Single-Walled Carbon Nanotube-Polymer Composite Thin Film for Flow Sensor Application

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We report a fabrication method for a composite thin-film flow sensor including a single-walled carbon nanotube (SWCNT) network and polydimethylsiloxane (PDMS), which is immersed in deionized water and NaCl solution. The morphology of SWCNTs on the surface of the composite thin film is characterized by scanning electron microscopy. The induced voltage generated along the direction of the flowing liquid depends significantly on the liquid concentration and flow velocity. Since the SWCNTs are coated with polymer chains and fixed into the PDMS matrix, the *I-V* curves of the composite thin film are completely coincident before and after several flow velocity measurements, and the repeated flow-induced voltage experiment shows that the composite thin film has a reliable electrical characteristic and a wide potential of device application.

1. Introduction

A carbon nanotube (CNT) is a type of carbon allotrope, which was discovered in 1991 by a Japanese scientist, Iijima.[1] It's thermal, mechanical, chemical stability, and large current-carrying capacities make it attractive for application in electrical interconnects,[2,3] field-effect transistors,[2,4] cold cathode field emitters,[5,6] and sensors.[7,8] CNTs can exhibit good conductor and semiconductor behaviors owing to their unique structures.[9] One of the primary hurdles in developing such novel CNT devices is the absence of a reliable method of fabrication.

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In a recent remarkable experiment, Ghosh and coworkers[10,11] observed that the flow of an ion-rich liquid, such as deionized water or HCl solution, through bundles of metallic single-walled carbon nanotube (SWCNT) networks generates a voltage in the nanotube along the direction of the liquid flow when CNT films are immersed in flowing liquids. Liu *et al.*[12] found that multiwalled carbon nanotubes (MWCNTs) also generate an electric voltage when NaCl solution flows through the nanotube network (NTN). These studies indicate that the voltage generation depends on the polar nature of the liquid. These studies reveal the potential application of a CNT flow sensor. Since the nanotubes are deposited on the substrate without being fixed, the CNTs are washed away by the liquid and the performance of the sensor is unstable. In addition, the unfixed CNTs relatively reduce the movement between fluid and NTN.

In this study, we provide a synthetic process for fabricating a SWCNT network/ polydimethylsiloxane (PDMS) composite thin film-based flow sensor. The SWCNTs are coated with PDMS polymer chains and fixed into the PDMS matrix to prevent the washing away of SWCNTs by liquid. The features of the electric voltage generated by ion-rich liquid are similar to those observed in previous studies.

2. Experiments

The SWCNTs used in this study were supplied by Chengdu Organic Chemicals Company, with an average diameter of about 2 nm, an average length of about 30 μm, and a purity above 90 wt%. The PDMS was a transparent flexible insulator and was supplied by Dow Corning Company.

The SWCNT suspensions were prepared by sonicating the raw materials in dimethylformamide (DMF, 99.9%, J. T. Baker) for 8 h at a power level of 80 W with subsequent centrifugation at 16,000 rpm for 1 h. The upper 10% of the supernatant was then carefully decanted. The resulting CNT suspension had a concentration of approximately 20 mg/L. The suspension was then ultrasonically treated for 2 h to sufficiently disperse the SWCNTs. The CNT networks[13] were then obtained by vacuum filtration[14] using a poly-tetrafluoro-ethylene (PTFE) filter with an average pore size of 220 nm, as shown in Fig. 1(a). To enhance the degree of the distribution uniformity of the CNT film, the vacuum level was controlled to extend the filtration time.[14]

The CNT film formed on the surface of the filter (Fig. 1(a)) was placed in a mould (Fig. 1(b)) and transferred to a substrate by direct PDMS molding (Fig. 1(c)). In this process, the PDMS was poured onto the filter surface and cured at 60°C for 8 h in a low-vacuum oven (5 Pa). After curing, the filter membrane was removed (Fig. 1(d)) and the CNT/PDMS hybrid thin film was formed on the PDMS substrate. The metal electrodes, 10 Å of chromium (adhesion layer) and 200 Å of gold, were deposited onto the surface of the CNT/PDMS composite thin film (Fig. 1(d)) by thermal evaporation.[15] Finally, the cured PDMS cover with a square cross-sectional flow channel was treated in an oxygen plasma for 1 min to form oxidized PDMS[16] and then bonded to the PDMS substrate (Fig. 1(e)). A schematic of the flow sensor is shown in Fig. 1(f). The CNT/PDMS composite thin film was placed at the center of the flow channel with an inner square side of 2 mm and a length of 60 mm to prevent any turbulent flow caused by the expansion of the flow
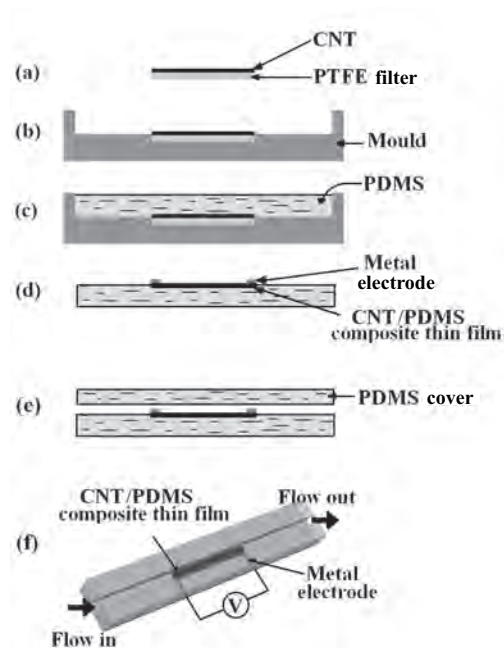
Fig. 1. Process of fabricating flow sensor: (a) SWCNT network is formed on PTFE filter membrane by vacuum filtration. (b) PTFE filter membrane with SWCNT network is placed in the mould. (c) PDMS is poured into the mould and cured. (d) Filter membrane is removed, the SWCNTs are transferred to PDMS, and then the metal electrodes of Cr and Au are deposited on the CNT/PDMS composite thin film by thermal evaporation. (e) PDMS cover is bonded to the PDMS substrate. (e) Schematic of flow sensor.

at the inlet of the channel. The flow velocity in the channel was controlled using a liquid flow controller (L23V02, Bronkhorst, Netherlands). The flow-induced voltage along the CNTs was measured using a digital multimeter/data acquisition system (Medel 2007, Keithley, USA).

Two liquids, namely, deionized water (DI water) and aqueous NaCl solution, were allowed to flow over the NTN/PDMS composite thin film in our experiments. Experimental conditions, such as liquid velocity and NaCl solution concentration were varied and the voltage between two electrodes was measured repeatedly.

3.   Results and Discussion

To investigate the morphology of SWCNTs in the NTN/PDMS composite thin film, scanning electron microscopy (SEM, Sirion 200, FEI, Holand) was used to obtain the microstructure of the thin film (Fig. 2). Since it was fabricated by vacuum filtration, the film was composed of highly entangled SWCNT bundles held together by a van der
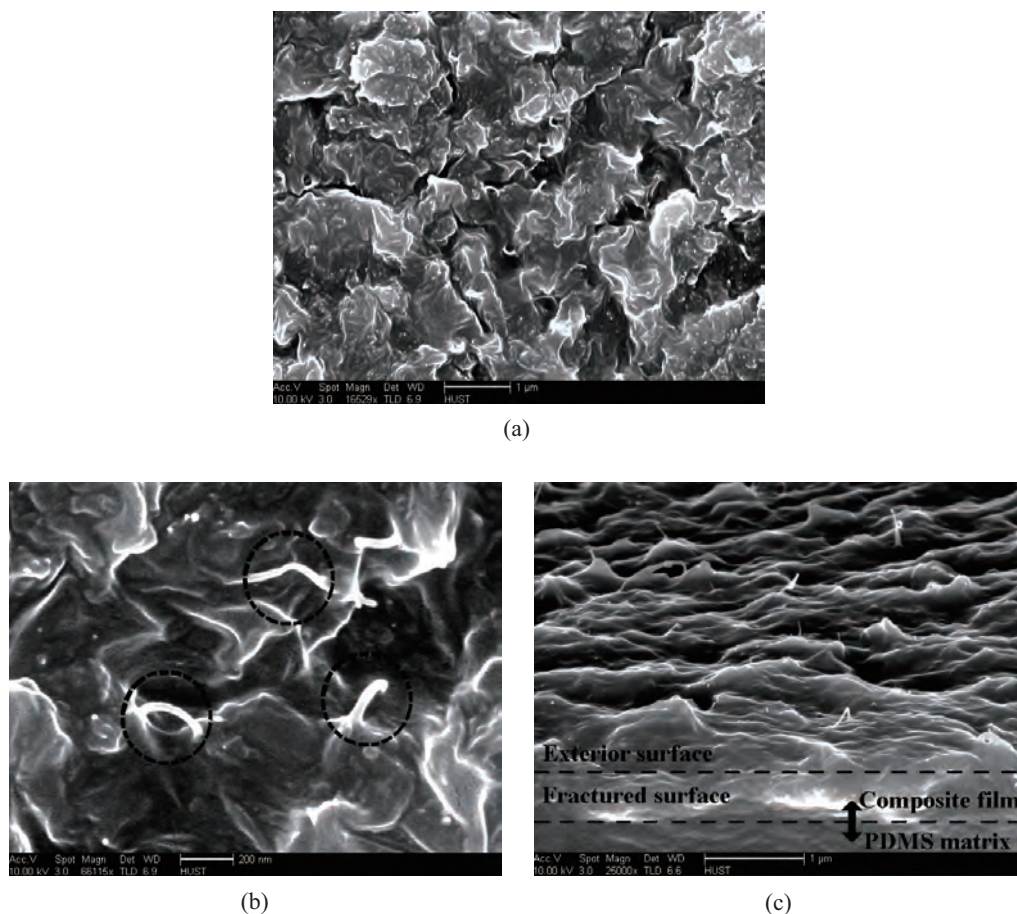
(a)

(b)

(c)

Fig. 2. SEM image of NTN/PDMS composite thin film: (a) Surface of NTN/PDMS composite thin film. (b) Highly magnified image of (a). (c) Surface and cross section of composite thin film.

Waals attraction force, and the SWCNTs appeared randomly oriented and uniformly deposited.[13]   As shown in Fig. 2(a), most of the SWCNT bundles are completely embedded in the cured PDMS matrix, and some of them lie near the surface protruding above the composite film. Figure 2(b) shows the highly magnified image in Fig. 2(a). It shows that the SWCNTs are coated with PDMS, suggesting that the SWCNTs are bonded to PDMS polymer chains and fixed during PDMS curing. The outer diameter of the tubes is consistent for the different morphologies and is on the order of approximately less than 50 nm. The thickness of the NTN/PDMS composite films is less than 1 μm, as shown in Fig. 2(c).

The dimensions of the NTN/PDMS composite thin film used in the flow sensor are about 20×2 mm^2. The Reynolds number (*Re*) (~30 for a velocity of 10 mm/s, DI water) of the chamber is much less than the critical value of 2000 for the turbulent flow in a pipe. Thus, the flow at the center of the chamber is laminar. There was an original voltage of about 3 mV when the flow sensor was immersed in solution, which was explained by Ghosh *et al.*[10] as an electrochemical potential difference at the interface of the SWCNT bundles with the metal electrodes. The difference between the measured and offset voltages is considered to be due to a flow-induced voltage.

For individual SWCNTs, a theoretical investigation method for electrical current generation has been proposed by Kral and Shapiro.[17] One mechanism of such current generation is the transfer of momentum from the flowing liquid molecules to the acoustic phonons in the nanotube as the phonon quasi-momentum, which in turn drags free carriers into the nanotube. The other mechanism involves the direct scattering of free carriers from the fluctuating Coulombic fields of the ions or polar molecules in the flowing liquid.

The relationship between the flow-induced voltage and the flow rate of DI water or NaCl solution is shown in Fig. 3. The voltage increases with increasing flowing velocity and saturates slowly. This sublinear dependence on the flow velocity indicates a pulsating asymmetric ratcheting mechanism.[10] The voltage generated under the condition of DI water is much smaller than that generated under the condition of NaCl solution. When NaCl solution with a concentration of 20 wt% flows over the sensor at a rate of 3 mm/s, the flow-induced voltage increases to 5.83 mV.

Figure 3 also shows the relationship between the flow-induced voltage and concentration of NaCl solution. When NaCl solutions with concentrations of 5, 10, and 20% flow over the sample at a rate of 3 mm/s, the induced-voltage reaches 5.71, 5.79, and 5.83 mV, respectively. The voltage induced by the liquid flow depends on the
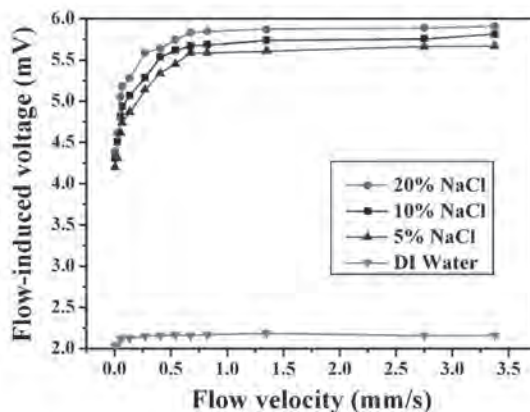

Fig. 3. Flow-induced voltage versus flow velocity.

concentration of the flowing liquid, suggesting that the mechanism involving fluctuating Coulombic fields dominates the phonon-mediated electron drag.[10]

   To investigate the stability of this NTN/PDMS composite thin film, several experiments were conducted. Figure 4(a) shows the flow-induced voltage measured repeatedly at the same velocities of 0.027, 0.0675, and 0.675 mm/s with 20 wt% NaCl solution, and the observed changes correspond to 0.8, 1.2, and 0.7%, respectively. When a DC voltage was applied between two electrodes, the film exhibited a linear relationship
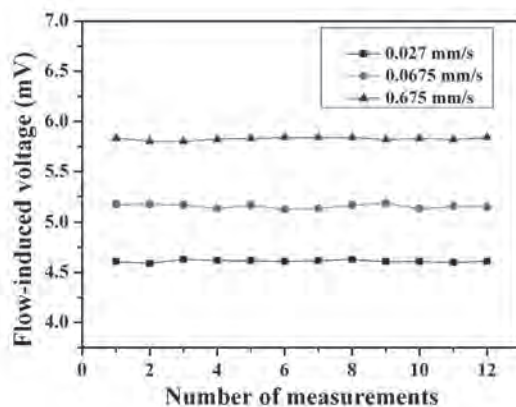
(a)
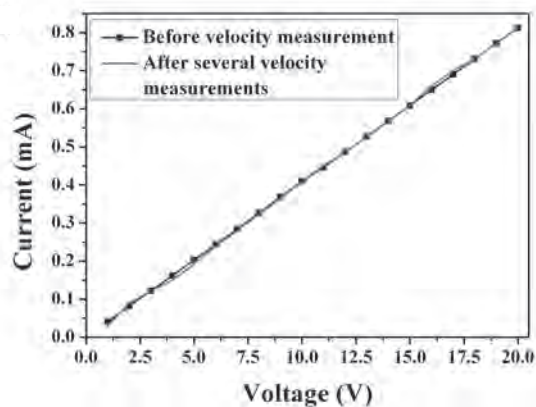
(b)

Fig. 4.   (a) *I-V* curve of NTN/PDMS composite thin film before and after velocity measurement. (b) Repeat voltage measurement at flow rates of 0.027, 0.0675, and 0.675 mm/s with 20 wt% NaCl solution.

between voltage and current. The *I-V* curve of the composite thin film was measured before and after several velocity measurements. As shown in Fig. 4(b), the two curves are almost coincident with each other, and the maximum change rate is about 0.197% at 2.5 V. These results show a stable electrical characteristic in the composite thin film and make it suitable for flow sensing.

4.   Conclusions

Experimental results show that the flow-induced voltage could be generated using NTN/PDMS composite thin films immersed in flowing liquids. The flow-induced voltage depends on the flow rate and concentration of the liquids. The SEM images of this thin film show that SWCNTs are coated with polymer chains and fixed in the PDMS matrix. The experimental results of repeated measurement and the *I-V* curve indicate that this NTN/PDMS composite is highly stable, which could lead to flow-induced nanotube flow sensors of practical significance. This sensor can be scaled down to dimensions on the order of micrometers, which makes it suitable for very small liquid volumes.

Acknowledgments

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