

Actuator Based on MWNT/PVA Hydrogels

Jiahua Shi,[†] Zhi-Xin Guo,^{*,†,‡} Bohan Zhan,[†] Hongxia Luo,[‡] Yongfang Li,[†] and Daoben Zhu[†]

Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China, and Department of Chemistry, Renmin University of China, Beijing 100872, China

Received: May 22, 2005; In Final Form: July 7, 2005

The first actuator based on multiwalled carbon nanotube (MWNT) hydrogels was developed through simple hydrogelation with poly(vinyl alcohol) (PVA). This actuator exhibited excellent actuating properties compared with the corresponding actuator based on poly(acrylic acid)/PVA hydrogels.

Carbon nanotubes have attracted an ever-increasing amount of scientific interest since their discovery in 1991.¹ It was first reported by Baughman et al. that sheets of single-walled carbon nanotubes (SWNTs) could be excellent electromechanical actuators, which was based on a combination of quantum chemical and double-layer electrostatic effects.² In addition to this so-called “non-faradaic actuation by double-layer charge injection” actuation process,^{2–4} several other types of actuation process of SWNTs such as electrostatic actuation,⁵ light-driven actuation,⁶ and pneumatic actuation⁷ have also been proposed. These results are critically important for the use of carbon nanotubes as robotics and microrobotics (e.g., microscopic pump), optical displays (interrupters), optical fiber switches, or medical prosthetic devices, which offer the interesting possibility for such various types of macro-, micro-, and nanoscopic applications. However, these carbon nanotube actuators were mainly based on SWNTs. It is therefore necessary to develop actuator systems based on multiwalled carbon nanotubes (MWNTs).^{8,9} Unlike SWNTs, sheets made from MWNTs are brittle and difficult to manipulate. In this communication, we report the first actuator based on MWNT hydrogels. We find that salts of carboxylic MWNTs show excellent actuating properties through simple hydrogelation with poly(vinyl alcohol) (PVA).

PVA is an excellent water-soluble matrix polymer for making hydrogels with certain polymers such as poly(acrylic acid) (PAA).¹⁰ To make MWNT/PVA hydrogels, commercially available MWNTs (CVD method, Shenzhen Nanotech Port Co., Ltd, China, denoted as p-MWNTs) were purified and converted into the acid form (MWNT-COOH, denoted as a-MWNT) by sonicating with nitric-sulfuric acid (3:1, v/v) in a water bath (Cole Palmer, model B3-R, 55 kHz) for 5 h at ca. 50 °C and then converted to the sodium salts (MWNT-COONa, denote as Na-MWNT) with aqueous NaOH.¹¹ The Na-MWNTs can form very stable dispersions in water which makes them form homogeneous mixtures with PVA very easily. The Na-MWNT/PVA composite hydrogels were prepared by repeatedly freezing and thawing a mixture of PVA and Na-MWNT aqueous solutions.¹² Briefly, appropriate amounts of Na-MWNT aqueous

dispersions were added to 10% of PVA solution in order to achieve homogeneous mixtures with MWNT loadings between 0.2 and 10% (w/w), respectively. Each of the mixtures was sonicated for 10 min at room temperature and then heated at 80 °C and subsequently transferred into a rotary evaporator at 50 °C for partial water evaporation. The PVA concentration of the resulting solution was kept as 10%. The resulting concentrated PVA/Na-MWNT mixture was poured into glass troughs and frozen at –20 °C for 12 h. The frozen mixture was then warmed for 12 h at room temperature. This freezing and thawing process was repeated thrice before the mixtures changed into hydrogels. Pure PVA hydrogels, PVA/p-MWNT composite hydrogels, and PVA/PAA composite hydrogels were also prepared according to the same procedure for comparison. The resulting hydrogels were swollen at room temperature and then cut into strips 20 mm long, 5 mm wide, and 0.6 mm thick. These strips were immersed in sodium carbonate aqueous solution for the bending measurements.

While pure PVA hydrogel strip was insensitive to DC electric field, p-MWNT/PVA hydrogel strips showed only a very minimal displacement. However, the Na-MWNT/PVA hydrogel strips exhibited significant and quick bending toward the cathode under DC electric field. Two frames were captured in Figure 1(a and b), which showed the muscle-like movement of the composite gel strip at different times.

These results clearly imply that the Na-MWNT plays an important role in the actuation process of the MWNT/PVA hydrogels. Considering the structures of p-MWNTs and Na-MWNTs, we suggest that Na-MWNTs act as polyelectrolytes in the composite. Therefore, the MWNT/PVA actuation differs from those observed with SWNTs^{2–7} and MWNTs^{8,9} reported before and arises from a different actuation mechanism, which can be explained by Flory’s theory of the osmotic pressure.¹³ It is well-known that polyelectrolyte gels show bending motion by swelling or shrinking of certain parts of the gels in an electric field.^{10,14} In Na-MWNT/PVA composite hydrogels, MWNT-COO[–] serves as polyions with negative charges. When the hydrogel strip is subjected to a DC electric field, counterions (Na⁺) of MWNT-COO[–] inside the strip move toward the negative electrode while the polyions MWNT-COO[–] are immobile, which is similar to the actuation principle of typical ionic polymer–metal composites (IPMCs) proposed by de

* Corresponding author. E-mail: gzhixin@ruc.edu.cn, fax: 86-10-62516660.

[†] Chinese Academy of Sciences.

[‡] Renmin University of China.

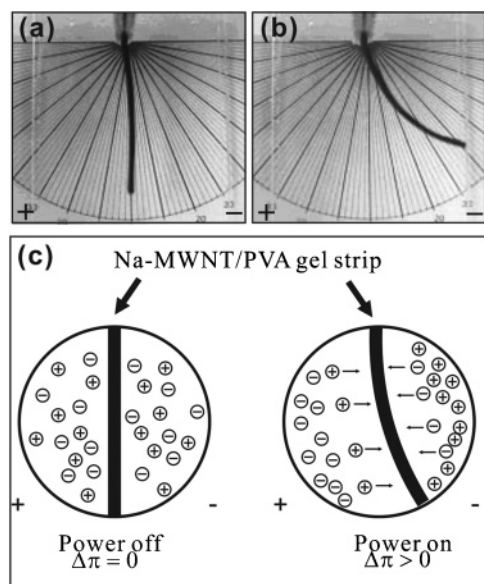


Figure 1. Photographs of the Na-MWNT/PVA composite hydrogel strip with 10% (w/w) loading of Na-MWNT at different times in 3 mM of Na_2CO_3 aqueous solution at 10 V/cm DC electric field at (a) 0 and (b) 30 s. Shown in (c) is the schematic illustration of bending mechanism of Na-MWNT/PVA hydrogel strip due to the change of the osmotic pressure under a DC electric field.

Gennes et al.^{15,16} The mobile ions in the surrounding solution also move toward their counter electrodes and come into the hydrogel strip. Then, the osmotic pressure of the gel strip near the positive electrode side (π_1) increases and becomes larger than that of the gel strip near the negative electrode side (π_2). Therefore, the osmotic pressure difference $\Delta\pi (= \pi_1 - \pi_2)$ occurs within the gel strip, which leads to swelling of the gel strip near the positive electrode side and shrinking of the gel strip near the negative electrode side; the gel strip is bent like a bimetal due to $\Delta\pi$. This is illustrated in Figure 1c.

To investigate further the electroresponsive behavior of the Na-MWNT/PVA composite hydrogels, we measured the bending angle of the composite hydrogel strip by varying several factors. Figure 2a exhibits the relationship between the amount of the Na-MWNTs and the bending angle of the gel strip in 70 s. As the content of the Na-MWNTs increased, the bending angle increased accordingly, which further proved that Na-MWNTs are the source of bending actuation of the composite hydrogels.

We also examined the influence of the Na_2CO_3 concentration on the bending behavior of the composite hydrogels in response to the electric stimulation. The bending angle of the gel strip within 70 s was recorded for each case. As shown in Figure 2b, at a DC electric field of 10 V/cm, the bending angle of the strip first increased and then decreased, while the concentration of Na_2CO_3 increased from 0.5 mM to 10 mM. When the concentration of Na_2CO_3 solution is 3 mM, the equilibrium bending angle reaches the maximum of 55 degrees. As described above, an increase in electrolyte concentration in a solution induces an increase of mobile ions moving from the surrounding solution toward their counter electrodes or into the gel strip. As a result, the bending angle of the gel should increase. However, if the concentration of the electrolyte is greater than the critical concentration (3 mM in our study), a shielding effect of fixed polyanions (MWNT- COO^-) by the ions in the electrolytic solute occurs, leading to a reduction in the electrostatic repulsion. This makes the mobile ion drift through the gel more difficult, resulting in a decrease in the bending.

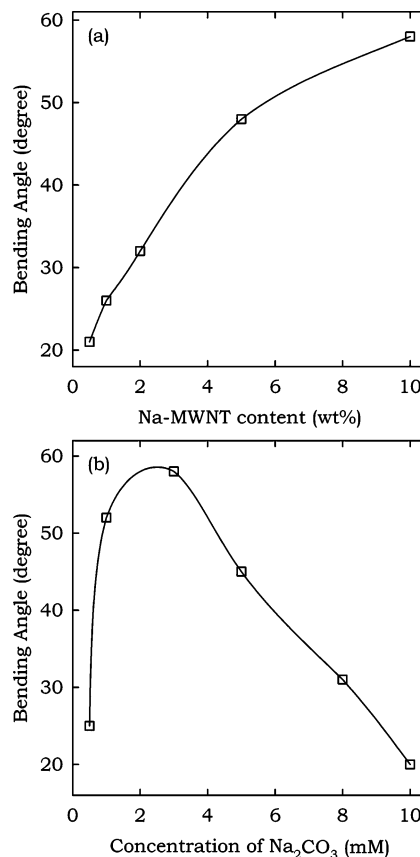


Figure 2. (a) Effect of Na-MWNT content on the bending angles of the Na-MWNT/PVA hydrogel strip in 3 mM of Na_2CO_3 aqueous solution at 10 V/cm DC electric field. The angles were recorded at 70 s for each sample; (b) The influence of Na_2CO_3 concentration on the bending angle of Na-MWNT/PVA hydrogel strip at 10 V/cm DC electric field. The Na-MWNT content is 10%.

Electric field is the driving force to make the composite hydrogels bend like artificial muscles. The influence of voltage on the bending behavior of the Na-MWNT/PVA hydrogel strips was also compared with that of Na-PAA/PVA hydrogel strips under same experimental conditions. Figure 3a shows the equilibrium bending angles of the hydrogels as a function of applied voltage. Clearly, while both of the bending angles of Na-MWNT/PVA and Na-PAA/PVA strips increased along with the increasing of the applied voltage, the Na-PAA/PVA showed smaller bending angles at each measured voltage, and tended to be closer to those of Na-MWNT/PVA at higher voltage. When the voltage was 10 V, the two samples exhibited similar equilibrium bending angles. For the bending speeds of the two samples, the Na-MWNT/PVA was always larger than those of Na-PAA/PVA at each of the measured voltages, and they all increased along with the increasing of the applied voltage (Figure 3b).

It is well-known that MWNTs exhibit good DC electrical transport properties.¹⁷ When applying a DC voltage to a Na-MWNT/PVA composite hydrogel strip in an electrolyte solution, the better DC electrical transport properties of MWNTs will make the movable counterions inside and outside the strip move faster, which makes the Na-MWNT/PVA composite hydrogel strip bend faster than the corresponding Na-PAA/PVA hydrogel strip.¹³ However, along with the increase of the voltage, the electric field will compensate the effect of conductivity of the Na-MWNT/PVA gel, which induces the equilibrium bending angles of the hydrogel strip close to that of the corresponding Na-PAA/PVA hydrogel strip.

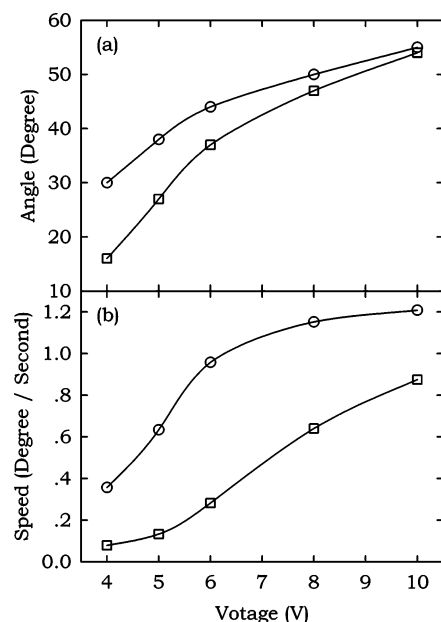


Figure 3. The equilibrium binding angles (a) and the bending speeds (b) of Na-MWNT/PVA (○) and Na-PAA/PVA (□) composite hydrogel strips (1:10, w/w) as a function of the applied voltage in 3 mM aqueous Na_2CO_3 solution.

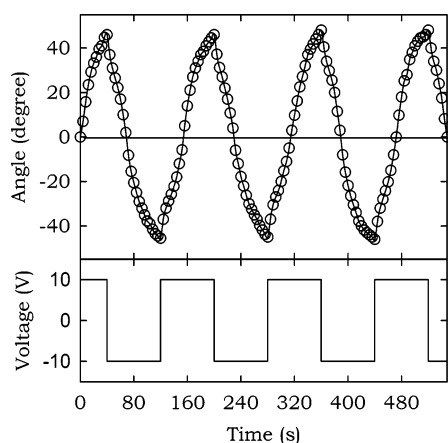


Figure 4. Reversible bending behavior of the Na-MWNT/PVA composite hydrogel strip (1:10, w/w) in 3 mM Na_2CO_3 aqueous solution by repeatedly changing the polarity of a 10 V/cm DC electric field.

As shown in Figure 4, the Na-MWNT/PVA hydrogel strip exhibited a reversible bending behavior when the polarity of the electric field was altered. The application of 10 V/cm voltage resulted in the bending of the hydrogel toward the cathode

(denoted by the positive bending angles). With the reversion of the polarity of the electric field by the application of -10 V/cm voltage, the mobile ions both outside and inside the hydrogel strip moved to the opposite direction, thus the strip bent reversely (denoted by the negative bending angles).

In conclusion, a novel type of actuators based on MWNT/PVA hydrogels was reported for the first time in this communication. The actuation is derived from Flory's theory of the osmotic pressure, which is quite different from those related to carbon nanotubes reported before. The new composite actuators are interesting structures, combining the properties of both classes of materials with potential applications ranging from microswitches to artificial muscles, robotics, optical displays, prosthetic devices, microscopic pumps and anti-vibration systems, which we are working for currently.

Acknowledgment. This research was sponsored by the National Natural Science Foundation of China (No. 50203015, No. 90306007, No. 20410019, and No. 50433020) and the Scientific Research Starting Foundation of Department of Chemistry, Renmin University of China.

References and Notes

- (1) Baughman, R. H.; Zakhidov, A. A.; de Heer, W. A. *Science* **2002**, *297*, 787.
- (2) Baughman, R. H.; Cui, C.; Zakhidov, A. A.; Iqbal, Z.; Barisci, J. N.; Spinks, G. M.; Wallace, G. G.; Mazzoldi, A.; DeRossi, D.; Rinzler, A. G.; Jaschinski, O.; Roth, S.; Kertesz, M. *Science* **1999**, *284*, 1340.
- (3) Fraysse, J.; Minett, A. I.; Jaschinski, O.; Duesberg, G. S.; Roth, S. *Carbon* **2002**, *40*, 1735.
- (4) Vohrer, U.; Kolaric, I.; Haque, M. H.; Roth, S.; Detlaff-Weglikowska, U. *Carbon* **2004**, *42*, 1159.
- (5) Kim, P.; Lieber, C. M. *Science* **1999**, *286*, 2148.
- (6) Zhang, Y.; Iijima, S. *Phys. Rev. Lett.* **1999**, *82*, 3472.
- (7) Spinks, G. M.; Wallace, G. G.; Fifield, L. S.; Dalton, L. R.; Mazzoldi, A.; Rossi, D. D.; Khayrullin, I. I.; Baughman, R. H. *Adv. Mater.* **2002**, *14*, 1728.
- (8) Spinks, G. M.; Wallace, G. G.; Baughman, R. H.; Dai, L. In *Electroactive Polymer (EPA) Actuators as Artificial Muscles: Reality, Potential and Challenges*, 2nd ed.; Bar-Cohen, Y., Ed.; SPIE: Bellingham, WA, 2001.
- (9) Hughes, M.; Spinks, G. M. *Adv. Mater.* **2005**, *17*, 443.
- (10) Shiga, T. *Adv. Polym. Sci.* **1997**, *134*, 131.
- (11) Qin, Y.; Shi, J.; Wu, W.; Li, X.; Guo, Z.-X.; Zhu, D. *J. Phys. Chem. B* **2003**, *107*, 12899.
- (12) Lozinsky, V. I.; Domotenko, L. V.; Vainerman, E. S.; Mamtsis, A. M.; Titova, E. F.; Belavtseva, E. M.; Rogozhin, S. V. *Colloid Polym. Sci.* **1986**, *264*, 19.
- (13) Flory, P. J. *Principles of Polymer Chemistry*, 15th ed.; Cornell University Press: Ithaca, New York, 1992.
- (14) Tanaka, T.; Nishio, I.; Sun, S. T.; Ueno-Nishio, S. *Science* **1982**, *218*, 467.
- (15) de Gennes, P. G.; Okumura, K.; Shahinpoor, M.; Kim, K. J. *Europhys. Lett.* **2000**, *50*, 513.
- (16) Shahinpoor, M.; Kim, K. J. *Smart Mater. Struct.* **2001**, *10*, 819.
- (17) Saito, R.; Dresselhaus, G.; Dresselhaus, M. S. *Physical Properties of Carbon Nanotubes*; Imperial College Press: London, 1998.