FLEXIBLE STRAIN SENSORS BASED ON PRINTED CARBON NANOTUBE LAYERS ON POLYDIMETHYLSILOXANE

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ABSTRACT

The unique mechanical and electrical properties of carbon nanotubes represent a potential for developing a piezo-resistive strain sensor for smart structures. This study demonstrated a new processing technique of multi-walled carbon nanotube strain sensors with tunable strain gauge factors. A digital-controlled spraying-evaporation deposition process that uses a 12-array bubble jet nozzle attached to a digital x-y plotter combined with a heated substrate which induces evaporation of the solvent was developed. The experimental results showed that the prepared carbon nanotube strain sensors are capable of measuring strains through highly linear electrical resistance change. The fabricated sensors exhibit a high stretchability (in excess of 45%) and sensitivity with a highest gauge factor of 35.75. The gauge factors of the fabricated strain sensors could be easily tuned by controlling the number of printed layers of carbon nanotubes. The cyclic loading-unloading test results revealed that the strain sensors exhibited excellent long-term durability. These superior sensing capabilities of the fabricated CNT/Polydimethylsiloxane (PDMS) strain sensors offer them potential applications in wearable smart electronics and structural health monitoring.

1. INTRODUCTION

Carbon nanotubes (CNTs) have attracted extensive attentions in the research community due to their unique electrical and mechanical properties [1-3]. The electrical resistance of CNTs is interestingly correlated to their mechanical deformation, which is called piezo-resistive effect [4]. This electrical characteristic of CNTs coupled with their high mechanical strength makes them a promising material for strain sensors. Piezo-resistive strain sensors are an interesting area of industrial and academic research due to the growing demand for flexible and wearable electronics [5-8], smart textiles [9] and structural health monitoring [10].

To create CNT based strain sensors with desired properties, various fabrication techniques have been employed to date, including compression molding [11], solution casting [12], contact film transfer [13, 14], screen printing [15, 16] and spray coating [17, 18]. For instance, CNTs were spray-deposited on a PDMS substrate to prepare a strain sensor, which could accommodate strain up to 150% for detection of large-scale human motions but show low sensitivity (~6 of gauge factor)[19]. Besides this, strain sensors based on

carbon nanotube and graphene were fabricated by compression molding method to investigate the synergistic effect of bi-filler on strain sensing. The produced strain sensors exhibited a high sensitivity with a gauge factor of 152.93 at 30 % strain[11].

However, most of previously-reported sensors were fabricated through expensive and complex processes without controllable sensitivity or good response linearity for measuring diverse human motions. These techniques are not able to manufacture multi-directional strain sensor. Additionally, some challenges in fabrication have prevented their widespread industrial applications. For instance, although the contact film transfer technique is able to produce CNT strain sensors with good sensitivity, transferring film to substrate is time-consuming and complex, often requiring a surface treatment of the substrate and multiple fabrication steps, which increase the overall cost of and limit the manufacturing scalability of this technique.

To overcome these problems, highly stretchable strain sensors were fabricated by using a digitally-controlled spray deposition modeling (SDM) printer to incorporate CNT layers into PDMS substrate. SDM is a digital-controlled additive manufacturing process in which the CNT ink droplets are supplied in the form of a stream to any desired location through an x-y axis movable nozzle. Thus, as nozzle moves, the CNT patterns could be printed continuously at different locations. The highest resolution of SDM is 100 dots per inch, which enables the CNT patterns to be printed over the same area with precision and accuracy. The SDM is also an additive manufacturing process, which enables the strain sensor to be built layer by layer and has a minimum loss of the supplied material. Strain sensors with different printing cycles of CNT layer were fabricated to investigate the effect of printing cycle numbers on the sensing properties. Two types of flexible strain sensors, unidirectional-type and rosette-type sensors, were fabricated and characterized.

2. EXPERIMENTAL DETAILS

2.1 Preparation of CNT inks

Multi-walled carbon nanotubes (MWCNT) (Chengdu Organic Chemical) with an average outer diameter of 30 nm was used in this study. The desired amount of MWCNT materials was initially dispersed into water using a sonication tip. A surfactant (Triton-X100, Fisher Bioreagents) was used to de-agglomerate the nanotubes to enhance their dispersion. The CNT ink with good dispersion of carbon nanotubes was achieved by sonication for 1 hour. The prepared CNT ink can remain stable for one week.

2.2 Preparation of CNT/PDMS strain sensor

The digital fabrication of CNT strain sensors is achieved by the process shown in Figure 1. The sensor design was first done in CAD software. To simplify the process only black and white images were used. A MATLab code was used to bring in 2D images and generate G-code that controls the motion of nozzle. PDMS and its curing agent (Sylgard 184 Silicone Elastomer Kit, Dow Corning) were mixed in 10:1 weight ratio and cured in oven at 100°C for 1.5 hrs. Acid treatment (H_2O_2:H_2SO_4 = 1:3, H_2O_2 30%; H_2SO_4 98%; purchased from Sigma-Aldrich) was performed to increase the hydrophilicity of PDMS substrate for aqueous ink printing. The CNT ink was then loaded into the cartridge to be sprayed on to a PDMS substrate. While the substrate was heated, 12-array bubble jet nozzles sprayed the ink material in the order given by the G-code. During the spraying process, water evaporated and CNTs were deposited on the substrate. The samples were printed at the speed of 15 mm/s using a nozzle set with 12 nozzle outlets to increase the productivity[20, 21]. Each nozzle outlet has the diameter of 80 μm. After the printing process, copper wires were attached to the end of CNT patterns and finally another layer of PDMS was cured on top of printed patterns to obtain the strain sensors.

2.3 Characterization

The surface morphology of CNT/PDMS strain sensor was examined using a scanning electron microscopy (SEM, Zeiss-Ultra 55) under an accelerating voltage of 10kV. The strain sensing tests were carried out on a MTS hydraulic 100kN test system. Specimens were stretched/released at a constant frequency of 0.2 Hz. Real-time electrical resistance was measured during the tests using a Fluke 45 digital multi-meter connected to a PC that records data through LabView software.

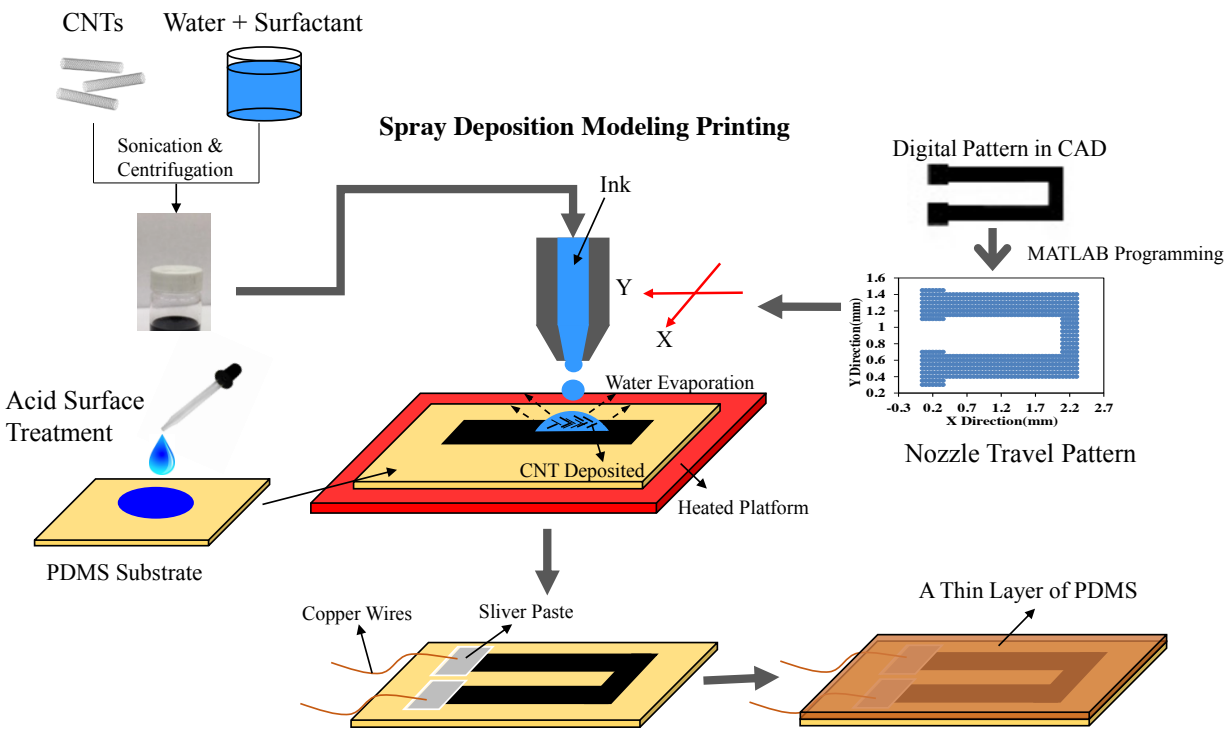

Figure 1. Schematic of the digital fabrication of CNT strain sensors through the SDM technique

3. RESULTS AND DISCUSSIONS

3.1 Structure and morphology

To identify the morphology of the printed pristine CNT layer on PDMS substrate, cross-section SEM images of CNT layers obtained by 10 and 50 printing cycles were shown in Figure 2(a) and (b), respectively. They clearly show that CNTs were uniformly deposited on PDMS substrate to form a dense and continuous conductive network without the agglomeration of CNTs, owing to the homogenous dispersion of CNTs in water as well as the optimized and effective SDM printing process. Figure 2(c) shows the morphology of the fractured surface of CNT/PDMS composite, where the PDMS resin fully impregnated throughout CNT networks indicating a good interfacial bonding between matrix and fillers.

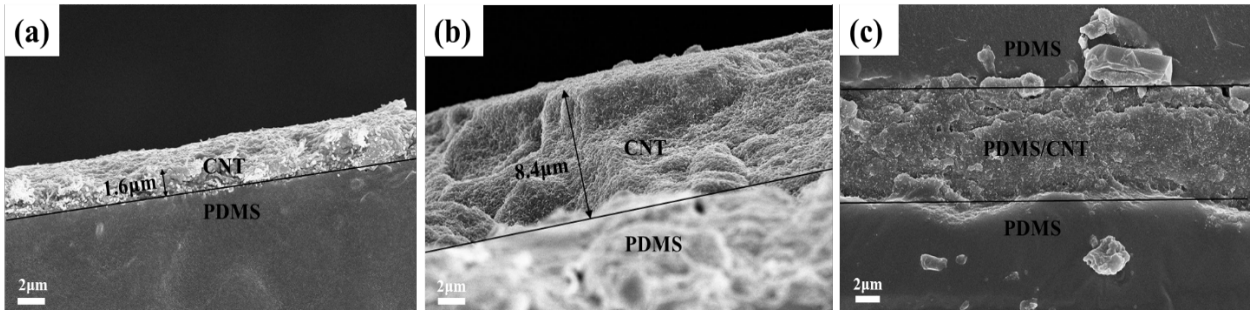

Figure 2. Cross-section SEM images of pristine CNT layers on PDMS substrate with (a) 10; (b) 50 printing cycles; (c) Cross-section SEM images of CNT/PDMS sensors with 50 printing cycles of CNT layer

3.2 Strain sensing capabilities

Strain sensors with different number of printed CNT layers were tested to examine the effect of the number of printed CNT layers on the sensitivity of strain sensors. The strain sensors with area of 15x50 mm^2 and thickness of 0.5mm were prepared for sensing testing, and were named as CPx, where x denotes the printing cycles of CNT layer. To study the change in their electrical resistance as a function of strain, the printed CNT strain sensors were extended up to 45% strain until the PDMS substrate was damaged. The representative resistance change-strain data recorded for the CNT strain sensors is shown in Figure 3(a). A gauge factor was used to characterize the strain sensing properties of carbon nanotube strain sensors[22]:

$$K = \frac{\Delta R / R_0}{\varepsilon} \tag{1}$$

Where: R_0 is the resistance of carbon nanotube strain sensor without strain, ΔR is the resistance change under strain, ε is the strain, and K is the gauge factor. The strain-dependent responses of the sensor were divided into two linear regions with the different slopes (gauge factors, GFs) at around 5% strain and similar observations were also reported[23-25]. In the high strain region, the resistance of the strain sensors increased with a relatively steep slope, which means that in this region, CNT strain sensor is more sensitive to strain. That is possibly due to the CNT networks were damaged suddenly at a high strain and the resistance increase faster than that of a low strain. The cracking occurred in the CNT networks under a high strain, so the contact resistance between carbon nanotubes changed fast. However, in the low strain region, the CNT network was only stretched slightly in the loading direction. The other conduction networks may form in other directions due to the compression in the perpendicular direction, so the resistance change was slow. Additionally, the deformation at a high strain could occur in individual carbon nanotube, which causes the intrinsic electrical resistance of carbon nanotubes increases significantly. Therefore, the sensors showed a higher sensitivity under a high strain. Nevertheless, these observations suggest that the printed CNT based strain sensor can efficiently work as strain sensors at a wide range of mechanical strains. For all the sensors, the resistance increased linearly with the strain (R^2>0.98) for a wide range of strains (from 5 to 45%). This linear increase in resistance with the strain indicates that these strain sensors are capable of measuring strain with high accuracy. Moreover, these sensors can measure much higher tensile strains compared to conventional metallic strain gauges which are limited to applications involving strains less than 5%[26].

As shown in Figure 3(b), strain sensors with more printed CNT layers showed a larger strain gauge factor indicating that the sensor sensitivity could be tuned by simply altering the number of printed CNT layers. The gauge factor varies from 8.74 to 35.75 in our experiments. For the strain sensor with small number of CNT layers, the resistance at an un-stretched state is high due to the loose CNT network. Compared with this original resistance value, the resistance change is small which can explain why this sensor has a low

gauge factor. In addition, a loose network could cause an inefficient load transfer within the CNT network. Therefore, the sensor with thin CNT layers has a lower sensitivity than that has thick CNT layers with the dense network. This behavior was also observed in previous reports[27, 28]. The highest gauge factor obtained in this study is 35.75, which is much higher than the value of ~2 reported for conventional metallic strain gauges[29].

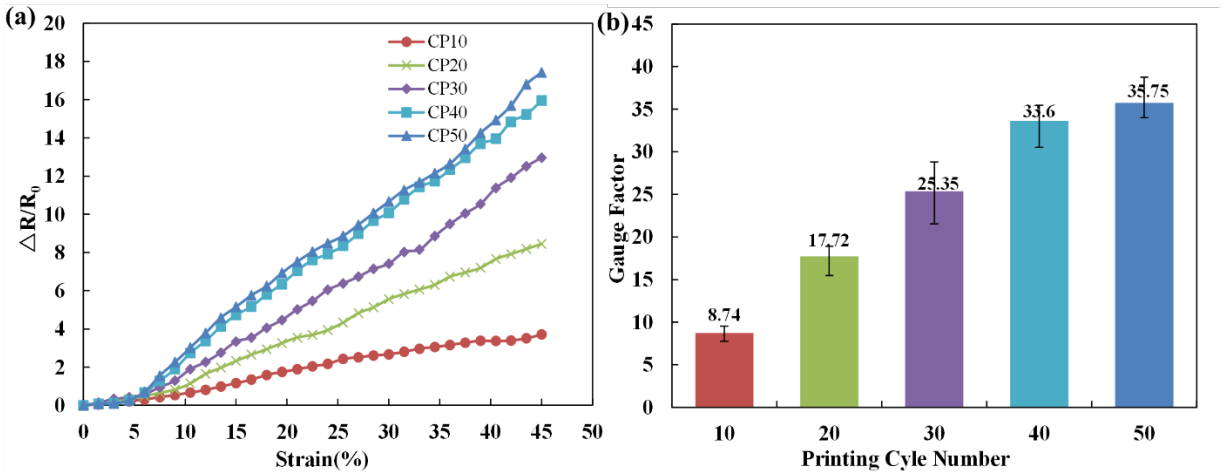

Figure 3. (a) Resistance change–strain relationship of sensors with different numbers of CNT layer (b) Corresponding gauge factors

To examine the strain-dependence behavior under a cyclic loading, repeated stretching and releasing cycles were applied to strain sensors. As shown in Figure 4(a), the printed strain sensor exhibited negligible hysteresis at the stretching/releasing cycle. The resistance increased upon stretching and the changed resistance recovered immediately upon unloading. This could be attributed to the strong interfacial bonding between the CNTs and PDMS in sensors. As shown in Figure 4(b), sensors under three different strains all present excellent resistance recoverability and reproducibility. These results indicated that the printed carbon-nanotube strain sensor exhibited good durability and stability under cyclic loading.

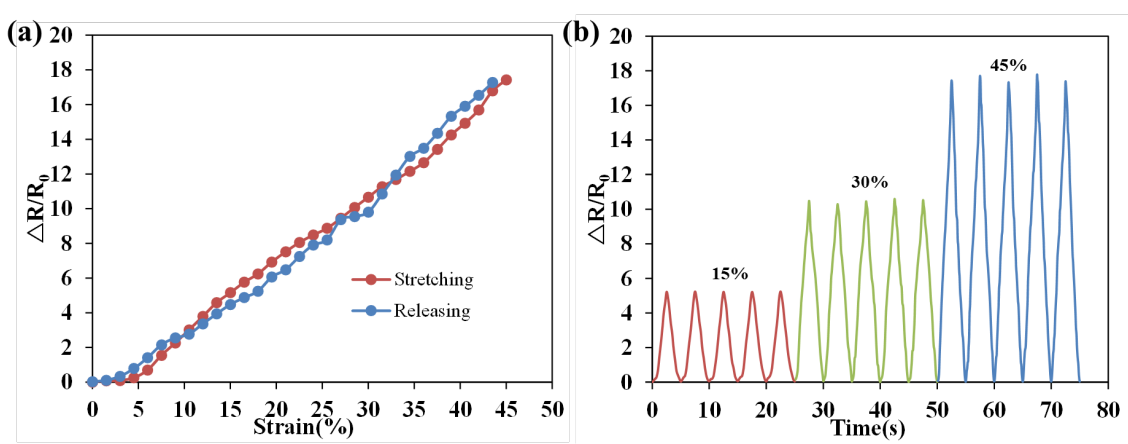

Figure 4. Pieoresistive response of CP50 (a) at first stretching/releasing cycle (b) under different strains

The fabricated strain sensors can be used for wearable electronics applications, because they are flexible to be easily attached to human body parts. To examine their capability of monitoring human motion, the CP50 strain sensors were attached to human wrist to monitor diverse motions. Human body deformation is generally multidirectional, which cannot be accurately monitored by single-directional strain sensors. Due to flexibility of the SDM fabrication, muti-axial strain sensors were fabricated to monitor complicated strain. A rosette-shaped strain sensor was fabricated with an intersecting angle of 120°. As shown in Figure 5(a), the fabricated rosette-shaped strain sensor was mounted on the tester's wrist. Figure 5(b) shows the corresponding electrical resistance changes of each individual sensors. The similar signal changes were observed when the same motion was repeated, which represents a good durability of fabricated sensors for monitoring motions.

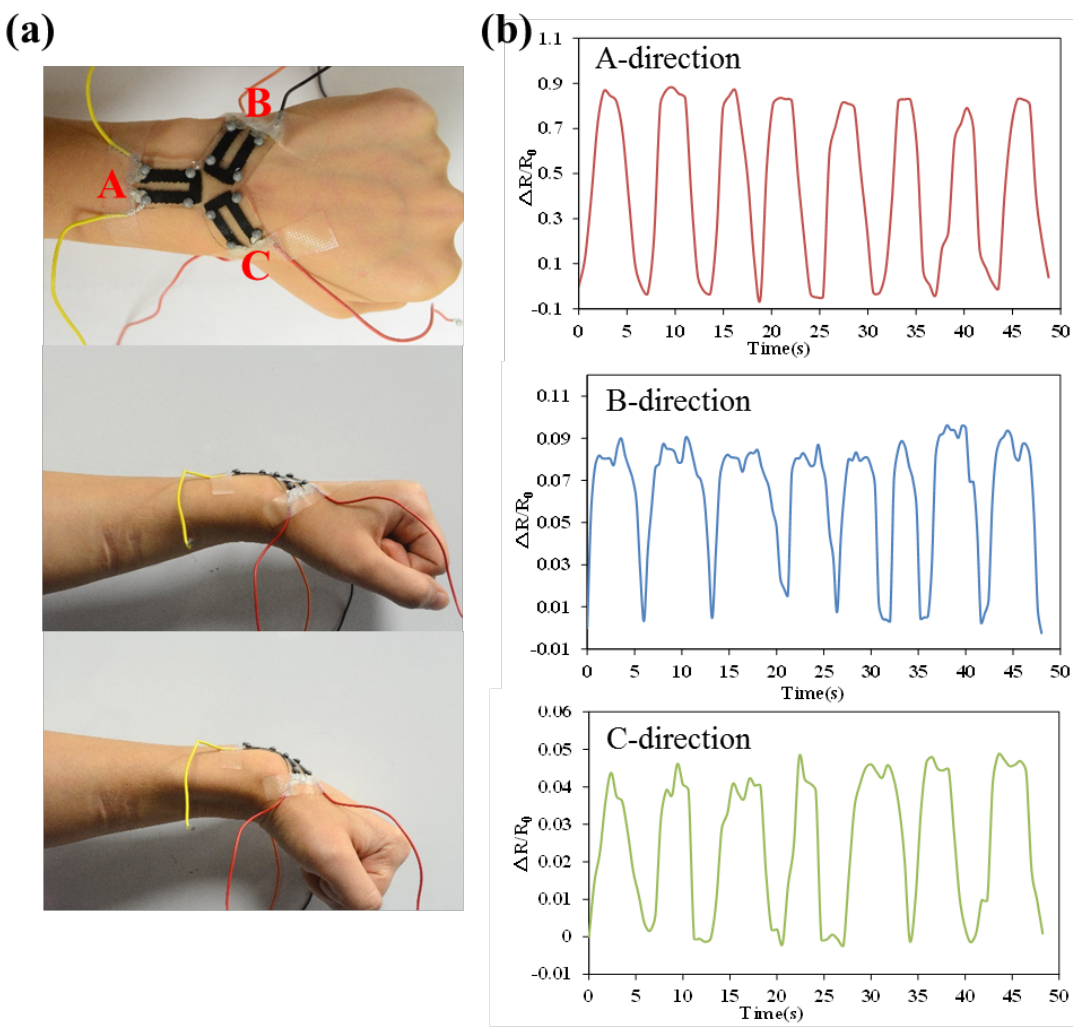

Figure 5. (a) Photographs of the rosette-type strain sensor attached to tester's wrist (b) electrical resistance changes of each individual sensors

4. CONCLUSIONS

This study employed a new spray deposition modeling technique to fabricate carbon nanotube strain sensors to monitor the strain based on the piezo-effect of carbon nanotubes. This fabrication technique has an exquisite print path control that enables the fabrication of CNT sensors with desired geometries and strain

gauge factors. The additive characteristic of this fabrication technique has an advantage of saving the material. A large scale production could be realized by applying multiple spraying nozzles. Therefore, this SDM technique can overcome the drawbacks of the conventional fabrication technique of CNT strain sensors and provide an efficient way to manufacture CNT strain sensors that could work at high strain and high sensitivity. Due to the flexibility of this SDM fabrication technique, the properties of strain sensors could be easily tuned by controlling the number of printing layers of CNT sensors.

The relationship between the change in electrical resistance and the applied strain of carbon nanotube sensors was studied. All the printed sensors exhibited good linearity of electro-mechanical response and high sensitivity in a wide range of strains (0 to 45%). Strain sensors were fabricated with different numbers of printed carbon nanotube layers from 10 to 50 layers and strain gauge factors were measured in a range of 8.74-35.75. It was concluded that as the number of printed CNT layers increases, the sensitivity of CNT strain sensors increases. Moreover, upon the dynamic cyclic loading, all the printed carbon-nanotube strain sensors exhibited excellent durability and stability at cyclic strain. It was also demonstrated that using the digital printing technique, multidirectional strain sensors could be manufactured to monitor complicated deformation of human motion.

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