Room temperature hydrogen gas sensor nanocomposite based on Pd-decorated multi-walled carbon nanotubes thin films

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ABSTRACT

Multi-walled carbon nanotubes (MWCNTs) are successfully processed in the form of thin films (buckypapers), and their morphology and electrical behaviour are characterized. The MWCNTs are synthesized by the floating catalyst chemical vapour deposition process. The effects of a sequence of treatments applied for MWCNTs purification on the buckypapers electrical behaviour are also examined. Nanocomposite thin films constituted of pristine and purified MWCNTs and Pd nanoparticles are prepared in order to evaluate their viability as H_2 sensors at room temperature. For this purpose, the electrical resistance of the nanocomposite films in atmospheres with different H_2 concentrations, is determined. Scanning electron microscopy (SEM) images show that the buckypapers and the nanocomposite films are 2D structures constituted by randomly oriented MWCNTs. The buckypapers present a semiconductor-like electrical behaviour as determined by the standard four point method. Room temperature resistivity values of around $10^{-3}\,\Omega\,m$ are assessed. Nanocomposite films show different electrical behaviour depending on the purification treatment applied to the MWCNTs employed. Furthermore, the electrical resistance of the nanocomposite films is found to increase when the measurements are performed in H_2 atmosphere. Values of H_2 sensitivity at room temperature of the nanocomposite films up to 2.15% are determined for H_2 average concentration higher than 350 ppm with short recovery time.

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1. Introduction

Gas sensors are widely used for environmental analysis in industry, medical diagnostics, and several other applications. Common gas sensors are based on metal oxide semiconductors such as tin oxide, zinc oxide, titanium oxide and aluminium oxide. Problems encountered with these sensors are lack of flexibility, poor response time, and operation at elevated temperature. Therefore, new materials are needed to serve as small, user-friendly and reliable gas sensing devices [1]. Since their discovery in 1991 [2], carbon nanotubes (CNTs) have attracted much attention as a feasible gas sensor material [3–6].

Recently, macroscopic forms of CNTs, such as arrays and films, have been reported making the macroscopic manipulation of CNTs practical for gas sensing application [7]. Carbon nanotube paper, which is a paper-like CNTs film, also known as buckypaper, is expected to have the same properties as CNTs. Up to the present, the most popular way of preparing buckypapers has involved the pro-

cedures of dispersion and filtration of functionalized CNTs [8–11]. Regardless of the form of CNTs in devices, nanotube-based sensors have unique advantages over other materials. Different proposals have been explored; fabrication of miniaturized devices, operation at low power levels, and integration in future nanodevices are envisaged as critical factors that determine the application of CNTs.

Detection of ammonia gas and water vapour using as grown multi-walled carbon nanotubes (MWCNTs) arrays has been reported [6]. It has also been reported that single-walled CNTs respond impractically to a broad range of common gases and volatile organic compounds [12]. In some cases, CNTs mixed with different metal oxides have been used to fabricate gas sensors. Modification of CNTs with functional groups, metal nanoparticles, oxides, and polymers has been proposed to change their electronic properties and to enhance the selectivity and response to specific gases through the interaction of the target molecules with the functional groups or additives [13]. In particular, detection of different gases has been reported modifying single-walled CNTs, using coatings of catalytic noble metals and mixtures of metal oxide semiconductors or polymers [14]. Metals exhibit a broad range of electronic, chemical and physical properties that are often highly sensitive to changes in their chemical environment [15]. They are mechanically and chemically robust and stable, and can operate at high temperature and in harsh environment. There have been some

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attempts to detect hydrogen using CNTs-based gas sensors, which are functionalized with catalytic palladium (Pd) or platinum (Pt) [16–18].

In the near future, hydrogen is expected to be widely used as an energy source for fuel cells. Accordingly, H_2 gas sensors are necessary to ensure safe operation of hydrogen-based energy equipments and infrastructures, such as H_2 gas stations or fuel cell vehicles. Suehiro et al. [18] developed an electrochemical functionalization method to fabricate a H_2 gas nanosensor by site-specific eletrodeposition of Pd nanoparticles on as grown single-walled CNTs, with a detection limit of 100 ppm and a linear response up to 1000 ppm of H_2 in air at room temperature. The carbon nanotube-based gas sensors utilize the change of electrical conductivity caused by the adsorption of gases. It is well established that at room temperature, the adsorbed H_2 molecules on the surface of Pd nanoparticles are dissociated as hydrogen atoms, which dissolve into Pd with high solubility, leading to a decrease in the work function of Pd. This causes electron transfer from Pd to CNTs, leading to a decrease in the nanotube conductance. The process is reversible as dissolved atomic hydrogen in Pd can be combined with O_2 in air to form water leaving the Pd–CNTs system and, enabling to recover the sensor's initial conductance [13].

Within this context, the present work deals with the study of the H_2 sensitivity of high purity nanocomposite thin films obtained by a simple and practical filtration method of Pd-decorated MWC-NTs dispersion in water. The aim of this study is two folds: (i) to process both pristine MWCNTs and further subjected to purification treatments in the form of buckypapers and, additionally, of nanocomposite thin films, and (ii) to understand the gas sensing behaviour and feasibility of the decorated carbon nanotubes as room temperature hydrogen sensor material. This work presents fabrication methods, structural properties, electrical behaviour, and H_2 sensing characteristics of the Pd–carbon nanotube based nanocomposite thin films.

2. Experimental

2.1. Carbon nanotubes preparation

Aligned MWCNTs arrays were lab-synthesized by the floating catalyst chemical vapour deposition process under flowing Ar/H_2. Analytical grade iron(II) phthalocyanine ($C_{32}H_{16}N_8Fe$) was used as precursor, according to the procedure reported earlier [19].

Oxidation was performed according to the procedure earlier reported [20]. It consisted of treating a batch of the as-synthesized CNTs (CNT-P, P for pristine) in an O_2 atmosphere (O_2 molar fraction of 0.10) at 375 °C for 90 min, using the same set-up employed for the synthesis. The oxidized CNTs are denoted as CNT-O (O for oxidized). It should be emphasized that many works in the literature concerned with gas-phase oxidation of CNTs have mainly involved pure air (i.e. O_2 molar fraction of 0.21), as oxidation agent. These conditions, however, have led to an over-oxidation of CNTs, often causing severe damage to the CNTs, in addition to removal of the amorphous carbon and other impurities, thus resulting in low yields of the oxidized CNTs [21]. Part of the oxidized sample was further separated for the preparation of macroscopic CNTs thin films, while the rest was subsequently subjected to acid treatment, to remove oxide nanoparticles.

The acid treatment consisted in contacting the oxidized sample with HCl aqueous solution (50 wt%), and gently mixing at room temperature. Afterwards, the CNTs were rinsed repeatedly with distilled water until neutral pH in wash water was attained. Then, the sample was dispersed in ethanol and the dilute dispersion was ultrasonicated at room temperature for 120 min. Ethanol was eliminated by evaporation and the sample was oven-dried overnight at

100 °C up to constant weight. The so-treated CNTs are denoted as CNT-A (A for acid treated).

Both the pristine MWCNTs and those further subjected to treatments have a length between 16 and 20 μm, with inner and outer average diameters of 24 and 50 nm, respectively [20,22].

2.2. CNTs macroscopic thin films preparation

The buckypapers films were obtained by filtration of a floccule-like aqueous suspension of MWCNTs. Typically, the CNTs, both pristine and further treated, were ultrasonically dispersed in distilled water for 90 min at room temperature. The suspension (0.3 mg/mL) was filtered through a polyamide membrane (Osmonic Inc., pore diameter 0.45 μm) employing a rectangular shape mould, and then dried overnight at room temperature. The resulting rectangular shaped MWCNTs film was easily peeled off from the polyamide membrane.

The nanocomposite was prepared by reduction of the mixtures of both pristine and further treated MWCNTs and palladium salt following a similar procedure to that described by Li et al. [23]. The carbon nanotubes (0.3 mg/mL) and $PdCl_2$ (1.0 mg/mL) were added to water to prepare a mixture by ultrasonic dispersion (60 min). Then, 5 mL of aqueous solution of $NaBH_4$ (0.01 M) was added dropwise, into 20 mL of the mixture, in a period of 20 min under ultrasonic treatment for the reduction of Pd^{2+}. Finally, the aqueous suspension (25 mL) of the so prepared Pd-decorated MWCNTs was diluted with distilled water (500 mL) and ultrasonicated for 2 h. Then, it was filtered through the polyamide membrane and repeatedly washed with distilled water using the same filtering device mentioned above.

2.3. Characterization of macroscopic CNTs based films

The morphologies of the CNTs buckypapers and nanocomposite films were observed on a Philips 500 scanning electron microscope (SEM) with an accelerating voltage of 25 keV. Measurements of electrical behaviour of both buckypapers and nanocomposite films were carried out in Ar atmosphere using a standard four-point method, varying the DC current intensity between 0 and 0.175 A. The resistances of the samples were determined by recording electrical voltage and current intensity at fifteen seconds interval until the system reached steady state. The electrical contacts to the sample were made with silver paste. Simultaneously, the temperature of the samples was measured with a copper-constantan (T-type) thermocouple.

The Pd-decorated MWCNTs nanocomposite films were characterized by determining the change in resistance when they were exposed to environments with different concentrations of hydrogen. All the measurements were performed at room temperature using a self built system device applying only 100 mW DC power. The testing chamber had a volume of 190 mL and was operated under normal pressure throughout the measurements. Argon used as carrier gas was fed continuously into the chamber at a flow rate of 30 mL/min. In order to obtain low concentrations of H_2 inside the testing chamber, small doses of hydrogen (30–500 $\mu L_{(STP)}$) were injected into the carrier flow. A mixing chamber of the same volume of the testing one (190 mL) was placed between the hydrogen feed and the testing chamber with the purpose of homogenization of H_2 molecules in the carrier gas flow. The instantaneously concentration of hydrogen inside the testing chamber was determined by gas chromatography. A lay-out of the equipment employed is shown in Fig. 1.

The response of the sensors (S) is defined as the percentage of the resistance change due to the exposure to a gas containing H_2 against the resistance measured without the presence of hydrogen,
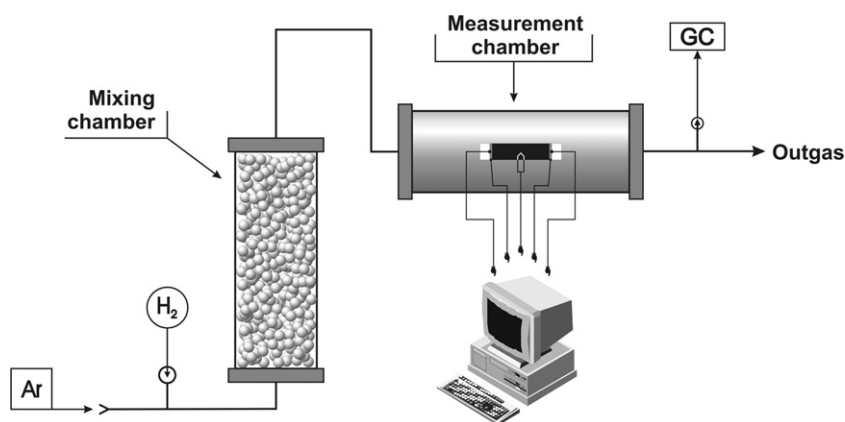
Fig. 1. Schematic representation of the experimental setup employed for characterization of the electrical and hydrogen sensing behaviour of the macroscopic CNTs based films.

according to:

$$S = 100 \left(\frac{R_{H_2} - R_{Ar}}{R_{Ar}} \right) \tag{1}$$

where R_{Ar} is the resistance of the film exposed only to the carrier gas (without H_2), and R_{H_2} is the resistance of the films after exposure to a gas containing hydrogen. The response magnitude of the sensors (S_{max}) is defined as the percentage of the maximum resistance change for a gas containing a given concentration of hydrogen. The response time is defined as the time to reach S_{max}, while the time of recovery is defined as the time to attain the steady state resistance once the atmosphere is free of hydrogen.

3. Results and discussion

3.1. Structure of buckypapers and nanocomposite films

Fig. 2 shows the SEM micrographs of the CNTs buckypapers films surface. It is worthy to mention that no surfactant was used for their processing so that high-purity buckypapers were obtained. As may be seen, the films are 2D like-structures constituted by randomly oriented MWCNTs, both pristine (Fig. 2a) and subjected to purification treatments (Fig. 2b and c), parallel to the filter surface. Cross linkages of straight MWCNTs can be observed, suggesting that good physical contact may be attained among nanotubes. The SEM images indicate that the sequence of treatments applied to the MWCNTs have no effect on the morphological conformation of the buckypapers.

The SEM micrographs of the surface of Pd-decorated MWCNTs nanocomposites thin films obtained with both pristine nanotubes and further treated ones are shown in Fig. 3. It is well known that CNTs are very hydrophobic and cannot be wetted by some liquids due to their high surface tension, hindering adhesion of most metals [24,25]. In contrast, in the present work, Pd nanoparticles form clusters well dispersed all over the MWCNTs surface, as can be observed in Fig. 3. This should imply that Pd nanoparticles are merged into clusters attached to the surface of the nanotubes in the aqueous suspension, instead of being filtered during the film formation. Fig. 3a shows that Pd nanoparticles clusters in the nanocomposite films based on the pristine MWCNTs (Pd–CNT-P) are larger than those present in the treated MWCNTs based composite films (Pd–CNT-O and Pd–CNT-A, in Fig. 3b and c, respectively). Thus, in the latter, the Pd nanoparticles decorating the nanotube surface seem to form nanoclusters partially interconnected, that could lead to improve the electrical contacts among the Pd-decorated nanotubes (Fig. 3b and c). The functional groups generated during the oxidation treat-

ment, such as carboxylic and hydroxyl groups attached to the outer surface of the CNT-O, could act as anchor seeds for Pd nanoparticles deposition [26].

3.2. Electrical behaviour characterization

For the electrical characterization, the rectangular shaped MWCNTs films were maintained over the polyamide membrane and cut into smaller rectangular probes to maximize the aspect ratio and minimize edge effects. Fig. 4 shows typically electrical responses for the pristine and further treated MWCNTs based buckypapers and nanocomposite films. For comparative purposes, voltage drops (ΔV_{Norm}, y-axis) generated between the extreme of the probes by the DC current (i. x-axis) and normalized by the aspect ratio of each probe, are plotted in Fig. 4. Thus, the slope of the curve in the linear region (below 60 mA) represents the room temperature resistivity (ρ_0) of the buckypapers and nanocomposite films. It can be appreciated that the treatments applied to the MWCNTs affect differently the electrical response of the films. In comparison with the CNT-P based buckypapers, the room temperature resistivity of those based on CNT-O is slightly increased, while the one corresponding to the CNT-A based buckypapers is slightly decreased. The values of ρ_0 of the CNTs based buckypapers are listed in Table 1. Zhang et al. [27] also determined that electrical resistivity of SWCNTs thin films (3×10^{-5} Ω m) increased when the nanotubes were previously subjected to an oxidative treatment with nitric acid. Enhancement in the resistivity of CNT-O buckypapers should be associated with the presence of oxide nanoparticles and oxide groups in the carbon nanotubes.

Moreover, all the Pd-decorated CNTs nanocomposite films show lower values of room temperature resistivity than the CNTs buckypapers, pointing out to an increase in the density of electrical contact points in the structure of the films (Fig. 4 and Table 1). In addition, the CNT-O based nanocomposite shows the lowest value of ρ_0, opposite to the CNT-O based buckypaper, which presents the highest value. Compared to the CNT-P based nanocomposites, the

Table 1
Values of room temperature electrical resistivity (ρ_0) for the buckypapers films and Pd-decorated nanocomposites.

	Buckypaper (ρ_0)[a]	Nanocomposite (ρ_0)[a]
CNT-P	1.0×10^{-3}	5.6×10^{-4}
CNT-O	1.2×10^{-3}	3.2×10^{-4}
CNT-A	7.8×10^{-4}	4.7×10^{-4}

[a] ρ_0 is determined as the slope, near the origin, of the curves plotted in Fig. 4 and it is expressed in Ω m.
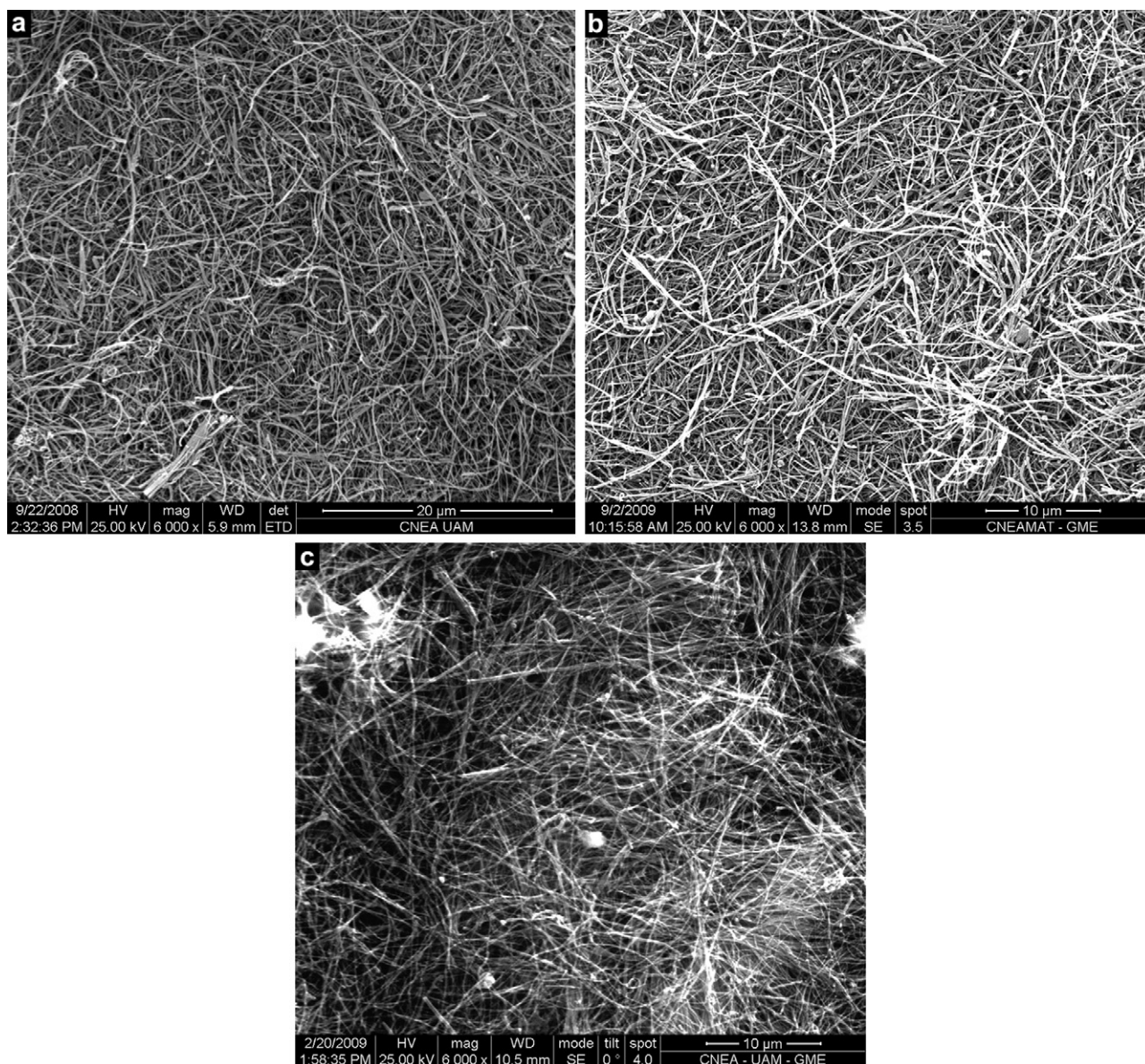
Fig. 2. SEM micrographs of the surface of the buckypapers based on pristine and further treated nanotubes, (a) CNT-P, (b) CNT-O, and (c) CNT-A.

lower value of ρ_0 would be related with a better distribution of Pd nanoparticles in smaller clusters enhancing the number of electrical contact points inside the film structure, as shown in Fig. 3b.

Furthermore, during the electrical characterization of the films, their temperature raised due to Joule effect, leading to a change in their inherent electrical resistivity. Thus, the temperature dependence of resistivity (ρ), estimated as the ratio between the normalized voltage drop and the DC current intensity, divided by ρ_0 for the buckypaper and nanocomposite films is plotted in Fig. 5. It can be seen that the electrical resistivity of both the pristine and further treated MWCNTs buckypaper films present strong semiconductor-like dependence with temperature, decreasing its resistivity when the temperature is increased. Regarding the Pd-decorated nanocomposite films, the resistivities of Pd–CNT-O and Pd–CNT-A films present slightly semiconductor-type temperature dependence, whereas the Pd–CNT-P sample exhibited metallic-like type dependence. The latter trend points to an extensive presence of large clusters of Pd nanoparticles contributing to the electrical resistance in addition to cross-linking among MWCNTs.

3.3. Hydrogen sensing of Pd–CNTs nanocomposite films characterization

To investigate the reproducibility of sensing, the Pd–CNTs nanocomposite films were tested for three sensing cycles by injecting doses of H_2 repeatedly. Fig. 6 shows the electrical resistance of the Pd–CNT-P based film as a function of time when exposed to H_2 dose of $500\,\mu L_{(STP)}$ for three times. The responses of the Pd-decorated CNTs nanocomposite film did not deteriorate after the third cycle, indicating that the sensing characteristics are repeatable.

Fig. 7 illustrates the measured response of the Pd-decorated nanocomposite films based on pristine and further treated MWC-NTs when H_2 dose of $500\,\mu L_{(STP)}$ was injected into the carrier gas flow. All the samples showed similar behaviour, namely an increase in electrical resistance in H_2 atmosphere reaching a maximum value to slightly decrease straight afterwards (saturation-like state); then, the increased resistance suddenly dropped to the original value as the H_2 concentration in the carrier vanished. This behaviour is similar to that reported earlier by Kumar and
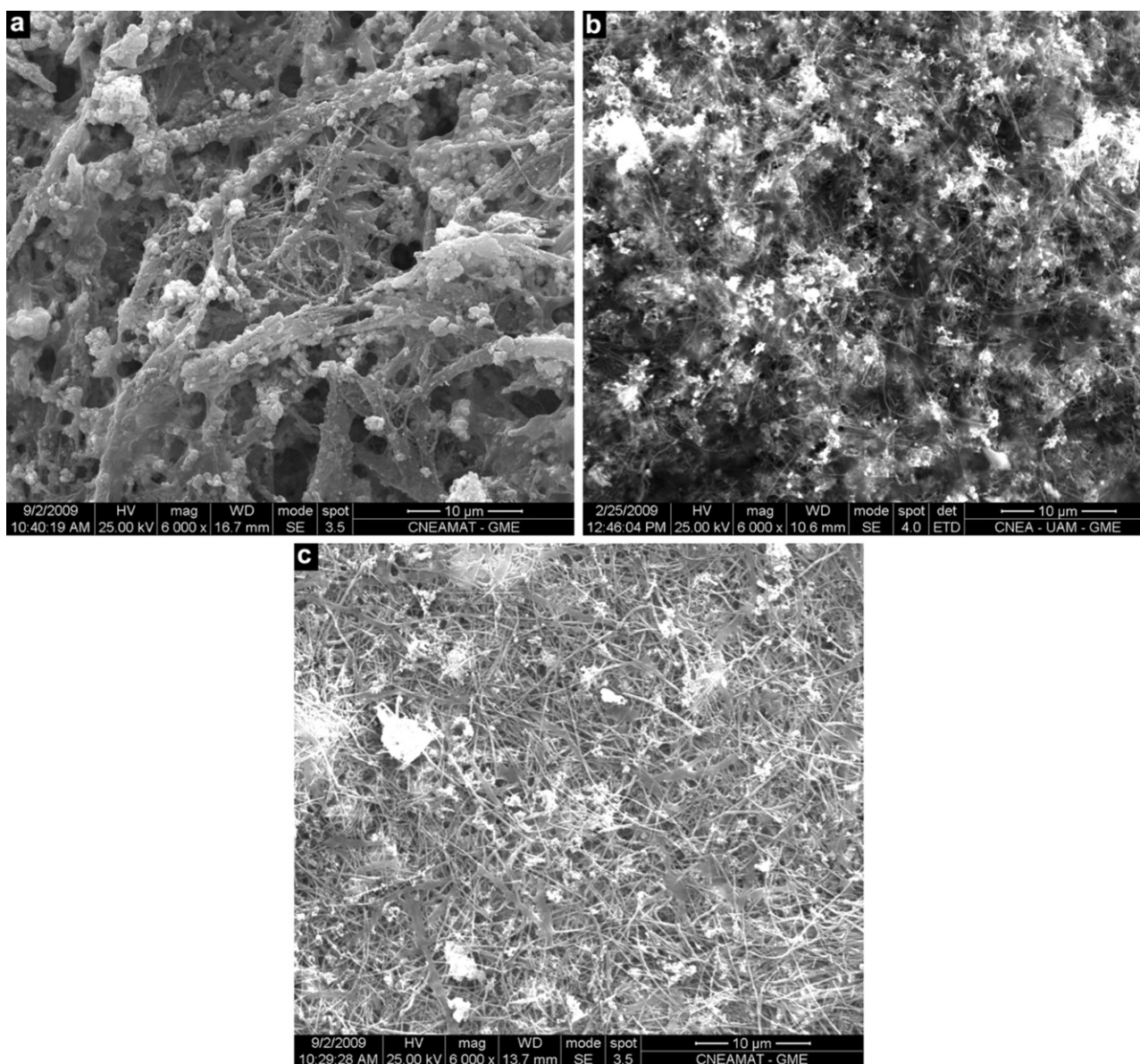
Fig. 3. SEM micrographs of the surface of the Pd-decorated carbon nanotubes based nanocomposite films, (a) Pd–CNT-P, (b) Pd–CNT-O, and (c) Pd–CNT-A.

Ramaprabhu [28] who studied the H_2 sensing performance of thin plastic substrates with Pd-nanoparticles decorated SWCNTs. Comparatively, the Pd–CNT-P and Pd–CNT-A based films exhibited similar response towards H_2, but the Pd–CNT-O based film showed a more pronounced one. This suggests that the latter would be more sensitive to the presence of H_2 molecules in the environment, due to the distribution of Pd nanocluster over the MWCNTs surface (Fig. 3b). The response magnitude and time of both Pd–CNT-P and Pd–CNT-A films were estimated as ~1.0% and ~150 s, respectively, while the same values associated with the Pd–CNT-O films were ~2.2% and ~200 s. Besides, the time of recovery of all of the samples was estimated to be ~210 s. In order to analyze the difference in the behaviour of nanocomposite sensors towards H_2, the presence of surface oxide groups and oxide nanoparticle produced, due to the intermediate oxidative stage in the sequential purification treatment, should be considered. In CNT-P, most catalytic Fe nanoparticles are encapsulated inside the nanotubes. Nevertheless, during the gas phase oxidation, they would be exposed as their corresponding oxides and oxygenated groups would be generated in active sites over nanotubes surface, but the removal of the oxide

nanoparticles occurs during the final acid treatment. Then, iron oxide nanoparticles and oxygenated groups such as –COOH and –OH, present in the MWCNTs, should act as additional anchoring sites for Pd^{+2} ions [27]. Considering these results, the Pd–CNT-O based sensor was selected to gain insight into its performance when different doses of H_2 gas were injected into the gas carrier flow.

The measured Pd–CNT-O based sensor response to different doses of H_2 injected (30 and 100 $\mu L_{(STP)}$) in the gas carrier flow is plotted in Fig. 8. For comparative purpose, the measured response to 500 $\mu L_{(STP)}$ dose of H_2 (injected) is also included. Fig. 8 shows that the dose of H_2 injected influences the Pd–CNT-O based sensor response. It can be appreciated that the sensor response magnitude reached similar values ($S_{max} \sim 2.2\%$) when the two higher doses of hydrogen (100 and 500 $\mu L_{(STP)}$) were injected, although the saturation-like state monitored under the former condition holds for a shorter period of time than that measured with the latter. These two characteristics combined together should indicate the presence of a threshold hydrogen concentration, above which the sensor response attains a maximum value, and remains practically constant as in a saturation-like state, until the concentration of H_2
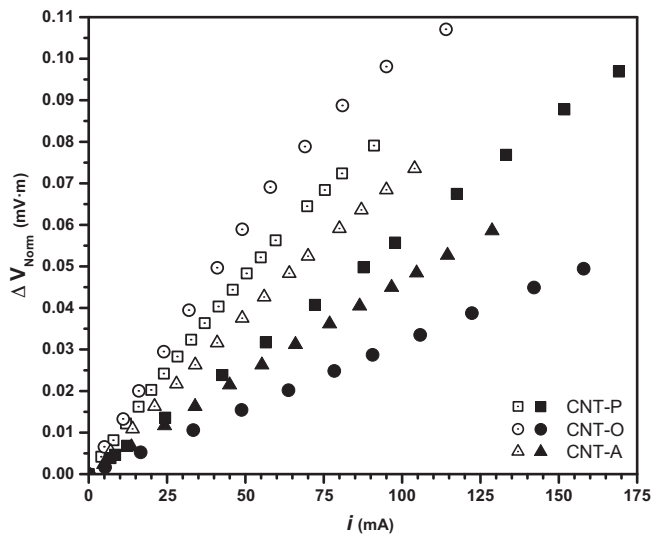
Fig. 4. Plot of normalized voltage drops as a function of DC current intensity for the buckypapers based on pristine and further treated CNTs (open symbols), and for the nanocomposite films (closed symbols).
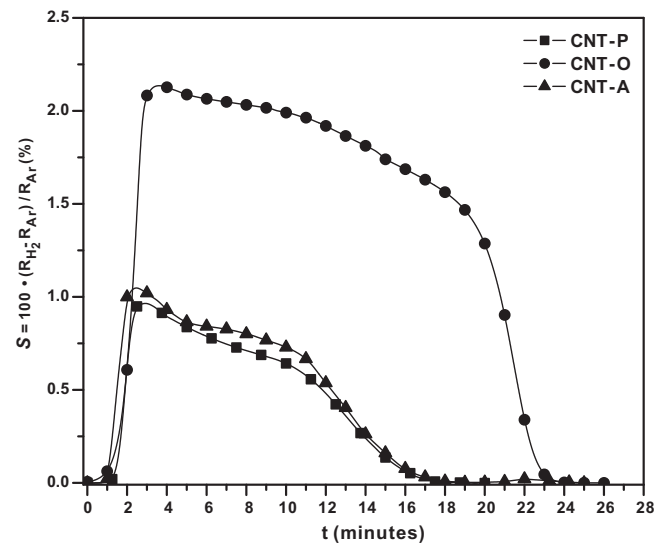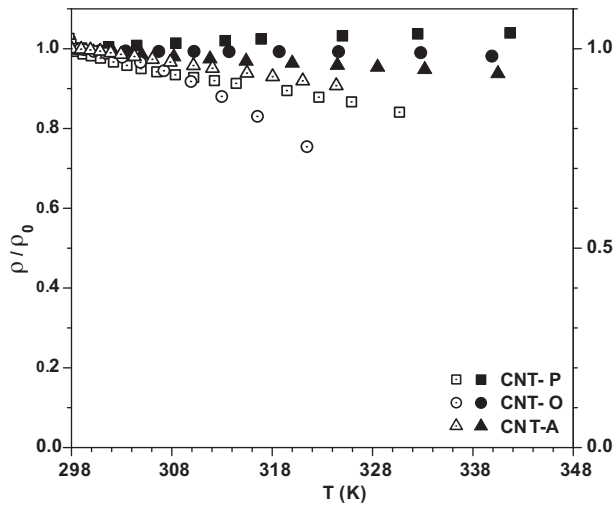

Fig. 5. Variation of the resistivity of the pristine and further treated CNTs based buckypapers (open symbols) and nanocomposite films (closed symbols) with temperature, ρ is normalized to ρ_0 at 298 K.
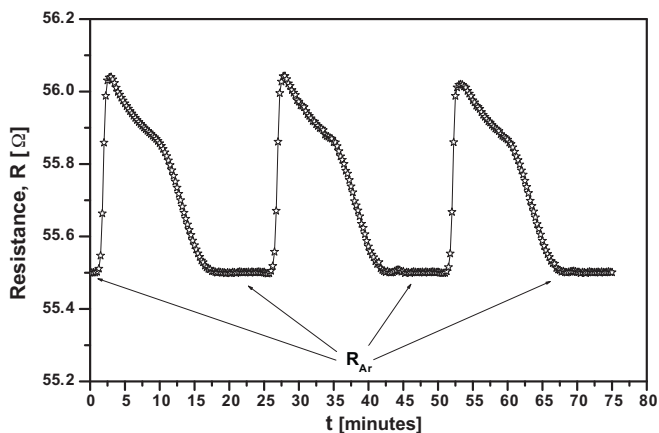

Fig. 6. Electrical resistance changes of the Pd–CNT-P based films as a function of time when exposed to H_2 dose of $500\,\mu L_{(STP)}$ for three cycles.

Fig. 7. Sensor behaviour of the Pd-decorated MWCNTs based nanocomposite films when H_2 dose of $500\,\mu L_{(STP)}$ was injected into the carrier system.

in the test chamber decreases below it. Nevertheless, after the H_2 dose of $30\,\mu L_{(STP)}$ was injected, the resistance change of the sensor reached a maximum ($S_{max} \sim 0.6\%$) and decreased to its original value straight afterwards, indicating that the threshold hydrogen concentration was never reached inside the test chamber.

In order to correlate the response magnitude of the sensor with the effective amount of H_2 inside the measurement chamber, an average hydrogen concentration ($\overline{[H_2]}_{t_p}$) was estimated, considering the time spent (t_p) until the S_{max} is reached since the dose of H_2 is injected into the carrier ($t_{inj} = 0$), and the following expression:

$$\overline{[H_2]}_{t_p} = \frac{\int_{t_{iny}=0}^{t_p} Q \cdot [H_2]_{(t)} \cdot dt}{\int_{t_{iny}=0}^{t_p} Q \cdot dt} \tag{2}$$

where $[H_2]_{(t)}$ represents the instantaneous hydrogen concentration inside the measurement chamber, determined by GC since the dose of H_2 is injected (t_{inj}), and Q, the carrier gas flow. The results calculated employing Eq. (2) along with the magnitude and time
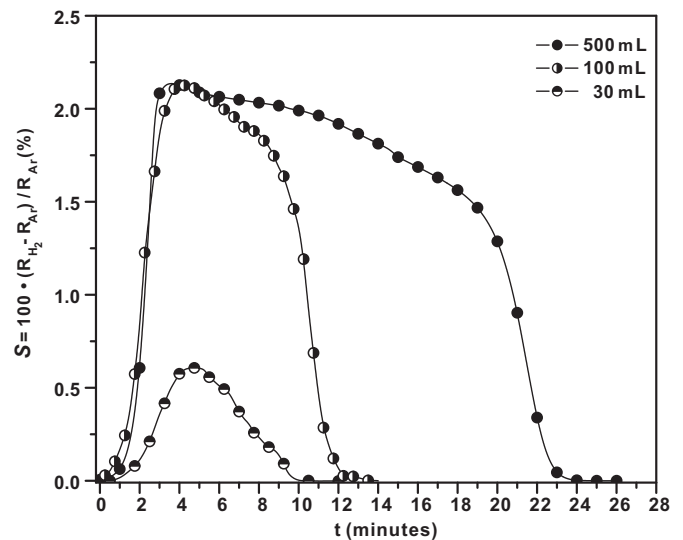

Fig. 8. Effect of the H_2 dose injected into the carrier flow on the response of the Pd-decorated oxidized MWCNTs based nanocomposite sensor (Pd–CNT-O based sensor).

Table 2
Characteristic values of Pd–CNT-O based nanocomposite films.

Dose of H_2 (μL_{STP})	Response time t_p (min)	Average H_2 conc. (ppm)	Response magnitude, S_{max} (%)
30	4.5	70	0.60
100	4.0	340	2.10
500	3.3	2100	2.15

of response of Pd–CNT-O based sensor (S_{max}), are comparatively summarized in Table 2.

The results reveal that the Pd-decorated CNT-O based nanocomposite films exhibited a reversible response to low concentrations of hydrogen at room temperature. Accordingly, they have potentialities to be used as low power devices for sensing H_2 at room temperature.

4. Conclusions

Room temperature H_2 sensing potentiality of nanocomposite films based on Pd decorated catalytically lab-synthesized MWCNTs, pristine and subjected to purification treatments, has been comparatively examined. The Pd-MWCNT film can be prepared by a simple process involving the reduction of palladium in solution and the subsequent filtering of the aqueous suspension of decorated nanotubes. The sensing capacity of the nanocomposite films has been measured by registering the change in their electrical resistance in H_2 atmosphere.

Present results show that the Pd-decorated MWCNTs nanocomposite films exhibit a reversible response towards hydrogen at low concentrations. Besides, their sensing capacity is affected by the different stages of purification applied to the carbon nanotubes. CNTs nanocomposite films based on Pd-decorated CNTs, pristine or completely free of catalyst particles, present a similar sensing behaviour, while the response of the oxidized Pd–CNTs based films is twice larger. Furthermore, the sensing behaviour of the Pd-decorated oxidized CNTs nanocomposites is modified by the H_2 concentration. The sensor magnitude of response at room temperature reaches a saturation-like state with a maximum associated value of 2.15% for an average hydrogen concentration above 350 ppm. The maximum value is 0.6% for an average hydrogen concentration of 70 ppm. The results reveal that the nanocomposite films prepared with the Pd-decorated oxidized MWCNTs have potentialities for their use as room temperature H_2 sensors devices.

Acknowledgements

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