Rapid dip-dry MWNT-rGO ink wrapped polyester elastic band (PEB) for piezoresistive strain sensor applications

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Herein, we report the fabrication as well as application of a multiwall carbon nanotube-reduced graphene oxide polyester band (MWNT-rGO@PEB) piezoresistive strain sensor for human-machine interface applications. The addition of unzipped functionalized MWNTs in the rGO ink assists in providing the propagation path for the charge carriers. The sensing mechanism involved for this strain sensor comprises two regimes, one with a gauge factor of 150 (0%–25%) and the other one with 650 (28%–40%) with the change in the resistivity at a low strain value since the fibres entangled together and wrapped with conductive rGO flakes get separated very slightly apart. At higher strain values, the flakes wrapped on the fibre backbones separated far apart, resulting in a disconnected percolation path for the charges. This kind of sensing mechanism has enough potential to detect small scale as well as large scale motions with excellent reproducibility over 2000 cycles. Some heath monitoring applications such as forearm motion, cheek bulging, and finger bending have been demonstrated in real time by using this piezoresistive strain sensor. The significant advantages of these sensors are their low cost, easy fabrication (one step), and versatility, which render them favourable for health-monitoring applications. Published by AIP Publishing.

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Strain sensors based on smart materials for monitoring physiological and biomechanical reactions of the human body are attaining more importance in the healthcare sector. Such sensors include wearable strain sensors that can be affixed to different parts of the body to monitor both small-scale motions such as breathing, heartbeat, and blood pulse and large scale motions such as sensing body postures and the movement of joints. Conventional strain sensors fabricated using semiconductors and thin metal wires are fragile and brittle making them ineligible for application as wearable devices. However, attempts have been made to fabricate flexible strain sensors using conductive elastomers and garments for body posture detection; however, they are uncomfortable to wear for a long time due to their bulky size and are impermeable to sweat.

Moreover, it is quite essential to miniaturize stretchable/wearable electronic devices in a compact form in order to satisfy the demands of the healthcare market. As of now, progressive attempts have been made to fabricate wire-shaped strain sensors as a reliable alternative to traditionally available bulk devices. The excellent properties of such wire-based strain sensors include their light weight, small size, flexibility and shape adaptability, ease of fabrication, and comfort enabling prolonged wearing during monitoring. Various conductive materials—for instance, gold and silver nanoparticles, silver nanowires, conductive polymers, carbon nanotubes, and graphene—have been employed to fabricate wire-based strain sensors. However, the expense of raw materials along with the complexity of the fabrication processes of carbon and its derivative based sensors (mentioned in Table S1 in the supplementary material) restricts the production of these wire-based sensors. Therefore, it is quite challenging to develop simple, low-cost wire-based wearable strain sensors that are capable of mass production.

In this study, we demonstrate the implementation of a very cheap polyester elastic band (PEB) composed of polyester and spandex as a piezoresistive strain sensor. The sensor was fabricated by dipping the band into a multiwall carbon nanotube-reduced graphene oxide (MWNT-rGO) ink multiple times while allowing it to dry in between each successive dip. To confirm the wrapping of fibres within the PEB with MWNT-rGO flakes, scanning electron microscopy (SEM) images at different positions as well as orientations (horizontal and vertical) were collected at different magnifications. The electrical measurements of the PEB band were recorded under different values of applied strain varied between 0% and 38%. Two linear regimes were observed, with a gauge factor (GF) of 150 calculated for strains between 0 and 15% and GF = 650 for strains between 28% and 38%. The reproducibility of the fabricated sensors has been confirmed by measuring over 2000 stretching cycles without any permanent deformation observed, with the signals collected highly stable and repeatable. We also demonstrated the application of the fabricated strain sensor for monitoring body motions including the forearm muscle, cheek bulging, and finger extension.
Graphite flakes were supplied by Talga Resources Ltd, via Talga Advanced Materials GmbH. Polyester elastic bands made of polyester and spandex were purchased from Lily Zhang Dongguan Limei Packaging Material Co., Ltd. China. These bands are white in color and commonly employed as the elastic band in face masks.

The synthesis procedure involved the preparation of the unzipped functionalized MWNT and its mixture with rGO ink has already been reported recently in our paper. The preparation of rGO involved three steps: (i) preparation of graphene oxide (GO) using Hummer’s method, (ii) reduction with hydrazine monohydrate and additive composed of benzisothiazolinone and methylisothiazolinone as chemical species, and (iii) finally, doping with functionalized unzipped MWNTs.

The fabrication involved washing a 5 cm length Polyester elastic band (PEB) with Iso-propanol (IPA) and acetone followed by drying at 60°C in an oven for 2h. The band was then dipped in the MWNT-rGO ink kept in the desiccator under vacuum to infuse MWNT-rGO flakes into PEB band fibres and dried at 70°C for 15–20 min. This process was repeated ten times in order to allow the complete wrapping of the PEB fibres from one end to other (shown in Fig. 1). As it can be clearly visualised in Fig. 1, the band swelled after the process, which can be further confirmed through the SEM images of the vertically oriented band as shown in Figs. 3(e) and 3(m) depicting the effect, before and after dipping. The effect can be attributed to the MWNT-rGO flakes getting wrapped on the fibre surface during the course of the above process.

Two wires as electrodes were connected at opposite ends of the PEB with silver paste (Alfa Aesar) and further encapsulated with Sil-Poxy Gel (Smooth-On, Inc.) in order to establish a firm connection as shown in Fig. S1(a). Subsequently, the MWNT-rGO@PEB piezoresistive strain sensor was mounted on an Ultimate Tensile Machine (UTM), Mark 10 model ESM303, and subject to strain varying from 0% and 40% [Figs. S1(b) and S1(c)]. Figure 2 graphically summarizes the various steps involved in the fabrication of the MWNT-rGO@PEB piezoresistive strain sensor.

The detailed discussion regarding the synthesis procedure of functionalized unzipped MWNTs and their mixture as MWNT-rGO ink along with the properties has already been reported in our earlier work. The morphologies of PEB before and after coating were examined by scanning electron microscopy (SEM) JSM-7600F with a resolution of 1.0 nm (15 kV); an accelerating voltage that ranged from 0.1 to 30 kV was used along with a focused electron beam. The samples were coated with gold for 60 s to make their surface conductive. Further, the samples (before and after coated PEB bands) for SEM imaging were placed in both vertical and horizontal orientations with respect to the plane of the copper grid, and images were collected at different magnifications to obtain more insight into the sample.

The electrical conductivity of the strain sensor while undergoing strain was measured with a KEYSIGHT model B2902A Source/Measurement Unit in the two wire connection mode. The strain behaviour of the MWNT-rGO@PEB strain sensor was investigated using UTM (Mark 10 model ESM303). To study the performance of the strain sensor under different values of applied strain (0%–40%), the sensor was affixed between the two grips of the testing machine while the wires connected at two ends of the strain sensor (electrodes) were connected to the KEYSIGHT in the two wire mode operation condition as shown in Fig. S1(b). Once strain of known magnitude was applied to the strain sensor, the real time response in terms of resistance was recorded by the measurement setup. Conductivity was measured with an applied bias of 1 V. The relative change in the resistance magnitude was calculated using the \( \frac{\Delta R}{R_0} = \left( R_1 - R_0 \right) / R_0 \) relation, where \( R_0 \) and \( R_1 \) are the resistances without and with applied strain, respectively. Thereafter, the gauge factor (GF) of the strain sensor was calculated using the slope of change in resistance \( [\delta(\Delta R/R_0)/\delta S] \) against applied strain.

Figure 3 presents the SEM images of the PEB before and after coating, with both vertical and horizontal orientations. It can be clearly seen that the PEB band is composed of thin fibres (25 μm thick) which are twisted together so as to form the elastic band. The vertical orientation [Figs. 3(e) and 3(f)] shows that the band is not perfectly circular in cross-section but rather has a star shape (with six corners) with the arms of the star interlinked at the centre. Since the fibres are tightly packed [as shown in Figs. 3(c), 3(d), 3(g),

![FIG. 1. The cleaned Polyester band thread (a) before and (b) after multiple dipping in the MWNT-rGO ink.](image-url)
and 3(b)], the space between them is very less requiring multiple dipping of the PEB band into the MWNT-rGO ink mixture. It can be observed from Figs. 3(d) and 3(h) that at higher magnification, the surface of the fibres in the pristine band is very smooth. After the PEB band is dipped in the MWNT-rGO ink, the MWNT-rGO flakes get wrapped on the PEB fibres and cover the maximum surface available on the PEB surface as shown in supplementary material Fig. S2. Moreover, as establishing a percolating network of MWNT-rGO flakes was difficult, the band was dipped into the ink repeatedly followed by drying at 70°C, resulting in a swollen band. The reiteration of the above procedure resulted in adherence of the MWNT-rGO flakes to the fibre skeleton which can be clearly seen in the magnified images shown in Figs. 3(g) and 3(h), with the surface of the fibres appearing rugged compared to the fibres in the undipped band [in Figs. 3(e) and 3(f)]. In order to get more insight, SEM images of the PEB after dipping are shown in supplementary material Fig. S2, representing magnified images of the MWNT-rGO wrapped fibres at different scales. A peel-off test using scotch-tape was performed to demonstrate the firm adherence of the MWNT-rGO ink (after drying) to the surface of as-fabricated piezoresistive strain. A video along with the digital images is provided in Fig. S3 of the supplementary material.

The cumulative results of the electrical measurements done using the MWNT-rGO@PEB sensor are shown in Fig. 4. The I-V characteristics as shown in Fig. 4(a) depict a huge increment in the electrical resistance value with the increase in the strain values (7.5%–20%). This can be further confirmed through comparative study of the real-time response curve behavior obtained through the MWNT-rGO@PEB strain sensor under different magnitudes of applied strain as shown in supplementary material Fig. S4(a). Simultaneously, Fig. 4(b) presents the plot of relative resistance change ($\Delta R/R_0\%$) as a function of applied strain to calculate the gauge factor (GF). The sensor exhibited different piezoresistive responses to the applied strain, with two response regimes being evident. Up until 28% strain, the relative resistance change was $\sim$1000%, with the relative resistance change increasing dramatically to $\sim$10,000% at 40% strain. This kind of response originates from structural deformation caused within the sensor during stretching. It can be intuited that excess stretching hampers the connectivity of these flakes via MWNTs, thus causing a significant increase in the electrical resistance, i.e., 4.47 MΩ at 0% strain to 355 MΩ at 40% strain. The sensitivity of the strain sensor or gauge factor (GF) was calculated for the two regimes using strain ranges 0%–15% and 28%–38%, with values of GF = 150 and GF = 650 calculated, respectively. The obtained results are quite convincing in terms of the fabrication process.
as well as GF values obtained through the MWNT-rGO@PEB strain sensor as compared to other reported literature studies summarized in Table S1 in the supplementary material.

The GF values of the MWNT-rGO@PEB sensor were observed to increase exponentially at higher values (above 20%) of applied strain implying higher sensitivity of the sensor at higher strain values. Moreover, the rGO ink has a great affinity towards the crimped and twisted fine polyester fibres [Figs. 3(g) and 3(h)]; as a result, delamination of the flakes from the backbone of the thread did not occur at higher strain values. However, the permanent deformation was induced in polyester fibres at higher values of strain, i.e., above 40%. Thus, it can be employed for health monitoring that includes small-scale as well as large scale motion.27

The efficacy of the strain sensor to determine the detection limit can only be explored by perturbing the sensor using applied strain in a stepwise fashion. Figure S5 in the supplementary material shows the stepwise response of the sensor with steps of 8%, 11%, 18%, and 22% strain. These values of strain were applied for a period of 20 s before increasing, with the sensor held at a maximum strain of 22% for approximately 53 s before lowering the applied strain in a reverse step-wise fashion. With decreasing strain, the resistance returns to a similar value indicating that the MWNT-rGO@PEB strain sensor can sustain different values of strain without undergoing any permanent deformation. Similarly, the cyclical response of the strain sensor was studied with different values of applied strain; Fig. 4(c) shows the response to six stretching-and-release cycles at 12%, 20%, 28%, and 38% strain. The signature of the curve shows excellent stability and elasticity of the sensor under different applied strains which is also reflected from Fig. S6 in the supplementary material. The reproducibility of the strain sensor was further evaluated with extensive cycling at 36% of applied strain. The sensor was exposed to periodic strain for 2000 cycles’ stress vs strain curve. Further, the performance of the MWNT-rGO@PEB piezoresistive strain sensor (as shown in Fig. S7 in the supplementary material) was also studied under a constant strain of 10% at different frequencies, say 0.0084 Hz, 0.015 Hz, 0.15 Hz, and 1.5 Hz. Thus, the above results clearly demonstrate efficient stability and durability of the fabricated sensor. However, there are certain limitations that can be reflected in the real-time response curve during dynamic study of the as-fabricated strain sensor. In order to make it available for the real-time application, we can infuse the elastomers, say PDMS, Ecoflex, etc., inside the MWNT-rGO ink coated band. Alternately, the conductive band can be sandwiched between two elastomer layers (top and bottom) with a finite width which provide enough space so as to get mounted easily. In both the cases, the elastomer will assist in managing the uniform distribution of strain throughout the band and will not impact the electro-mechanical properties of the band over time.

The potential for the MWNT-rGO@PEB sensor for application in health monitoring applications was studied by measuring the response of the sensor to small-scale motions such as cheek bulging and forearm motion and to large scale motions such as finger extension.

Figure 5(a) shows the electrical signal response associated with monitoring of forearm muscle movements. The sensor was affixed on the muscle using tape near the top and bottom ends of the electrodes. Figure 5(a) shows the response of the sensor to clenching and release of the fist and (b) cheek bulging and large-scale motion, say tracking finger bending at (a) 45°, (b) 60°, and (c) 90°, respectively.

FIG. 5. Response of the MWNT-rGO@PEB strain sensor to monitor small-scale motion such as (a) motion of forearm muscles during clenching and release of the fist and (b) cheek bulging and large-scale motion, say tracking finger bending at (a) 45°, (b) 60°, and (c) 90°, respectively.
increased bending is expected due to the decreased interconnectivity associated with increased distortion. Thus, an increase in resistance with the increase in the bending angle was observed.

In conclusion, we have demonstrated the fabrication as well as application of the MWNT-rGO@PEB piezoresistive strain sensor for sensing of human motion. The proposed sensing mechanism is speculation for this strain sensor that comprises two regimes, a low strain regime (0%–28% strain) where there is a modest increase in resistance with strain associated with a slight separation of conductive rGO flakes and a high strain regime (28%–40% strain) where the flakes wrapped on the elastic fibres are separated far apart such that percolation path for conduction is broken with an associated steep increase in resistance. This sensing mechanism is capable of monitoring small-scale and large-scale motions such as forearm motion, cheek bulging, and finger bending in the real-time curve.

See supplementary material for digital images of the MWNT-rGO@PEB based strain sensor mounted on UTM at 0% and 40% strain, SEM images of the MWNT-rGO ink coated PEB fibers, demonstration of the peel-off test using scotch-tape of MWNT-rGO ink adhered onto the PEB surface, comparative real-time curve and response time behavior, four-step up cycle measurements, real-time resistive curve along with different values of applied strain, and the effect of frequency on the real-time resistance curve under 10% of applied strain.

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