

Gas sensors based on decorated carbon nanotubes

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1. Introduction

Sensors are devices that detect or measure physical or chemical quantities, providing an immediate feedback on the environment. Sensing gas molecules is crucial for many process control technologies, and advances in chemical and physical sensors continue to get improved sensitivity, lower power consumption and faster response.

The potential uses of chemical sensors include: monitoring and control of environment pollution; advanced diagnostics for point care in medical applications; small, low-power, fast, and sensitive tools for process and quality control in industrial applications; detection of warfare and security threats. In all these applications, there is a strong demand for improved sensitivity, selectivity, stability, and low-power consumption beyond what is offered by commercially available sensors.

To meet this demand, nanotechnologies are employed, providing new materials, devices, and systems with structures and components that can exhibit novel and significantly improved physical and chemical properties because of their nanoscale size. One class of this kind of materials are carbon nanotubes (CNTs) that can be the multi-walled (MWCNTs) discovered in 1991 by Iijima (Iijima 1991), or single-walled (SWCNTs) reported simultaneously by Bethune and Iijima (Iijima and Ichihashi 1993), (Bethune et al., 1993) two years later.

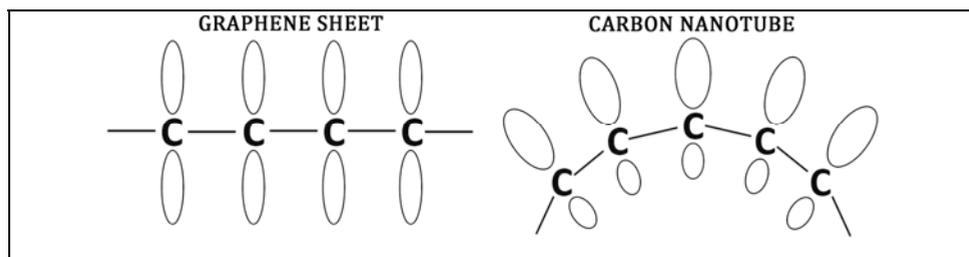


Fig. 1. Schematic of electron distribution off plane in graphene and CNT.

Carbon nanotubes are high-aspect ratio cylinders formed by rolled-up graphene sheets. In graphene, outer-shell electrons of each carbon atom occupy the planar sp^2 hybrid orbital to form three in-plane σ bonds and one out-of-plane π bond. While the σ bonds make graphene more strong in-plane than diamond, the σ electron is delocalized over the plane and makes it more thermally and electrical conductive (M. Meyyappan, 2005). Due to the nanotube surface curvature, the sp^2 graphene bonds are slightly out of plane (Fig.1). This change causes σ - π re-hybridization in which three σ bonds are slightly out of plane and the π bond is more delocalized outside the tube (Haddon and Chow 1999). This results in higher chemical reactivity of nanotubes (especially of small diameter ones) compared with graphene.

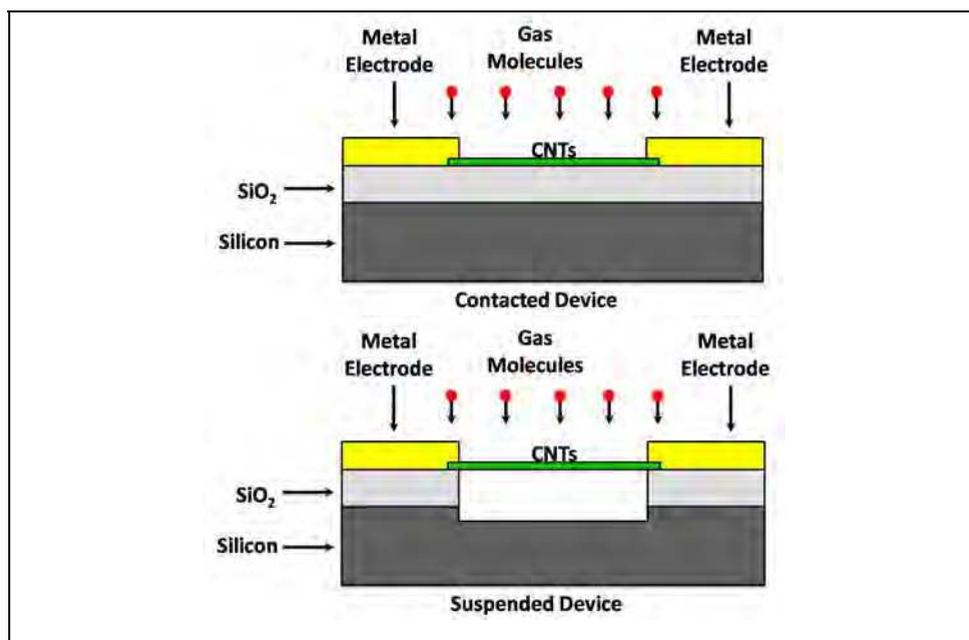


Fig. 2. Chemiresistor in supported/contacted (top) and suspended (bottom) configurations.

These characteristics boosted numerous researches in the area of CNT- based sensors during the last decade. The first CNT gas sensor was demonstrated by Kong *et al.* (Kong *et al.*, 2000). Using a semiconductor SWCNT as a channel to conduct the source-drain current in a field-effect transistor (ChemFET) configuration, detection of nitrogen dioxide (NO_2) and ammonia (NH_3) was demonstrated. The sensing mechanism in CNT based gas sensors is charge transfer occurring during interaction of gas molecules with the CNT surface, resulting in modification of the CNT conductivity. Since then, CNT-FET sensors were successfully used for detection of O_2 , NO_2 , Br_2 , I_2 , NH_3 , and other gases, (Kong *et al.*, 2000a), (Lee *et al.* 2000), (Bockrath *et al.* 2000), (Park and McEuen 2001), (Someya *et al.* 2003). The CNT-FET configuration has some advantages like a very low initial current (and thus, low noise) and low power consumption. It should be noted, however that fabrication of CNT-FET sensors is technologically very challenging, since all known methods of SWCNT

synthesis produce a mixture of metallic and semiconducting SWCNTs, and reliable technologies of their separation still have to be developed.

Other CNT based sensor configuration is a chemiresistor, very popular due to its simplicity. In this case, the changes in resistance of the metallic (usually, multi-walled) CNTs induced by gases, are detected. To improve sensitivity, large area interdigitated electrodes can be used, with the gaps filled with a big number of nanotubes. This kind of devices has been successfully used to detect gases and organic vapors, including at room temperature, at mW power consumption (Li et al. 2003), (Suehiro, Zhou and Hara 2003). In principle, the MWCNTs based sensors must be less sensitive than those based on SWCNTs, as the measured current (and the associated noise) is supposed to pass through the whole volume of a MWCNT including all internal walls, whereas the reaction with gases should affect mainly the current fraction through the outermost wall. However, recent studies of MWCNT electrical properties (Moshkalev et al., 2008) have revealed that for distances shorter than $\sim 1 \mu\text{m}$, current redistribution between graphitic shells is small (see Fig. 3). That means that for side contacted MWCNTs and short gaps between electrodes, the major fraction of the current passes through the outermost wall. In terms of sensing configuration, this can effectively transform a short side-contacted MWCNT in a big-diameter "single-wall" metallic CNT, providing higher signal-to-noise ratio in gas sensing.

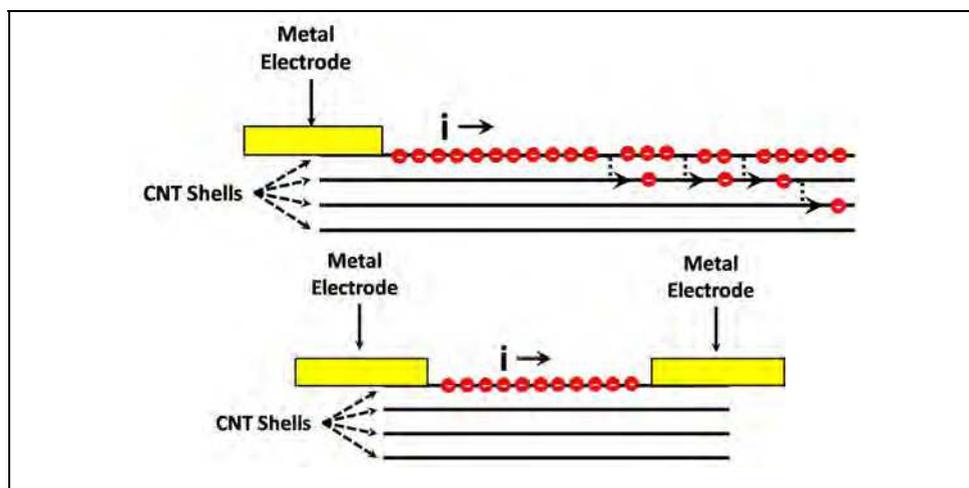


Fig. 3. Schematic representation of current redistribution between shells for long (top) and short (bottom) MWCNT.

High surface-to-volume ratio, high conductivity (for metallic tubes) and mechanical stability make CNTs very attractive for gas sensing applications. However, nanotubes do not show high reactivity towards many gases of interest, and their sensitivity to gases (when available) is not selective. These shortcomings can be, at least in part, circumvented by functionalization of CNTs with nanoparticles (NPs). Combining unique properties of CNTs and nanoparticles, the resulting hybrid nano-composite CNT/NP structures can get new properties different from those for their parts while separate.

Nanoparticles exhibit many amazing properties not found in conventional materials (Zhu et al. 1987), (Siegal et al., 1987). They can show unique physical and chemical characteristics due to their high surface-to-volume ratio and a high density of chemically active surface sites like corners or edges. Particles size is expected to influence three important groups of properties in any material. The first one is related to the structural characteristics, namely, the lattice symmetry and cell parameters (Ayyub et al. 1995). The size of particle induces structural distortions associated with changes in cell parameters, and has been observed in various nanoparticles of Al_2O_3 (Samsonov, Sdobnyakov and Bazulev 2003), (Ayyub et al. 1988), CeO_2 (Hernández-Alonso et al., 2004), ZrO_2 (Garvie and Goss 1986). Other important effect is related to the electronic properties. In nanostructures, so-called quantum size or confinement effects can be observed, which essentially arise from the presence of discrete, atom-like electronic states (Moriarty 2001), (Pacchioni, Ferrari and Bagus 1996), (FernandezGarcia, Conesa and Illas 1996). The third group of properties influenced by size appears due to specific structural and electronic characteristics of nanoparticles. In their bulk state, one material has wide band gaps and a low reactivity (Rodriguez 2002), the decrease in the average size of particles alters the electronic band structure of the material, and this can have a strong influence on the conductivity and chemical reactivity (Hoffmann et al., 1988), (Lucas et al. 2001). Furthermore, the presence of under-coordinated atoms (like corners or edges) or oxygen vacancies in oxide nanoparticles should produce specific geometrical arrangements as well new electronic states above the valence band of the corresponding bulk material enhancing in this way the chemical activity of the system (Anchell and Hess 1996), (Ferrari and Pacchioni 1995).

The recently demonstrated possibility to attach metal or metal oxide nanoparticles to CNTs opens the way to development of new hybrid materials combining the unique physical and chemical properties of CNTs and nanoparticles. The main reason to decorate nanotubes by nanoparticles in gas sensing applications is to provide selective sensitivity towards different gases.

In this chapter we present a family of novel gas sensors based on decorated and pristine CNTs. Basically, the discussion will be centered in chemiresistor devices. Advantages of using arrays of such sensors in different configurations (e.g., supported or suspended, pristine or decorated nanotubes) are discussed.

2. Preparation of samples and decoration

2.1 Methods of CNTs growth

There have been numerous reviews on the synthesis of carbon nanotubes, which are members of the fullerene family (Dai 2002), (Liu, Fan and Dai 2004), (Ferrones 2004). The most common methods for growing CNTs are the electric arc discharge, laser ablation and chemical vapor deposition techniques.

In the arc discharge technique (Iijima, 1991) a low-voltage, high-current power supply is used to produce an arc across small gap between two graphite electrodes in the presence of catalytic metals. The high temperature provides the energy for CNTs formation.

The laser ablation technique (Thess et al. 1996) uses graphite targets with small admixtures of cobalt/nickel placed in a 1200°C quartz tube furnace with an inert (Ar or He) atmosphere and vaporized by a laser pulse. CNTs are formed during the condensation of vapor phase.

The CVD process (Endo et al. 1993) encompasses a wide range of synthesis techniques, from the gram-quantity bulk formation of nanotube containing materials to the formation of

individual aligned SWCNTs on SiO₂ substrates for use in electronics. The majority of CNT methods are direct descendents of basic CVD. Basically, a carbonaceous gas flows over transition metal nanoparticles at medium to high temperature (550 to 1200°C) and reacts with the nanoparticles to produce CNTs. The mechanisms of nucleation of multi-walled nanotubes in CVD are subject of current studies (Moshkalev and Verissimo 2007).

2.2 Methods of purification

Independently on the method of fabrication, there is always significant quantity of impurities in produced carbon deposits. In the last years, several methods to remove the impurities has been developed (Zhu et al. 2004), (Shelimov et al. 1998), (Bandow et al. 1997), (Holzinger et al. 2000), (Duesberg et al. 1998b), (Duesberg et al. 1998a), (O'Connell et al. 2002).

Briefly, one of the popular procedures used to purify as-produced CNT materials consist in heating the material for 2 or 3 hours in air atmosphere at 330 °C, to reduce the amorphous carbonaceous material. The crystalline carbon material is burnt out at much higher temperatures. The thermally treated material is refluxed in nitric acid for 12 hours at 60 °C to remove catalytic metal inclusions. The resulting solution is washed with distilled water until pH 7 and dried at 80 °C for 6 hours.

2.3 Methods to prepare solutions with CNTs

For a variety of applications where separate nanotubes are required, making a good dispersion of CNT in a solution is of critical importance. It is known that CNTs are not wetted by water, so that solutions of nanotubes in water are not stable. On the other hand, due to strong Van der Waals interactions between nanotubes they tend to aggregate in solutions.

The poor wettability can be overcome using surfactants. Surfactants like DNA, polymers, Sodium dodecyl sulfate (SDS) and dimethylformamide (DMF) were successfully utilized for this propose. These reagents coat CNT surfaces with micelles, forming a hydrophobic core and a hydrophilic surface. After addition of the surfactant, the mixture is dispersed using ultrasonic bath, and stirred. A superior fraction of this solution is extracted and used for deposition of nanotubes.

2.4 Deposition techniques – Dielectrophoresis

Deposition of CNTs in a desired position and formation of reliable electrical contacts are among the biggest challenges on the way to mass production of CNTs-based devices. Many techniques of deposition or controlled growth have been developed in the last years. One possibility is to grow CNTs directly on the electrode by catalytic CVD (Kong, 2000b), (Pengfei et al. 2003), (Valentini et al. 2003). Others methods use CNTs prepared beforehand (Varghese et al. 2001), (Chopra et al. 2002). The CNTs containing solutions are dropped on the desired position, followed by a drying or spin coating process (Varghese et al., 2001). However, the number of nanotubes is not well controlled and their orientations are random. Dielectrophoresis (DEP) technique using ac electric fields (Suehiro et al. 2003), (Gelamo et al., 2009a) has proven to be a very efficient technique for deposition of aligned nanotubes in desired position between metallic electrodes. In a DEP process, elongated polarized objects are aligned and attracted to the area of strongest electric field (Pohl, 1978).

Using this technique Gelamo *et al.* (Gelamo *et al.*, 2009b) were able to deposit MWCNT between tungsten, nickel and titanium electrodes with gaps $\sim 1 \mu\text{m}$ (Fig. 4 and 5). They report the possibility to deposit one or various CNTs, changing the process parameters (density of solution, bias, frequency, time).

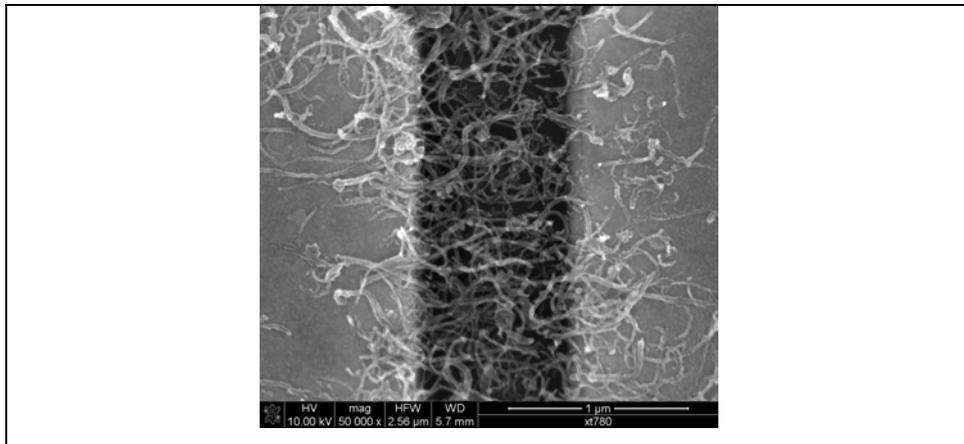


Fig. 4. SEM image of nanotubes deposited over metal electrodes by dielectrophoresis in a supported configuration.

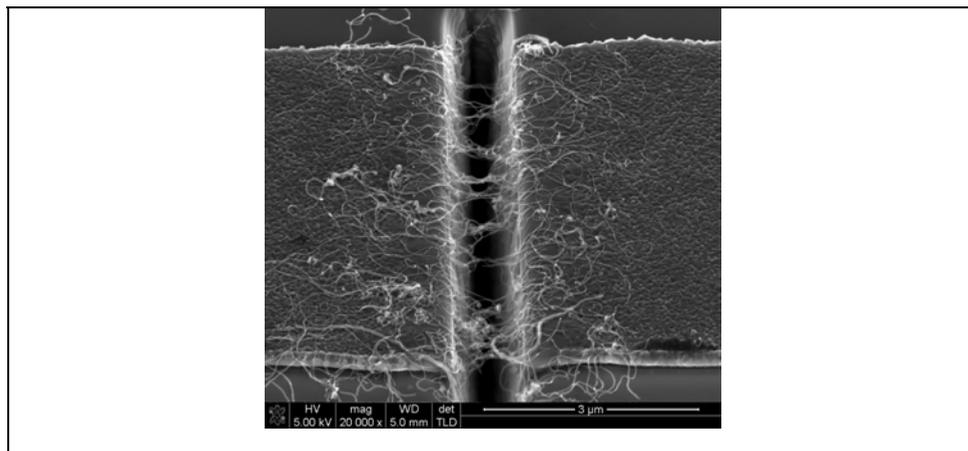


Fig. 5. SEM image of nanotubes deposited over metal electrodes by dielectrophoresis in a suspended configuration.

2.5 Chemical methods to decorate CNT

Direct growth of nanoparticles on the surface of CNTs using chemical routes offers many advantages, in particular the ability to control the size and distribution of particles, by adjusting various parameters of the solution.

In this method the CNTs are previously treated with strong acids or oxidizing agents such as H_2SO_4 , H_2NO_3 , KMnO_4 and O_3 , to produce oxygen functional groups that serve as precursors for nanoparticles growth.

Multi-walled carbon nanotubes were chemically oxidized using nitric acid aiming the functionalization of nanotube walls with oxygen-containing functional groups such as hydroxyl (-OH), carbonyl (-C=O), and carboxylic (-COOH) ones. The outermost walls functionalization is an important step to the direct synthesis of metal oxide nanoparticles on the MWCNTs surface since these oxygen-containing groups act as sites for nucleation of nanoparticles, see Fig. 6

We recently successfully synthesized cerium-praseodymium mixed oxide nanoparticles on MWCNTs in a hydrolysis reaction. Praseodymium and cerium carbonates were used as precursors in a hydrolysis reaction, realized under controlled pH, assisted by ultrasonic bath. The optimized pH value of the solution was near 3 and was adjusted by using HCl. The mixture was stirred and the precipitate filtered and dried.

2.6 Physical methods to decorate CNT

Physical metal deposition processes also have been successfully applied for CNTs decoration. The main methods used so far were electron-beam evaporation, sputtering and thermal evaporation. Electron beam evaporation was used to decorate CNT with Pd (Kong, Chapline and Dai 2001), Pt, Sn, Rh (Star et al. 2006). Using sputtering (Lu et al. 2004) and (Sayago et al. 2007) SWCNTs were decorated with Pd. MWCNTs were decorated with Ti (Gelamo et al. 2009), Pt and Au (Penza et al. 2007). The differences in chemical reactivities of metal nanoparticles resulted in selective detection of gases like of H_2 , CH_4 , CO , H_2S , NH_3 , NO_2 and O_2 .

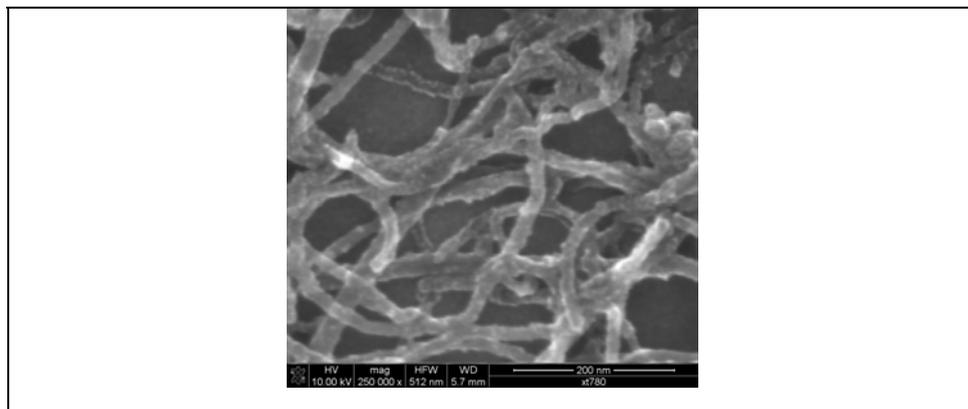


Fig. 6. SEM image of nanotubes decorated with SnO_2 nanoparticles.

2.7 Thermal treatment

The electrical transport properties of a CNT-based device are dependent on the metal-CNT contact properties. For metal electrodes, a junction with semiconductor SWCNT may result in a Schottky barrier (SB) and a junction with metallic CNT may produce an ohmic contact. To develop and design CNT-based devices, low values of contact resistances are required.

High contact resistances result in higher noise, especially at elevated working temperatures, and this is critical for noise generated by the device. The lowest detectable gas concentration is limited by signal-to-noise ratio (R); when R is higher than 3 the signal is considered to be a true signal (Currie 1995).

One important technique to reduce the contact resistance is the thermal treatment (TT). After the CNTs have been deposited under the metal electrodes the resistance of the device is normally very high.

The electrical characterization before TT has shown a typical rectifying behavior for metal-MWCNT junctions, see Fig. 7. This can be attributed to the presence of water, surfactants and oxide layers in the interface between the nanotubes and electrodes (Zhang et al., 1999).

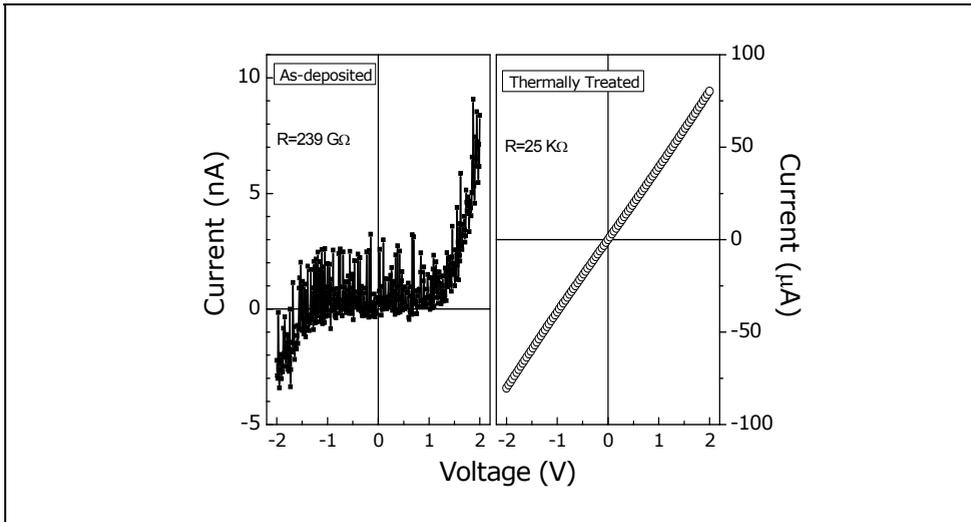


Fig. 7. Current-voltage curves for as-deposited (left) and thermally treated (right) nanotubes.

The main reasons to use TT in ultra-high vacuum or an inert atmosphere to improve the nanotube-metal contact resistance are:

- i) Avoid any reaction with atmosphere (oxygen) and remove water and volatile reactants from the surfaces
- ii) The reaction between CNT and metal on the contact may occur at the interface between them once a sufficient temperature is reached. The reaction CNT-metal may produce a metal carbide in the junction forming a low-resistance ohmic contact and reliable mechanical connection between them.

Experiments with TT in high vacuum at temperatures between 400-800 °C resulted in significant improvement of contact resistance between Ti electrodes and nanotubes (from ~240 GΩ to 25 kΩ), with high linearity of I-V dependencies at low biases (Fig. 7). Observation by SEM proved integrity of nanotubes and electrodes after this treatment.

3 The influence of substrate

3.1 Supported MWCNTs

There are just a few works where the effects of a substrate on electrical and thermal properties of nanotubes have been studied. Recently Gelamo *et al.* (Gelamo *et al.*, 2009a) have studied the effect of a CNT contact with the substrate using pristine MWCNTs (in a chemiresistor configuration), deposited by DEP over Ti electrodes and followed by annealing in vacuum. It was observed that MWCNTs were almost equally sensitive to the gases tested (N_2 , Ar, O_2). This can be seen in Fig. 8, where results with pulsed injection of the gases (at the same peak pressure of 30 mTorr) are presented. Hereafter, the sensor response is given by a relative change of electrical current after gas admission into the chamber. For chemically inert gases like Ar and N_2 , the observed current change can be attributed only to the electrothermal effect, associated with Joule heating of CNTs by electric current (Wei *et al.* 2004) and their cooling by gas. After evacuating the gas, fast recovery of signal (heating of nanotubes) is evident. Note that practically the same response is observed for O_2 , indicating that under the present process temperature (200 °C), chemical interaction of oxygen with CNTs is negligible. The resistance of metallic MWCNTs is known to depend on temperature, and the thermal coefficient of resistance (TCR) was estimated to be $\sim 0.26\% K^{-1}$ (Pop *et al.* 2007). When a gas is injected into the chamber, cooling by gas results in reduction of the CNT temperature (ΔT_{gas}) and corresponding current increase. The estimates give $\Delta T_{gas} \sim 15$ °C for the data shown in Fig. 8. Other possible mechanisms of cooling, besides the heat conduction by gas, are: i) by radiation and ii) heat conduction to the substrate and iii) heat conduction to the Ti electrodes. Cooling by radiation should be relatively low at the present temperatures.

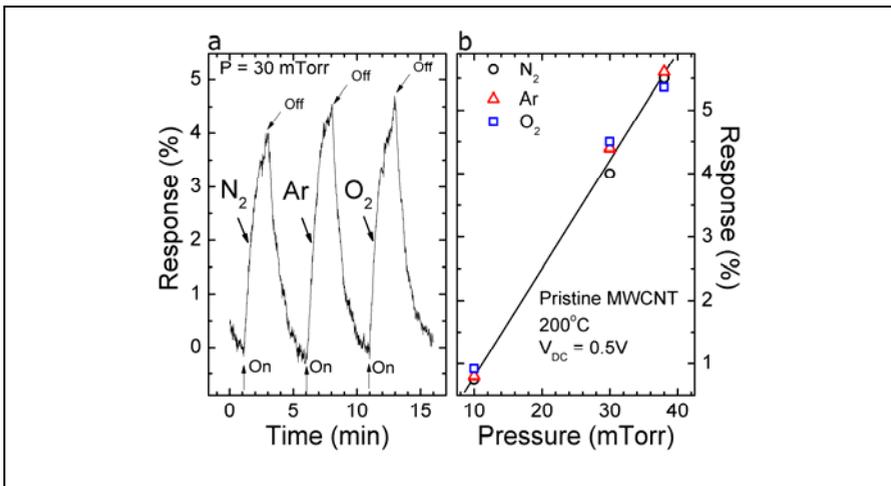


Fig. 8. Sensor response to 30 mTorr pulses of N_2 , Ar and O_2 (left) and dependence of response on gas pressure (right) using pristine MWCNTs.

This results show that the chemiresistor configuration using supported pristine MWCNTs can be used as a low-pressure gauge for pressures between 10^{-3} and 10^{-1} Torr, with no selectivity to simple gases like Ar, N₂ or O₂ (Fig. 8).

3.2 Suspended vs. supported MWCNTs

In order to evaluate relative contributions of different mechanisms of heat conduction, supported and suspended configurations were compared using N₂ (Fig. 9). For the latter, heat transfer to the substrate is eliminated (FIB was used to mill the gap between electrodes), and other parameters (the gap width, gas pressure, process temperature, applied voltage, and number of CNTs bridging the gap that determines the initial current value) were kept about the same. It is possible to see a dramatic reduction (by a factor of 30) in response to the gas for suspended CNTs. In some cases, this reduction was even more pronounced, up to 10^2 or even more, see below. This finding clearly indicates the major role of the substrate in CNTs cooling, while the cooling due to direct interaction between the gas and CNT surface and due to heat conduction to electrodes is of minor importance.

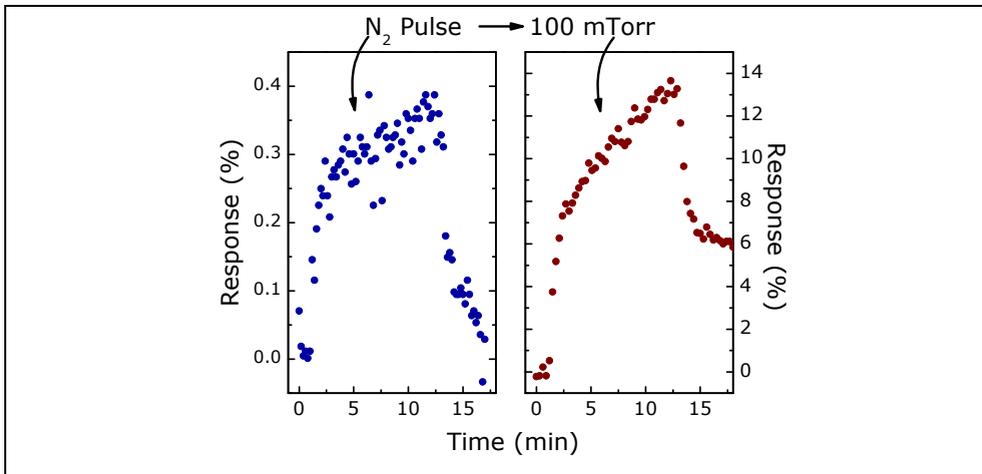


Fig. 9. Sensor response to N₂ pulse at T = 200°C for pristine CNTs, in suspended (left) and supported (right) setups.

Strong difference in self-heating of supported and suspended single-wall carbon CNTs by electric current was observed also by Pop *et al.* (Pop *et al.* 2005). The mechanisms responsible for enhanced heat transfer to the substrate in thermal contact with CNTs are not completely clear at the moment. This result is somewhat surprising as stronger heat conduction along CNTs to metal electrodes could be expected, considering data on thermal conductivity for the materials involved, available in literature: 1.4 W/mK (for silica), 22 W/mK (Ti), 11.7 W/mK (TiO₂) and 300-6600 W/mK (CNT) (Pop *et al.*, 2005), (Berber, Kwon and Tomanek 2000).

It is possible that a high thermal resistance at the area of contact between CNTs and metallic electrode hampers the heat transfer. Further, the observed strong heat transfer to the substrate (SiO₂) effectively increases the area of thermal contact between the gas and the

CNT/substrate system. In other words, cooling by gas occurs not only at the CNT surface but at much higher surface of a SiO₂ substrate which is in thermal contact with the CNT. This explains strongly enhanced sensitivity to gases for supported CNTs. On the other hand, the observed strong effect of substrate could be used to control the sensitivity of pressure measurements just by changing the area of thermal contact between the CNT and substrate, or by choosing substrates with different thermal properties.

4. Decorated MWCNTs and selectivity to gases

4.1 Supported MWCNTs

As commented above, the technologies of nanotubes decoration by nanoparticles that were developed last years can be used to promote selectivity to gases (Gelamo et al., 2009a). Here, we used decoration by Ti nanoparticles to detect selectively O₂ and the result using this device in a presence of N₂, Ar and O₂ at different pressures is shown below, see Fig. 10.

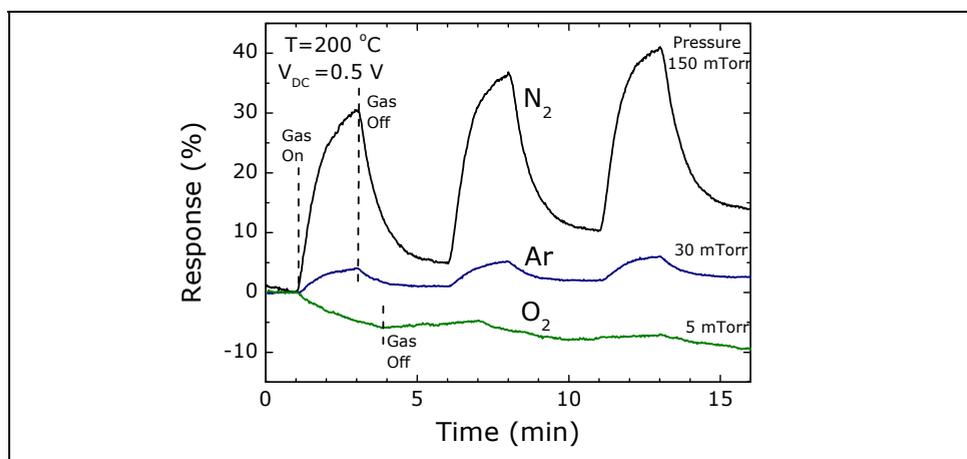


Fig. 10. Sensor response to pulses of different gases.

Tests varying O₂ pressure showed that two mechanisms (chemical and electrothermal or ET) can be observed at the same time in a CNTs/NPs system, see Fig. 11. For O₂ pressures ≤ 10 mTorr, the chemical effect at NPs (current decrease) is notable, while for pressures > 30 mTorr, the ET effect starts to prevail. For intermediate O₂ pressures, a superposition of positive and negative contributions of two effects can give results that might appear confusing (e.g., these contributions in some cases can be mutually canceled for a specific pressure), though characteristic times for these effects are much different. In particular, interesting behavior can be seen in Fig. 11, when the current drops abruptly after O₂ pumping out (at $t = 15$ min) for pressures higher than 70 mTorr. This is a result of fast rise of the CNTs/NPs system temperature after the gas removal (no more gas cooling), and corresponding decrease of CNTs resistance. Note that apparently much smaller rise of current is observed when gas is injected ($t = 1$ min), since the corresponding current rise is mostly compensated by its almost simultaneous decrease due to the chemical effect. As a result, in contrast to N₂ when a good linearity with pressure is observed, the signals for oxygen (measured at $t = 5$ min) tend to saturate for small pressures (~ 10 mTorr), see Fig. 12.

When Ti decorated MWCNTs are exposed to N_2 , only ET effect is observed, with the response similar to that for pristine MWCNTs. Figure 12 shows the device responses to injection of O_2 at various pressures. For O_2 , tendency for saturation at very low pressures can be seen, while for N_2 the response is linear for the pressure range used.

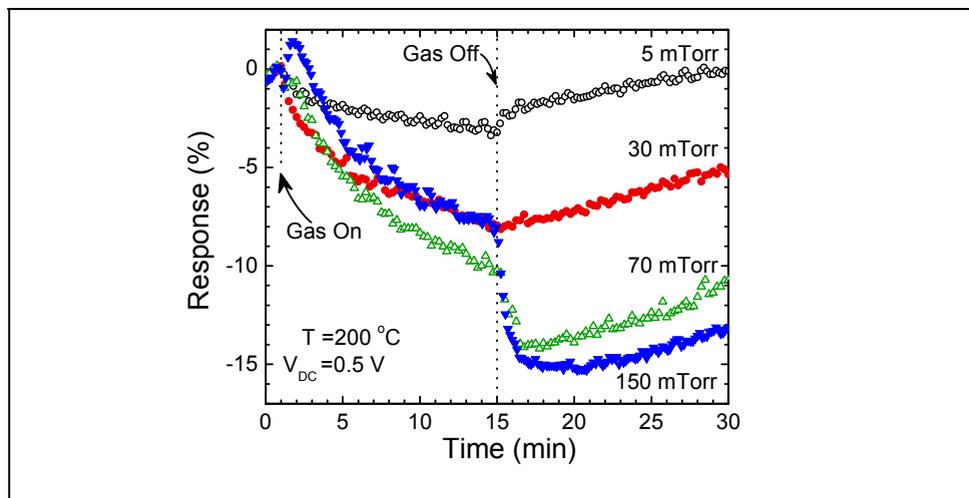


Fig. 11. Response to O_2 , supported MWCNTs: effect of pressure variation, pulsed gas injection. Gas is on at $t = 1$ min and off at 15 min.

4.2 Suspended MWCNTS

As previously discussed above, there is a significant heat transfer from the CNTs self-heated by current to the substrate (oxidized Si). Thus it is clear that by eliminating the heat losses to substrate, significant increase of nanotube (and attached nanoparticles) temperature can be achieved. To prepare suspended nanotubes, first a FIB system was used to mill $5 \mu\text{m}$ deep and $1 \mu\text{m}$ wide cuts between electrodes and after this MWCNTs were DEP deposited. Thin Ti film (1-2 nm) was then deposited by sputtering on the surface of nanotubes (Fig. 5).

In this case, due to much stronger self-heating, selective gas measurements turn out to be possible even at a *room* substrate temperature (Fig. 13), with greatly enhanced sensitivity (by an order of magnitude, at much lower substrate temperature), as compared with supported CNTs. Faster sensor response can be also clearly seen. Some reports give values of Joule heating for suspended MWCNTs exceeding $1000 \text{ }^\circ\text{C}$ (Cai, Akita and Nakayama 2004), but this seems to be unlikely for the present conditions, as heating above $600 \text{ }^\circ\text{C}$ at the presence of oxygen would eventually burn out the nanotubes that was not observed in our experiments. However, local CNTs/NPs heating under present conditions evidently can reach very high values (up to $300\text{-}400 \text{ }^\circ\text{C}$ or even more, Gelamo et al., 2009b) under low pressure conditions when cooling by gases is negligible. This makes possible very intense interaction of oxygen with partially oxidized Ti NPs.

Besides the enhanced device response under exposition to O_2 , other interesting parameter that changes greatly is the response time, see Fig. 14 where results for both supported and suspended configurations are presented. This parameter can give important information

about characteristic times of processes occurring during chemical interaction of nanoparticles and gas, and can be useful to analyze the underlying mechanisms. For supported MWCNTs, longer response times (near 5 min.) are an indication of slow processes of heat transfer to the substrate. For suspended nanotubes, the response time is an order of magnitude smaller (0.5-0.8 min.), and its value is still higher than that residence time for gas molecules in the chamber (~0.2 min.). Probably, this time is determined by chemical interaction between O₂ and Ti particles. Careful study of the interaction mechanisms is subject of future work.

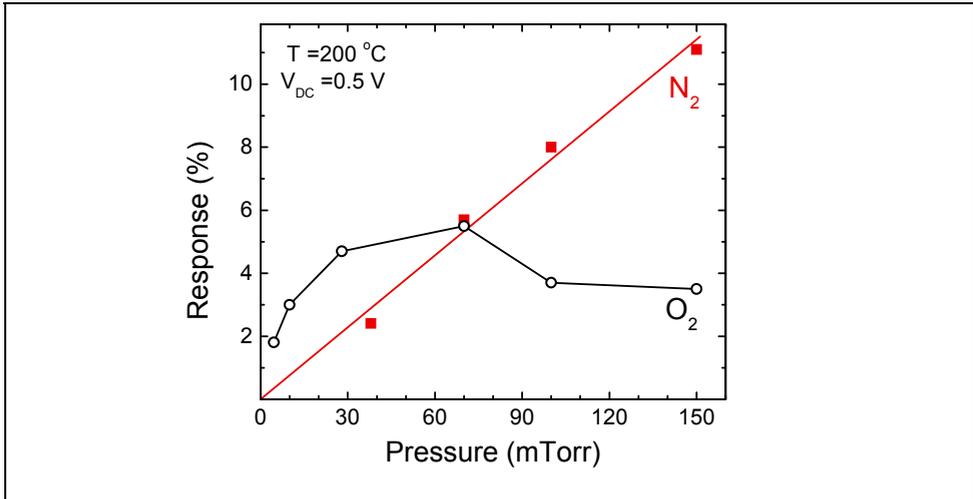


Fig. 12. Dependence of response on pressure for O₂ and N₂ using Ti decorated supported MWCNTs.

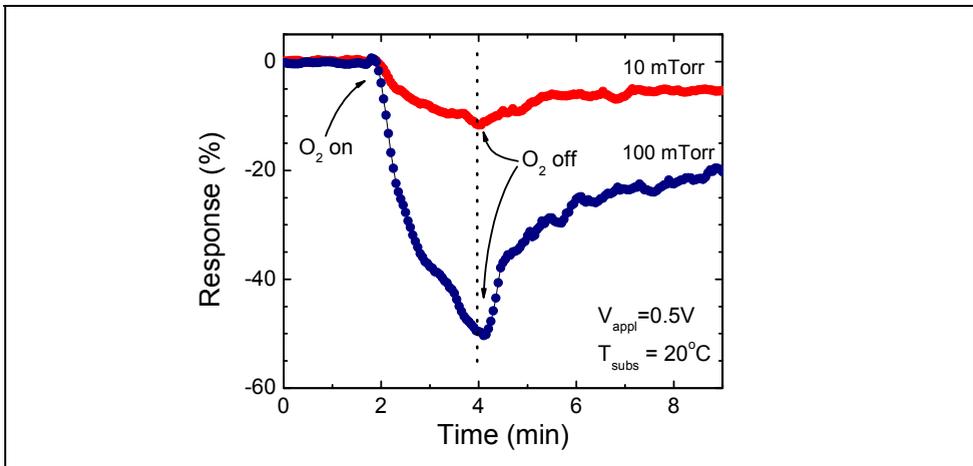


Fig. 13. Response to O₂, suspended MWNCTs, O₂ peak pressures of 10 mTorr and 100 mTorr, respectively.

5. Conclusions

The study of gas sensors based on short MWCNTs in a chemical resistor configuration (where nanotubes can be heated considerably by current) has revealed two main effects occurring under exposure to simple low-pressure gases like Ar, N₂ and O₂, and manifestation of the effects is significantly different for supported (over SiO₂) and suspended nanotubes (Gelamo et al., 2009a):

- i) thermoelectric effect, due to cooling of nanotubes upon injection of gas. This cooling results in a current increase, indicating positive TCR values for MWCNTs used, and happens both with pristine and decorated nanotubes. For the latter, nanoparticles should have the same temperature as nanotubes. No significant difference was observed for the cooling efficiency between three gases studied (Ar, N₂ and O₂);
- ii) chemical effect due to interaction of Ti nanoparticles with O₂, resulting in a current decrease.
- iii) for supported nanotubes, heating appears to be much weaker due to strong heat losses to the substrate, in this process the substrate surface layer also attains high temperature. Upon injection of gas, the nanotube and substrate surface layer that are in a thermal contact are cooled down together, and this increases the sensitivity to gas pressure, due to effectively larger area of interaction with gas;
- iv) for suspended nanotubes, self-heating is much stronger (no heat losses to the substrate, and losses to the metal electrodes and by radiation are smaller). On the other hand, the area of interaction with gas (the nanotube surface area) is much smaller as compared with supported nanotubes, so that nanotubes cooling by gas, under the same conditions, is much smaller for suspended ones (at least, two orders of magnitude). That means that suspended nanotubes can be used for pressure sensing at much higher gas pressures (>1 Torr), as cooling rate is proportional to the gas pressure;
- v) for suspended nanotubes decorated with Ti nanoparticles, much higher sensitivity to O₂ (chemical effect) is achieved as compared with supported ones, due to much stronger self-heating of nanotubes (and attached nanoparticles), so that measurements at room substrate temperature are possible.

Finally, a CNT/NP hybrid material has been applied for low-pressure gas sensing applications in chemical resistor configuration. In this configuration, multi-wall carbon nanotubes serve as a conductive channel (for electrical signal acquisition), a heating element (for local heating of attached nanoparticles), and a substrate for NPs deposition (for selective gas sensitivity), whereas nanoparticles are employed to provide selective sensitivity to specific gases.

Self-heating by Joule effect, especially strong for suspended nanotubes, provides enhanced sensitivity to gases using CNT/NP material. In contrast to sensors based on self-heated nanowires, where functions of heating and gas sensing are coupled in the same element, in the CNT/NP system these functions are associated with two different elements, that can be beneficial for the sensor performance. It is a flexible configuration allowing pressure and gas sensing in a wide dynamic range using arrays of sensors (suspended or supported, decorated or pristine CNTs) at room substrate temperature and very low power ($\sim 10^{-5}$ W) consumption.

Measurements have been realized for gases O₂, Ar and N₂, with gas pressures varying from a few to 150 mTorr due to current experimental limitations, however, the range of measurable pressures (and gases) can be further expanded.

Finally, the opportunity to perform experiments at locally elevated temperatures using CNT/NP structures can be interesting for studies of temperature activated processes such as catalysis.

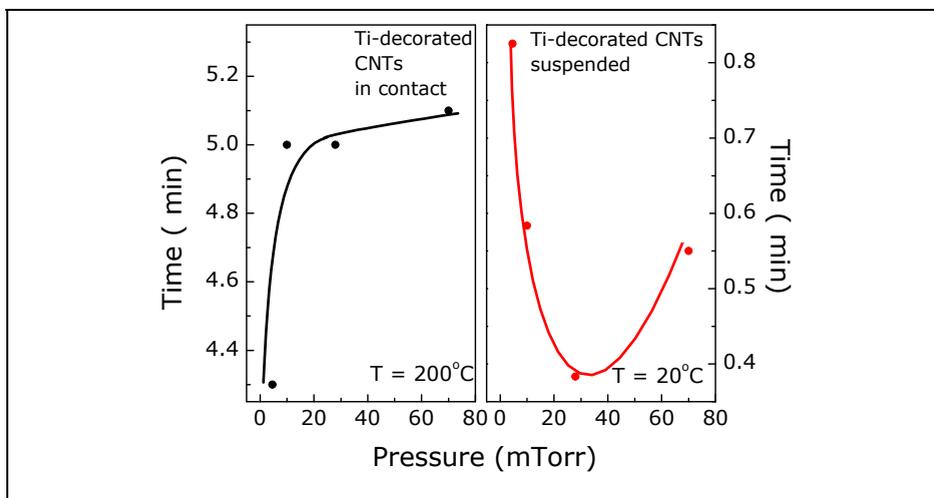


Fig. 14. Characteristic times for sensor response upon gas injection.

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6. References

- Anchell, J. L. & A. C. Hess (1996) H₂O dissociation at low-coordinated sites on (MgO)(n) clusters, n=4,8. *Journal of Physical Chemistry*, 100, 18317-18321.
- Ayyub, P., M. Multani, M. Barma, V. R. Palkar & R. Vijayaraghavan (1988) Size-induced structural phase-transitions and hyperfine properties of microcrystalline Fe₂O₃. *Journal of Physics C-Solid State Physics*, 21, 2229-2245.
- Ayyub, P., V. R. Palkar, S. Chattopadhyay & M. Multani (1995) Effect of crystal size-reduction on lattice symmetry and cooperative properties. *Physical Review B*, 51, 6135-6138.
- Bandow, S., A. M. Rao, K. A. Williams, A. Thess, R. E. Smalley & P. C. Eklund (1997) Purification of single-wall carbon nanotubes by microfiltration. *Journal of Physical Chemistry B*, 101, 8839-8842.
- Berber, S., Y. K. Kwon & D. Tomanek (2000) Unusually high thermal conductivity of carbon nanotubes. *Physical Review Letters*, 84, 4613-4616.
- Bockrath, M., J. Hone, A. Zettl, P. L. McEuen, A. G. Rinzler & R. E. Smalley (2000) Chemical doping of individual semiconducting carbon-nanotube ropes. *Physical Review B*, 61, 10606-10608.

- Cai, X. Y., S. Akita & Y. Nakayama (2004) Current induced light emission from a multiwall carbon nanotube. *Thin Solid Films*, 464, 364-367.
- Chopra, S., A. Pham, J. Gaillard, A. Parker & A. M. Rao (2002) Carbon-nanotube-based resonant-circuit sensor for ammonia. *Applied Physics Letters*, 80, 4632-4634.
- Currie, L. A. (1995) Nomenclature In Evaluation Of Analytical Methods Including Detection And Quantification Capabilities (Iupac Recommendations 1995). *Pure and Applied Chemistry*, 67, 1699-1723.
- Dai, H. J. (2002) Carbon nanotubes: Synthesis, integration, and properties. *Accounts of Chemical Research*, 35, 1035-1044.
- Duesberg, G. S., M. Burghard, J. Muster, G. Philipp & S. Roth (1998a) Separation of carbon nanotubes by size exclusion chromatography. *Chemical Communications*, 435-436.
- Duesberg, G. S., J. Muster, V. Krstic, M. Burghard & S. Roth (1998b) Chromatographic size separation of single-wall carbon nanotubes. *Applied Physics a-Materials Science & Processing*, 67, 117-119.
- Endo, M., K. Takeuchi, S. Igarashi, K. Kobori, M. Shiraiishi & H. W. Kroto (1993) The production and structure of pyrolytic carbon nanotubes (PCNTS). *Journal of Physics and Chemistry of Solids*, 54, 1841-1848.
- FernandezGarcia, M., J. C. Conesa & F. Illas (1996) Effect of the Madelung potential value and symmetry on the adsorption properties of adsorbate/oxide systems. *Surface Science*, 349, 207-215.
- Ferrari, A. M. & G. Pacchioni (1995) Electronic-structure of F and V centers on the MgO surface. *Journal of Physical Chemistry*, 99, 17010-17018.
- Garvie, R. C. & M. F. Goss (1986) Intrinsic size dependence of the phase-transformation temperature in zirconia microcrystals. *Journal of Materials Science*, 21, 1253-1257.
- Gelamo, R. V., F. P. Rouxinol, C. Verissimo, A. R. Vaz, M. A. B. de Moraes & S. A. Moshkalev (2009) Low-temperature gas and pressure sensor based on multi-wall carbon nanotubes decorated with Ti nanoparticles. *Chemical Physics Letters*, 482, 302-306.
- Haddon, R. C. & S. Y. Chow. 1999. Hybridization as a metric for the reaction coordinate of the chemical reaction. Concert in chemical reactions. *Pure & Appl. Chem.*, Vol. 71, 289-294.
- Holzinger, M., A. Hirsch, P. Bernier, G. S. Duesberg & M. Burghard (2000) A new purification method for single-wall carbon nanotubes (SWNTs). *Applied Physics A-Materials Science & Processing*, 70, 599-602.
- Iijima, S. (1991) Helical microtubules of graphitic carbon. *Nature*, 354, 56-58.
- Iijima, S. & T. Ichihashi (1993) Single-shell carbon nanotubes of 1-nm diameter. *Nature*, 363, 603-605.
- Kong, J., M. G. Chapline & H. J. Dai (2001) Functionalized carbon nanotubes for molecular hydrogen sensors. *Advanced Materials*, 13, 1384-1386.
- Lee, R. S., H. J. Kim, J. E. Fischer, J. Lefebvre, M. Radosavljevic, J. Hone & A. T. Johnson (2000) Transport properties of a potassium-doped single-wall carbon nanotube rope. *Physical Review B*, 61, 4526-4529.
- Li, J., Y. J. Lu, Q. Ye, M. Cinke, J. Han & M. Meyyappan (2003) Carbon nanotube sensors for gas and organic vapor detection. *Nano Letters*, 3, 929-933.
- Liu, J., S. S. Fan & H. J. Dai (2004) Recent advances in methods of forming carbon nanotubes. *MRS Bulletin*, 29, 244-250.

- Lu, Y. J., J. Li, J. Han, H. T. Ng, C. Binder, C. Partridge & M. Meyyappan (2004) Room temperature methane detection using palladium loaded single-walled carbon nanotube sensors. *Chemical Physics Letters*, 391, 344-348.
- Lucas, E., S. Decker, A. Khaleel, A. Seitz, S. Fultz, A. Ponce, W. F. Li, C. Carnes & K. J. Klabunde (2001) Nanocrystalline metal oxides as unique chemical reagents/sorbents. *Chemistry-A European Journal*, 7, 2505-2510.
- Moriarty, P. (2001) Nanostructured materials. *Reports on Progress in Physics*, 64, 297-381.
- Moshkalev, S. A. & C. Verissimo (2007) Nucleation and growth of carbon nanotubes in catalytic chemical vapor deposition. *Journal of Applied Physics*, 102, 044303.
- O'Connell, M. J., S. M. Bachilo, C. B. Huffman, V. C. Moore, M. S. Strano, E. H. Haroz, K. L. Rialon, P. J. Boul, W. H. Noon, C. Kittrell, J. P. Ma, R. H. Hauge, R. B. Weisman & R. E. Smalley (2002) Band gap fluorescence from individual single-walled carbon nanotubes. *Science*, 297, 593-596.
- Pacchioni, G., A. M. Ferrari & P. S. Bagus (1996) Cluster and band structure ab initio calculations on the adsorption of CO on acid sites of the TiO₂(110) surface. *Surface Science*, 350, 159-175.
- Park, J. W. & P. L. McEuen (2001) Formation of a p-type quantum dot at the end of an n-type carbon nanotube. *Applied Physics Letters*, 79, 1363-1365.
- Pengfei, Q. F., O. Vermesh, M. Grecu, A. Javey, O. Wang, H. J. Dai, S. Peng & K. J. Cho (2003) Toward large arrays of multiplex functionalized carbon nanotube sensors for highly sensitive and selective molecular detection. *Nano Letters*, 3, 347-351.
- Penza, M., G. Cassano, R. Rossi, M. Alvisi, A. Rizzo, M. A. Signore, T. Dikonimos, E. Serra & R. Giorgi (2007) Enhancement of sensitivity in gas chemiresistors based on carbon nanotube surface functionalized with noble metal (Au, Pt) nanoclusters. *Applied Physics Letters*, 90, 3.
- Pohl, H. A. (1978). *Dielectrophoresis: The Behavior of Neutral Matter in Nonuniform Electric Fields*. Cambridge: Cambridge University Press.
- Pop, E., D. Mann, J. Cao, Q. Wang, K. Goodson & H. J. Dai (2005) Negative differential conductance and hot phonons in suspended nanotube molecular wires. *Physical Review Letters*, 95, 4.
- Pop, E., D. A. Mann, K. E. Goodson & H. J. Dai (2007) Electrical and thermal transport in metallic single-wall carbon nanotubes on insulating substrates. *Journal of Applied Physics*, 101, 093710.
- Rodriguez, J. A. (2002) Orbital-band interactions and the reactivity of molecules on oxide surfaces: from explanations to predictions. *Theoretical Chemistry Accounts*, 107, 117-129.
- Samsonov, V. M., N. Y. Sdobnyakov & A. N. Bazulev. 2003. On thermodynamic stability conditions for nanosized particles. *Surface Science*, 526, 532-535.
- Sayago, I., E. Terrado, M. Aleixandre, M. C. Horrillo, M. J. Fernandez, J. Lozano, E. Lafuente, W. K. Maser, A. M. Benito, M. T. Martinez, J. Gutierrez & E. Munoz (2007) Novel selective sensors based on carbon nanotube films for hydrogen detection. *Sensors and Actuators B-Chemical*, 122, 75-80.
- Shelimov, K. B., R. O. Esenaliev, A. G. Rinzler, C. B. Huffman & R. E. Smalley (1998) Purification of single-wall carbon nanotubes by ultrasonically assisted filtration. *Chemical Physics Letters*, 282, 429-434.

- Someya, T., J. Small, P. Kim, C. Nuckolls & J. T. Yardley (2003) Alcohol vapor sensors based on single-walled carbon nanotube field effect transistors. *Nano Letters*, 3, 877-881.
- Star, A., V. Joshi, S. Skarupo, D. Thomas & J. C. P. Gabriel (2006) Gas sensor array based on metal-decorated carbon nanotubes. *Journal of Physical Chemistry B*, 110, 21014-21020.
- Suehiro, J., G. B. Zhou & M. Hara (2003) Fabrication of a carbon nanotube-based gas sensor using dielectrophoresis and its application for ammonia detection by impedance spectroscopy. *Journal of Physics D-Applied Physics*, 36, L109-L114.
- Terrones, M. (2004) Carbon nanotubes: synthesis and properties, electronic devices and other emerging applications. *International Materials Reviews*, 49, 325-377.
- Thess, A., R. Lee, P. Nikolaev, H. J. Dai, P. Petit, J. Robert, C. H. Xu, Y. H. Lee, S. G. Kim, A. G. Rinzler, D. T. Colbert, G. E. Scuseria, D. Tomanek, J. E. Fischer & R. E. Smalley (1996) Crystalline ropes of metallic carbon nanotubes. *Science*, 273, 483-487.
- Valentini, L., L. Lozzi, C. Cantalini, I. Armentano, J. M. Kenny, L. Ottaviano & S. Santucci. (2003). Effects of oxygen annealing on gas sensing properties of carbon nanotube thin films. *Thin Solid Films*, 436, 95-100.
- Varghese, O. K., P. D. Kichambre, D. Gong, K. G. Ong, E. C. Dickey & C. A. Grimes (2001) Gas sensing characteristics of multi-wall carbon nanotubes. *Sensors and Actuators B-Chemical*, 81, 32-41.
- Wei, J. Q., H. W. Zhu, D. H. Wu & B. Q. Wei (2004) Carbon nanotube filaments in household light bulbs. *Applied Physics Letters*, 84, 4869-4871.
- Zhu, J., M. Yudasaka, M. F. Zhang & S. Iijima (2004) Dispersing carbon nanotubes in water: A noncovalent and nonorganic way. *Journal of Physical Chemistry B*, 108, 11317-11320.
- Zhu, X., R. Birringer, U. Herr & H. Gleiter (1987) X-ray-diffraction studies of the structure of nanometer-sized crystalline materials. *Physical Review B*, 35, 9085-9090.



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This book has been outlined as follows: A review on the literature and increasing research interests in the field of carbon nanotubes. Fabrication techniques followed by an analysis on the physical properties of carbon nanotubes. The device physics of implemented carbon nanotubes applications along with proposed models in an effort to describe their behavior in circuits and interconnects. And ultimately, the book pursues a significant amount of work in applications of carbon nanotubes in sensors, nanoparticles and nanostructures, and biotechnology. Readers of this book should have a strong background on physical electronics and semiconductor device physics. Philanthropists and readers with strong background in quantum transport physics and semiconductors materials could definitely benefit from the results presented in the chapters of this book. Especially, those with research interests in the areas of nanoparticles and nanotechnology.

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