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Pressure-dependent electrical conductivity of freestanding three-dimensional carbon nanotube network

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The dependence of electrical conductivity on compression of a freestanding three-dimensional carbon nanotube (CNT) network is investigated. This macrostructure is made of mm-long and entangled CNTs, forming a random skeleton with open pores. The conductivity linearly increases with the applied compression. This behaviour is due to increase of percolating pathways—contacts among neighbouring CNTs—under loads that is highlighted by *in situ* scanning electron microscopy analysis. The network sustains compressions up to 75% and elastically recovers its morphology and conductivity during the release period. The repeatability coupled with the high mechanical properties makes the CNT network interesting for pressure-sensing applications.
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Owing to their excellent electrical conductivity and superior mechanical properties, carbon nanotubes (CNTs) are exploited as building blocks in several nanoscale devices.[1] These properties make CNTs particularly suitable for strain sensor applications especially when dispersed in polymers to form a composite material. In the literature, a plethora of examples of CNT-polymer composite strain sensors are indeed described.[2] In this case, the sensor fabrication involves dispersing small amounts of CNTs into a polymer matrix to form a CNT percolating network for electron conduction. The addition of CNTs dramatically increases the conductivity by forming electric pathways in the otherwise insulating polymer,[3] thus showing that the overall conductivity critically depends on the number of conductive paths. However, these sensor materials have two issues that have to be still addressed: repeatability and stability. Repeatability problems refer to plastic deformations of polymers under high loads, whereas stability issues arise when the sensor works in harsh conditions, like in solvents or at high temperature. These issues could be overcome by using thin (2D) films made only of CNTs as strain gauges,[4] but they show very low strength and permanent deformation after a strain of only 0.04%. Zhao *et al.*,[5] who succeeded in developing a macroscopic (3D) strain sensor based on CNT yarns, give a good alternative. This kind of sensor shows excellent repeatability and stability, however, it can work just under tensile strains because of the geometry of the system. Pushparaj *et al.*[6] report on a pressure sensor made of a macroscopic block of well-aligned CNTs. The sensor sustains compressions up to 50% but shows strain sensitivity[7] smaller (∼0.6) than that of metal alloys today used for foil-type strain gauges (>1). Herein, we develop a compressive strain sensor entirely made of entangled freestanding CNTs forming a macroscopic (mm^3 in size) solid, as reported in Fig. 1(a). The presented material shows a strain sensitivity double with respect to that previously reported by Pushparaj *et al.*[6] and can elastically sustain compression loads as high as 75% without showing sizeable plastic deformation. This macrostructure is synthesized as described in details elsewhere.[8] In brief, a sulphur-assisted chemical vapour deposition strategy is employed with ferrocene being the catalyst source. Within this synthesis method, the resulting solid is made of different kinds of multi walled CNTs.[8] Particularly, the presence of sulphur in the sp^2-carbon lattice leads to pentagon/heptagon rings which modify the CNTs' straight tubular morphology.[9] These obtained curved and interconnected carbon nanostructures form a random skeleton with open micrometre-size pores as highlighted by scanning electron microscopy (SEM) analysis reported in Fig. 1(b).

To test the strain sensor capabilities of the produced material, we set up an experiment similar to that used in Ref. 6, where the metallic electrodes are located at top and bottom of the sensor and the compression is applied to the whole sample. For the experiment, the static electrical conductivity (σ) is calculated from I-V plots acquired by a commercial sourcemeter (Keithley 2602A). The initial value of σ is 0.035 ± 0.002 S/cm thus highlighting the metallic character of the synthesized macrostructure. In Fig. 2, σ is plotted against the compressive load (ε), clearly showing the dependence of the electrical properties of the present CNT network on its morphology. In particular, as one can see, the conductivity linearly scales with the compression and increases of about 615% at compressive strain as high as 75% (black squares in Fig. 2). The resulting sensitivity[7] of the presented pressure-sensor is 1.15, a value double with respect to that reported in Ref. 6 for a sensor made of well-aligned CNTs. It is also worth noting that σ elastically restores the initial value during the release period (red dots in Fig. 2) apart from a small hysteresis, which can be ascribed to a sort of arrangement within the CNT network after the compression of about 75%. The conductivity increase under compression is ascribed to a growing number of contact locations (N_j) among adjacent CNTs that creates, in the network, new percolating pathways for charge carriers. In

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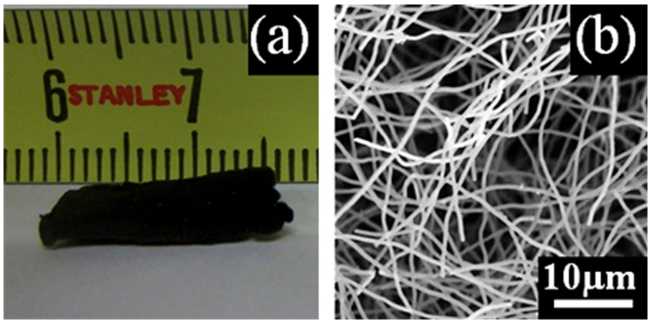

FIG. 1. (a) Snapshot of the freestanding CNT network and (b) its porous microstructure as shown by scanning electron microscopy.

fact, when a pressure is applied to the sample, the inter-tube pores are squeezed (likewise the pores in a sponge) so that the CNT network becomes denser and eventually more CNTs touch each other. Removing the compressive load from the sample results in a complete recovery of its original shape and consequently of initial number of tube contacts so that σ regains the starting value as well. This finding proves that both the electrical conductivity and the compressive strain response of the CNT-based sensor are fully reversible.

To straightforwardly display the increase of contact points among CNTs under loads with an experimental evidence, we report in Figs. 3(a) and 3(b) two SEM images acquired on the same volume without and with applied strain, respectively. Within this experiment, the compression on the sample is applied by a nano-tweezer. Under loads, it is evident that the CNT density in the scanned volume increases and the CNTs are closer to each other. To better highlight the CNT approaching, we have applied a z-threshold filter to the SEM pictures reported in Figs. 3(a) and 3(b) (Figs. 3(c) and 3(d), respectively). SEM reproduces 2D images, where the third dimension (z) is given by the greyscale which ranges from 0 to 1. The filter thereby works eliminating the elements that have z-coordinate lower than the threshold which has been previously chosen with the same percentage of greyscale in the two images. From the comparison, it is clear that we have a higher number of CNTs above the threshold when compression is applied, proving that the CNT density is increased.

Recently, Lyons *et al.*[10] have numerically predicted a linear relationship between σ and N_j for CNT films. In this

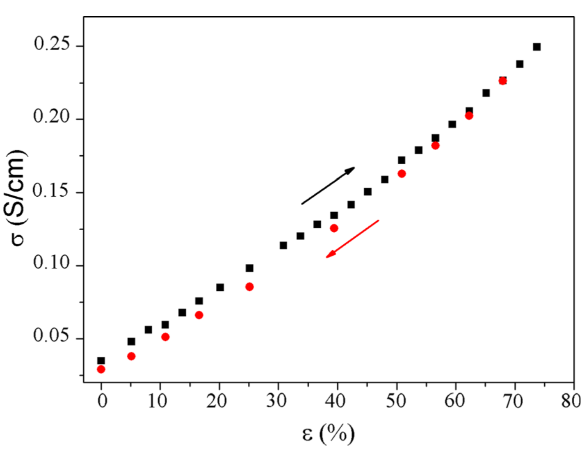

FIG. 2. Conductivity as a function of compressive strain under load (black squares) and release (red dots).

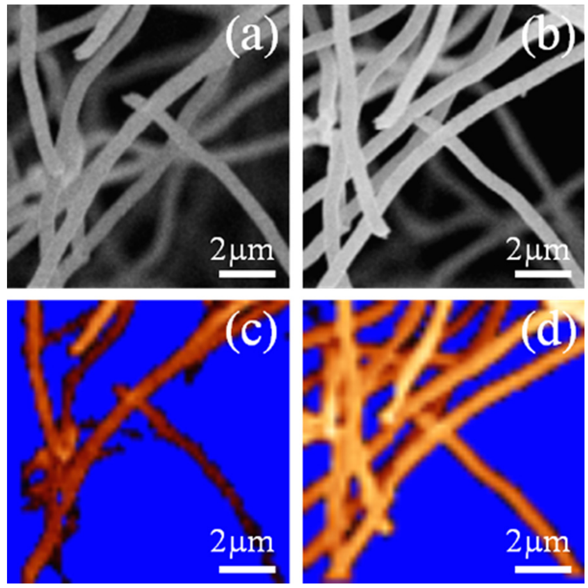

FIG. 3. SEM pictures of the CNT network acquired without (a) and with (b) applied strain. (c) and (d) are, respectively, the (a) and (b) images with a z-threshold filter applied to highlight the density change under load.

sense, from the comparison between our experimental data and the simulations in Ref. 10, we can state that, in a random CNT network, N_j linearly scales with ε.

Finally, in order to confirm the experimental findings minimizing the contribution of contact resistance and electrode distance to the conductivity change, we acquire the σ vs. ε plot with a different experimental set-up. As shown in Fig. 4(a), the CNT network is fixed on a rigid support in a SEM while the compression is applied by a nano-tweezer at the centre of the sample far away from the metal electrodes that are located at the edges. In this way, the contact resistance and the electrode distance are kept unchanged during the experiment so that their contribution to the measured conductivity change is negligible. For the experiment, the strain is directly evaluated from the SEM images reported in Fig. 4(b). The relative σ vs. ε plot is shown in Fig. 4(c). As one can notice, the linear trend is still found thus confirming that the sensing mechanism is the increase of contact points (i.e. percolating pathways) among adjacent CNTs. However, in this configuration, the conductivity change ($\Delta\sigma$, and consequently the sensitivity of the sensor) is lower than that measured in the previous experiment at the same compressive range. Actually, this behaviour is expected, as in the second experiment the pressure is applied just on a reduced area and the number of pressure-induced contact points among CNTs is thereby smaller. This result confirms that the sensing element of the CNT network is the number of contact points among neighbouring CNTs. As matter of fact, the higher sensitivity shown by the present entangled CNT network with respect to that reported for well-aligned CNT block in Ref. 6 can be easily understood. In addition, the random skeleton with the open pores gives to our sensor mechanical properties similar to that of sponges, so that the network can be compressed up to 75% without showing sizeable plastic deformation. On the contrary, in the case of aligned CNTs it was reported a maximum load value of 50%.

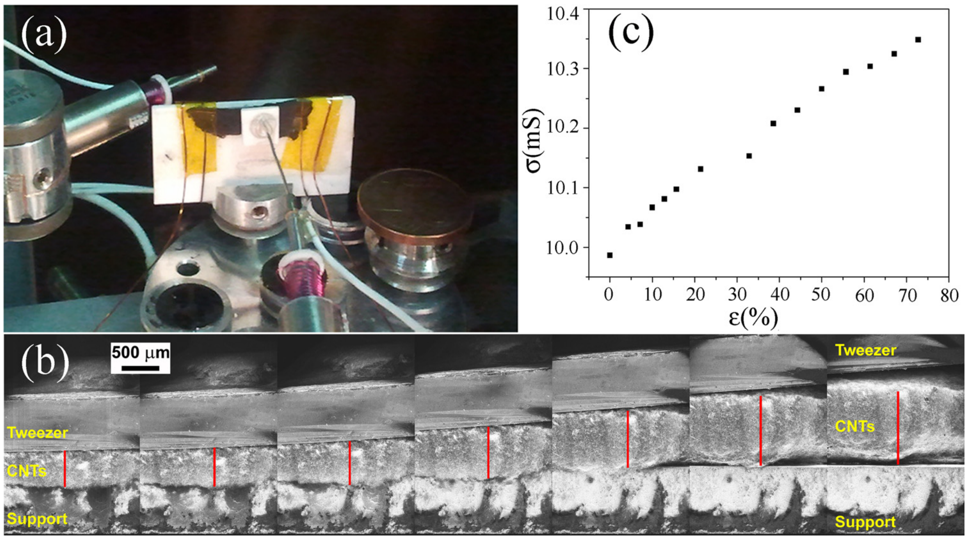

FIG. 4. (a) Photo of the experimental set-up used for acquiring the σ vs. ε plot in a SEM. (b) Some of the SEM images acquired at different compressions. The CNT network is sandwiched between the nano-tweezer and a rigid support. (c) Conductance vs. strain plot acquired with the configuration shown in (a).

In conclusions, we have investigated the relationship between the electrical conductivity and the compression of a freestanding 3D percolating network entirely made of highly entangled CNTs. The conductivity linearly scales with the applied compressive loads and in particular increases up to 615% for compression of 75%. The sensing mechanism resides in the increase of contact points (i.e., percolating pathways) among adjacent CNTs due to the squeezing of the inter-tube pores under compression. This phenomenon has been underlined by *in situ* SEM investigations. When the compression goes over, the electrical conductivity regains its initial value as the initial number of tube contacts has been restored. The high mechanical properties, the reversible electrical conductivity change, the ability to be compressed up to 75% the original size, and the CNT chemical stability make the present CNT network very interesting for pressure-sensor applications.

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