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Effect of aligned ferromagnetic particles on strain sensitivity of multi-walled carbon nanotube/polydimethylsiloxane sensors

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A strain sensor using chain-structured ferromagnetic particles (FPs) in a multi-walled carbon nanotube (MWCNT)/polydimethylsiloxane (PDMS) nanocomposite was fabricated under a magnetic field and its strain sensitivity was evaluated at different material proportions. When the proportion of MWCNTs that are well dispersed in PDMS is higher than the percolation threshold, the strain sensitivity reduces with the increase of MWCNTs, in general; whereas a higher volume fraction of FPs produces a higher strain sensitivity when the chain-structure of FPs sustains. The mechanisms causing this interesting phenomenon have been demonstrated through the microstructural evolution and micromechanics-based modeling. These findings indicate that an optimal design of the volume fraction of FPs and MWCNTs exists to achieve the best strain sensitivity of this type of sensors. It is demonstrated that the nanocomposites containing 20 vol. % of nickel particles and 0.35 wt. % MWCNTs exhibit a high strain sensitivity of $\sim$80. *© 2015 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License.* [http://dx.doi.org/10.1063/1.4917070]

Multi-walled carbon nanotubes (MWCNTs) have attracted significant attention because of their unique material properties in mechanical, thermal, and electrical aspects.[1,2] MWCNT-polymer composites have been used as strain sensor since MWCNTs change the composite from nonconductive to conductive, while the nanocomposites can sustain a high strain with excellent flexibility.[3,4] However, the dispersion of MWCNTs in a polymer is still very challenging.[5,6] In addition, when a MWCNT composite sensor is subjected to a mechanical load, it may exhibit a lower strain sensitivity with an increase in the amount of MWCNTs in the polymeric matrix. This is a result of the affine transformation of the MWCNT network during deformation which cannot change the effective electrical conductivity significantly except for the change of the contact resistance between MWCNTs. However, the change of contact resistance generally exhibits inconsistent trends during cyclic loading,[7] which significantly limits the application of this type of sensors.

To manipulate the microstructure of MWCNT-polymer composites for better performance, filler materials were aligned in the matrix by means of mechanical, electrical, and magnetic methods.[8–10] Among them, the magnetic method has been commonly used. For example, Shi *et al.*[11] coated ferromagnetic particles (FPs) on MWCNTs and made well-aligned coated MWCNTs in the polystyrene matrix under a high magnetic field. On the other hand, pure FPs made of nickel, iron, and cobalt only require a low magnetic field to align particles into chains in the matrix because of their high magnetic susceptibility. These long chain-structured particles could also serve as an effective path for electron transfer, leading to an increase of the electrical conductivity of the nanocomposite.

We[12] recently invented a strain sensor made of MWCNTs and FPs in polydimethylsiloxane (PDMS) for a large strain capacity and a high sensitivity. MWCNTs and FPs were well mixed in a prepolymer and the FPs were aligned into chains under the magnetic field.[13–15] The mixture was cured and solidified into a thin film, which was tailored into a tape with the chain direction normal to the width direction. Although the electrical conductivity of PDMS is extremely low, a properly chosen volume fraction of MWCNTs can significantly improve the effective conductivity of the mixture for good measurability. Moreover, FP chains further improve the effective conductivity of the composite.

Fig. 1 illustrates the application of this sensor made of the MWCNT/PDMS nanocomposite containing chain-structured FPs. Along the chain direction, the electrical conductivity of the sensor, which is a tape attached on the sensing surface, is much higher than in other directions. Electrodes are attached onto the tape along the width direction with a certain spacing, and gauge leads are used to setup
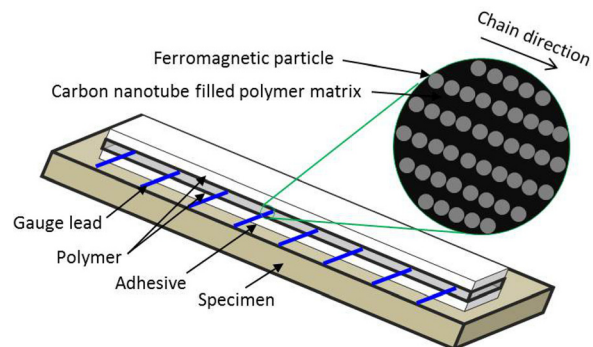

FIG. 1. CNT/polydimethylsiloxane (PDMS) nanocomposite with chain-structured FPs to measure strain in the chain direction.
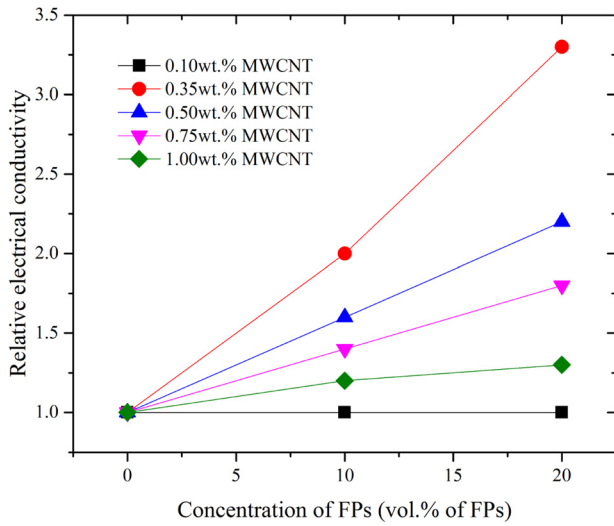
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FIG. 2. Relative electrical conductivity of the nanocomposites with aligned FPs.

the measurement circuit. Because PDMS is so compliant, the tape will deform together with the specimen surface, which can lead to significant change of the electrical conductivity of the tape and can therefore sense the strain and fracture of the specimen surface through the change in the electrical conductivity. This letter will report the experimental results of electrical conductivity and strain sensitivity of the nanocomposites with the aligned FPs and discuss the mechanism on how the aligned FPs improve the effective electrical conductivity as well as strain sensitivity.

The preparation of the nanocomposites was explained in the supplementary material (see supplementary material[16]).

In strain sensing applications, we will use the change of electrical resistance in the chain's direction to measure the strain. Therefore, we focus on the electrical conductivity of the nanocomposite in the chain's direction, which is in parallel to the magnetic field in the fabrication process. It has been observed in Fig. S4(b) that the effective electrical conductivity of MWCNT/PDMS nanocomposites increases along with the concentrations of MWCNTs and aligned FPs. Adding FPs reduces the percolation threshold of the MWCNT/PDMS nanocomposites from $\sim$0.35 wt. % without FPs to $\sim$0.20 wt. % with 20 vol. % of FPs. Although MWCNTs were well dispersed in the matrix to form a network, disjoint parts have constantly been observed in the MWCNT network, especially when the concentration of MWCNTs is low. In this case, the FPs may act as a filler to connect MWCNT network, leading to a lower percolation threshold as well as a higher electrical conductivity. Fig. 2 illustrates the effective electrical conductivity of the nanocomposites as a function of concentration of FPs, which is normalized by the electrical conductivity of the MWCNT/PDMS composites with 0% of FPs. Adding FPs in the nanocomposites generally enhances their effective electrical conductivity. However, in absence of MWCNTs, the increase of electrical conductivity of the composite is negligible; whereas at a low concentration of MWCNTs, say 0.35 wt. %—the percolation threshold of the MWCNT/PDMS, the increase of the relative electrical conductivity reaches $\sim$3.3. Otherwise, continuously increasing MWCNT concentration $>$0.35 wt. % reduces the relative electrical conductivity although the absolute value increases.

To use the proposed nanocomposite for strain and fracture sensing, the change of electrical conductivity with the
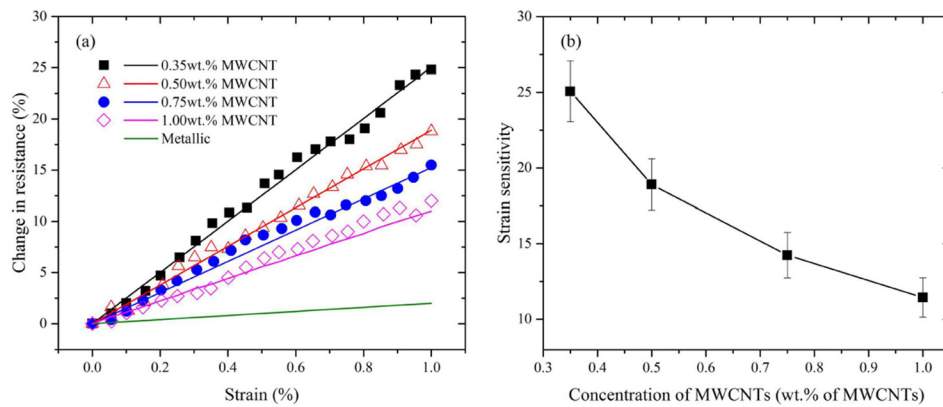

FIG. 3. Electromechanical responses of MWCNT/PDMS composites: (a) Change of the resistance vs. strain and (b) strain sensitivity vs. the concentration of MWCNTs.
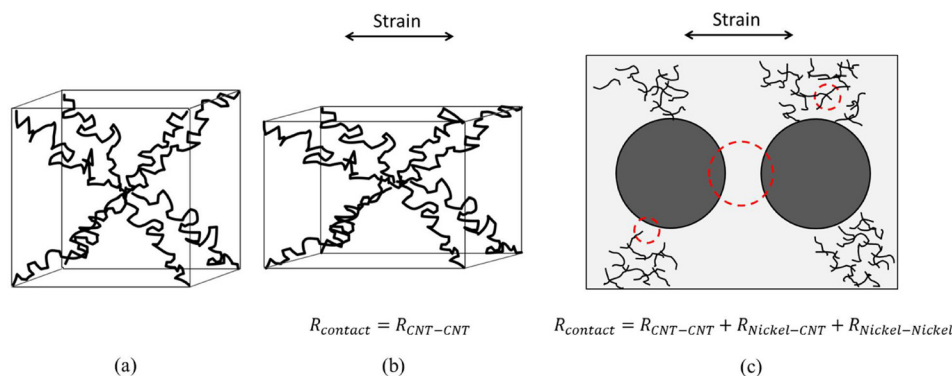

$$R_{contact} = R_{CNT-CNT}$$

$$R_{contact} = R_{CNT-CNT} + R_{Nickel-CNT} + R_{Nickel-Nickel}$$

(a)   (b)   (c)

FIG. 4. Schematic illustration of MWCNT/PDMS nanocomposites with aligned FPs: (a) Eight-chain model of MWCNT/PDMS without strain;[19] (b) deformed unit cell of MWCNT/PDMS with strain; and (c) MWCNT/PDMS with chain-structured FPs during deformation.

strain will play a key role in this application. A traditional metallic strain gauge, Vishay CEA-13–250UW-120, has been used as a reference. Fig. 3 shows the strain sensitivity of the nanocomposite, which is calculated by the linear regression of the measurement data of the change in resistance versus strain. Three replicas for each MWCNT concentration have been measured and the variation ranges are provided with the error bars. The samples have much higher values of the strain sensitivity compared to the metallic strain gauge, which is generally between 2.0 and 2.5. A decrease of the strain sensitivity of the nanocomposite with increasing the MWCNT concentration is observed, which is consistent with the experimental results in the literature.[17,18]

For MWCNT/PDMS nanocomposites, the electron transport is mainly through the MWCNT network when the concentration of MWCNTs is higher than the percolation threshold. Fig. 4(a) schematically illustrates the mechanism using the eight-chain model.[19] The deformation of the network of curved MWCNTs will not change the effective electrical resistance of the network during the affine transformation from Figs. 4(a) and 4(b) as long as the resistance of single MWCNTs and their connections do not change. However, the contact resistance between MWCNTs in the polymer may change significantly with the spacing between MWCNTs at their joints, as shown in Figs. 4(b) and 4(c). When the MWCNT concentration is low, the major electron paths are few, the change of contact resistance at any connection point may produce considerable impact to the overall electrical conductivity. Therefore, the strain sensitivity is high. However, because the contact resistance may not restore the same value when the load is removed, inconsistent trends may be observed in the cycle loading condition. When the MWCNT concentration is higher, even if one path is cut, other paths may still remain the conductivity well. Therefore, the strain sensitivity is reducing as adding more MWCNTs, especially when the MWCNT concentration is much higher than the percolation threshold.

When FPs are added into the MWCNT/PDMS nanocomposites, they may significantly change the electron transport pattern. FPs exhibit a spherical shape, so that the contact
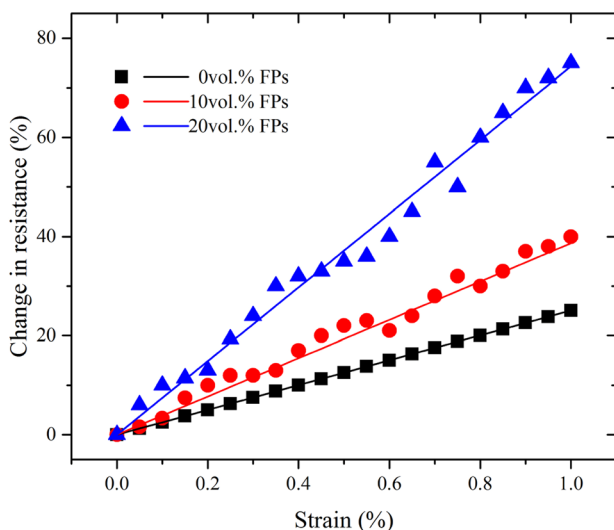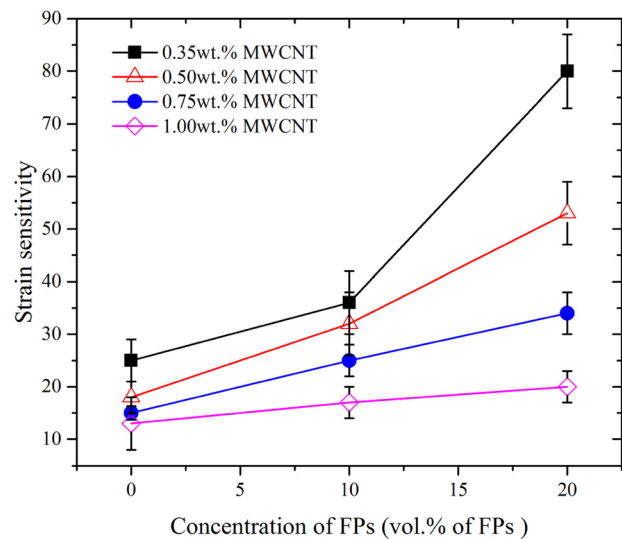

FIG. 6. Strain sensitivity of MWCNT/PDMS composite with aligned FPs for different concentrations of MWCNTs.

point is relatively small compared to a fiber-like shape of MWCNTs and the direct contact resistance between FPs plays a minor role. The electron transport mainly goes through the CNT network and CNT-FP-CNT network as shown in Fig. 4(c). Therefore, MWCNT/PDMS nanocomposites with aligned FPs also exhibit different electromechanical behaviors. Fig. 5 shows the electromechanical response of 0.35 wt. % MWCNT/PDMS nanocomposite with different volume fractions of FPs. All nanocomposites containing FPs were much more sensitive to the tensile strain than the nanocomposite without FPs. Increasing FPs in MWCNT/PDMS nanocomposites led to a higher strain sensitivity to mechanical force.

Fig. 6 shows the strain sensitivity for MWCNT/PDMS nanocomposites with aligned FPs for different concentration of MWCNTs. Interestingly, increasing the concentration of FPs led to higher strain sensitivity, while increasing the concentration of MWCNTs resulted in lower strain sensitivity. In particular, the strain sensitivity dramatically increased at lower contents of MWCNTs, which reached ~80 for the nanocomposites containing 20 vol. % of nickel particles and 0.35 wt. % MWCNT. The FP particle-to-particle spacing change caused by the strain led to the significant change of effective electric resistance, which resulted in the huge strain sensitivity of this strain gage.

In conclusion, MWCNT/PDMS nanocomposites with aligned ferromagnetic particles were fabricated using the external magnetic field. Adding aligned nickel particles into MWCNT/PDMS composites that leads to new electron transport paths reduces the percolation threshold of the nanocomposites, increases the effective electrical conductivity due to the filler effect, and improves the strain sensitivity of this sensor. MWCNTs provide the electron transport network in the PDMS matrix. Without FPs, the MWCNT/PDMS nanocomposites exhibited lower strain sensitivity with the maximal strain sensitivity of ~25 at the percolation threshold of 0.35 wt. % of MWCNTs. Using 20 vol. % of nickel particles in 0.35 wt. % MWCNT/PDMS nanocomposite, we obtained a high strain sensitivity of ~80. The reinforcing mechanisms

FIG. 5. Electromechanical responses of 0.35 wt. % MWCNT/PDMS composite with chain-structured nickel particles.

have been discussed. Rigorous measurements to obtain the optimal design of the sensor are underway.

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