

# Multi-walled carbon nanotube films for the measurement of the alcoholic concentration

Chiara Giordano<sup>1,2</sup>, Giovanni Filatrella<sup>1</sup>, Maria Sarno<sup>3,4</sup>, Antonio Di Bartolomeo<sup>2,4</sup> ✉

<sup>1</sup>Department of Sciences and Technologies, University of Sannio, Via Port'Arsa 11, I-82100 Benevento, Italy

<sup>2</sup>Physics Department 'E. R. Caianiello', University of Salerno, Via Giovanni Paolo II, 132, I-84084, Fisciano, Salerno, Italy

<sup>3</sup>Industrial Engineering Department, University of Salerno, Via Giovanni Paolo II, 132, I-84084, Fisciano, Salerno, Italy

<sup>4</sup>Interdepartmental Centre NanoMates, University of Salerno, Via Giovanni Paolo II, 132, I-84084, Fisciano, Salerno, Italy

✉ E-mail: adibartolomeo@unisa.it

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The work shows that a multi-walled carbon nanotube (MWCNT) film can be used as the sensing element of a low-cost sensor for the alcoholic concentration in liquid solutions. For this purpose, they investigate the electrical resistance of the film as a function of the isopropanol concentration in a water solution. The analysis reveals a growing resistance with increasing isopropanol concentration and a fast response. The sensing element is re-usable as the initial resistance value is restored once the solution has evaporated. The electrical resistance increases linearly when the MWCNT film is exposed to common beverages with increasing alcoholic content. This work paves the way for the development of low-cost, miniaturised MWCNT-based sensors for quality monitoring and control of alcoholic beverages and general liquid solutions.

**1. Introduction:** The availability of nanostructured materials has generated huge opportunities for the realisation of new highly sensitive, low-cost, portable and small-size sensors, which operate at very low power consumption. Carbon nanotubes (CNTs), since they were discovered by Iijima in 1991 [1], have been drawing great research interest because of their one-dimensional morphology and unique chemical, electrical and mechanical properties [2–5]. Thus, the preparation, properties, and applications of CNTs have been the subject of an intense activity. CNTs are graphene sheets rolled up to form hollow cylinders with single-wall CNTs (SWCNTs) or multi-wall CNTs (MWCNTs). SWCNTs have diameters of few nanometres, and length of at least of 1–100  $\mu\text{m}$  [6]. MWCNTs consist of multiple layers of graphene wrapped up around the same central axis to form tubes with diameters up to hundreds of nanometres and lengths that can reach several centimetres. The structure of the CNT inherently provides unique electrical, physical, and chemical properties. Mechanically, due to the C–C  $\sigma$ -bonds, CNTs are among the strongest fibres that are known to date. CNTs also possess a high thermal stability, both in a vacuum and in the air. In terms of electrical properties, SWCNTs can be either metallic or semiconducting, depending upon the tube diameter and chirality (the direction in which the graphene sheet is rolled to form the tube) [7], while, for the large diameter and different wall tube chiralities, MWCNTs have a metallic behaviour.

The extremely high surface-to-volume ratio makes CNTs ideal for sensing purposes, as the interaction of CNTs with the analyte is maximised [8, 9]. Hence, CNT-based sensors have been long sought by the biomedical, automotive, manufacturing, food and fishing industry, as well as for application in agriculture and environmental control [10]. In particular, it has been demonstrated that CNTs are sensitive to gases, which, adsorbed on their surface, easily change their conductivity, capacitance, dielectric constant etc. The voltage response of the CNTs as a function of time has been used to detect  $\text{H}_2$  and  $\text{CO}_2$  at various concentrations while supplying a constant current to the system [11]. The sensitivity of the response to gas molecules has been related to the extent of electron transfer and the binding energy [12]. SWCNT films have been used for alcohol detection through a change of mass detected by a frequency shift of the SWCNT film

deposited onto a quartz crystal microbalance [13]. Alcohol vapour sensors consisting of SWCNT field effect transistors (FET) with a significant change in the FET drain current by exposure to various kinds of alcoholic vapours were reported in [14]. Similarly, ethanol vapour detection was demonstrated using metal–CNT hybrid materials synthesised by infiltrating SWCNTs with transition metals such as Ti, Mn, Fe, Co, Ni, Pd or Pt [15]. Alcohol vapour detection was also achieved using MWCNT films, whose resistance was found to increase with the flow rate of the alcohol vapour carried by an inert gas [16]. Sin *et al.* [17] demonstrated that the functionalisation with carboxyl groups grafted along the sidewall and ends of MWCNTs can increase the variation of the resistance to alcohol vapours. It was proposed that the polar –COOH groups enhance the response to the alcohol vapours, as the dipole–dipole interactions with –COOH increases the absorption efficiency of the volatile polar organic molecules [18].

In 2009, it was reported that the electrical resistance versus temperature of a freestanding MWCNT film, known as buckypaper, has a monotonic behaviour, and it was proposed that the buckypaper could be used as a small-size temperature sensor with long-term stability, fast response, and high sensitivity on a wide range of temperatures [19].

In this study, differently from previous works, we demonstrate that an easy-to-fabricate MWCNT film can be directly exposed to a liquid solution and exploited as a chemical sensor to monitor the alcoholic concentration. Indeed, the electrical resistance of the buckypaper increases monotonically and reversibly with the alcoholic concentration of the liquid solution. Liquid drops, with different alcohol contents, are easily adsorbed on or desorbed from the MWCNT film, and the element responds with a variation of the resistance that is proportional to the alcoholic concentration, enabling the discrimination of liquid solutions based on their alcoholic concentration. Furthermore, we confirm that the MWCNT film is sensitive to temperature (temperature sensor), and has a positive temperature coefficient of resistance ( $dR/dT > 0$ ) typical of metals.

**2. Device fabrication and measurements:** MWCNTs were synthesised by an ethylene catalytic chemical vapour deposition

on Co/Fe–Al<sub>2</sub>O<sub>3</sub> catalyst, following a procedure described elsewhere [19, 20]. After that, 0.5 g of MWCNTs were suspended in 100 g of water and sonicated for 15 min (see Fig. 1) [21]. The solution was then vacuum filtered onto a membrane support. After drying, films of different thickness and densities were removed from the support. This procedure allows some control of the thickness and the density of the buckypaper [20].

The obtained films are stable, freestanding, and bendable; they can be easily manipulated or contacted without breaking.

Figs. 2a and b show an optical and a scanning electron microscopy (SEM) image of the buckypaper. The nanotubes are multi-walled with the external and the internal diameter in the range from 10 to 30 nm, and from 5 to 10 nm, respectively, as obtained from the transmission electron microscopy (TEM) characterisation reported in a previous work [22].

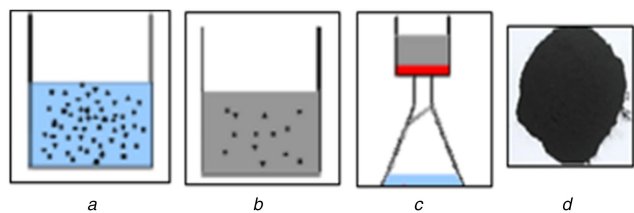
The buckypaper sample used for the resistance measurement was held by silver paint on a glass support, as shown in Fig. 2c where the electric measurement setup is sketched. It consists of a small rectangle of about 3 cm length, 0.5 cm width, and 400  $\mu$ m diameter. Copper wires (diameter 0.2 mm) were connected to the sample surface by silver paint.

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 and pressure. We forced a current ( $I_{\text{force}}$ ) and measured a voltage ( $V_{\text{meas.}}$ ), thereby obtaining  $R = V_{\text{meas.}}/I_{\text{force}}$ . To avoid Joule heating of the sample, we kept  $I_{\text{force}}$  below 1 mA (corresponding to <3  $\mu$ W power dissipation).

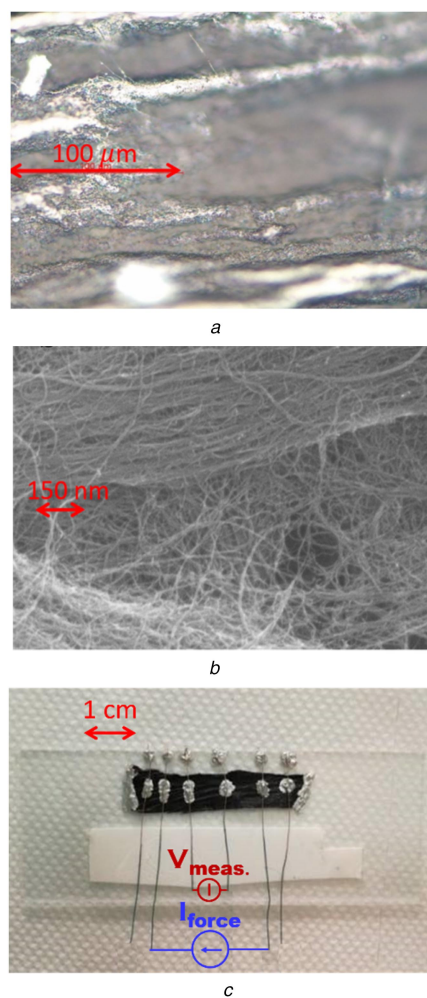
**3. Results and discussion:** We start with a short discussion on the electrical properties and the temperature response of the buckypaper. After that, we focus on the effects of alcohol on the electrical resistance, from which we demonstrate that the buckypaper can be conveniently exploited for the measurement of the alcoholic concentration of an aqueous solution.

**3.1. Electric characterisation:** Fig. 3a shows the typical current–voltage ( $I$ – $V$ ) characteristic of the buckypaper in two- and four-probe configuration at room temperature and pressure. The MWCNT film is highly conductive and the linear  $I$ – $V$  behaviour confirms its ohmic nature. The electrical resistance, obtained from the slope of the  $I$ – $V$  characteristics in Fig. 3a, determined with the two-probe method is 4.32  $\Omega$  and becomes 2.30  $\Omega$  using the four-probe method. Hence, we estimate that the contribution of wires and contacts to the total resistance of the sample is about 2  $\Omega$ . To focus only on the properties of the buckypaper and to avoid the effect of the contacts, in the following, we systematically use the four-probe configuration that eliminates the contact and the wire resistance.

Fig. 3b shows the electrical resistance as a function of time and evidence that the resistance of the buckypaper is stable over time since it remains almost constant at 2.26  $\Omega$  for 16 h. The slight trend up, starting after 7 h, corresponds to day/night increase of the temperature of the laboratory. The inset of Fig. 3b displays



**Fig. 1** Production of a film of MWCNTs (buckypaper)  
a MWCNTs are added to an aqueous solution  
b A MWCNT dispersion is obtained after sonication  
c The MWCNT dispersion is filtered under vacuum  
d Finally a free-standing MWCNTs film is obtained



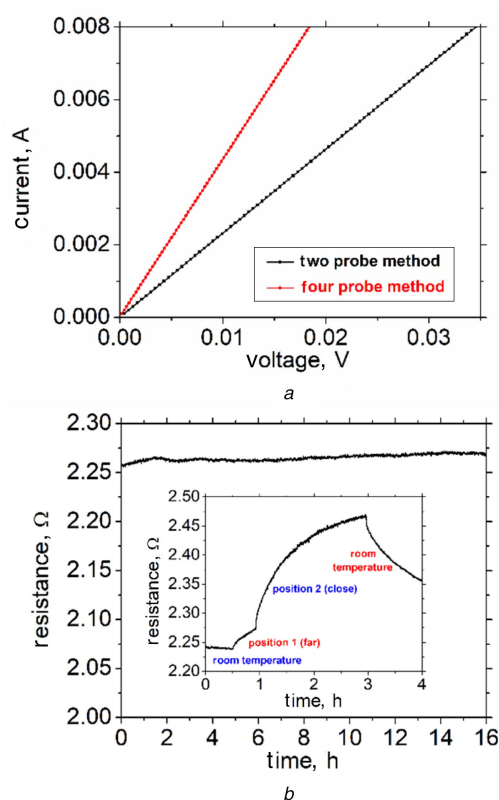
**Fig. 2** SEM and TEM images of the sample

a Optical image of the sample  
b SEM image of the buckypaper showing a network of nanotubes bundles  
c The sample used in the experiments contacted by six copper wires. Four wires were used simultaneously during the alcoholic test concentration experiment for the four-probe resistance measurement, in which a current was forced between the intermediate wires while a voltage was measured between the innermost ones

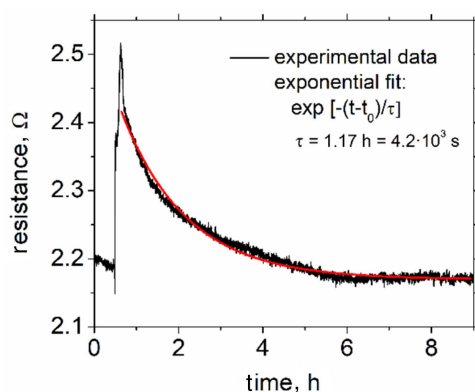
the increasing electrical resistance for growing temperature resulting from a hot plate placed at different distances (denoted as positions 1 and 2) from the sample; the final decay corresponds to the removal of the hot plate. It is clear that the warming up of the sample yields an increase in the resistance.

The resistance dependence on temperature is a further indication of the metallic behaviour of the buckypaper under study, which is a direct consequence of the high density of MWCNTs in it [19]. The fast response and high sensitivity to temperature is a remarkable advantage of the buckypaper and can be exploited to realise a small-size thermistor with a temperature coefficient of resistance around  $7 \times 10^{-4} \text{ K}^{-1}$  as we reported in a previous publication [19].

**3.2. Alcoholic sensor:** In the following, we consider the sample as an alcohol sensor by studying its response to isopropanol and then to isopropanol/water solutions. Fig. 4 shows the time evolution of the resistance when an isopropanol drop (0.05 ml) was poured on the portion of the buckypaper between the two contacts used for the voltage sensing in the four-probe measurement configuration. The small volume assures that the drop is confined away from the two leads and there is no reaction of the analyte with the silver paint contacts. The figure shows that the electrical

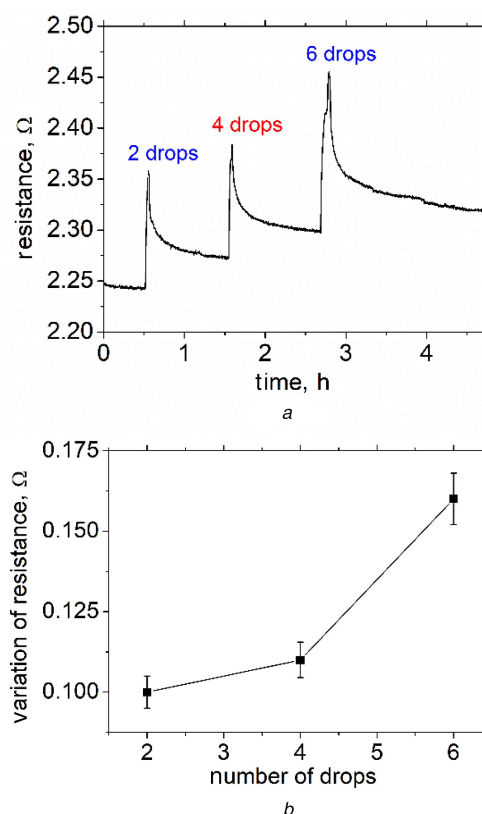


**Fig. 3** Electrical characterisation of the buckypaper  
*a* Current–voltage ( $I$ – $V$ ) characteristics of the buckypaper measured in two-probe (upper red line) and four-probe (lower black line) configurations  
*b* Four-probe electrical resistance of the buckypaper as a function of the time. The resistance stays constant for several hours; the fluctuations are due to minor room-temperature variations. The inset shows the response of the sample to temperature changes induced by a hot plate, placed at different distances from the buckypaper. The sample electrical resistance is highly sensitive to temperature



**Fig. 4** Resistance of the buckypaper versus time coated with a 0.05 ml isopropanol drop. The sample is highly sensitive to the isopropanol, which causes a sudden increase in its resistance. The resistance slowly returns to the baseline while the isopropanol evaporates

resistance is suddenly increased by the presence of isopropanol and that it slowly decreases while the isopropanol evaporates. We point out that the buckypaper and the isopropanol liquid drop are at the same temperature (room temperature), therefore the sudden increase in resistance cannot be ascribed to a drop-induced temperature change. The decrease follows an exponential law, as shown by the fitting curve. The electrical resistance returns to the baseline value after few hours. It is important to notice that



**Fig. 5** Sensor response to increasing number of isopropanol drops  
*a* Electrical resistance versus time, showing that adding isopropanol drops causes a sudden increase of the resistance  
*b* The variation of the electrical resistance of the buckypaper versus the deposited amount of isopropanol(drops). The variation of the resistance, for each peak, is the difference between the maximum and the starting value of the resistance

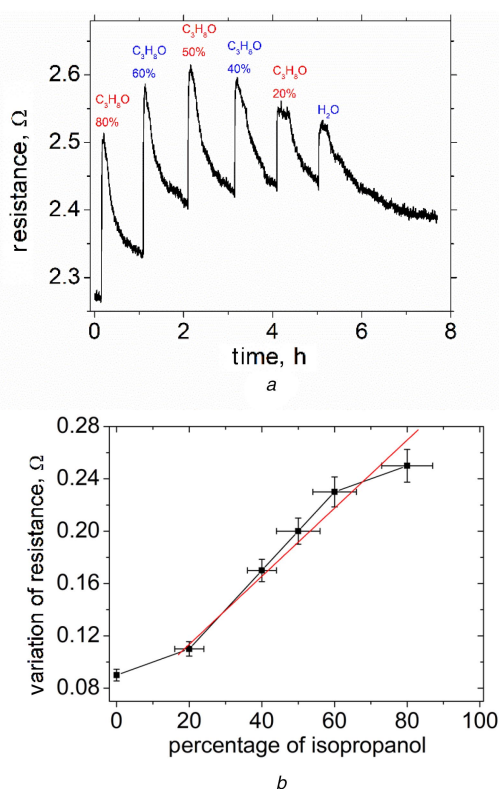
the sensors recovery time, i.e. the time needed for the resistance to return to the baseline, is dominated by the slow evaporation of the alcohol. Such time can be shortened by heating the sample by an increased forcing current, which speeds up the evaporation process.

Fig. 5*a* shows the electrical resistance versus time obtained by pouring an increasing amount of isopropanol on the buckypaper, determined by the number of drops.

The growing up-steps in the resistance (Fig. 5*b*) are expected considering that a wider buckypaper area is wetted. The error bars result from the instrumental incertitude and error propagation. We notice that the general up-trend of the resistance in Fig. 5*a* is due to the fact that we did not wait long enough for the fully restore of the baseline after each drops' evaporation. The sensor response is connected to the extent of the interaction area between the CNTs and the alcohol. Consistently with our finding, a substantial increase of the resistance of entangled networks of pristine MWCNTs, exposed to vapours of linear alcohols (such as methanol, ethanol, 1-propanol, 1-butanol, and 1-pentanol), was reported in [23].

When the liquid solution comes in contact with the CNT film, the solute molecules are polarised by the fringing electric fields radiating from the CNTs and are attracted to their surface, causing a change of the CNTs electric resistance. Molecules with a higher dipole moment, such as water or alcohol, are attracted with higher efficiency [24]. Furthermore, polar COOH groups possibly created during the fabrication/purification process on the CNT surface could contribute to the adsorption efficiency of alcohol molecules by hydrogen bonding. Consequently, a charge transfer between the CNT to the adsorbed molecules, which reduces the





**Fig. 6** Sensor response to aqueous solutions with different isopropanol concentration

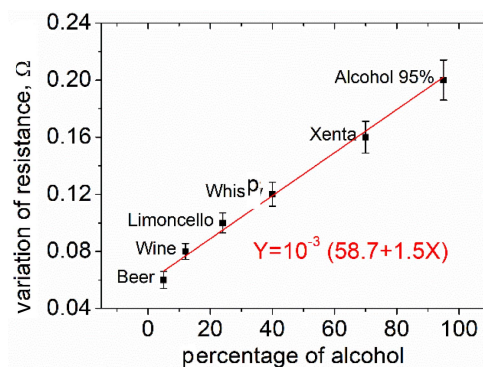
a Time-variations of the buckypaper resistance, induced by different isopropanol/water solutions

b Change in the electrical resistance as a function of the concentration of isopropanol. The variation of the resistance is the difference between the maximum of the resistance and its starting value for each peak

intrinsic doping of the nanotubes, likely causes the observed increase of the electrical resistance of the buckypaper with the alcohol concentration. Furthermore, the molecules adsorbed on the CNT surface can induce a change in the structure of the buckypaper and make the CNT–CNT contacts looser, thereby increasing the tunnelling barrier and the inter-tubes contact resistance. The above two mechanisms, i.e. the reduction of the MWCNT electron density and the increase of contact resistance between touching tubes, likely concur to cause the observed variation of resistance.

Next, we consider aqueous solutions consisting of different percentages of isopropanol and water (Fig. 6). Indeed, the sudden increase of resistance varies with the concentration of isopropanol in the solution. As shown in Fig. 6b, the sensor is capable of discriminating different isopropanol concentrations in the solution, exhibiting a monotonic variation of resistance with the percentage of isopropanol. We notice that this behaviour is consistent with Fig. 5.

A natural problem that arises is the sensitivity of the buckypaper element to alcoholic beverages. Hence, we have checked the buckypaper resistance when the sample was exposed to alcoholic beverages, such as beer (5%), wine (12%), limoncello (24%), whisky (40%), xenta (75%), and pure alcohol (95%). The purpose was to figure out if the buckypaper was able to discriminate the concentration of alcohol in common beverages. To prevent the deposition of unwanted substances, present in the beverages, we cleaned the sample by water, which was poured on the buckypaper and let evaporate before each measurement. Fig. 7 shows the response to a single drop of several alcoholic beverages with augmenting alcohol volume content. Although the response might be contributed by chemicals present in the beverages, the linear



**Fig. 7** Electrical resistance measured when the sensor is exposed to a drop of several alcoholic beverages with increasing alcoholic content

increase of the resistance, consistently what has been observed for the isopropanol solutions, is mostly caused by the alcoholic concentration. The alcohol concentration response can be evaluated as  $S = (1/\Delta R_0)(d\Delta R/dP) = 2.6\%$  per unit of alcohol volume percentage (here  $P$  is the alcohol volume percentage,  $\Delta R$  is the variation of resistance, and  $\Delta R_0 = 58.7 \text{ m}\Omega$  is the extrapolated variation of resistance for an alcohol-free beverage). This result indicates a high sensitivity of the MWCNT film to the alcoholic graduation of liquid solution and constitutes the proof-of-concept of the proposed sensor. Once optimised and properly calibrated, the sensor has great potentiality for real-life applications, such as for the control of the alcohol content in cosmetic products or in worldwide highly-consumed alcoholic beverages.

**4. Conclusion:** In this work, we have demonstrated that a MWCNT film (buckypaper) responds to the alcoholic concentration of liquid solutions. The observed increase of the electrical resistance with the alcohol concentration can be ascribed to stress due to either alcohol molecules captured around the CNTs surface or to charge transfer between the CNT and the alcohol molecules.

The buckypaper shows an ohmic behaviour, with a positive temperature resistance coefficient, typical of a metal. We have proved that a steep rise of the resistance results from the exposure of the buckypaper to water drops with increasing content of isopropanol. The device shows repeatability and reusability since its electrical resistance returns to the initial value when the solution drops evaporate. More importantly, we have demonstrated that the MWCNT-based sensor has the potentiality to discriminate the concentration of alcohol in common alcoholic beverages. The sensor exhibits a linear and rapid response and can be used to monitor a sudden change of the alcohol concentration in a solution.

This work paves the way towards practical application of MWCNT films in the control of the alcoholic concentration of liquid substances.

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