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## Novel Carbon Nanotubes-Based Hybrid Composites for Sensing Applications

Nicola Donato, Mariangela Latino and Giovanni Neri

*Dept. of Matter Physics and Electronic Engineering*

*University of Messina*

*Dept. of Chemical Science and Technologies*

*University of Rome Tor Vergata*

*Dept. of Industrial Chemistry and Materials Engineering*

*University of Messina*

*Italy*

### 1. Introduction

In this chapter book is reported about the development and applications of carbon nanotube (CNT)-based hybrid composites material for gas sensing devices. Gas sensors are employed in many applications spanning from security, environmental and pollution monitoring, healthcare, indoor and outdoor fields. The great number of practical applications is due to their low cost, small dimensions, easiness of use and attitude for being organized in arrays. Metal oxides and conductive polymers are the conventional sensing elements in use today. Hybrid composites are materials offering new advantages and are promising candidates for the development of high performance sensor devices. Further, with the advent of new synthesis methods at the nanoscale, this let chemical gas sensors to improve their properties and figures of merit. Indeed, owing the small size and large surface to bulk area ratio of the grain nanoparticles, this results in an increased sensitivity. However, dealing with the fabrication of sensors with nanostructured materials some problems must be taken into account, such as the synthesis and deposition methods of the sensing material (finalized to optimize grain size, porosity, film thickness, etc.) and the optimization of the sensor parameters (operating temperature, sensitivity, response and recovery time).

In the chapter book there will be reported the main transduction phenomena involved on the working conditions of resistive sensor devices based on hybrid composites. Then the authors will focus the attention on two composite typologies: inorganic/CNT and organic/CNT composite materials.

The first topic, about inorganic-carbon nanotube composites, will deal about the development of sensing materials based on metal oxide/CNTs composites. It will be shown as it is possible to enhance gas sensing properties towards specific gas targets using CNTs as conductive media to help to transduce any adsorption/chemical reaction on the semiconducting layer into an electrical response, i.e. by means of resistive sensors. The case that will be reported, is about the development of resistive devices obtained by employing a Pt/TiO<sub>2</sub>/CNT composite as sensing layer for monitoring high hydrogen concentration in inert atmosphere at near room temperature.

The second topic is about the development of novel organic/CNTs semiconductor composites for resistive gas sensors. Organic materials based on  $\pi$ -conjugated molecules are intensively studied nowadays in the field of organic semiconductors as a complement to the shortcomings of inorganic semiconductors. Organic semiconductors offer, with respect to current inorganic-based technology, greater substrate compatibility, device processability, flexibility, large area coverage, and reduced costs. However, in many cases, the reduced conductivity of these materials hindered their use in resistive sensors. Carbon nanotubes provide in this case an easy method to modulate their electrical transport properties. A diaza-perylene/CNT composite will be reported as an example in the monitoring of vapour of protic solvent (e.g. water, acetic acid).

## 2. Main transduction and sensing mechanisms for resistive gas sensors

In the last years, the ask for real-time, compact and low cost chemical gas sensors has been increased, due to their employment in many fields of science and technology. The applications span from homeland and work-place security, antiterrorism and defence scenarios, to automotive and biomedical employments. For instance, homeland security and defence applications need effective portal monitoring, chemical weapons sensing, and water quality testing. Devices that can serve as personal exposure monitors, provide advance warning of food spoilage, and enable breath analysers to uncover pre-symptomatic disease are also under development and diffusion in the market. The increasing demand for small scale solid-state sensors for automotive exhaust gas mixtures are also of great interest due to the improvements of the emission control legislations. The turning point for these devices is to satisfy the requirements of high levels of sensitivity and specificity in small, economical packages. These requirements are mainly fulfilled by resistive solid state sensors, making these devices the most promising in the market for gas and volatile organic compounds (VOCs) detection.

In the planar configuration, they are composed of a porous thick/thin film as a gas sensing element, deposited onto a ceramic substrate with interdigitated electrodes (Fig. 1). Resistive solid state sensors performances have been improved by optimizing the sensing layers properties, for example by using nanostructured materials (G. Neri, 2010). It is well known that the sensing characteristics of a chemoresistive sensor depend primarily on the nature of the sensing layer. In this respect, most of conventional sensors used films based on metal oxides such as  $\text{SnO}_2$ ,  $\text{ZnO}$ , or conducting polymers. In the first type of sensors, i.e. metal oxide semiconductor (MOX) sensors, power supply is generally required to heat the sensitive layer deposited on the interdigitated contacts to an operating temperature of few hundred degree Celsius e.g. from  $200^\circ\text{C}$  to  $1000^\circ\text{C}$  supplied by means of a heater. The latter operate at lower temperatures, are highly sensitive and selective, but their life time is limited. Additionally, some organic materials are not compatible with micro-electronic fabrication technologies and, therefore, not suitable for large scale production. The most important aspect to focus is that gas sensors need to operate at elevated temperatures to avoid selectivity problems. The most suitable sensing material is that providing the right balance between sensor performance and power consumption (lower operating temperatures).

The employment of carbon nanotubes, as intrinsic sensing materials or as composite materials, where a metal oxide or polymer is deposited on carbon nanotubes (Y. P. Sun et al., 2002), provide an easy diffusion for chemical gas accessing through over the bulk

material. Indeed, the use of CNTs can bring some advantages such as introducing identical open gas nano-channels through bulk material, achievement of a great surface to volume ratio, and providing good gas-adsorption sites due to inside and outside of metal oxide/CNTs composites.

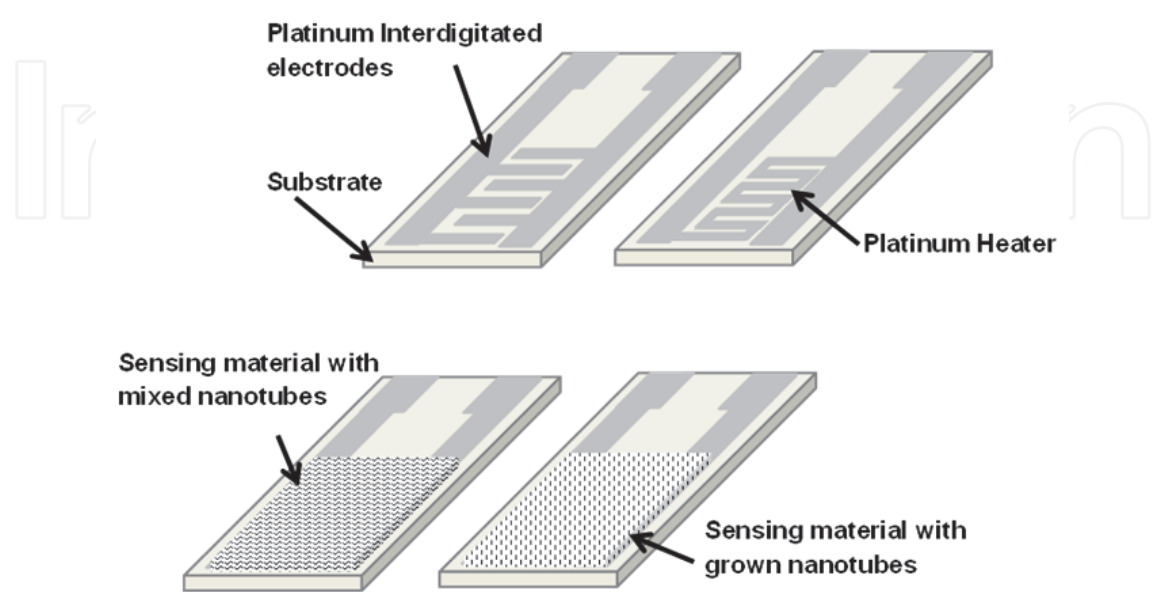


Fig. 1. Planar structure of chemoresistive sensor with top side coated thick/thin film and heater on the backside.

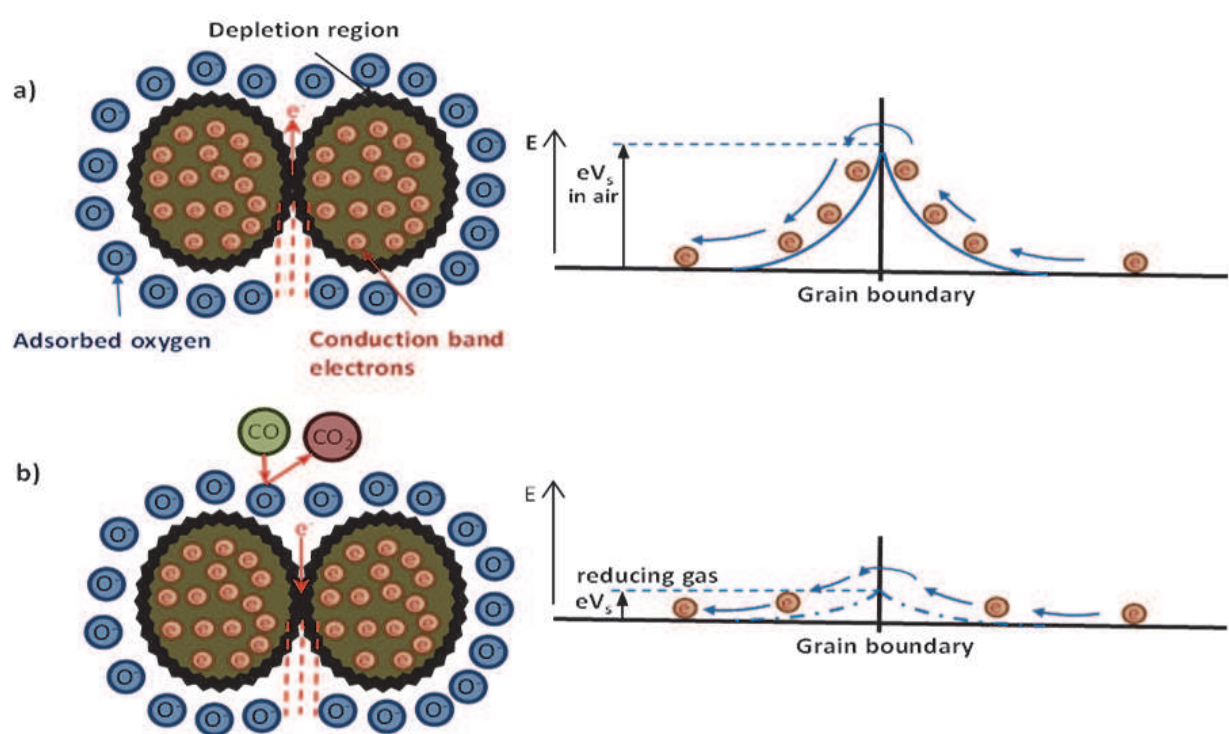


Fig. 2. Mechanism of gas sensing operating on n-type metal oxide semiconductors with reducing gases.

The transduction mechanism for gas detection on resistive sensors is based on the variation of the electrical resistance (conductance) due to target gas adsorption (Y. Shimizu and M. Egashira, 1999). By measuring the resistance variation it is possible to determine the presence and the concentration of the gas in the ambient surrounding the sensor. To better understand the operating sensing mechanism, the responses of resistive gas sensors have been widely explored with respect to surface adsorption, chemical reaction, and resulting conductivity changes. Several sensing mechanisms are possible, on the basis of the different sensing material. With conventional n-type metal oxide semiconductors-based sensors (e.g. ZnO, SnO<sub>2</sub>) the response to the presence of a target gas relies on the surface reactions which occur between adsorbed oxygen species and the probed gas (A. Gurlo et al, 2006). In air, point a), oxygen adsorbed on the surface traps free electrons because of its high electron affinity, forming a potential barrier at the grain boundaries, determine the electrical resistance value. When the sensor is exposed to an atmosphere containing reducing gases, e.g. hydrocarbons, CO, ethanol, etc., point b), the gas molecules adsorb on the surface and reacts with active oxygen species. Reactions with surface oxygen species will vary depending upon the temperature and the reactivity of the sensing material. These reactions/interactions decrease the potential barrier allowing electrons to flow more easily, thereby reducing the electrical resistance, as a function of the concentration of the target gas. By employing polymer films as sensing layer, weak intermolecular interactions, rather than redox chemistry, can be envisaged as the main pathway of the sensing mechanism. In some cases these interactions require specialized functions of the molecules, making these chemoresistive sensors more selective than those based on metal oxide semiconductors.

The development of nanostructured sensing materials can be considered the right trade-off between the traditional approach and the new one, devoted to the development of new sensing materials. In such scenario carbon nanotubes can be employed by mixing them with polymer host, or by functionalizing them to specific gas targets by means of coating them with nanostructured metal oxides or directly grown on the transduction substrates.

This variety of sensing materials and of transduction mechanisms, contributes to develop chemoresistive sensors with enhanced performance tuned towards specific applications. Some examples from our laboratory are here reported, highlighting how carbon nanotubes can be used to modulate the conduction of the sensing layer and/or to enhance sensing properties toward specific gas target or volatile organic compounds of chemoresistive gas sensors.

### **3. Role of carbon nanotubes in hybrid sensing materials**

In general, nanostructured materials offer a huge number of possibilities to enhance the property of sensing of the developed devices. Carbon nanotubes, for example, are suitable candidates to serve as a constituent in functional materials as they provide properties such as a well defined structure, high chemical stability, high surface area and a good thermal conductivity.

Since the discovery of CNTs in 1991 by Iijima (S. Iijima, 1991), a great deal of effort has been devoted not only to study the chemistry and fundamental electronic and physical properties but also the application and integration of this new class of materials into electronic devices. They are viewed as single or multiple sheets (from 2 to 50) of graphene to build single-walled carbon nanotubes (SWCNTs), with a diameter in the range of 0.4–3 nm, or coaxial multiwalled carbon nanotube (MWCNTs) with an interlayer spacing of 0.34 nm and



diameter in the range from 4 to 30 nm. The length of nanotubes is in the range of several hundred micrometers to millimeters.

Here we focused our attention only on the MWCNTs and, otherwise not specified, the discussion is referred to this nanotube typology. From an electrical point of view, MWCNTs can be divided in two broad classes - metals and semiconductors. In metallic conductors, electric current generally flows freely and there is no energy gap between the valence and the conducting states. In a semiconductor, such an energy gap exists and therefore a higher voltage is needed to make electric current flow. Whether a carbon nanotube is a metal or semiconductor depends upon their diameter and chirality.

Semiconducting carbon nanotubes have been proposed for applications as chemical and biochemical sensors (Kong et al, 2000; Star et al, 2003; Kauffman et al, 2008). CNTs-based gas sensors have received considerable attention because of their outstanding properties towards a wide variety of gases that may be detected, such as high sensitivity and especially lower operating temperature, compared with the other types of gas sensors (Pengfei et al., 2003; Valentini et al., 2003).

To date CNTs have shown sensitivity towards such gases as  $\text{NH}_3$ ,  $\text{NO}_2$ ,  $\text{H}_2$ ,  $\text{CH}_4$ ,  $\text{CO}$ ,  $\text{SO}_2$ ,  $\text{H}_2\text{S}$ , and  $\text{O}_2$ . CNTs-based gas sensing utilizes a change in an electrical property due to adsorption of gas molecules as the output signal. The response is attributed to the p-type conductivity in semiconducting MWCNTs and the electrical charge transfer is found to be the major sensing mechanism at low temperature. Target gas molecules (e.g.,  $\text{NH}_3$ ,  $\text{NO}_2$ , etc.) directly adsorb onto the CNT surface inducing electron transfer and changing the electrical conductivity of the nanostructure. Figure 3 depicts in a schematic way as the conductance of a carbon nanotube is modified when electron donor ( $\text{NH}_3$ ) or acceptor ( $\text{NO}_2$ ) gaseous molecules are in the atmosphere surrounding the sensor.

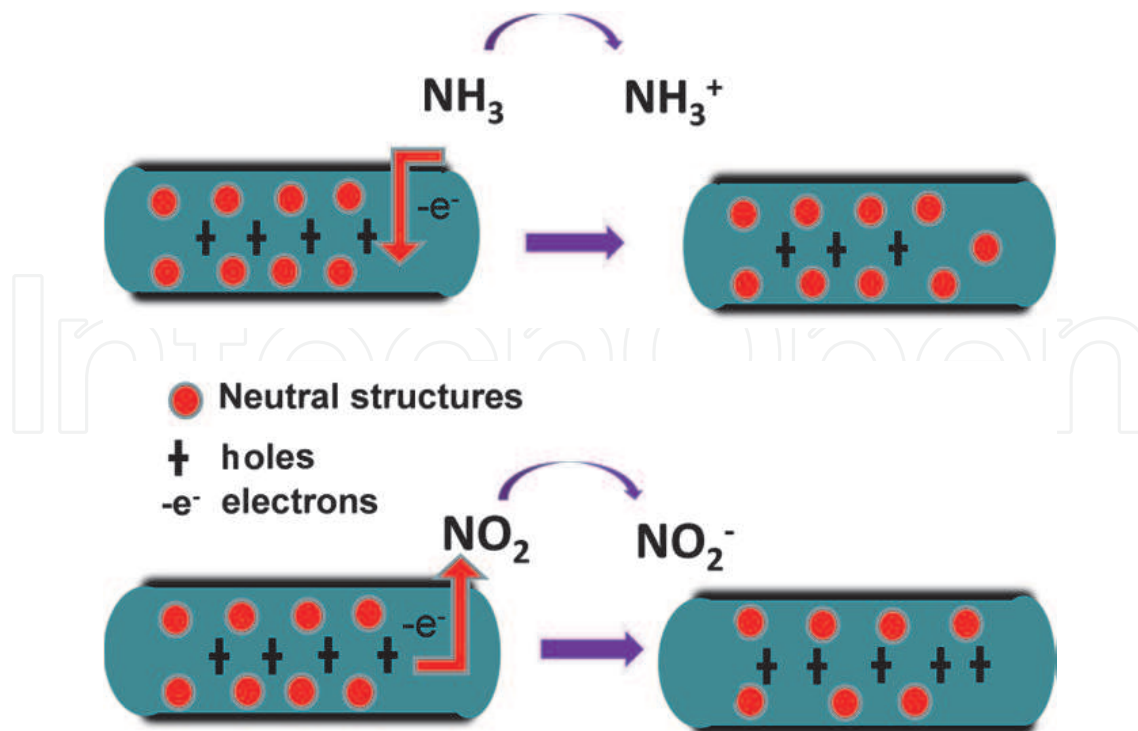


Fig. 3. Mechanism of gas sensing operating on p-type CNT semiconductors with reducing/oxidizing type gases.

$\text{NH}_3$  transfers electrons to the underlying nanotube structure. As MWCNTs behave as a p-type semiconductor, the transferred electrons will recombine with 'hole' carriers, thereby decreasing the charge carrier concentration in the support and a consequent increasing the electrical resistance. In the presence of  $\text{NO}_2$ , the reverse mechanism takes place and as a result of the presence of this gas the carbon nanotube electrical resistance decreases.

In order to enhance the sensitivity of resistive gas sensors, the addition of semiconducting metal oxides ( $\text{SnO}_2$ ,  $\text{TiO}_2$ ,  $\text{V}_2\text{O}_5$ , etc.) or polymers to carbon nanotube network (and vice versa, coating carbon nanotubes by metal oxides or polymers) has been widely exploited today (W.-D. Zhang and W.-H. Zhang, 2009).

The examples reported in the above references demonstrated that the presence of carbon nanotubes as a component in nanocomposites can help to improve the sensing properties. From a practical point of view, MWCNTs act as conductive media to transduce adsorption/chemical reaction processes into an electrical response, able to be measured and recorded with conventional or custom electronics.

The interaction between the carbon nanotube and the matrix is then essential in order to have a synergic action. This is favoured, making the carbon nanotube surface more reactive by creating functional groups on its. A functionalization process, for example by a strong oxidation in  $\text{HNO}_3$  of the nanotubes, is then often required to produce  $\text{COOH}$  and  $\text{OH}$  groups along the sidewall and the caps of the CNTs. These functional groups can physically/chemically interact with functional groups in the matrix, resulting in a strong interfacial adhesion and a better dispersion of surface modified CNTs in the polymer or metal oxide matrix. Obviously, these groups can act as anchoring sites for deposition of film of polymer or metal oxides on the surface of the carbon nanotube.

#### **4. Cases studies in the development of selected hybrid composite sensing materials**

This section is mainly focused on the development of two sensing material composite typologies: inorganic/MWCNT and organic/MWCNT ones.

The first case, will deals about the development of sensing materials based on metal oxide/MWCNTs composites. Metal oxides are well known for their electrical semiconducting properties that make them suitable for sensing applications. However, the full potentiality of these materials is only partially exploited, owing by the difficulty inherent to high resistance values they present at low temperatures. The possibility of an efficient electrical conductance promotion when adding a conductive second phase, such as MWCNTs, opened many opportunities. It is very important further to recognize that the amount of such second phases required to get a reasonable reduction in resistivity is very smaller. Due to their high aspect ratio, quite low percolation thresholds have been reported for metal oxide/CNTs composites (E. Flahaut, et al., 2000). Conductivity values after percolation seem to depend more on the CNT type and purity as well as on the composite processing procedure.

In the case study here reported, we focused first our attention about the development of resistive devices obtained by employing a Pt-doped  $\text{TiO}_2$ /MWCNT composite as sensing layer for monitoring high hydrogen concentration in inert atmosphere at near room temperature. Hydrogen-based systems truly promise a futuristic energy scenario, where hydrogen fuel will be used in fuel cells for civil transportation and in rockets for space vehicles. All these applications necessitate then the development of hydrogen sensor

devices, which allow its safe and controlled use (V. M. Aroutiounian, 2005). Numerous metal oxide thin films work at high temperature in air as effective resistive hydrogen sensors, allowing detection of this gas down to very low concentration. However, many of these devices need ambient oxygen to operate, and moreover they fail to detect hydrogen at high concentrations due to saturation effects. Then, there is also great interest to detect high concentrations of hydrogen in reducing or inert atmosphere, by means of devices operating at temperature as low as possible, preferably room temperature.

The second topic is about the development of novel organic/MWCNTs semiconductor composites for resistive gas sensors. The preparation of organic materials stable in air, solution-processable and with suitable electrical conductivity, is a fundamental step in organic electronics. To obtain this, MWCNTs can be dispersed in organic material hosts to enhance the conduction properties, offering an attractive route to introduce new electronic properties based on electronic interactions between the two composite constituents (M.S.P. Shaffer and A.H. Windle, 1999).

#### 4.1 Hydrogen sensor based on Pt/TiO<sub>2</sub>/MWCNT composites

TiO<sub>2</sub>/carbon nanotube composites attracted more attention because of their potential in gas sensing. Moreover, such composites, exhibiting enhanced photocatalytic activity, because CNT could acts as an electron sensitizer and donator to accept the photo-induced electron (e<sup>-</sup>) into the conduction band of TiO<sub>2</sub> particles under UV light irradiation, are promising candidate to fabricate UV-photoactivated sensors.

We prepared CNT/TiO<sub>2</sub> composites with different MWCNTs loading ranging from 0 to 70 wt%, by a sol-gel method. MWCNTs were first functionalised by a nitric acid treatment at 110°C for 18 h, in order to create on the surface of the nanotubes, suitable functionalized groups, facilitating the interaction with titania. The typical morphology of the resulting composite materials is reported in the SEM and TEM micrographs of Fig. 3, showing the titania particles dispersed in the mats of carbon nanotubes.

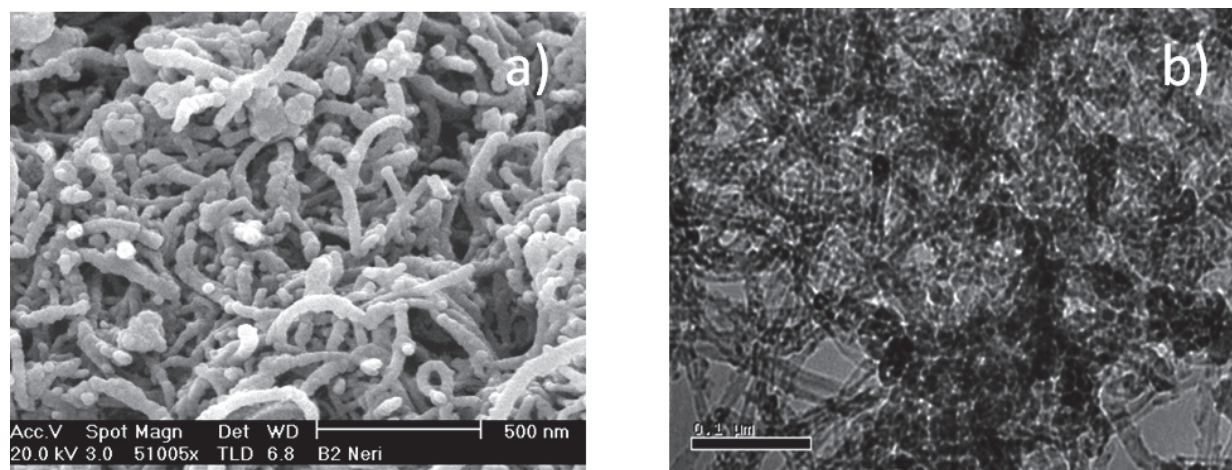


Fig. 4. a) SEM and b) TEM micrographs showing the morphology of the TiO<sub>2</sub>/MWCNT composite.

The comparison of XRD spectra registered on all samples with titania reference-spectra showed only the presence of the diffraction peaks of crystalline anatase. Micro-Raman analysis also evidenced a marked similarity with the spectrum of anatase.



Subsequently, 2 wt% of Pt was introduced by the wetness impregnation method, by using a solution of platinum acetylacetonate in acetone. The resulting Pt/TiO<sub>2</sub>/MWCNT composites were treated at 200°C for 2 h in a mixture of 5% H<sub>2</sub> in argon. XRD and micro-Raman spectra of the ternary composites do not differ from those reported for the parent TiO<sub>2</sub>/MWCNT. Pt diffraction peaks are absent, suggesting the noble metal is in an amorphous state and/or having very small size. In agreement, small platinum nanoparticles wrapped on the composite surface were observed by transmission electron microscopy.

Sensing tests were carried out in an apparatus, interfaced with a PC, composed by a stainless steel box, where is allocated the sensor, and connected to gas supply (He and H<sub>2</sub>) and a power supply able to set and control the operating temperature (in the range 25-100 °C), and measuring the resistance values of the sensor when it is maintained under H<sub>2</sub>/He mixtures flow (100mL/min) by means of a resistance meter. The sensor response is given as  $[(R-R_0)/R_0] \cdot 100$ , where  $R_0$  is the resistance recorded under He and  $R$  the resistance recorded under H<sub>2</sub>/He mixture. Before carrying out the sensing measurements, sensors were pre-treated "in situ" upon different experimental conditions. This treatment allowed to obtain a better baseline stability (Fig. 5). In this regard, it can be hypothesized that during storage in air, Pt particles oxidize at least in the surface and a reductive treatment at higher temperature "in situ" is necessary to establish the optimal working steady-state conditions.

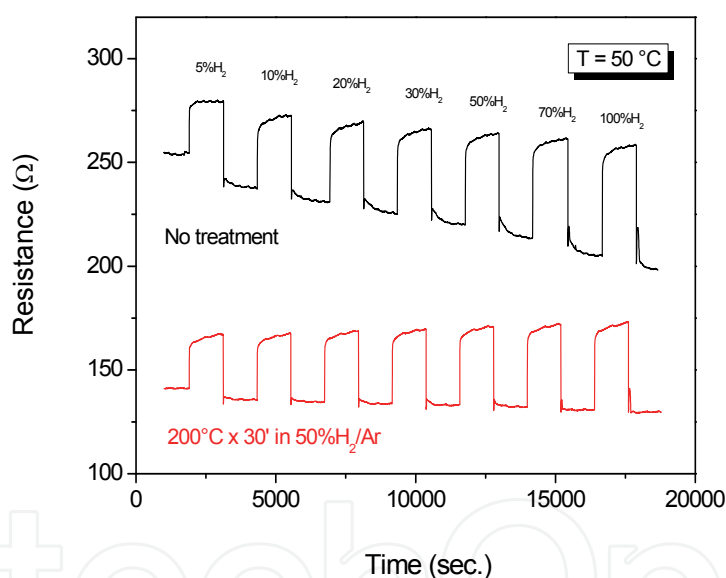


Fig. 5. Resistance variations registered for the Pt/TiO<sub>2</sub>/MWCNT composite sensor, after different "in situ" reducing treatments.

The behaviour of the composite sensors was, as expected, strongly related to Pt presence, MWCNTs loading and working temperature. Pt was found to be essential to have a measurable response to H<sub>2</sub>. As platinum is known to be an efficient catalysts for hydrogen dissociation, it is plausible that its role is related to the promotion of this reaction on the metal surface at low temperature. The hydrogen atoms so formed are much reactive, favouring the hydrogen sensing mechanism at near room temperature.

The best sensing performance were obtained for a MWCNTs loading of about 35 wt% (Fig. 6a). Furthermore, the comparison of the response of the Pt/TiO<sub>2</sub>/MWCNT sensor, with that of TiO<sub>2</sub>/MWCNT and Pt/MWCNT sensors, clearly indicated that hydrogen monitoring take place only with the three-component sensor, suggesting a synergic action between the metal

oxide, noble metal and carbon nanotubes. A linear relationships between the response and hydrogen concentration was well established for the sensor having a MWCNTs loading of about 35 wt% (Fig. 6b).

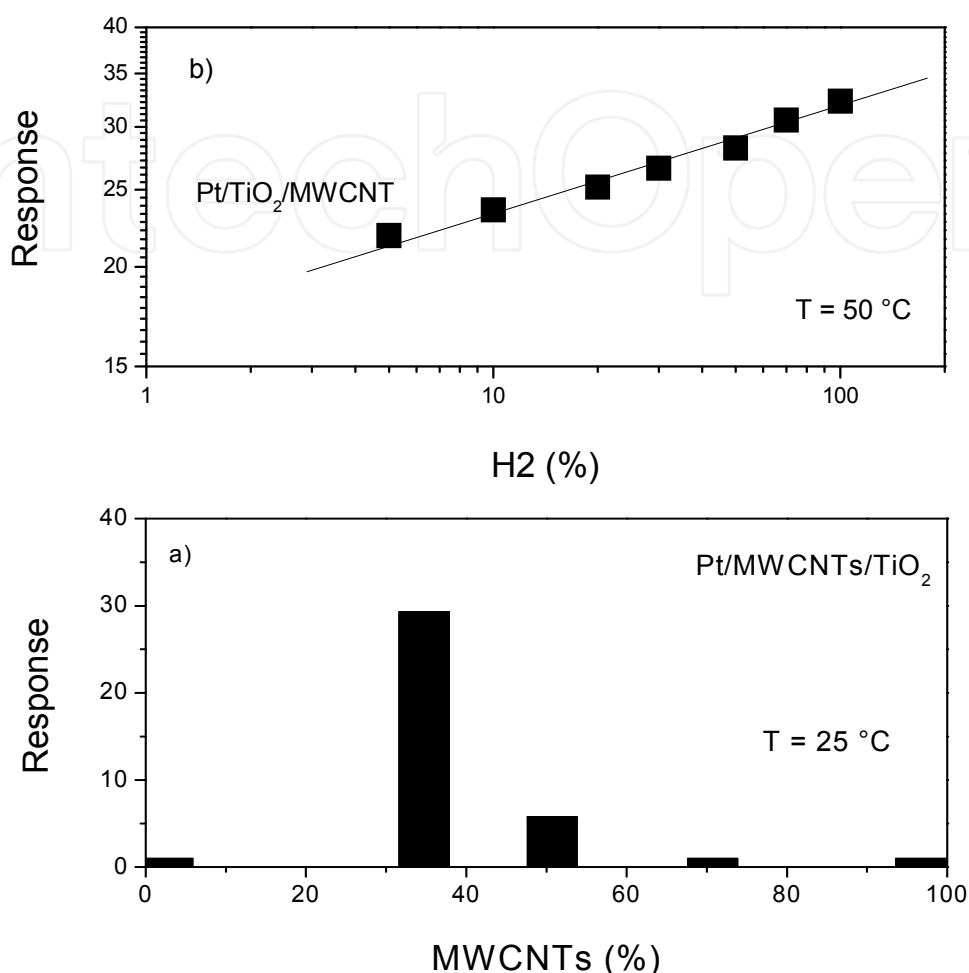


Fig. 6. a) Response to hydrogen of sensors having different carbon nanotube loading. b) Calibration curve of the Pt/TiO<sub>2</sub>/MWCNT sensor with a carbon nanotube loading of about 35 wt%.

In order to formulate an hypothesis about the sensing mechanism, it is should be remarked that the sensor measurements were conducted in absence of oxygen. Then, the usual mechanism involving the removal of chemisorbed oxygen by hydrogen cannot be invoked in this case. We think the sensor response can be attributed to a “spill-over” mechanism, in which hydrogen molecules are chemisorbed and dissociated by platinum, and finally spill out of the Pt, diffusing into the TiO<sub>2</sub> surface layer. This agrees with the fact that both the platinum and TiO<sub>2</sub> are necessary for obtain the sensor response. MWCNTs act providing a preferential pathway to the current flow and a larger specific surface area for the adsorption of hydrogen atoms.

According to current view, once the active hydrogen atom is chemically adsorbed at the interstitial positions in the oxide lattice structure, partial electron charge transfer occurs to the n-type TiO<sub>2</sub> and the conductance should increases (O. K. Varghese et al., 2003). Vice versa, we observed that the sensor resistance increases in hydrogen. In literature this has

been explained suggesting a p-type behaviour of the metal oxide (F. Hossein-Babaei et al., 2005), or an  $H \rightarrow TiO_2/MWCNT$  charge transfer which reduces the hole concentration in the carbon nanotube structure, increasing the resistivity in the system (R. A. Guirado-Lopez et al., 2007).

In order to get a deeper insight into the sensing mechanism more systematic investigations are however necessary, aimed at clarifying the role of MWCNTs- $TiO_2$  interaction. The response can arise from the modulation of nanotube themselves, the junctions between platinum electrodes and the nanotubes, or between two adjacent nanotubes. For example, it has suggested that  $NH_3$  mainly interacts with carbon nanotubes themselves. In contrast, other authors suggested that the modulation of nanotube metal electrode junctions influence the response to  $NH_3$ , or that both nanotube channels and nanotube electrode junctions play a role in the detection process of  $NH_3$  (A. Salehi-Khojin et al., 2011).

Due to the extremely practical importance, further investigations are also planned aiming to optimise the formulation of the sensing layer devoted to the development of a prototypal hydrogen sensing device.

#### **4.2 Organic/MWCNTs composites: semiconductor composite for resistive gas sensors**

In the framework of a research oriented to study new  $\pi$ -electron organic systems for sensing applications, we have focused the attention on the aza-helicenes (with 5 or 6 or even more ortho-condensed benzenic or pyridinic rings) and aza-perylenes (with 5 benzenic or pyridinic peripheral rings) compounds. These organic molecules appear very promising for gas sensing, due to the presence of a reactive nitrogen functionality on the pyridinic ring, which could be able to interact reversibly with specific gases. Most important, the possible existence of a charge transfer might considerably alter the electronic structure of the conduction channels in the highly conjugated molecule system, modifying as a consequence the transport properties making them very attractive for fabricating resistive chemosensors.

Recently, several authors have explained the electrical properties of composites in which CNTs are dispersed in an insulating polymer matrix based on percolation theory (Allaouia et al., 2002). The use of CNTs in a polymer composite is found to reduce the percolation threshold to a very low filler volume than in the case of carbon black/polymer matrix.

Here, we report data obtained in the investigation of the electrical and sensing properties of 7,8-diazabenzoperylene (DABP)/CNTs composites. The molecular structure of DABP is shown in Figure 7. DABP was synthesized through photochemical reactions carried out as reported elsewhere (Bazzini, C., et al., 2005).

DABP is a dark orange solid material with high melting point (226-234°C), and results stable in air. It shows moreover a good solubility in many organic solvents, allowing preparing processable solutions for thin films deposition. However, notwithstanding the large conjugation, the conductivity of DABP is low, and not suitable for the application in chemoresistive sensors. Therefore the organic material was mixed with a suitable amount of multi-walled carbon nanotubes, in order to enhance the conductivity of the sensing film.

The composite sensor was fabricated depositing by drop-coating from dichloroethane solution thin films of DABP/MWCNTs on an alumina substrate provided with interdigitated electrodes. The sensor was preliminary conditioned in air for 2 h at room temperature. Electrical tests were carried out at room temperature (25 °C). I/V curves were acquired by means of a Keithley 2400 source meter. The relative humidity (RH) and organic

vapours were generated by using a bubbler connected to a mass flow control system, in order to vary their concentration.

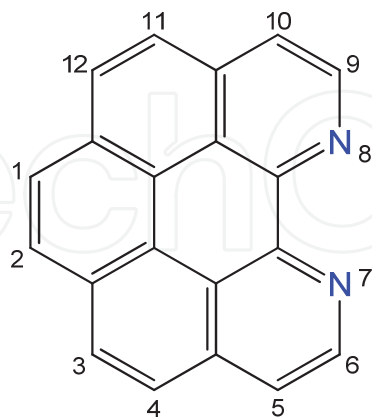


Fig. 7. Molecular structure of 7,8-diazabenz[ghi]perylene (DABP).

Electrical properties of the pure DABP film and DABP/MWCNTs composite, were studied in order to evaluate the effect of the CNTs on the films conductivity. Figure 8 shows the output currents of a DABP/MWCNTs composite film at room temperature as a function of input bias.

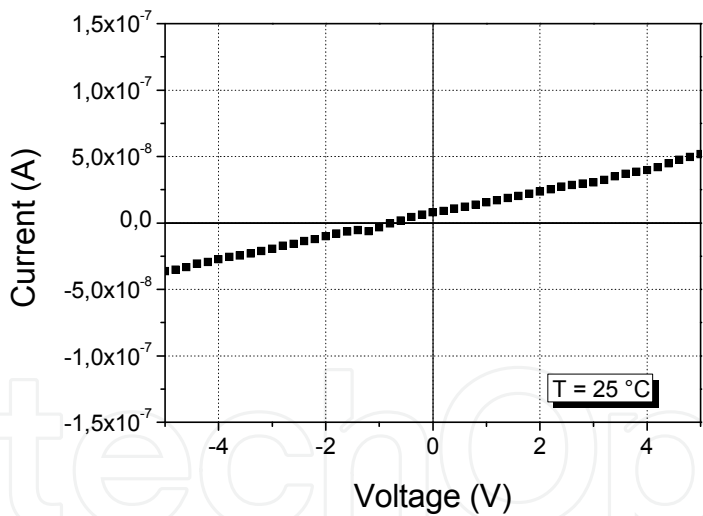


Fig. 8. I/V characteristics of a DABP/MWCNTs composite film.

While the output signal of the pure DABP film is not measurable due to its very low conductivity, the output signal is remarkably enhanced with the addition of carbon nanotubes, thus indicating the improvement in conductivity of the active layer. The dependence of conductivity on the CNT content in the composites is in agreement with previously reported results of polymer/CNT composites in which the conductivity exhibits percolation behaviour (J. N. Coleman et al., 1998). The effect of humidity on the electrical characteristics of the DABP/MWCNTs composite has evidenced a large variation of the sensor current with humidity change, suggesting that it can be used as resistive sensor for monitoring relative humidity (Figure 9).



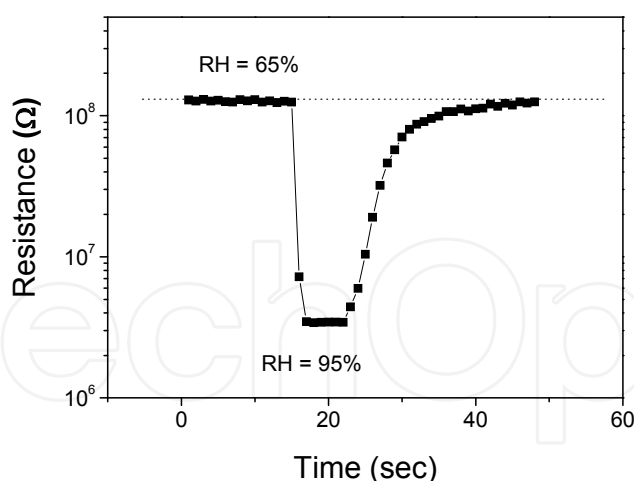


Fig. 9. Transient response of the composite sensor to different relative humidity variations.

It can be noted a strong decreases of resistance as the relative humidity value increase. Moreover, the response is well reversible, exhibiting a fast response/recovery time.

Experiments have also shown that no significant variations of current occurs on devices based only on DABP or MWCNTs, confirming that changes observed on the composite sensor are due to the synergic action between carbon nanotubes and the organic material.

According to other authors (J. Roithová et al. 2007), we explained this behaviour assuming that DABP manifests a strong affinity for protons. The electron transferring (hopping) assisted by the presence of a proton trap such as the heterocyclic nitrogen may be considered responsible of the resistance variations observed in humid ambient.

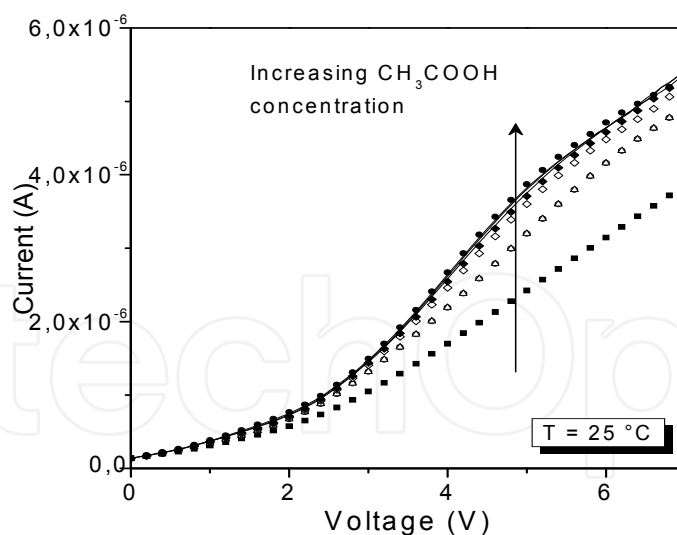


Fig. 10. I/V characteristics of DABP/MWCNTs composite film-based sensor at different acetic acid concentrations.

To support the above hypothesis, experiments aimed to investigate the effect of gases of different chemical nature (e.g. cyclohexane and acetic acid) have been carried out. The results of the tests have shown that the DABP/MWCNTs composite film-based sensor displays large variations of the electrical resistance with varying the concentration of acetic acid (Figure 10).

No significant variations were instead observed when cyclohexane vapours contacted the sensor, confirming that the interaction between the nitrogen(s) of the DABP and proton of water and acetic acid is the mechanism leading to the current variation registered. This opens the possibility to design and develop selective sensors for protic solvents.

## 5. Applications of MWCNT's based sensors

MWCNT's based gas sensors are one of the turning point for the development of high performance gas sensors. While there are many research activities focused on this direction, few are the commercial applications based on low cost reliable devices. These devices should have, among the others, low power consumption. The main contribution to power consumption of such sensor devices is the part employed in setting and controlling the optimal operating temperature value and, by a consequence of this, to reduce the power consumption is need to work at operating temperature values close to room temperature ones.

Nanomix employs carbon nanotubes based network to develop sensing systems for biomedical applications. This company developed a breath analysis system for the monitoring of nitric oxide (NO) as biomarker that has been shown to be correlated with asthma, an inflammatory airway disease. The breath analysis is one of the emerging biomedical applications involving gas sensors. By monitoring specific targets (biomarkers) in the alveolar air it is possible to monitor several diseases in the metabolic functions. This technique could be a cheaper and low intrusive test for early diagnosis of many human diseases allowing a large scale prevention and improving the quality of life (Nanomix website, 2011).

Applied Nanotech Holdings Inc. developed Enzyme coated Carbon Nanotubes (ECNT) as a small dimensions enzymatic biosensor suited for medical, environmental and chemical analysis. The carbon nanotubes are employed in the development of a three dimensional network promoting enhanced enzyme loading and increasing the analyte exposure. By choosing the proper enzyme for the specific analyte it is possible to enhance the performance of the device. These kinds of devices can be employed in arrays as electronic tongues, and they can analyse a large number of analytes from a single drop of blood or urine for metabolic analysis or as electronic nose for toxic gas detection and chemical warfare sensing (Applied Nanotech Holdings Inc. website, 2011).

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Since their discovery in 1991, carbon nanotubes have been considered as one of the most promising materials for a wide range of applications, in virtue of their outstanding properties. During the last two decades, both single-walled and multi-walled CNTs probably represented the hottest research topic concerning materials science, equally from a fundamental and from an applicative point of view. There is a prevailing opinion among the research community that CNTs are now ready for application in everyday world. This book provides an (obviously not exhaustive) overview on some of the amazing possible applications of CNT-based materials in the near future.

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Phone: +86-21-62489820  
Fax: +86-21-62489821



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