the plane of the film, although their arrangement within the plane was random.

The combination of DNA as ion-conducting binder and MWNT electron system allows free transport of ions between the nanotubes and an external electrolyte. Fig. 4(a) shows considerably rectangular shapes, which is indicative of the capacitive behavior of carbon materials, and indicated that the high electrical conductivity is maintained in the swollen state. This rectangular CV shape represents the rapid response of current to changes in potential, which is essential to ensure optimum energy storage during the fast charge and discharge processes. A pair of broad redox peaks associated with the bonding of the phosphate groups or DNA base pairs through π-stacking charges along the nanotubes[11] is apparent, but the CV is dominated by the double-layer capacitance at the MWNT−electrolyte interface. Additionally, the anodic current peak
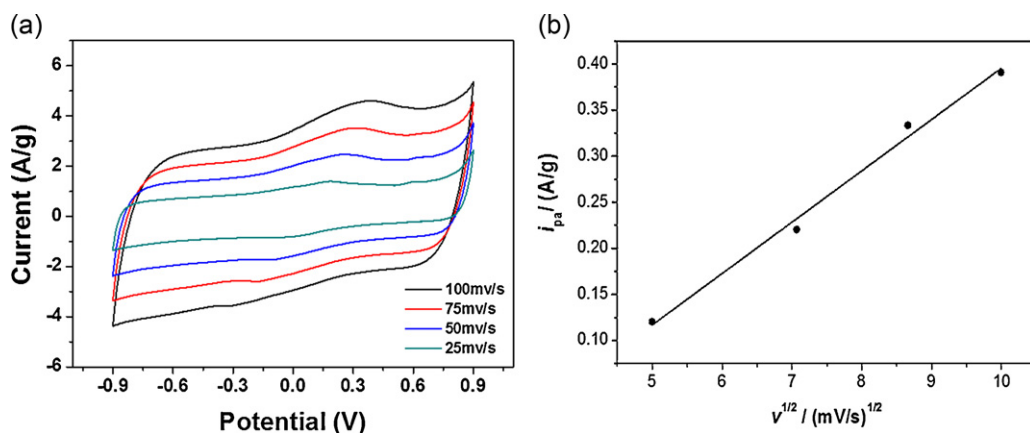
Fig. 4. (a) Cyclic voltammogram of a DNA/MWNT fiber film during potential cycling (scan rate = 25 mV/s, electrolyte: 2 M NaCl aqueous solution). (b) Potential scan rate versus peak anodic current, I_{pa}, for the DNA/MWNT fiber.

is proportional to the square root of the potential scan rate as predicted by the Randles−Sevcik equation for a diffusion-controlled electrochemical process (Fig. 4(b)) [12]. This result indicated that DNA was strongly bound to the MWNT surface. A linear relationship showed that there was no transition in the mass transfer regime on the explored timescale. In the case of electron hopping between redox sites homogeneously distributed in an isotropic medium, a proportionality of the peak current with the square root of scan rate was expected, since hopping can be assimilated to a diffusion process. Therefore, π–π interactions between the DNA and the walls of the MWNTs provide a medium for facilitating electron transfer.

Double-layer charging injection is a particularly promising mechanism for nanotube actuation, wherein improved capacitor charging results in relatively large changes in covalent bond lengths [13]. The high affinity of DNA for MWNTs ensures that the MWNT bundles are separated into individual MWNTs. Immersion of the DNA-coated MWNTs into NaCl electrolyte produced a layer of Na⁺ ion water clusters at the negatively charged DNA/MWNT nanocomposite surface by condensation of monovalent counterions around the DNA phosphate group, and formed an energetically favorable charge-transfer complex [14]. When an electrochemical charge is injected onto the surface of the DNA/MWNT nanocomposite, the layer of ion water clusters in the double layer at the surface of the DNA-coated MWNTs becomes thicker than in the swollen state. The amount of charge that can be stored at the DNA/MWNT fiber/electrolyte interface from the electrolyte ions contributes to the quantum chemical and double-layer electrostatic effects

responsible for the actuation strain [11]. An average capacitance of 50 ± 5 F/g (where *g* is the joint weight MWNT) was found, and this value was considerably higher than that of previous 'pristine' MWNTs (~30 F/g)[15]. These results showed that the DNA binder is an excellent ion conductor, allowing the double layer charge to accumulate at the individual MWNT surface.

In Fig. 5(a), the strain profile of the DNA/MWNT fibers shows expansion by reduction and contraction in 2 M NaCl electrolyte solution. The actuation profiles indicate typical behavior of an MWNT actuator. To confirm the major effect generated by DNA as an ion-conducting binder, we measured the electrochemical activity in aqueous electrolytes applied by electric potential. The actuation properties of DNA/MWNT fibers were determined during square wave potential cycling between 0 and −0.9 V versus Ag/AgCl, at the scan rate of 25 mV/s in a 2 M NaCl solution under an isotonic stress of approximately 540 kPa (Fig. 5(b)). The DNA/MWNT fiber shows excellent actuation stability with an expansion/contraction joined by mechanical entanglement and van der Waals' forces at the area of contact [3], and this could be attributed to the highly interconnected morphology of the DNA/MWNT fibers, caused by the ion-conducting binder that mechanically stabilizes the MWNT assembly. Moreover, by increasing the concentration of Na⁺, the disentangled dsDNA induced tighter or more compact aggregation of the dsDNA by screening the PO_2^- groups and a higher density of ionic cross-links between the dsDNA and cations. This ionic cross-linked nanowire network of randomly entangled DNA-coated MWNTs with cations can improve
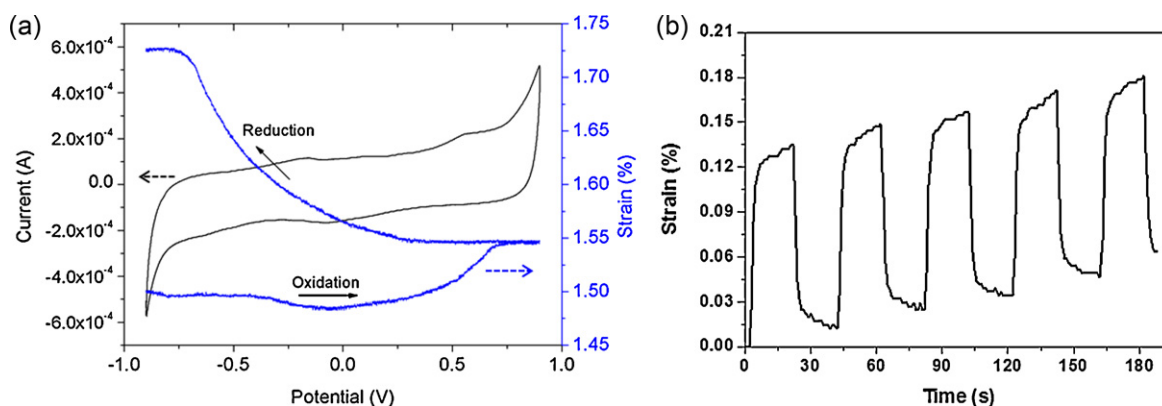

Fig. 5. (a) Strain versus potential (blue line) for DNA/MWNT fiber in 2 M NaCl during cycling voltammetry (black line) (between +0.9 V and −0.9 V versus Ag/AgCl, scan rate = 25 mV/s, electrolyte = 2 M NaCl aqueous solution, applied load was ~560 kPa). (b) Strain versus time of DNA/MWNT fiber with applied square wave voltage (between 0 V and −0.9 V versus Ag/AgCl, electrolyte was 2 M NaCl aqueous solution, applied load was 540 kPa). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

mechanical properties [16]. The robust DNA/MWNT fibers (MWNT content: 70 wt%) showed a strain of ∼0.15% under low potentials and this value compares favorably with previous MWNT tower.

This excellent actuation behavior is caused by the good electric/electrochemical properties of DNA-coated MWNTs. The fibers showed good electrical conductivity. The measured conductivity in DNA/MWNT fibers was ∼60 S/cm. Electron transport in MWNT networks is determined by conduction within the MWNTs and between nanotubes at junction points. This high conductivity can be attributed to the highly interconnected morphology of the ion-conducting binder that mechanically stabilized the MWNT assembly, reduced the overall junction resistance, and maintained electrical connectivity between nanotubes. In addition, the DNA has electrical characteristics similar to semiconducting diodes, in that current flows in only one direction [17]. The semiconducting nature of the DNA may be also lower the junction resistance because of the tunneling effect arising from π–π interactions between the DNA and the walls of the nanotubes[18].

4. Conclusion

We demonstrated conducting and electrochemically active nanocomposites formed by assembly of DNA on the surface of MWNTs. The improved electrical conductivity was attributed to the highly interconnected morphology of the ion-conducting binder reducing the junction resistance. As a result, the DNA/MWNT fibers showed good actuation performance with improved electrostatic double layer capacitance effect by the DNA-coated MWNT assembly. The DNA was also effective in acting as a mechanical binder when immersed by ionic interaction in liquid electrolytes. Their electrically conductive network is useful as biological electrodes facilitating electron transfer between electrolyte/DNA-coated MWNTs. Consequently, the DNA/MWNT fiber possessing good electrical, strain, and capacitance behavior would produce a useful electro-chemo-mechanical system, and could be the basis for new intelligent materials for biomedical applications.

References

[1] S.R. Shin, C.K. Lee, I.S. So, J.H. Jeon, T.M. Kang, C.W. Kee, et al., DNA-wrapped single-walled carbon nanotube hybrid fibers for supercapacitors and artificial muscles, Advanced Materials 20 (2008) 466.
[2] R.R. Johnson, a.T.C. Johnson, M.L. Klein, Probing the structure of DNA–carbon nanotube hybrids with molecular dynamics, Nano Letters 8 (2008) 69.
[3] M. Hughes, G.M. Spinks, Multiwalled carbon nanotube actuators, Advanced Materials 17 (2005) 443.
[4] J. Chen, a.I. Minett, Y. Liu, C. Lynam, P. Sherrell, C. Wang, et al., Direct growth of flexible carbon nanotube electrodes, Advanced Materials 20 (2008) 566.
[5] Y. Min, M. Akbulut, K. Kristiansen, Y. Golan, J. Israelachvili, The role of interparticle and external forces in nanoparticle assembly, Nature Materials 7 (2008) 527.
[6] J.C.G. Jeynes, E. Mendoza, D.C.S. Chow, P.C.P. Watts, J. McFadden, S.R.P. Silva, Generation of chemically unmodified pure single-walled carbon nanotubes by solubilizing with RNA and treatment with ribonuclease A, Advanced Materials 18 (2006) 1598.
[7] D. Liu, S. Balasubramanian, A proton-fuelled DNA nanomachine, Angewandte Chemie (International Ed. in English) 42 (2003) 5734.
[8] H. Takahashi, S. Numao, S. Bandow, S. Iijima, AFM imaging of wrapped multiwall carbon nanotube in DNA, Chemical Physics Letters 418 (2006) 535.
[9] S.H. Lee, C.K. Lee, S.R. Shin, S.I. Kim, I. So, S.J. Kim, The peculiar response of DNA hydrogel fibers to a salt and pH stimulus, Macromolecular Rapid Communications 30 (2009) 430.
[10] G.M. Segers-Nolten, N.M. Sijtsema, C. Otto, Evidence for Hoogsteen GC base pairs in the proton-induced transition from right-handed to left-handed poly(dG-dC).poly(dG-dC), Biochemistry 36 (1997) 13241.
[11] S. Gupta, Charge transfer in carbon nanotube actuators investigated using in situ Raman spectroscopy, Journal of Applied Physics 95 (2004) 2038.
[12] T.K. Tam, M. Ornatska, M. Pita, S. Minko, E. Katz, Polymer brush-modified electrode with switchable and tunable redox activity for bioelectronic applications, Journal of Physical Chemistry C 112 (2008) 8438.
[13] Y. Bar-Cohen, Electroactive polymer (EAP) actuators as artificial muscles: reality, potential, and challenges, Society of Photo Optical (2004).
[14] A. Savelyev, G.a Papoian, Electrostatic, steric, and hydration interactions favor Na(+) condensation around DNA compared with K(+), Journal of the American Chemical Society 128 (2006) 14506.
[15] G. Arabale, D. Wagh, M. Kulkarni, I. Mulla, S. Vernekar, K. Vijayamohanan, et al., Enhanced supercapacitance of multiwalled carbon nanotubes functionalized with ruthenium oxide, Chemical Physics Letters 376 (2003) 207.
[16] C.K. Lee, S.R. Shin, J.Y. Mun, S.-S. Han, I. So, J.-H. Jeon, et al., Tough super-soft sponge fibers with tunable stiffness from a DNA self-assembly technique, Angewandte Chemie (International Ed. in English) 48 (2009) 5116.
[17] V. Bhalla, R.P. Bajpai, L.M. Bharadwaj, D.N.A.electronics, EMBO Reports 4 (2003) 442.
[18] G. Lu, P. Maragakis, E. Kaxiras, Carbon nanotube interaction with DNA, Nano Letters 5 (2005) 897.

Biographies

Su Ryon Shin has received her Ph.D. degree in 2009 at Hanyang University in Korea under professor S.J. Kim. Her research interests were development of DNA based molecular actuators or machines.

Chang Kee Lee has received his Ph.D. degree in 2009 at Hanyang University in Korea under professor S.J. Kim. His research interests were development of artificial muscles based on biofunctional hydrogels.

Tae Won Eom has received his B.S. degree in 2010 at Hanyang University in Korea, and his major was biomedical engineering.

Sung-Ho Lee is a researcher of the Creative Research Initiative Center for Bio-Artificial Muscle. His research interests include biofuel cells and biomaterials for implantable medical device.

Cheong Hoon Kwon is a research professor of the Creative Research Initiative Center for Bio-Artificial Muscle at Hanyang University. Her research is focused on enzyme-based high power biofuel cell, electrochemical actuation and analysis.

Insuk So is a professor at department of Physiology, Seoul National University. His research area of interests includes smooth muscles, ion channels, and electro physiology.

Seon Jeong Kim is a professor of Biomedical Engineering at Hanyang University, and director of the Creative Research Initiative Center for Bio-Artificial Muscle. His research interests include stimuli responsive hydrogels, fabrication of multifunctional fibers using electrospinning and wet-spinning, biofuel cells, and biomaterial based actuators ranging from microscale to nanoscale for artificial muscles.