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Proceeding Paper

Sensors Based on Multiwalled Carbon Nanotubes †

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Abstract: In this study, we exploit films of multiwalled carbon nanotubes (MWCNTs) as the sensing element of new and low-cost sensors for temperature, pressure and humidity. Aqueous solutions of functionalized MWCNTs are vacuum filtered to produce freestanding films of randomly oriented MWCNTs, known as buckypaper, with thickness in the range 200–500 μm. The electric resistance of the buckypaper, patterned in strips with widths of a few mm and lengths of up to a few cm, is investigated as a function of temperature, pressure and humidity. The electric resistance of the buckypaper shows a monotonic decrease for increasing temperature over the 80–380 K range. Owing to the high porosity, the buckypaper structure can be changed by the application of a force. A compressive force applied over the buckypaper surface improves the electric contact between the MWCNTs and results in a decrease in the electric resistance. The exposure of the buckypaper to liquid or vapour water increases its electric resistivity. The experimental data presented in this work confirm that the electrical conduction of a buckypaper is highly sensitive to environmental conditions and that the buckypaper is an interesting material with promising applications in a variety of low-cost sensors with high sensitivity and fast response.

Keywords: sensors; carbon nanotube; heat sensor; pressure sensor; humidity sensor

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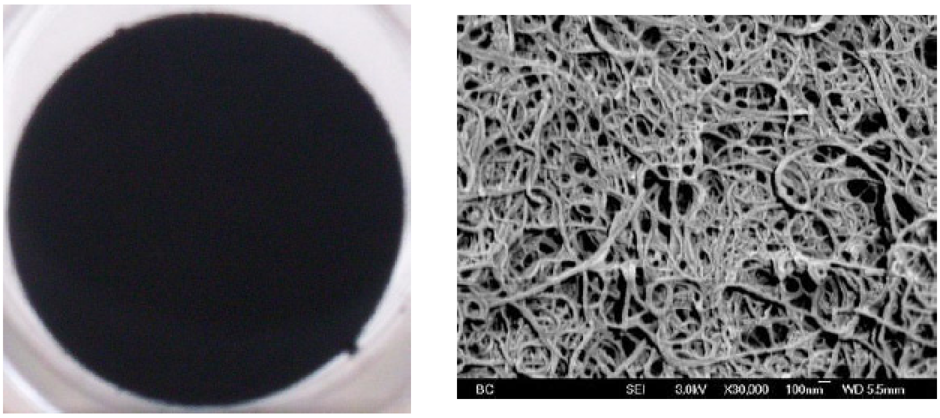
1. Introduction

Carbon nanotubes (CNTs), since they were discovered by Iijima [1], have been drawing great research interest because of their one-dimensional morphology and their chemical, electrical and mechanical properties [2–4]. Carbon nanotubes are graphene sheets rolled up to form hollow cylinders with single walls (SWCNTs) or multiwalls (MWCNTs). Buckypaper is an arrangement of carbon nanotubes. These CNTs can be arranged to enhance specific properties, such as strength, heat dissipation and electrical conduction [5–7].

There are plans to develop a new generation of sensors based on buckypapers because they are cheap and highly sensitive and have real-time response. In this work, we investigate the electrical and mechanical properties of MWCNT buckypapers as a function of temperature, pressure and humidity.

2. Materials and Methods

The buckypaper shown in Figure 1a is a sheet of carbon nanotubes that must be purified to become suitable for aqueous processing. The purification of the carbon nanotubes takes place in hydrochloric acid to dissolve residual iron-particle catalysts. Once the nanotubes have been acid treated and washed with deionized water, they are re-suspended in deionized water. After sonication, a stable nanotube suspension is obtained. A volume of this suspension is poured into a filtration unit. Both vacuum based and pressurized filtration units can be used to pull/push the suspension through the filter membrane. Nanotubes deposit on the filter surface, and its concentration dictates the resulting thickness of the paper. After deposition, the nanotube paper is removed from the supporting filter membrane. The obtained buckypaper is shown in Figure 1b and is ~ 50% dense.



(**a**) (**b**)

Figure 1. Buckpaper film. (**a**) Photo of MWCNT buckypaper; (**b**) typical scanning electron microscope (SEM) image of buckypaper.

Resistance measurements on the sample kept inside a glass box were performed by a Keithley 4200-SCS using a two- or four-probe configuration, at room temperature. We forced a current I and measured a voltage V, thereby obtaining R = V/I. To avoid Joule heating of the sample, we kept I below 2 mA.

3. Results

We start with a short discussion about the electrical properties and the temperature response of the buckypaper. After that, we focus on the effects of heat, pressure and humidity on the electrical resistance, from which we demonstrate that the buckypaper can be conveniently exploited to develop a new generation of cheaper, highly sensitive and fast response sensors.

3.1. Electric Characterization

The MWCNT film is highly conductive, and the linear Current–Voltage (I–V) behaviour, shown in Figure 2, confirms its ohmic nature. The electrical resistance, obtained from the slope of the I–V characteristics of Figure 2, determined with the two-probe method is 180.3 Ω, and becomes 125.5 Ω using the four-probe method. Hence, we estimate that the contribution of wires and contacts to the total resistance of the sample is about 54.8 Ω. To focus only on the properties of the buckypaper and to avoid the effect of the contacts, in the following, we systematically used the four-probe configuration, which eliminated the contact and the wire resistance contribution.

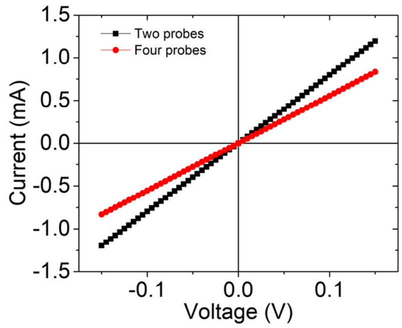


Figure 2. Current–Voltage (I–V) characteristics of the buckypaper measured in four- (**black line**) and two-probe (**red line**) configurations.

3.2. Thermal Response

The sample was made with a piece of buckypaper with a length of 2.6 cm and width of 0.2 cm, placed on a glass substrate and contacted with silver paste, as schematically shown in Figure 3a. The specimen was placed on a base and connected to the Keithley 4200-SCS. The temperature was monitored through a thermocouple placed near the sample. The sample was posed under an infrared lamp. The starting temperature was 290K and warmed up to 368K; later, the lamp was switched off, and the resistance was also evaluated during cooling. Two measurement cycles were carried out both in heating and in cooling.

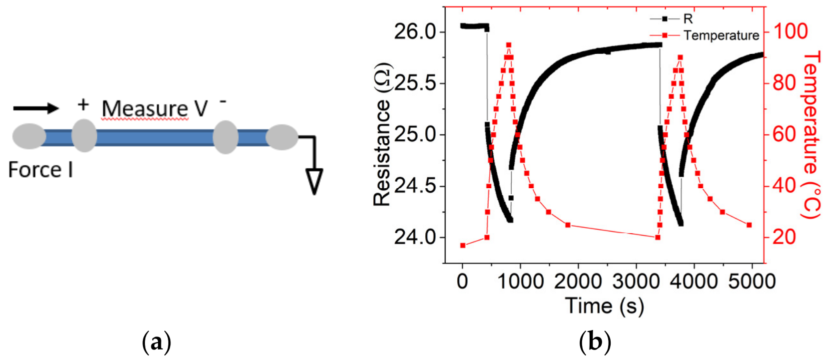


Figure 3. (**a**) Schematic of the sample used for four-probe electrical measurement. The current is forced in the external probes, and the voltage is measured between the inner ones. (**b**) Temperature and resistance as a function of time.

Figure 3b shows that the resistance decreased rapidly as the temperature increased in the range of 293–303 K. In first cycle, the resistance decrease was estimated approximately at 3.7%. After the lamp was switched off, there was an increase in resistance.

In the next step, the sample was placed in a liquid nitrogen thermostatic chamber to evaluate the response of the sensor in a range between 80 and 293 K. Starting from a value of 293 K, the sample was brought to lower temperatures until it reached a minimum temperature of 80 K. The resistance was measured with 5 K steps, and its value increased. Similar results were obtained in the next heating cycle, as shown in Figure 4a. As in the cooling cycle, the resistance was measured with 5 K steps, until returning to the initial value, obtaining similar values.

As shown in Figure 4b, the measure was repeated in a range between 80 and 380 K, and the thermal response had the same trend measured during the first range.

Therefore, it can be deduced that the buckypaper is responsive to temperature changes over a wide range.

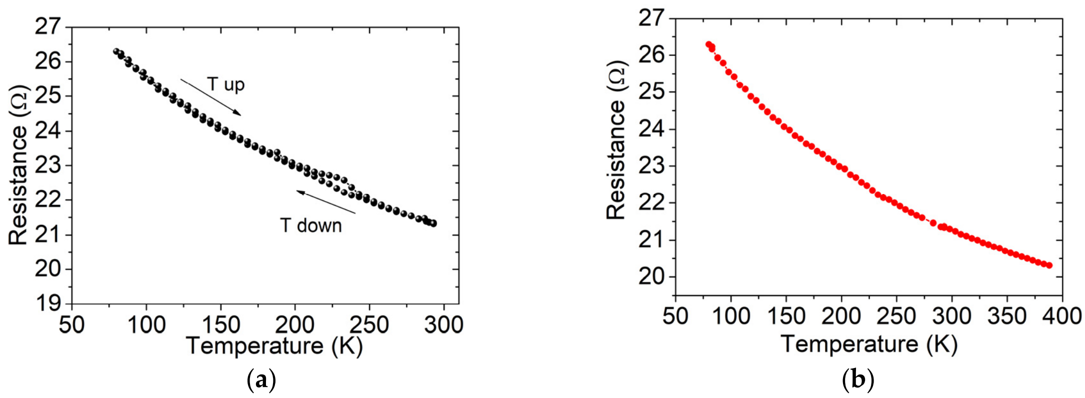


Figure 4. Trend of resistance as a function of time. (**a**) Measurement of two cycles, cooling and heating, between 80 and 293 K. (**b**) Heating cooling between 80 and 380 K.

3.3. Pressure Response

A sample consisting of a buckypaper strip was sandwiched between two glass substrates, and a pressure was mechanically applied to it. Figure 5 shows that the application of a pressure between 10 and 50 kPa resulted in a decrease in the resistance, which was almost reversible. The dips in the resistance correspond to the application and release of a pressure over time.

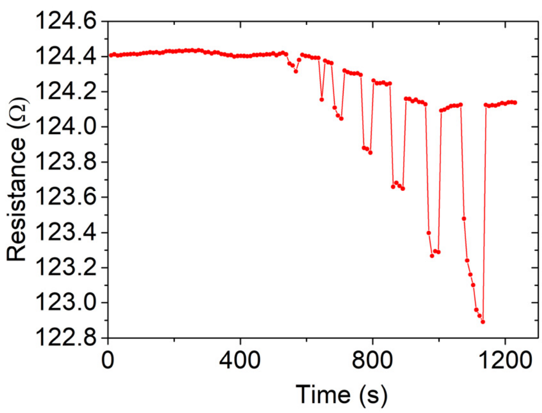


Figure 5. Resistance variation when a pressure is applied and released repeatedly over time.

The resistance of buckypaper decreased with increasing pressure because the adhesion between the nanotubes improved. There was only a slight variation in the pristine state, indicating that there were minor changes in the microscopic structure of the buckypaper.

3.4. Humidity Response

The same sample of the temperature experiment (Figure 3) was used to evaluate the resistance as a function of humidity. Using a micropipette, different volumes of deionized water were poured onto the sample. Pouring 2 μL of water onto the sample, the resistance increased significantly and then returned to the starting value after the evaporation of the water. Repeating the procedure, the same response was obtained. The results were the same, increasing the volume to 4 and 6 μL, as shown in Figure 6.

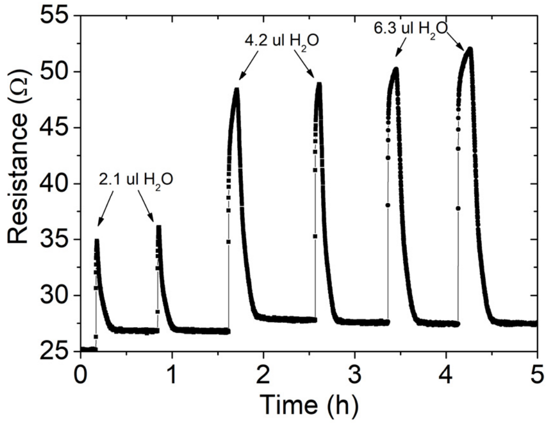


Figure 6. Resistance of the buckypaper when different volumes of water are poured on it.

The resistance increased with increasing volumes of water deposited on the buckypaper. After evaporation, the resistance returned to the initial value, indicating no permanent effects. Figure 6 indicates that a buckypaper, after proper optimization, is a water drop sensor.

4. Conclusions

In this work, we fabricated MWCNT buckypapers and investigated their electrical properties. We showed that the electrical resistance is sensitive to temperature, pressure and water. This study demonstrates that MWCNT buckypapers are promising for temperature, pressure and water sensing. Their easy miniaturization makes it possible to conceive buckypaper-based multipurpose sensors, able to measure different physical quantities simultaneously.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

References

1. Iijima, S. Helical microtubules of graphitic carbon. *Nature* **1991**, *354*, 56–58.
2. Giubileo, F.; Iemmo, L.; Luongo, G.; Martucciello, N.; Raimondo, M.; Guadagno, L.; Passacantando, M.; Lafdi, K.A. Di Bartolomeo: Transport and field emission properties of buckypapersobtained from aligned carbon nanotubes. *J. Mater. Sci.* **2017**, *52*, 6459–6468
3. Passacantando, M.; Bussolotti, F.; Santucci, S.; di Bartolomeo, A.; Giubileo, F.; Iemmo, L.; Cucolo, A.M. Field emission from a selected multiwall carbon nanotube. *Nanotechnology* **2008**, *19*, 395701.
4. Di Bartolomeo, A.; Scarfato, A.; Giubileo, F.; Bobba, F.; Biasiucci, M.; Cucolo, A.M.; Santucci, S.; Passacantando, M. A local field emission study of partially aligned carbon-nanotubes by atomic force microscope probe. *Carbon* **2007**, *15*, 2957–2971.
5. Voskanian, N.; Olsson, E.; Cumings, J. Field-Dependent Heat Dissipation of Carbon Nanotube Electric Currents. *Sci. Rep.* **2019**, *9*, 10785.
6. Li, Z.; Xu, J.; O'Byrne, J.P.; Chen, L.; Wang, K.; Morris, M.A.; Holmes, J.D. Freestanding bucky paper with high strength from multi-wall carbon nanotubes. *Mater. Chem. Phys.* **2012**, *135*, 921–927.
7. Sensors and sensitivity: Carbon nanotube buckypaper films as strain sensing devides. *Compos. Sci. Technol.* **2011**, *71*, 373–381.