Electromechanical Actuation with Controllable Motion Based on a Single-Walled Carbon Nanotube and Natural Biopolymer Composite

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ABSTRACT This paper reports novel electromechanical behavior for a natural biopolymer film due to the incorporation of a conductive carbon nanotube network. Through simple solution blending and casting, high weight fraction single-walled carbon nanotube—chitosan composite films were fabricated and exhibited electromechanical actuation properties with motion controlled by low alternating voltage stimuli in atmospheric conditions. Of particular interest and importance is that the displacement output imitated perfectly the electrical input signal in terms of frequency ($<$10 Hz) and waveform. Operational reliability was confirmed by stable vibration testing in air for more than 3000 cycles. Proposed electrothermal mechanism considering the alternating current-induced periodic thermal expansion and contraction of the composite film was discussed. The unique actuation performance of the carbon nanotube—biopolymer composite, coupled with ease of fabrication, low driven voltage, tunable vibration, reliable operation, and good biocompatibility, shows great possibility for implementation of dry actuators in artificial muscle and microsystems for biomimetic applications.

KEYWORDS: SWCNT dispersion · chitosan · electromechanical actuation · electrothermal · tunable vibration

There is a growing interest in the realization of systems with life-like or biomimetic movements. However, such motions are difficult to achieve with conventional actuators, thus researchers are pursuing the development of new artificial muscle-like actuators. The discovery of the electromechanical actuation properties of single-walled carbon nanotubes (SWCNTs) introduced a unique material enabling the conversion of electrical stimulus to mechanical displacement due to the double-layer charge injection.[1] Complex behavior of multiwalled carbon nanotubes has also heralded some interesting insights into the possibility of designing a nanoelectromechanical system.[2−5] Within the past few years, various carbon nanotube (CNT) actuators have been developed, including individual tubes and assemblies of these nanotubes in yarns and sheets.[6−11] Recently, a new class of active system, carbon nanotube/polymer composite actuators, has received great attention with regard to macroscopic artificial muscle applications.[12,13] It has been demonstrated that successful introduction of the highly conductive CNTs could significantly enhance the polymer nanocomposite's electrical, thermal, mechanical, and interface properties, thus providing a suitable material for novel artificial muscle-like actuator investigations.[14,15]

In this paper, we report an electroactive biopolymer/CNT composite actuator. The biopolymer used here is chitosan (CS), the second most abundant naturally occurring biomolecule after cellulose, which has been shown to be a biocompatible, low-cost, and smart polymer material with useful biological and chemical properties.[16] In addition, chitosan has also proved to be a good dispersant which can debundle CNTs at very high concentration.[17−19] These unique properties make chitosan an excellent candidate for numerous applications especially in CS−CNT-based electrochemical sensors and actuator in electrolyte solutions.[20−22] Up to now, there are few reports for the electromechanical actuation of the solid-state CNT/chitosan composite in air. We have recently discovered that the electroactive actuation properties can be achieved in air for CS after being dispersed with SWCNTs. The actuated vibrational motion, including the frequency and waveform, could be controlled by the applied low alternating voltages. The proposed mechanism of alternating current-induced periodic thermal expansion and contraction of the CNT/CS composite film is discussed. The discovered unique phenomenon may

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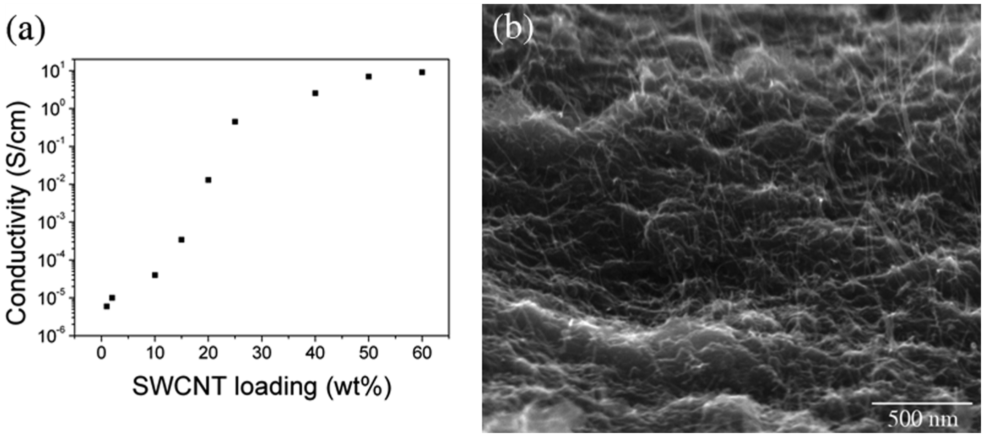

Figure 1. (a) Electrical conductivity as a function of the SWCNT loading amount in the composite. (b) SEM image of the cross section for the composite film containing 25 wt % SWCNTs.

provide a foundation for design and fabrication of CNT/biopolymer composite actuators with tunable electromechanical motion in the biomimetic field.

RESULTS AND DISCUSSION

Figure 1a shows the electrical conductivity of the composite films with different SWCNT loading. It can be seen that, as the SWCNT loading is increased, electrical conductivity increased significantly. The composite loaded with a higher than 25 wt % of SWCNTs can achieve electrical conductivity of more than 0.5 S/cm. Figure 1b shows the SEM image of the cross section of the 25 wt % SWCNT/CS composite film, which clearly reveals that the SWNTs are randomly dispersed in the chitosan matrix to form a well-resolved carbon nanotube conductive network.

The schematic setup of the electromechanical actuation test is shown in Figure 2. The strip sample was fixed and suspended on a glass substrate with two copper electrodes, which were connected to a function generator (Agilent 33220A). The laser spot was located on the midpoint of the strip. When an alternating voltage was applied, vibrational displacement was simultaneously measured. In addition, vibrational motion of the strip was recorded by an optical microscope. Figure 3 gives the optical images of the suspended 25 wt % SWCNT/CS strip response after turning on the alternating voltage. The strip plumped up at its middle part and reached its largest displacement at 5 V. Video records of long-time and real-time vibration of the 25 wt % SWCNT/CS strip under the positive sine wave voltages (0−5 V) with different frequencies of 0.5 and 2 Hz are also provided (see videos in the Supporting Information).

Figure 4 shows the displacement responses of the 25 wt % SWCNT/CS strip under different applied voltages. The dimensions of this strip are 6.0 mm × 2.2 mm (length × width) with a thickness of around 50 μm. It can be seen in Figure 4a that, when a 0.1 Hz sine wave voltage of ±2.5 V was applied, the displacement rose up and down following the absolute value variation of voltage amplitude, resulting in a double frequency sinusoidal vibrational motion. Due to the fact that the actuated displacement is irrelevant to the voltage direction, positive alternating wave voltages are employed in the other testing. Figure 4b−d gives the cycling vibrational displacements of the 25 wt % SWCNT/CS strip under 0.1 Hz positive wave voltage (0−5 V) with three kinds of different waveforms: sine wave, triangle wave, and square wave. It can be seen that the motion output imitated the applied voltage input perfectly. The frequencies and waveforms of the displacement are almost consistent with those of the applied voltages, indicating that controllable actuation behavior of the biopolymer−CNT composite was achieved.

The actuation motion of the 25 wt % SWCNT/CS strip under the applied sine voltages (0−5 V) with different fre-

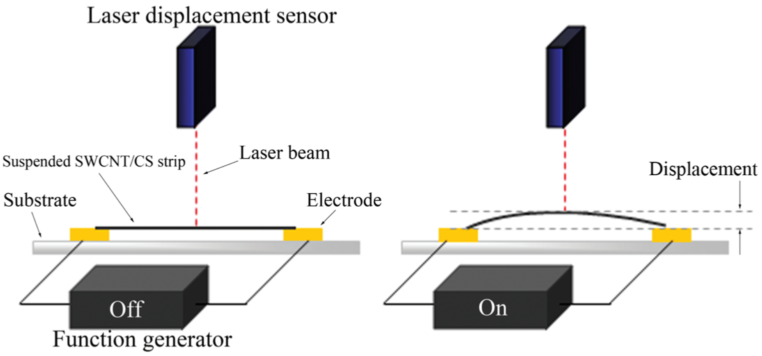

Figure 2. Schematic setup of the electromechanical actuation test before and after voltage is applied.

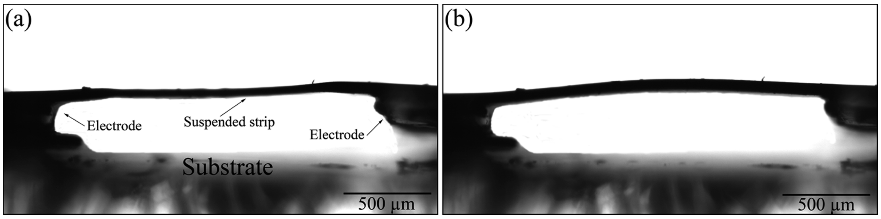

Figure 3. Side view optical images of the suspended strip with the voltage off (a) and on (b). The lower part is the glass substrate, and the black line is the 25 wt % SWCNT/CS composite. The applied voltage is 0.1 Hz alternating sine wave voltage of 5 V.

quencies is shown in Figure 5a. It can be seen that, with an increase of the voltage frequency, the actuation amplitude decreases a lot. The motion response can be observed with the applied voltage frequency of up to 10 Hz but was not detected when the frequency was higher than 10 Hz. Because CS is a kind of hygroscopic matrix, which is capable of moisture absorption,[23] the influence of absorbed water on the actuation properties was also investigated. It was found that there is no significant difference in the displacement output for the 25 wt % SWCNT/CS samples with and without drying treatment (above 100 °C for 1 h). Furthermore, operational reliability of the SWCNT/CS strip was examined by applying the alternating sine wave voltage (0.1 Hz, ±2.5 V) continuously. After more than 3000 cycles, no significant performance degradation for vibrational motion in air is exhibited, as shown in Figure 5b.

In order to understand the function of the SWCNTs in the composite actuator, CS samples with different CNT loadings were subjected to the same 0.1 Hz positive sine wave voltage (0−5 V) electromechanical characterization. It was found that, with reduced nanotube content, smaller displacements were observed. For the pure CS matrix, no displacement was observed. As indicated from Figure 1a, the higher the CNT doping, the higher the electrical conductivity, and therefore a larger current can pass through the sample under the same applied voltage. When an alternating current passes through a thin conductor, periodic heating takes place following the variation in the current strength. The generated temperature waves were then propagated into the surrounding medium, which caused the thermal expansion and contraction of the layer near the conductor.[24] Depending on the medium's properties, the thermal response will be different. Fan *et al.* reported the thermophone effect due to the air oscillation in the vicinity of carbon nanotube thin film.[25] In our system, CNTs were wrapped and dispersed in a polymer. CNT network played the same function as a conductive path heating source in the CS matrix. Therefore, alternating current-induced temperature undulation resulted in the cycling thermal expansion and contraction of the poly-

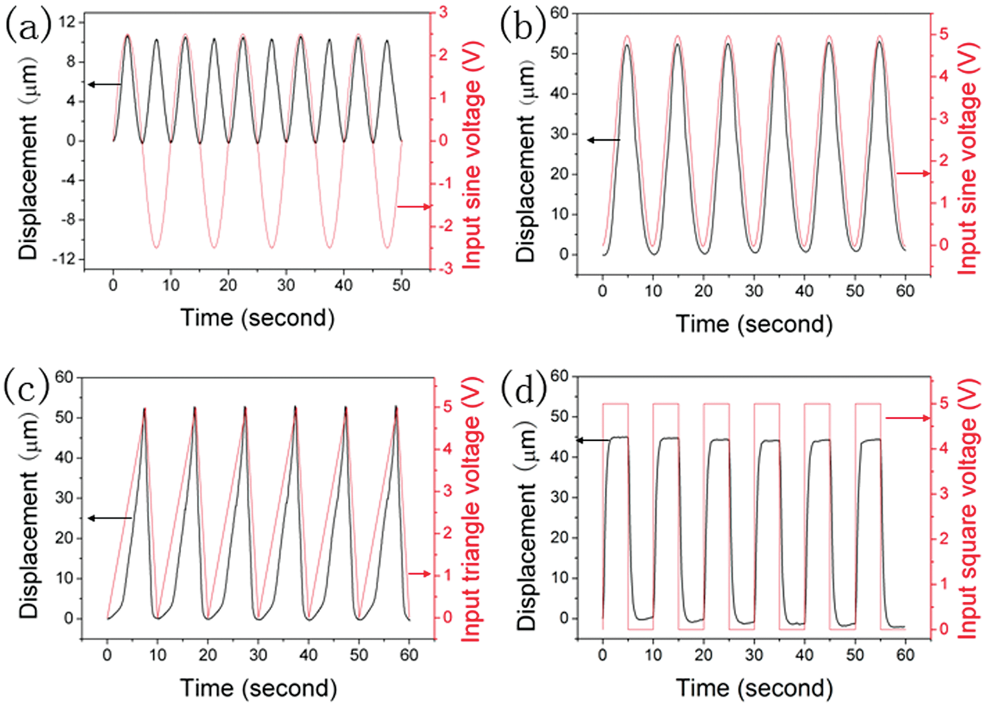

Figure 4. Displacement vibration of the 25 wt % SWCNT/CS strip with different alternating wave voltages: (a) 0.1 Hz sine wave voltage of ±2.5 V, (b) 0.1 Hz positive sine wave voltage (0−5 V), (c) 0.1 Hz positive triangle wave voltage (0−5 V), (d) 0.1 Hz positive square wave voltage (0−5 V).

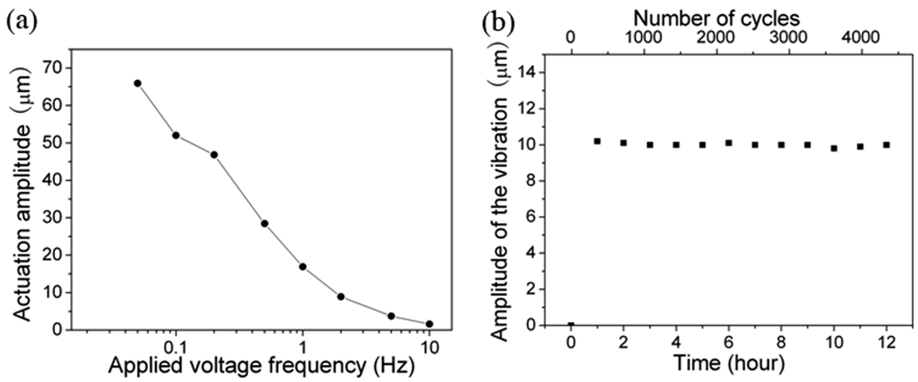

Figure 5. (a) Actuation amplitude of the 25 wt % SWCNT/CS strip as a function of frequency of the applied sine wave voltage (0−5 V). (b) Cycle life of the suspended 25 wt % SWCNT/CS strip with 0.1 Hz sine wave voltage of ±2.5 V.

mer medium, which depended greatly on the composite conductivity, and then enough current strength generated. In order to further confirm this mechanism, the temperature change during the actuation process is also measured, as shown in Figure 6. It can be seen that the induced temperature undulation is nearly in line with the actuated displacement, which could firmly support our electrothermal mechanism. This effect is also observed in Figure 4a as the frequency of the displacement output was double that of the electrical input. When a sine wave voltage was applied, the generated alternating current periodically heated the polymer both in positive and negative half-cycles, resulting in a double frequency temperature oscillation and then double frequency vibrational motion output. Additionally, the doped SWCNTs play not only the role of the enhanced electrical conductivity of composites but also the active cooling system due to their excellent electrical and thermal conductivity.[26,27] It can be found in Figure 4d that the actuated displacement rose due to the heating when a square wave was applied but fell more quickly than it rose due to the fast cooling when the voltage was closed. As a result of the balance reached between the electrical current-generated heating and easy cooling with the SWCNTs, the displacement also displaying a steady state during the period of a constant voltage was maintained. Accordingly, in the case of pure CS, almost no current went through as it is an insulator, and then no actuation took place. For the well-dispersed CNT samples, such as the 25 wt % SWCNT/CS composite, a larger displacement can be observed compared to those with low CNT doping. For those samples loaded with SWCNTs much higher than 25 wt %, the lower content polymer could still lead to lower thermal expansion. Meanwhile, excess current and heating destroyed the polymer matrix, and durable actuation performance in air was not maintained. At high voltage frequency, where not enough current strength was generated, the following thermal-mechanical effect does not exist, which can be demonstrated in Figure 5a. When the alternating voltage was applied, a constant current was also selected and passed through the SWCNT/CS composites. The results show that with 1 mA current and the same operation time the actuated displacement of the 25 wt % SWCNT/CS composite is 11.8 μm, while that of the 20 wt % SWCNT/CS composite is as large as 70.4 μm. The reverse of the trend we mentioned under alternating voltage further indicates that the current-induced thermal mechanism is indeed responsible for actuation. Namely, the actuator with largest CNT content will have the lowest resistance and will heat up the least at a constant current compared to those with lower CNT contents. Thus actuation strain should be smallest in the actuator with higher CNT content.

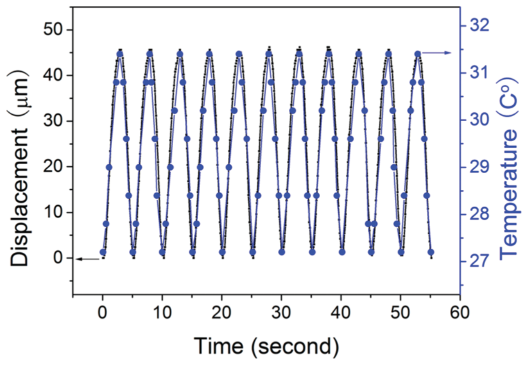

Figure 6. Actuated displacement (black lines) and temperature undulation (blue circles) of the 25 wt % SWCNT/CS strip under the applied 0.2 Hz sine wave voltage (0−5 V).

CONCLUSION

In summary, we have demonstrated the electromechanical behavior of natural biopolymer due to introducing the carbon nanotube conductive network. Under low alternating wave voltage, the CNT/CS composite film simultaneously vibrates in atmospheric conditions. Frequency and waveform of the motion are consistent with those of the applied voltage. It is believed that the vibrations are mostly controlled by thermal expansion and contraction of the polymer matrix, which is caused by periodically heating when an alternating current is passed through the CNT conductive network. The unique actuation performance of the

CNT/biopolymer composite system, coupled with ease of fabrication, low driven voltage, tunable vibration, reliable operation, and good biocompatibility, shows the great possibility for implementation of actuators for artificial muscles, microelectromechanical systems (MEMS), and biotechnology applications, such as microactuators for microrobots in biological environment, actuators for microfluidic devices, and so on.

EXPERIMENTAL SECTION

SWCNTs (purity $>$90 wt %, average diameter $<$2 nm) were obtained from Shenzhen Nanotech Port Co., Ltd. Chitosan (deacetylation degree 85%, purity 89 wt %, water 11 wt %, and average molecular weight of 400 kDa) was used as received from Jinan Haidebei Marine Bioengineering Co. Ltd. CS composite films with different SWCNT loading amounts (1$-$60 wt %) were typically prepared as follows: Chitosan was first added into a 4% acetic acid solution and stirred for 0.5 h to obtain a clear solution. SWCNTs were then added into the clear chitosan solution with ultrasonic treatment (Fisher Scientific Model 500 Digital Sonic Dismembrator) for 30 min without the help of any surfactants. Solid films with a thickness of $\sim$50 μm were prepared by evaporating the suspensions in an oven at 80 °C. The films were cut into strips for characterization and electromechanical testing.

Electrical measurements on the composite films were performed by the van der Pauw method[28] using a Keithley 4200 instrument. Morphologies of the SWCNT/CS composite films were characterized by a Quanta 400 FEG field emission scanning electron microscope (FESEM). Electromechanical actuation for the SWCNT/CS strip in air was measured by a laser displacement sensor (LK-G80, Keyence, Japan) and optical microscope (Nikon Ti-E) using a freely suspended configuration.

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Supporting Information Available: Video records of long-time and real-time vibration of the 25 wt % SWCNT/CS strip under the positive sine wave voltages (0$-$5 V) with frequencies of 0.5 and 2 Hz. This material is available free of charge *via* the Internet at http://pubs.acs.org.

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