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Latest Advances in Modified/Functionalized Carbon Nanotube-Based Gas Sensors

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1. Introduction

A gas sensor is a device that when exposed to gaseous species, is able to alter one or more of its physical properties, so that can be measured and quantified, directly or indirectly. These devices are used for applications in homeland security, medical diagnosis, environmental pollution, food processing, industrial emission, public security, agriculture, aerospace and aeronautics, among others. Desirable characteristics of a gas sensor are selectivity for different gases, sensitivity at low concentrations, fast response, room temperature operation (some applications may require high temperature), low power consumption, low-cost, low maintenance and portability. Traditional techniques like gas chromatography (GC), GC coupled to mass spectrometry (GC-MS), Fourier transmission infrared spectroscopy (FTIR) and atomic emission detection (AED) provide high sensitivity, reliability and precision, but they are also bulky, time consuming, power consuming, operate at high temperature, and the high maintenance and requirement of trained technicians translate in high costs. In an effort to overcome those disadvantages, research in the area has been focused on the search for functional sensing materials.

Carbon nanotubes (CNTs) have been have been focus of intense research as alternative sensing material because of their attractive characteristics like chemical, thermal and mechanical stability, high surface area, metallic and semi-conductive properties and functionalization capability [1]. CNTs are graphene sheets rolled in a tubular fashion. Different types of CNTs can be synthesized: single walled carbon nanotubes (SWCNT), double wall carbon nanotubes (DWCNTs) and multi walled carbon nanotubes (MWCNT).

The publication of the first CNT-based sensor for NH_3 and NO_2 detection using an individual semiconducting SWCNT [2] triggered the research activity in this area. Pristine CNTs have shown to be chemically inactive to gas molecules in general. However, their modifica-

tion/functionalization capability has been exploited throughout the last years, especially for the development of devices with enhanced selectivity and sensitivity for the room temperature detection of a wide variety of gases. Numerous articles and reviews focused on different aspect of CNTs-based sensors and summarizing their progress and potential have been published throughout the years. Some of them are listed in references [3-34]. A most recent review [35] addressing the technological and commercial aspects of CNTs sensors presents evidence of the continuous active research in the area and that they have real potential to complement or substitute current technologies.

This chapter presents a summary of selected original research articles that have been published between 2010 and present in which the main subject are modified/functionalized SWCNTs, DWCNTs and MWCNTs and their use as gas sensing material. The majority of the references included in this chapter content are based on experimental results. However, theoretical studies based on computational science are also included because of their importance in the study of CNT-based sensors. The use of different methods of calculations and simulation has been useful to design new structures and materials and to study, evaluate and predict the interactions and adsorption energies between those materials and gaseous molecules. First, we present current research activities on pristine CNTs-based sensors and the different approaches used to improve their sensitivity and selectivity without modifying the CNTs structure, followed by the review of CNTs modified with conducting polymers, metallic nanoparticles (NPs), nanostructured oxides and sidewall modification, doping and others. Different modification/functionalization techniques like chemical deposition, plasma, sputtering and electrodeposition are discussed. Gas sensors based on changes of electrical conductivity caused by adsorption of gas molecules (resistors) are the most common sensor type discussed in this review. Other sensing platforms like surface acoustic wave (SAW) and quartz microbalance (QMB) are also included.

2. Unmodified carbon nanotubes

Pristine CNTs are known for their high stability because of their strong sp^2 carbon-carbon bonds and thus insensitive when used as sensing material for certain gases. However, the detection of NO, NO₂ and NH₃ has been previously reported. In order to improve their sensitivity and recovery time, different approaches like dispersion techniques to debundling the CNTs ropes, humidity assisted detection, application of an electric field, continuous use of ultraviolet (UV) light and even separation of semi-conductive types from conductive have been reported. The detection of NO, NO₂ and NH₃, as well as other gases like formaldehyde and dimethyl methylphosphonate (DMMP) with pristine SWCNTs are discussed in this section.

A MWCNTs based sensor was used for the detection of 50 ppm of nitrogen monoxide (NO) [36]. With the purpose to increase the sensitivity, an electric field was applied between two copper plates as electrodes, one of them containing MWCNTs-silicon wafer. It was found that when a positive potential was applied to the copper plate and the negative potential applied to the copper plate containing the MWCNTs-sensor, NO, being an electron acceptor,

moves to the electron enriched zone, which is the one containing the MWCNTs-sensor and thus enhancement in the sensitivity is observed. The stronger the applied electric field, the better the sensitivity. However, applying a negative electric field was applied to the copper plate and a positive potential was applied to the copper plate containing the MWCNTs-sensor, the NO molecules moved away from the MWCNTs sensor and thus a decrease in the sensitivity is observed. The more negative the applied electric field, the lower the sensitivity of the sensor. Recovery of the sensors was achieved by applying reverse potential from the one used to perform the gas sensing experiments.

Cava, et al. proposed the use of a homogeneous film of MWCNTs prepared by the self-assembly technique and use it as an active layer for an oxygen gas sensor with increased sensitivity [37]. When the sensors were exposed to 10% O₂ in Nitrogen at 160 °C, the electrical resistance decreased and showed a better oxygen sensitivity when compared to sensors prepared under the same condition but using the drop-cast method. The reason for this is that the self-assembly technique provides a better distribution of the nanotubes and thus promoting a better gas adsorption between nanotubes (inter-tube contact).

The high van der Waals attraction between CNTs causes them to remain in bundles or agglomerated. This can represent a problem for their application as gas sensors because it results in less adsorption/interaction (binding) sites, which translates in less sensitivity. Considering this, different dispersion techniques were used by Ndiaye and coworkers for the preparation of CNTs based sensors for NO₂ detection [38]. SWCNTs were dispersed in a surfactant, sodium dodecylbenzene sulfonate (NaDDBs) and an organic solvent, chloroform (CHCl₃), drop-casted in IDEs and tested for the detection of 50, 100, 120, 200 ppb of NO₂ at 80 °C. Sensors prepared with SWCNTs dispersed in NaDDBs showed better sensitivity than those with SWCNTs dispersed in chloroform. The explanation to this is that the surfactant was more effective in debundle the SWCNTs than the organic solvent. It was stated that even though the surfactant was not completely removed after several rinsing steps and heating treatment at 150°C, it does not have significant effect on the electronic behavior of the sensor. Both surfactant-dispersed and organic solvent-dispersed samples showed a decrease in resistance with increasing temperature, which demonstrate the semi-conductive behavior of the SWCNTs and thus no effect of the solvent.

A SWCNT-based gas sensor selective for NO₂ and SO₂ at room temperature and ambient pressure was developed by Yao *et al.* [39]. High sensitivity and selectivity for 2 ppm of each gas was achieved by controlling the humidity levels. For instance, at low humidity levels, the sensors showed to be selective for NO₂ and insensitive to SO₂. At high humidity levels (92%), both gases were detected. However, NO₂ showed a decrease in resistance and SO₂ showed an increase in resistance.

Continuous *in situ* UV illumination on SWCNTs during gas sensing experiments was used to enhance the sensor's overall performance in the detection of NO, NO₂ and NH₃ (Figure 1) [40]. Changes in conductance ($\Delta G/G_0$) as function of time were recorded and used to prepare calibration curves in order to determine sensors sensitivity. It was found that the continuous exposure of the sensors to UV light under inert atmosphere (N₂, Ar) regenerating the surface, therefore, enhances their sensitivity for the detection of NO and NO₂. Linear responses

were achieved at low concentrations and up to 50 ppm. Detection limits (DL), derived from the noise of the baseline and the slope obtained from the calibration curve, were found to be as low as 590 parts per quadrillion (ppq) and 1.51ppt for NO and NO₂, respectively. For NH₃ it was found not only that the *in situ* UV illumination reverses the direction of the changes in conductance, but it was also confirmed that it helps to improve the DL from 5.67 ppm to 27.8 ppt when tested under identical conditions. The achieved DL outperformed by several orders of magnitude the sensitivity of other CNTs-based NO, NO₂ and NH₃ sensors that have been previously reported. This is attributed to the UV light inducing surface regeneration and actively removal of all gases adsorbed on SWCNTs surface. It is worth noticing that this *in situ* cleaning with continuous UV-light exposure without device degradation was just achieved under inert atmospheres.

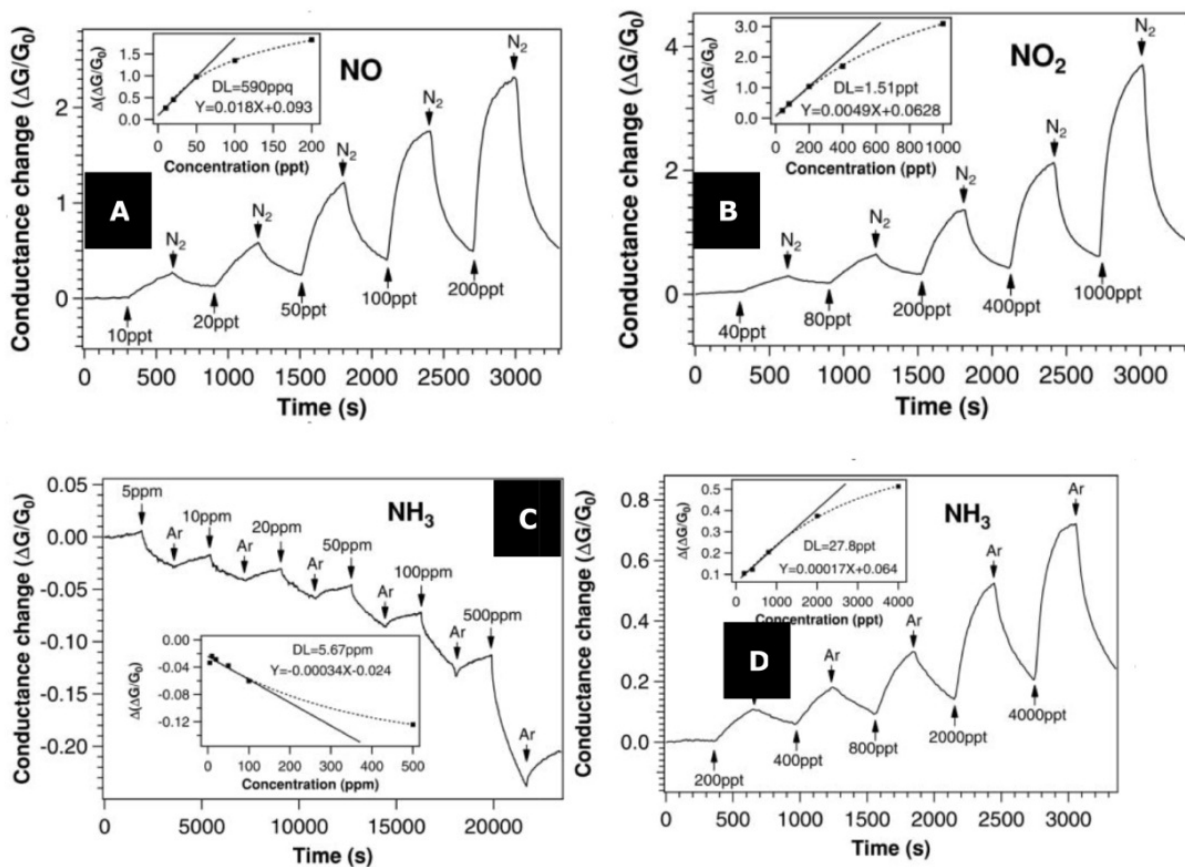


Figure 1. SWCNTs-sensor responses to (A) NO (10 – 200ppt) under *in situ* UV illumination, (B) NO₂ (40 – 1000 ppt) under *in situ* UV illumination, (C) NH₃ (5 – 500 ppm) without *in situ* UV illumination, and (D) NH₃ (200 – 4000 ppt) under *in situ* UV illumination. (From Chen *et al.* [40]. Copyright © 2012, with permission from Nature Publishing Group.)

Battie and coworkers used sorted semi-conducting SWCNTs as sensing film for the detection of NO₂ and NH₃ [41]. The density gradient ultracentrifugation (DGU) technique was used to separate semi-conducting from as produced SWCNTs. Films of as produced and sorted semi-conducting SWCNTs were exposed to NO₂ and NH₃ in air. Both films showed

decrease in resistance and increase in resistance as exposed to NO_2 and NH_3 , respectively. Full recovery was achieved by applying heat after NH_3 exposure and vacuum after NO_2 exposure. However, semi-conducting SWCNTs films were more sensitive for NH_3 than to NO_2 at different concentrations at ppm level.

Horrillo *et al.* used SWCNTs films for the room temperature detection of Chemical Warfare Agents (CWA) [42]. Changes in resistance were measured as samples were exposed to simulants of CWA at different ppm levels, DL of 0.01 ppm, 0.1 ppm and 50 ppm were achieved for DMMP, dipropylene glycol methyl ether (DPGME) and dimethylacetamide (DMA), respectively. The most remarkable advantage is that the sensors perform better and at more sensitive at room temperature, when tested at different temperatures.

3. Surface modified carbon nanotubes

CNTs modified with different functional groups have been used for the development of sensors for detection of volatile organic compounds (VOCs) in the environment as well as in exhaled breath. For the detection of VOCs in air, Wang *et al.* worked in the preparation of a sensor array based on MWCNTs covalently modified with different functional groups like propargyl, allyl, alkyltriazole, thiochain, thioacid, hexafluoroisopropanol (HFIP) [43] and Shrisat, *et al.* reported another one based on SWCNTs modified with different porphyrins (organic macrocyclic compounds) like octaethyl porphyrin (OEP), ruthenium OEP (RuOEP), iron OEP (FeOEP), tetraphenylporphyrin (TPP), among others [44]. Penza *et al.* also worked in the modification of MWCNTs with TPP for the room temperature detection of VOCs [45]. In this case, the TPP contained two different metals, Zn (CNT:ZnTPP) and Mn (CNT:MnTPP). Sensors were exposed to ethanol, acetone, ethylacetate, toluene and Triethylamine at ppm levels and all showed increase in resistance when exposed to the different gases. CNT: MnTPP showed the highest sensitivity towards all gases with respect to unmodified CNTs but for triethylamine and CNT: ZnTPP was more sensitive to ethylacetate.

Two different CNT-based sensor arrays have been reported for the detection and pattern recognition of VOCs present in exhaled breath samples for medical diagnosis, Tisch *et al.* presented a sensor array containing different nanomaterials including organically functionalized random networks of SWCNTs for the detection of VOCs related to Parkinson disease and that were present in exhaled breath collected from rats [46]. Ionescu and coworkers reported a sensor array based on bilayers of SWCNTs and polycyclic aromatic hydrocarbons (PAH) for the detection of multiple sclerosis in exhaled human breath [47]. In general, the incorporation of organic functional groups provided not only enhanced sensitivity but also provided better selectivity for each gas when compared to pristine CNTs. The use of statistical techniques like principal component analysis (PCA), discriminant factor analysis (DFA) and linear discriminant analysis (LDA) was possible to determine the discrimination capability of the sensors toward each VOC.

SWCNTs were functionalized with tetrafluoroquinone (TFQ) at the room temperature for detection of dimethyl methylphosphonate (DMMP) at parts per trillion (ppt) levels (Fig-

ure 2) [48]. The conductance of the TFQ-SWCNTs samples increased as function of concentration when exposed to DMMP in N_2 in a concentration range from 20ppt to 5.4ppb. Sensors showed fast response and ultra sensitivity down to 20ppt when compared to unmodified SWCNTs sensor, which had a DL of nearly 1 ppm. The presence of TFQ clearly showed to improve the sensitivity and this is because it provides additional binding sites thru hydrogen bonds between hydroxyl groups in TQF and DMMP. In addition, TQF tailors the electronic properties of SWCNTs via hole doping.

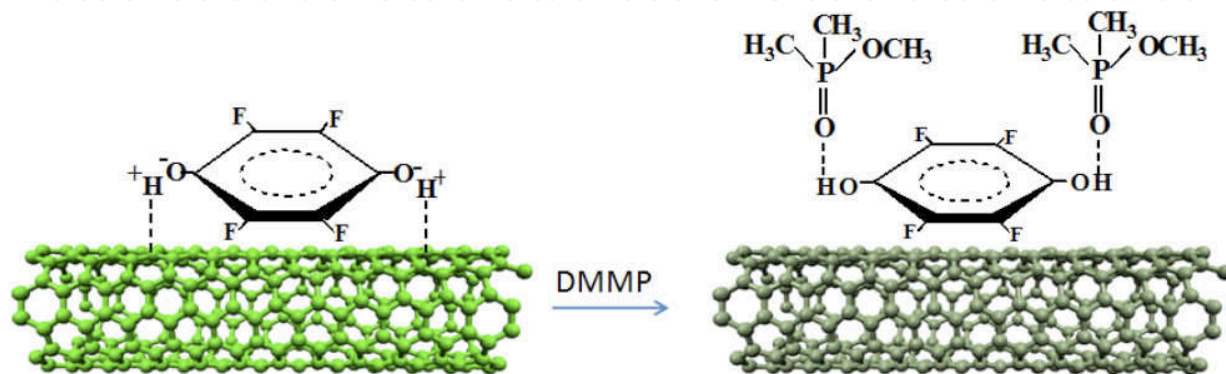


Figure 2. Representation of the possible sensing mechanism of DMMP with TFQ functionalized SWCNTs. (From Wei *et al.* [48]. Copyright © 2011, with permission from Institute of Physics Publishing.)

Wang *et al.* deposited a uniform network of SWCNT with carboxylic groups ($-COOH$) on a flexible poly (dimethyldiallylammonium chloride) (PDDA) modified polyimide (PI) substrate for DMMP detection at room temperature [49]. Changes in resistance as function of time were measured as the sensors were exposed to DMMP in N_2 at a concentration range of 1-40 ppm. Calibration curve showed a [17] linear increase of resistance as function of concentration and responses were found to be fast, stable and reproducible. Sensors showed to be selective to DMMP in presence of other volatile organic vapors like methanol, xylene and hexane, among others. Changing the carrier gas from N_2 to air caused the responses to DMMP to be lower which might be due to influence of oxygen and humidity contained in air. The apparent enhanced performance of this SWCNTs ($-COOH$) flexible sensor when compared to sensors prepared on Si/SiO₂ rigid substrates is attributed to the presence of PDDA, which is a polymer that absorbs DMMP. There is no information on the adsorption of DMMP by PDDA and its possible effect in the recovery of the sensors.

MWCNTs were oxidized with KMnO₄ to add oxygenated functional groups, mainly ($-COOH$) for the detection of organic vapors [50]. Oxidized MWCNTs in form of a bucky paper were exposed to different concentrations of acetone. Variations in electrical resistance were recorded for both unmodified and oxidized MWCNTs. Oxidized MWCNTs showed higher sensitivity to acetone (2.3 vol. %) than unmodified ones, and good selectivity when sensing other oxygen containing vapors such as diethyl ether and methanol. The sensors also showed complete reversibility and high reproducibility for all tested vapors.

MWCNTs were chemically treated with acid to obtain hydroxyl groups (OH) and used as sensing material for humidity sensors [51]. Changes in resistance were measured as the RH was varied from 11% to 98%. It was observed that the resistance increased as sensors were exposed to the different humidity levels. It was found that acid treated SWCNTs were more sensitive to humidity than pristine MWCNTs. The higher sensitivity of Acid treated SWCNTs is attributed to their higher surface and thus more adsorption sites that result from the acid treatment. Sensors showed fast response and to be stable. As with most humidity sensors, the recovery time was longer than response time due to slow desorption of water molecules.

Purified MWCNTs were treated with oxygen plasma or fluorine plasma and used for the detection of ethanol (Figure 3) [52]. Changes in resistance as function of time were recorded for the sensors when exposed of 50-500 ppm of ethanol vapor in air. Samples treated with oxygen plasma for 30 sec and with fluorine plasma for 60 sec showed the highest sensitivity to 100 ppm of ethanol, compared to pristine MWCNTs and other oxygen and fluorine plasma treated for different duration time. However, fluorine plasma treated samples showed the better sensitivity and reduced response and recovery time. The improvement of the fluorine plasma treated samples is explained by the difference in electronegativity between oxygen and fluorine.

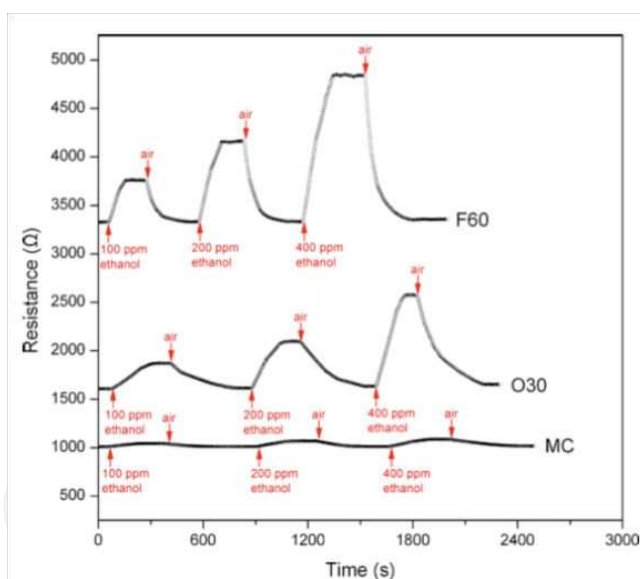


Figure 3. Responses of pristine (MC), oxygen plasma treated (O30) and fluorine plasma treated (F60) MWCNTs to 100-400 ppm of ethanol. (From Liu *et al.* [52] Copyright © 2012, with permission from Elsevier.)

Thermally fluorinated MWCNTs (TFC) were used for NO gas detection at room temperature [53]. The effect of thermal fluorination process was performed at various temperatures (100 -1000 °C) and 200 °C was found to be the optimum fluorination temperature. TFC samples prepared at temperatures higher than 200 °C showed a decrease of the fluorine functional groups, and even fluorine-assisted pyrolysis and fluorine-induced reorientation of the MWCNTs structure occurred at 1000 °C. TFC prepared at 200 °C showed high sensitivity,

stability, reproducibility and full recovery, when their gas sensing properties were evaluated towards the detection of 50 ppm NO in dry air. Interestingly, the presence of fluorine reverses the electron transfer process, when compared to pristine MWCNTs, allowing them to go from NO to MWCNTs and thus causing an increase in resistance. The fluorination not only helped to enhance the sensitivity but also made the sensors insensitive to humidity changes.

MWCNTs were modified with amino groups for the detection of formaldehyde at ppb level [54]. Changes in resistance as function of time were measured as the sensors were exposed to formaldehyde in a concentration range between 20 and 200 ppb. Sensors containing MWCNTs with higher amino group content (18%) were 2.4 and 13 times more sensitive to formaldehyde than samples containing 5% amino groups and pristine CNTs, respectively. Short response times are due to a chemical reaction between the aldehyde and amino group. For the same reason, the recovery times are longer, since chemical desorption is a slow and irreversible process. SWCNTs with 18% amino groups showed to be selective to formaldehyde when tested against interferences like acetone, CO₂, ammonia, methanol and ethanol.

Silicon (Si) nitrogen (N), and phosphorous-nitrogen (P-N) were used to modify MWCNTs and study their gas sensing properties for hydrogen peroxide, sodium hypochlorite and 1, 2-dichloromethane, nitrogen, and ammonia [55]. Samples of Si-MWCNTs, N-SWCNTs, and P-N-SWCNTs were prepared by aerosol chemical vapor deposition. It is known that the incorporation of heteroatoms in the CNT structure changes its morphology and thus the reactivity. To evaluate the gas sensing properties of the prepared materials, changes in resistance as function of time were recorded when they were exposed to the different gases. Exposure to N₂ caused the removal of physisorbed water molecules and thus a decrease in the resistance values. Sodium hypochlorite and dichloroethane caused decrease in resistance of pristine MWCNTs and Si-MWCNTs due to charge transfer (electrons) from CNTs to Chlorine atoms and increase in resistance of N-P MWCNTs. Ammonia showed the opposite effect in resistance. These results demonstrate the p-type semiconductor behavior for pristine MWCNTs and Si-MWCNTs and n-type of N-MWCNTs and N-P-MWCNTs. All sensors recovered in 10 min for all gases with the exception of ammonia that exceeded 1 hour.

In an effort to enhance the selectivity of SWCNTs-based vapor sensors, Battie *et al.* worked in the preparation of SWCNTs covered with a mesoporous silica film [56]. Sensors were fabricated by covering a SWCNTs film with a mesoporous silica film via by sol-gel deposition technique. Characterization of the sensors was done by measuring changes in resistance when exposed to 200 ppm of NO₂, NH₃, and H₂O in dry air. A sensor of SWCNTs without the mesoporous silica film prepared and tested under the same conditions. While the SWCNTs sensor showed to be sensitive to the three gases, the sensor based on SWCNTs film covered with mesoporous silica film showed to insensitivity to H₂O, and its sensitivity for NH₃ was considerably reduced. These observations can be explained considering the polarization capabilities and dipole moments of the silanol

groups contained in the mesoporous silica layer and the gas molecules. The silanol groups allow the mesoporous silica film to act as a diffusion barrier and allow the physical interaction and entrapment of highly polarized molecules like H₂O and NH₃, avoiding them to get in contact with the SWCNTs layer. On the other hand, the sensitivity to NO₂ was greatly enhanced, compared to the SWCNTs sensor. Compared to H₂O and NH₃, NO₂ has a weaker dipole moment and its diffusion thru the mesoporous silica gel and to the SWCNTs film results easier and thus its enhanced and selective detection.

Computational studies based on SWCNTs doped with heteroatoms have been also reported. *Ab initio* (ABINIT) simulations of CNTs doped with heteroatoms like boron, oxygen and nitrogen were performed to predict the behavior of the doped CNTs and to study their application as gas sensors for Cl₂, CO, NO and H₂ [57, 58]. Density functional theory (DFT) applied in the ABINIT code and the Generalized Gradient Approximation (GGA) were used to perform the calculations. The calculations demonstrated that doping the CNTs with B, O, and N causes a shift in the conduction band of the CNTs. For B and O, the conduction band shifts downward and creates a p-type semiconducting material. On the other hand, N dopant causes the conduction band to shift upward and create an n-type semiconducting material. Calculations also demonstrated that Cl₂, NO, H₂ and CO considerably affects the NTs density of states (DOS) and Fermi level as the gases become close to their surface. B-doped CNTs can detect CO, NO and H₂ gas molecules, O-doped can detect H₂, Cl₂ and CO and N-doped can detect CO, NO and Cl₂.

Similarly, Hamadani *et al.* presented a computational study of Al-substituted SWCNTs (10, 0) (2.5% and 25%) and their use as CO gas sensor [59]. DFT calculations (local density approximation with ultrasoft pseudopotential) were used to study the electronic properties of Al-substituted SWCNTs and how those properties are affected by the adsorption of CO molecules. Substitution of one carbon atom with an Al atom causes deformation of the 6-membered ring and increasing the bond length. Doping with Al also alters the DOS and band structure of the CNTs. Since Al has one electron less than C in the valence shell, introduces one electron holes in the band structure, therefore the tube is changed to p-type semiconductor. Calculations showed low adsorption energy for CO on pristine CNTs and that CO does not cause significant changes in the electronic band structure and DOS when adsorbed on pristine CNTs. These results confirm that pristine CNTs are insensitive to CO as result of their weak physical interaction. When CO is adsorbed on both 2.5% and 25% Al-substituted SWCNTs, it causes severe changes in the Band structure near Fermi level. Those changes strongly depended on the site of CNTs and the direction in which the CO molecule interacts. For instance, the most stable adsorption structure is when the C of the CO interacts with the middle point of a C-C bond of CNTs. Even when the adsorption energies of CO in 25% Al-substituted SWCNTs were higher than in 5% Al-substituted SWCNTs, the fact that the conductivity of the proposed material changes, makes them suitable for their use as CO gas sensing material.

Metal oxide	Nanotube Type	Op T. °C	Target (gas)	DL	Response Time	Ref.
ZnO SnO ₂ TiO ₂	MWNTs	RT	Ethanol	100ppm*	NS	[60]
Co ₃ O ₄	SWNTs	RT, 250	NO _x	20ppm	NS	[61]
			H ₂	4%		
ZnO	Pd-COOH SWCNTs	RT	NH ₃	50ppm*	NS	[62]
	F-SWCNTs					
	N-SWCNTs					
SnO ₂	SWNTs	200	NO ₂	2ppm	NS	[63]
SnO ₂	MWNTs	RT, 150	NO ₂	1ppm	3min (150C) 4min (RT)	[64]
			CO	2ppm	5min	
WO ₃	MWNTs	350	H ₂	100ppm*	Ns	[65]
SnO ₂	MWNTs	320	Ethanol			[66]
			LPG		21s	
SnO ₂	O-doped	RT	NO ₂	100ppb	7min	[67]
	N-doped				1min	
	B-doped				1min	

*Lowest tested concentration

Table 1. Summary of metal oxide NPs used to modify CNTs for gas sensor applications.

4. Conducting polymers and CNT composites

Conducting polymers have been widely used to enhance the sensing properties of CNTs-based sensors. CNTs unique characteristics combined with polymer's delocalized bonds, high permeability and low density have demonstrated that it is possible to detect many different gases with high sensitivity, fast response and good reproducibility. Previous reports on polymer/CNTs-based sensor have been summarized and reviewed [7-9, 12]. However, some challenges to overcome are aggregation or agglomeration of CNTs, thermal stability and selectivity, among others. Polymer/CNTs composites used in resistors, SAW and QMB type of sensors are discussed.

CNTs were used to improve Polyaniline (PANI) poor thermal stability (Figure 4) [68]. The proposed solution to this was the uniform incorporation of CNTs in the polymer network.

Considering that one of the problems of MWCNTs is their aggregation and agglomeration, they were oxyfluorinated under different conditions in order to obtain a better dispersion in aqueous solution and it was found that the better dispersion was obtained with the MWCNTs with the highest oxygen content. The oxyfluorinated MWCNTs were then mixed with aniline and ammonium persulfate (APS) and other chemicals, for in-situ polymerization. Changes in resistance as function of time were used to characterize and evaluate the resulting PANi/MWCNTs composite was for the detection of ammonia (NH_3) in a concentration range of 1-50 ppm. PANi/MWCNTs composite with the highest oxygen content had a uniform composition, improved thermal stability and highest and faster response for 50 ppm of NH_3 . The composite was able to detect 1 ppm and showed excellent repeatability for cycling exposures to 50 ppm and it needed heat treatment to accelerate the NH_3 desorption and thus the recovery of the sensor. A possible drawback is the selectivity to NH_3 among gases that can extract protons (H^+) from PANi.

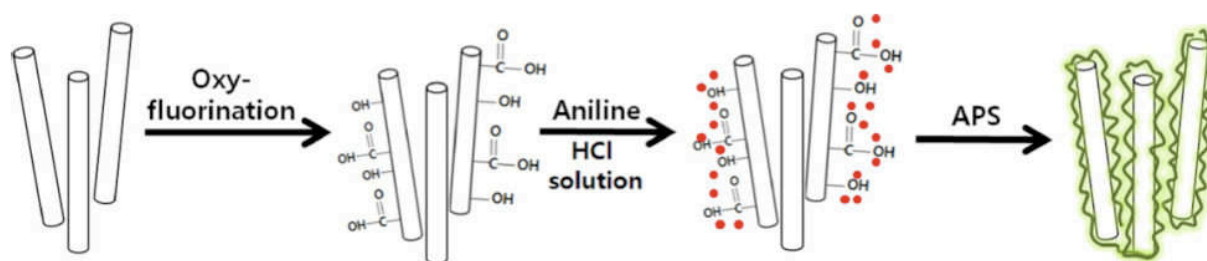


Figure 4. Illustration of the steps to obtain oxyfluorinated CNTs modified with PANI. (From Yun et al. [68]. Copyright © 2012, with permission from Elsevier.)

Mangu *et al.* also worked in the preparation of PANi-MCNTs as well as Poly (3, 4-ethylenedioxythiophene) poly (styrenesulfonate) (PEDOT:PSS)-MWCNTs composites for the detection of 100 ppm of NO_2 and NH_3 [69]. This group studied the effect of dissolving the polymers in different solvents for the gas sensing properties. PANi was dissolved in dimethyl sulfoxide (DMSO), *N, N*-dimethyl formamide (DMF), ethylene glycol (EG) and 2-propanol. PEDOT: PSS was dissolved in DMSO, DMF and 0.1M sodium hydroxide (NaOH). Each polymer solution was spin-coated in plasma treated MWCNTs and evaluated as sensing material. All PANi-MWCNTs composited showed an increase in resistance for NH_3 and a decrease in resistance for NO_2 , which is typical of p-type semiconducting composite films. All PANi-MWCNTs composites were selective to NO_2 . However, better sensitivities were achieved when PANi was dissolved in 2-propanol and DMSO for NH_3 and for NO_2 , respectively. On the other hand, all PEDOT:PSS-MWCNTs composites were also excellent for the detection if both NO_2 and NH_3 . PEDOT: PSS-MWCNTs (prepared without any solvent) showed to be more sensitive to NH_3 and PEDOT:PSS dissolved in NaOH to NO_2 .

Sayago, *et al.* have worked on the preparation of different composites using polymers with small percentages of CNTs as sensitive layers for surface acoustic wave (SAW) gas sensors [70-72]. Composites of polyisobutylene (PIB), polyepichlorohydrin (PECH) and polyetherur-

ethane (PEUT) with 2% and 5% of MWCNTs were prepared and used to detect volatile organic compounds (VOCs) at room temperature using SAW-sensor arrays. All the samples showed responses (frequency shifts) for octane and toluene (25-200 ppm), even though some samples were more sensitive than the others. For instance, samples with PIB/5%MWCNTs showed higher sensitivity for octane while PECH/2%MWCNTs and PEUT/2%MWCNTs were more sensitive to toluene. The difference in sensitivity is attributed to the difference in affinity between polymers and VOCs due to their respective polarities. The detection and recovery times were fast and fully reversible, which means that the main interaction is physisorption. The role of the MWCNTs is unknown. In general, their presence in the composite showed to improve sensitivity and reduce the limits of detection (LOD) but did not affect selectivity, response and recovery times.

Another SAW gas sensor was reported by Viespe *et al.* for the detection of methanol, ethanol, toluene using different polyethyleneimine (PEI)-based nanocomposite as sensitive layer, including MWCNTs-PEI [73]. In general, frequency shifts were proportional to the gas concentration and MWCNTs-PEI sensors showed better response time and higher sensitivity than the PEI-sensor. However, it did not show the best LOD when compared to the other PEI-based nanocomposite. The MWCNTs-PEI sensors showed higher sensitivity towards toluene and lower sensitivity to methanol when compared to ethanol.

Biopolymer/CNTs composites for chemical vapor sensors were produced by using two different biopolymers, cellulose, the most naturally abundant one and poly (lactic acid) (PLA). Considering that previous studies have shown that a homogeneous distribution of MCNTs in the cellulose matrix can improve the polymer's mechanical and electrical characteristics, MWCNTs were functionalized with imidazolide groups and covalently attached it to cellulose chains [74]. The resulting material, a paper-like film, was then used as sensing element for the detection of methanol, ethanol, 1-propanol and 1-butanol at ppm levels. Responses were measured by changes in resistance and were found to be reversible and consistent for all the tested vapors. However, the sensor only showed linear responses as function of concentration for 1-propanol in the range of 400-3600 ppm. The other composite, PLA/MWCNTs was prepared by doping the biopolymer with 2 and 5% of MWCNTs and annealing, in order to understand the effect of MWCNTs in the crystallinity of the polymer and its performance in the detection of toluene, water, methanol and chloroform [75]. PLA/2%-MWCNTs showed highest responses for all gases, when compared to PLA/3%-MWCNTs. However, it was found that all samples were selective to chloroform. Moreover, annealing the samples showed a decrease in the responses that were significantly lower than the untreated ones. Annealing did not affect the selectivity to chloroform but it considerably affected its sensitivity.

Plasma-treated MWCNTs (p-MWCNTs) polyimide (PI) composite films (p-MWCNTs-PI) were developed by Yoo *et al.* in an effort to overcome some of the problems presented by PI-based resistive-type sensors, e. g. nonlinear sensitivity to relative humidity [33]. When tested as sensing material for 10-95% relative humidity (RH), p-MWCNTs-PI showed better sensitivity and linear response (resistance) as function of humidity, when compared to pristine-MWCNT-PI and pristine PI. The increase of p-MWCNTs content in p-MWCNTs-PI films not

only showed improved the linearity and sensitivity but also lower resistance values. Lower resistance values might improve the performance at low RH range, a problem that PI resistive-type sensors present because of their high resistance values.

Yuana and coworkers prepared a sensor array based on polymer/MWCNTs composites for the selective detection of chloroform (CHCl_3), tetrahydrofuran (THF) and methanol (MeOH) [76]. Ethyl cellulose (EC), poly [methyl vinyl ether-alt-maleic acid] (PMVEMA), hydroxypropyl methyl cellulose (HPMC), poly (alpha-methylstyrene) (PMS), poly (vinyl benzyl chloride) (PVBC) and poly (ethyleneadipate) (PEA) were the polymers used to prepare the polymer/MWCNTs composites and to provide uniqueness to each sensor in terms of their physical and chemical characteristics like molecular structure, polymer length, polarity and intermolecular forces. Changes in resistance as function of time were recorded for the sensor array when exposed to the different gases at different temperatures (30 40, 50, 60 °C) and 50-60% R. H. The sensors showed to be selective to the three gases at the different temperatures when in presence of vapor molecules of chloride, cyclic oxide and hydroxide groups. The decreasing order of sensitivity concurred with the order of decreasing conductivity: PEA/MWCNTs >EC/MWCNTs >PMVEMA/MWCNTs >PVBC/MWCNTs >HPMC/MWCNTs >PMS/MWCNTs.

SWCNTs modified with Poly- (D) glucosamine (Chitosan) (SWCNTs-CHIT) were as high performance hydrogen sensor [77]. Three types of sensors were prepared: SWCNTs deposited on glass substrate (type 1), SWCNTs deposited over a glass substrate modified with CHIT-film (type 2), Chit-film deposited over SWCNTs deposited over a glass substrate. Each type of sensor showed a different changes in resistance when exposed to 4% H_2 in air. Increase in resistance was observed for three types of sensors and good recovery but for type (3) sensor. Sensors modified with CHIT showed better sensitivity. Moreover, the authors explained that the improved sensitivity was far higher than that reported for Pd-SWCNTs based sensors, which are commonly used for H_2 detection. The enhanced performance of SWCNTs-CHIT can be explained by the strong interaction/binding of the H_2 molecules with/to the $-\text{OH}$ and $-\text{NH}_3$ groups contained in CHIT, which also explains the poor recovery of type 3 sensor.

SWCNTs were modified with Polypyrrole (PPy) and 5, 10, 15, 20-tetraphenylporphyrine (TPP) to prepare composites for the detection of 1-butanol in nitrogen using a quartz microbalance (QMB) [78]. The QMB gold electrodes were coated with PPy/SWCNTs-COOH, PPy/SWCNTs-COOH/SWCNTs-TPP via electropolymerization. Frequency shifts of the quartz crystal resonator as function of time were measured for the sensors when exposed to 1-butanol in ppb concentration range. Even though both composites showed good and higher response magnitudes than QMB prepared with other composites that did not contain CNTs, PPy/SWCNTs-COOH/SWCNTs-TPP showed better performance than PPy/SWCNTs-COOH. The results demonstrate that the incorporation of CNTs enhanced the sensitivity towards the detection of 1-butanol.

Lu *et al.* reported a sensor array containing pristine SWCNTs, Rh-loaded SWCNTs, PEI/SWCNTs and other CNTs with different coatings and loadings for the detection of hydrogen

peroxide (H_2O_2) [79]. The measurements of changes in resistance as function of time were used to analyze the sensor array performance when exposed to H_2O_2 . Pristine SWCNTs showed strong increases in resistance and fast responses for H_2O_2 and an estimated DL (by IUPAC definition) of 25 ppm. But when the sensor array was exposed to H_2O and CH_3OH in order to test its selectivity, pristine SWCNTs showed also good responses for both chemicals, which means that the discrimination capabilities towards H_2O_2 are limited. On the other hand, the PEI/SWCNTs sensors were sensitive to H_2O_2 , showing decreases in resistance for each exposure. The PEI/SWCNTs did not show significant changes in resistance when exposed to H_2O and CH_3OH , which makes it selective to H_2O_2 under the tested conditions.

Polymer	CNT Type	Sensor Configuration	Target	DL	Ref.
PECH, PEUT, PIB	MWCNTs	SAW	Toluene	1.7-12.2ppm	[70 72]
			Octane	9.2-12.7ppm	
				NS	
Cellulose	MWCNTs	Resistor	Methanol	650ppm*	[74]
			Ethanol	672ppm*	
			1-propanol	635ppm*	
			1-butanol	687ppm*	
PANi	MWCNTs	Resistor	NH_3	1ppm	[68]
PEDOT:PSS	MWCNTs	Resistor	NH_3	100ppm*	[69]
			NO_2		
PI	MWCNTs	Resistor	Humidity	10%*	[33]
PEI	MWCNTs	SAW	Ethanol	176.5	[73]
			Methanol	184.2	
			Toluene	170.6	
PLA	MWCNTs	Resistor	VOC	NS	[75]
CHI	SWCNTs	Resistor	H_2	4%*	[77]
EC	MWCNTs	Resistor	THF, CH_2Cl_2 , MeOH	NS	[76]
PMVEMA					
HPMC					
PMS					

PVBC					
PEA					
PPy	SWCNTs	QMB	1-butanol	46ppb*	[78]
PPT					
PEI	SWCNTs	resistor	H ₂ O ₂	NS	[79 80]

* Lowest detected concentration

Table 2. Summary of polymers used for the preparation of polymer/CNTs-based sensors.

5. Metal nanoparticlesdecorated CNTs

Electronic, physical and chemical properties of metallic nanoclusters are usually sensitive to the changes in environment [81]. CNTs decorated with metallic nanoparticles (NPs) have been widely used to achieve selectivity and improve the sensitivity, response time and DLs for a variety of gas detections. Layer by layer, electrodeposition, chemical deposition, electrochemical deposition and sputtering are the methods used to prepare the metallic NP-CNTs composites discussed in this section.

SWCNTs films were modified with Pd NPs using sputtering method [82]. After apply different deposition times (40 – 160 s), it was found that 120 s was the optimum deposition time to obtain enhanced sensor response for 1% H₂ in dry air at 50 °C. A typical response curve (i_{gas}/i_{air} vs. time) showed differences in response and recovery between the first and following H₂ sensing cycles. FTIR studies were used to support and explain those differences and mechanisms of detection. The first cycle showed an overall larger electrical current in the presence of H₂ and then it reached a new steady state. When the atmosphere was change to dry air, the current did not go to its original value but remained in the steady state, which is considered as an irreversible response. The explanation to this is that is atomized by the Pd NPs and spilled to the surface of the MWCNTs, occurring the chemical and irreversible reaction of hydrogenation of the carbonyl groups of the MWCNTs at the first cycle. The second cycle and following ones started at the steady state where the first cycle finished and the electrical current showed a decrease in the presence of H₂ and when the atmosphere was changed to dry air, the electrical current recovered back to where the cycle started. This reversible behavior is explained as physisorption of H₂ molecules onto Pd/SWCNTs.

Pd/MWCNTs and Pt-Pd/MWCNTs composites were tested for the detection of H₂ in a concentration range of 20 ppm– 2% in N₂ and 200 ppm – 2% in air [83]. Composites were prepared by growing CNTs yarns and then covered them with a layer of Pd NPs or sequentially deposited layers of Pd and Pt NPs, using a recently developed technique called self-fuelled electrodeposition (SFED). Exposure to 1% H₂ using N₂ with 1% air as carrier gas. As with other Pd/CNTs-based sensors [82], an initial irreversible drop in resistance was ob-

served, and after that, the sensor reached a steady state. A stable baseline was established just after a couple of exposure/recovery cycles. Pd-MWCNTs was not able to detect H₂ concentrations below 20 ppm but with the Pt-Pd/MWCNTs composites it was possible to detect concentrations as small as 5 ppm (0.0005%). The sensor saturated at 100 ppm and higher concentrations. When the same experiments were performed using air as carrier gas, it was found that the detection limit for both composites decreased.

A Pd/MWCNTs flexible substrate H₂ sensor was fabricated using the layer-by-layer technique [84]. For this, an Au IDE was sputtered over a polyester (PET) film, followed by the fabrication of a poly (4-styrenesulfonic acid-*co*-maleic acid)/poly (allylamine hydrochloride) (PSSMA/PAH) bilayer film. Then, a MWCNTs layer was deposited over the PSSMA/PAH bilayer film and decorated with Pd NPs using chemical deposition. The sensors were exposed to H₂ in a range of concentrations between 200 and 40000 ppm at room temperature and 53% RH. The rapid response and higher sensitivity of the Pd/MWCNTs when compared to plain MWCNTs is attributed to the well known catalytic effect of Pd NPs. Because the detection mechanism is the dissociation of the H₂ molecules on the surface of the Pd NPs, the linear relation was found to be between the sensor's response and the square root of the concentration. It also showed to be selective to H₂ at concentrations higher than 1000 ppm (vs. NH₃, CO, CH₄ and others), to be highly reproducible, to have long-term stability and comparable to similar sensors fabricated in rigid substrates.

Zilli *et al.* demonstrated that the H₂ sensing capacity of the Pd/MWCNTs nanocomposite is affected by the different stages of purification of the CNTs [85]. Pd NPs were chemically deposited on pristine MWCNTs (Pd-CNT-P), gas-phase oxidized MWCNTs (Pd-CNT-O) and gas-phase oxidized/acid treated MWCNTs (Pd-CNT-A) and used as H₂ sensing material. All three nanocomposites showed increase in resistance as function of time in the presence of 500 μL_(STP) of H₂ and an immediate decrease when the H₂ disappeared from the testing chamber. However, Pd-CNT-O showed to be more sensitive than Pd-CNT-P and Pd-CNT-A, which both showed similar responses. The reason for these results is that for CNT-P, catalytic Fe NPs, used for the CNT growth, are encapsulated inside the CNTs and in CNT-A, the Fe NPs were removed during the acid treatment. After the gas-phase oxidation process (CNT-O), the Fe NPs become exposed and at the same time, oxygen-containing groups are formed in the surface of CNTs, which act as additional anchoring site for Pd NPs and thus making the Pd-CNT-O sample more sensitive to H₂.

Pd/SWCNT composites were prepared by using a poly (amido amine) (PAMAM) dendrimer assisted synthesis, followed by a pyrolysis step to remove the dendrimers [86]. For H₂ sensing experiments, the samples were deposited over Ti/Au electrodes and changes in resistance as function of time were measured. The Pd/SWCNTs samples showed to be more sensitive to 10, 000 ppm of H₂ at room temperature, when compared to samples of chemically reduced Pd on SWCNTs (without the presence of dendrimer) and Pd/PAMAM-SWCNTs. Moreover, these samples were able to detect all of the concentrations in a 10-100 ppm range. It was concluded that not only the dendrimers provided more nucleation sites for the Pd NPs and thus higher NPs density, but also that the removal of the dendrimers thru the py-

rolysis step reduces the distance between the NPs and the SWCNTs and consequently reduces the delay in electron transfer, allowing faster response times.

Double wall carbon nanotubes (DWCNTs) have shown to have longer length, compared to SWCNTs, provide a better percolation behavior, the possibility of modifying the outer layer without modifying the inner one and flexibility are some of their attractive characteristics. Considering those characteristics, Rumiche *et al.* evaluated Pd NPs/ (DWCNTs) composites as room temperature H₂ sensor (Figure 5) [87]. Different amounts of DWNTs (15 and 20 μL) were deposited over silicon oxide substrates and decorated with 1, 3 and 6nm layers of Pd NPs. To evaluate their sensing properties, changes in resistance as function of time were recorded when exposed to 3%, 2%, 1%, 0.5%, 0.3%, 0.2%, 0.1%, and 0.05% of H₂ in dry air. Samples containing 1nm Pd layer were unsuccessful detecting any of the tested concentrations. On the other hand, samples containing 3 and 6nm Pd layer showed overall similar performance in terms of increases of resistance and recovery. When analyzing the results for the lowest tested H₂ concentration (0.05%) it was found that the increase in resistance was comparable for samples with same Pd layer thickness and different DWCNTs content (e. g. 3nm thick Pd layer deposited over 15μL DWCNTs was comparable to of 3nm thick Pd layer over 20μL DWCNTs). However, the increase in Pd coating thickness produced a reduction in the response. The obtained results confirmed that the combination of the amount of DWCNTs and the Pd-layer thickness directly affects the sensitivity of the sensors.

Another H₂ sensor based on N-doped MWCNTs electrochemically decorated with Au NPs (Au-NMWCNTs) was presented by Sadek and collaborators [88]. N-doped MWCNTs were chosen because they have enhanced surface reactivity and chemically active sites for the nucleation of Au NPs during the electrodeposition process. NPs of different sizes were obtained with variation of electrodeposition potential. Changes in resistance as function of time were used to evaluate the performance of the Au-NMWCNTs sensors when exposed to different H₂ concentration between 0.06% and 1%. Sensitivity, response time and recovery time highly depended on the size of the AuNPs: the smallest the size the better the sensitivity and the shorter the response and recovery times.

Penza *et al.* worked in the modification of SWCNTs with Pt, Ru and NiNPs to monitor toxic, landfill, and greenhouse gases (CO₂, CH₄, NH₃, and NO₂) [89, 90]. Pt NP layers with thickness of 8, 15 and 30 nm were sputtered over SWCNTs films and exposed to the different gases at an operation temperature of 120°C. Changes in resistance as function of time showed that Pt-SWCNTs had better sensitivity than unmodified SWCNTs. It was also found that the sensitivity depended on the layer thickness. For instance, 8 nm Pt layer-SWCNTs showed highest sensitivity for NO₂ and CH₄ and 15 nm Pt layer-SWCNTs showed better sensitivity for NH₃ and CO₂. In a similar study, a sensor array containing Pt, Ru, and Ag NPs sputtered over SWCNTs with a thickness of 5nm was able to detect and selectively discriminate between landfill gases. Concentrations as low as 100 ppb of NO₂ were selectively detected at a temperature of 120 °C.

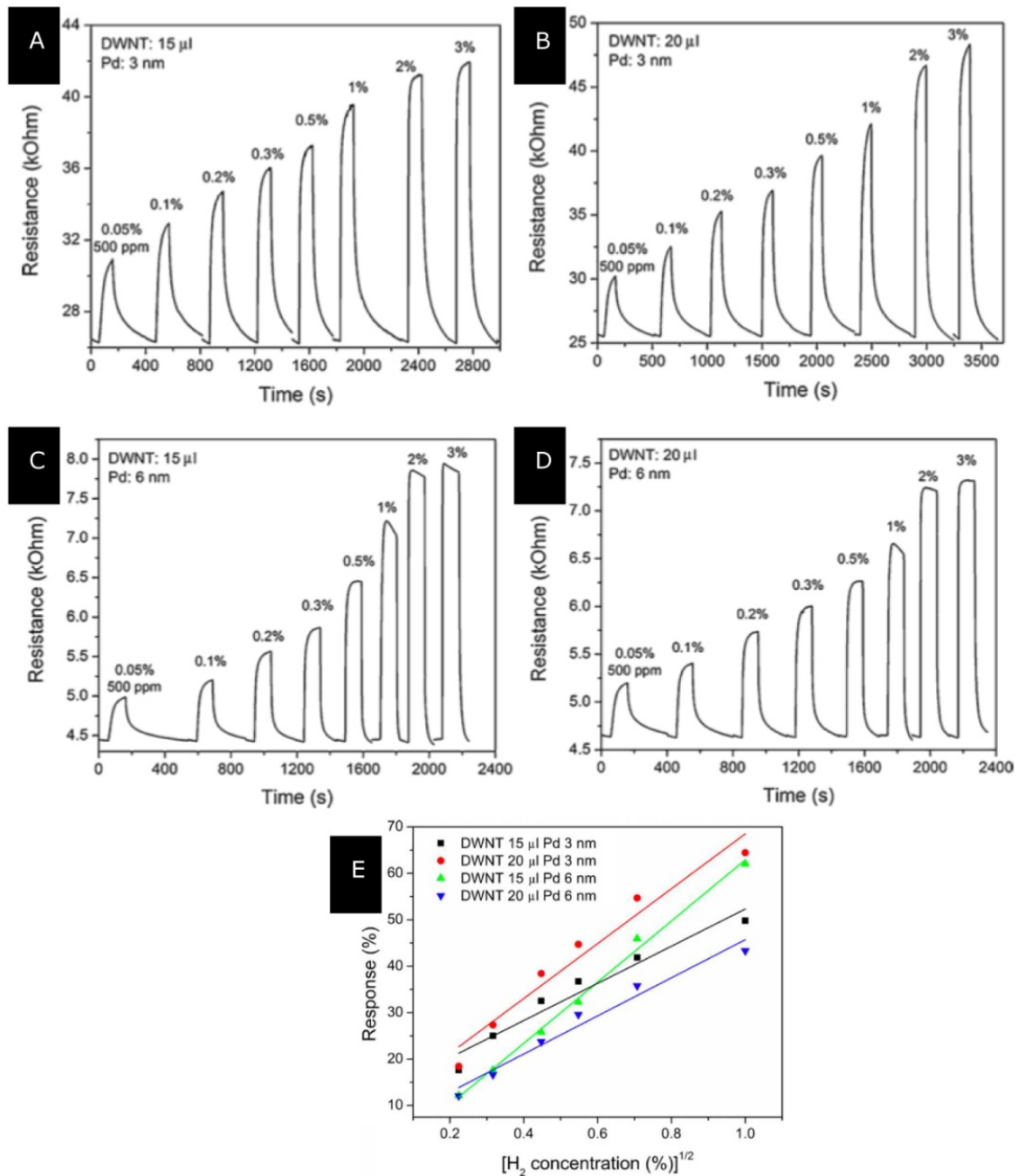


Figure 5. A-D) Responses of the different Pd/DWCNTs composites when exposed to H₂. (E) Calibration curves for the samples presented in figures (A-D). (From Rumiche *et al.* [87] Copyright © 2012, with permission from Elsevier.)

Lu *et al.* used pristine SWCNTs, fluorinated SWCNTs (F-SWCNTs) and rhodium doped SWCNTs (Rh-SWCNTs) and other various coatings and dopings on the SWCNTs for the room temperature detection of formaldehyde (HCOH) [80]. The measurements of changes in resistance as function of time when the array was exposed to the different concentrations of formaldehyde were used to analyze the sensor array performance. When exposed to 0.71 ppm formaldehyde, pristine SWCNTs showed the higher re-

response, followed by Rh/SWCNTs and F-SWCNTs, which were less sensitive. The other CNTs with different coating and loadings were insensitive to formaldehyde. However, when the array was exposed to formaldehyde at concentrations as low as 0.01 ppm (10ppb), Rh/SWCNTs sensor showed to be more sensitive and the presented an estimated DL (by IUPAC definition) of 10ppb. The DL for pristine SWCNTs and F-SWCNTs sensors were 15ppb and 20ppb, respectively. The three sensors presented very fast response (~18sec) and recovery time of approximately 1 minute.

Theoretical studies have been used to study the interaction between Pd and Pt NPs decorated CNTs and a wide variety of gases for different applications. Zhou *et al.* used the density functional theory (DFT) to study the adsorption and interaction of SO₂, CH₃OH, and CH₄ with Pd-SWCNTs [91]. The replacement of a central C atom of the CNTs with a Pd atom causes structural deformations. As SO₂ is adsorbed, there is a charge transfer from Pd-SWCNT to SO₂. As for CH₃OH, the appropriate adsorption conformation is thru the lone pair of the oxygen of CH₃OH and thus occurring an overall charge transfer from CH₃OH to Pd-SWCNT. The interaction between Pd-SWCNT and CH₄ is similar in that the charge transfer occurs from Pd-SWCNT to the gas. However, the interaction between Pd-SWCNTs and CH₄ is not as strong as the interaction between Pd-SWCNT and SO₂ or even CH₃OH.

NP	NT Type	Target	Sensor Configuration	DL	Ref.
Pd	MWCNT	H ₂	Resistor	1%	[82]
Pd	MWCNTs	H ₂	Resistor	10000ppm*	[84]
Pd	MWCNTs	H ₂	Resistor	NS	[85]
Pd-Pt	MWCNTs	H ₂	Resistor	5ppm	[83]
Pd	SWCNTs	H ₂	Resistor	10ppm	[86]
Pd	DWCNTs	H ₂	Resistor	0.05	[87]
Pt, Ru, Ag	SWCNTs	CO ₂ , CH ₄ , NH ₃ , NO ₂	Resistor	100ppb NO ₂	[89 , 90]
Au	N-doped MWCNTs	H ₂	Resistor	0.06%*	[88]
Rh	SWCNTs	HCOH	Resistor	10ppb	[80]

*Tested concentration

^For concentrations >1%

Table 3. Metallic nanoparticles used to decorate SWCNTs for gas sensing applications

Li and co workers investigated the adsorption of CO and NO on SWCNTs-decorated with Pd and Pt using first-principle calculations [92]. It was found that the electronic properties of SWCNTs change upon modification with Pd or Pt atoms. The semi-conductive band gap is decreased compared to pristine SWCNTs. The reason for the observed decrease in the band

gap is due to charge transfer from the Pd and Pt atoms to the surface of the SWCNTs. Different from pristine SWCNT that show poor adsorption, Pd-SWCNTs and Pt-SWCNTs showed to chemisorb CO molecules as well as NO. However, Pt-SWCNTs showed bigger binding energy and charge transfer than Pd-SWCNTs. The formation of C-Pd, N-Pd, C-Pt, and N-Pt bonds demonstrate that the metal atoms provide additional adsorption sites for gases and open the possibility to use both materials as sensors for the detection of CO and NO.

6. Nanostructured oxides mixed with CNTs

Sensors made of metal oxides films have been used for a long time because of they provide high sensitivity for the detection of a wide variety of gases. However, their major drawback is their elevated operating temperatures. The development of metal-oxide NPs based films and nanocomposites has shown advantages like higher surface area and porosity, high catalytic activity, efficient charge transfer and adsorption capacity. However, it has been demonstrated that the improvements in gas detection at low temperature for CNTs/MO-based sensors is due to the introduction of CNTs in the nanocomposite.

Tin oxide (SnO_2)/MWCNTs were synthesized using different ratios of tin dioxide precursor and plasma treated MWCNTs (Figure 6) [64]. The composites was tested for 2, 10, 20 ppm for CO and 50, 100, 500, 1000 ppb of NO_2 in dry air at both room temperature and 150 °C. Pure tin oxide films and pure plasma treated MWCNT were also tested for comparison purposes. Pure tin oxide films were unresponsive to all of the tested concentrations at the two different temperatures because both room temperature and 150 °C are too low when compared to the operation temperature for pure tin oxide-based sensors. On the other hand, pure plasma treated MWCNT responded to both gases at room temperature but not at 150 °C. As for the SnO_2 /MWCNTs composite, higher sensor response for both gases was achieved from samples prepared with an intermediate ratio of tin dioxide precursor and plasma treated MWCNTs (i. e. 20mL and 12mg, respectively), especially when operated at room temperature. Response time for 1 ppm of NO_2 was 3 minutes at 150 °C and 4 minutes at room temperature. Response time for 2 ppm of CO is stated to be 5 minutes but the temperature was not specified. SnO_2 /MWCNTs showed higher sensor response to NO_2 than to CO, and was also sensitive to humidity changes.

Different composite synthesis temperature can affect the sensor performance. SnO_2 /SWCNTs composites were synthesized at different oxidizing temperatures (300-600 °C) for testing the effect of temperature in their morphology, structure and gas sensing properties in the detection of NO_x [63]. The synthesized composites were exposed to 60 ppm of NO_x at 200 °C and it was found that the ones synthesized at 400 °C showed higher response. From here, composites synthesized at 400 °C were exposed to 30 ppm NO_x at different operating temperatures and it was determined that the optimum operation temperature was 200 °C. Concluding that the optimum oxidizing and operating temperatures were 200 °C and 400 °C, respectively, the samples were then exposed to different concentrations of NO_x . Under the aforementioned conditions, the SnO_2 /SWCNTs composite showed improved performance for the detection of NO_x when compared to thin films of SWCNTs or SnO_2 .

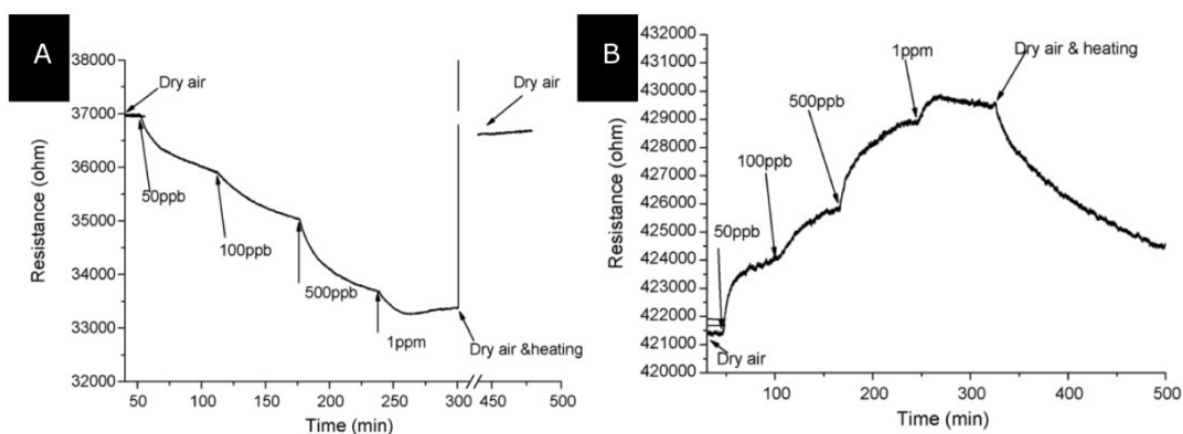


Figure 6. Response of SnO₂/MWCNTs to NO₂ at (A) room temperature and (B) 150 °C. (From Leghrib *et al.* [64]. Copyright © 2010, with permission from Elsevier.)

Wongchoosuk, *et al.* were the first to report the preparation of MWCNT-doped tungsten oxide (WO₃) thin films for H₂ sensing application [65]. The thin films of MWCNT-doped WO₃ and undoped WO₃ (for comparison purposes) were prepared using the electron beam (e-beam) evaporation technique and exposed to 1000 ppm of H₂ at different temperatures (200-400 °C). It was determined that 350 °C was the optimum operation temperature. Overall, MWCNT-doped WO₃ thin films showed higher responses for H₂ at any operating temperature when compared to the undoped WO₃ thin film. To demonstrate selectivity, the response of the MWCNT-doped WO₃ thin films was measured in presence of H₂, ethanol (C₂H₅OH), methane (CH₄), acetylene (C₂H₂) and ethylene (C₂H₄) at ppm level concentrations and operating temperature of 350 °C. It was concluded that the MWCNT-doped WO₃ thin films were selective to H₂ because they showed stronger response for H₂, much weaker responses for C₂H₅OH, CH₄, C₂H₂ and insensitivity ethylene (C₂H₄).

MWCNTs treated with nitric acid were used to fabricate MWCNTs-doped SnO₂ sensors for the detection of ethanol and liquid petroleum gases (LPG) [66]. Sensors were tested to 100-1000 ppm of ethanol and 1000-10,000 ppm of LPG at different operation temperatures in the range of 10-360 °C. The detection of both chemicals was improved when the operating temperature was 350 °C or lower and it was determined that the optimum operating temperature is 320 °C. The MWCNTs-doped SnO₂ composite showed better selectivity for LPG than for ethanol and the calibration curve showed the sensors saturated at concentrations higher than 5000 ppm. The 90% response and recovery time were 21s and 36s, respectively. When undoped SnO₂ sensors were exposed to 250 ppm of ethanol and 2500 ppm of LPG, they showed higher sensitivity to ethanol than to LPG at operation temperature range of 190 - 360 °C. Considering the obtained results, the selectivity of the MWCNTs-doped SnO₂ composite for LPG can be attributed to the presence of MWCNTs but further studies are required.

Nanocomposite structures of cobalt oxide (Co₃O₄) and SWCNTs were prepared using a polymer assisted deposition (PAD) method [61]. For this, polyethyleneimine (PEI) was the polymer used to bind the cobalt ions from and adjust the viscosity of the solution during the deposition process in order to get a homogeneous distribution of the particles on the

SWCNTs thin film. The $\text{Co}_3\text{O}_4/\text{SWCNTs}$ composite sensor was tested for the detection of NO_x in a concentration range of 20-100 ppm at room temperature. It showed proportional increases in response as function of concentration, poor recovery at room temperature and good recovery at 250 °C. Higher responses of the $\text{Co}_3\text{O}_4/\text{SWCNTs}$ composite when compared to pristine CNTs are attributed to the high adsorption power of Co_3O_4 particles. The composite was also exposed to 4% of H_2 in air, and showed enhanced responses than pure SWCNTs at room temperature and than Co_3O_4 films at both room temperature and 250 °C.

MO NPs (ZnO , SnO_2 , TiO_2) and MWCNTs composites were simultaneously grown on silicon and silica on silicon substrates by catalytic pyrolysis method and used for gas sensing [60]. Current differential-voltage (ΔI -V) curves were recorded for all the prepared composites, while to 100 ppm ethanol. $\text{TiO}_2/\text{MWCNTs}$ showed better sensitivity (defined as $\Delta I/I$ -V) when compared to pure MWNT film, ZnO/MWCNTs and $\text{SnO}_2/\text{MWCNTs}$.

N-doped, B-doped and O-doped CNTs were used to prepare doped-CNTs/ SnO_2 hybrids [67]. All doped-CNTs and doped-CNTs/ SnO_2 hybrids were used to study the effect of functional groups on their gas sensing properties for 100, 200, 500, 1000ppb of NO_2 at room temperature. The responses were as follows: B-doped hybrid > N-doped hybrid > O-doped hybrid. All doped-CNTs/ SnO_2 hybrids responded better than N-doped and B-doped and O-doped CNTs. B-doped-CNTs/ SnO_2 hybrids showed an improvement in the response time when compared to bare CNTs and recovered its baseline, which was not achieved with B-doped CNTs. The high sensitivity and improved performance achieved with the B-doped and N-doped-CNTs/ SnO_2 hybrids for low concentrations of NO_2 at room temperature are attributed to two main factors: the interaction of the N_2 gas with the n- SnO_2 /p-CNTs heterostructure that affects the conduction of the CNTs and the addition of new functionalities (i. e. B and N atoms) to the CNTs surface that affects the electronic density of states and Fermi level and consequently, its conductivity.

A combination of ZnO layer with functionalized MWCNTs for the room temperature detection of NH_3 has been reported by Tulliani and coworkers [62]. Samples of Pd-doped/ COOH -MWCNTs, N-MWCNTs, and F-MWCNTs were deposited over a screen-printed ZnO layer. The materials were evaluated by measuring changes in resistance as the sensors were exposed to NH_3 at room temperature, in a concentration range 0-75 ppm and different relative humidity levels. The sensor based on ZnO with Pd-doped/ COOH -MWCNTs was the only one that showed sensitivity to humidity. When exposed to NH_3 , all sensors showed a decrease in electrical resistance but did not show better DL than other graphite-based sensors prepared under the same conditions.

7. Conclusion

Modification and functionalization of CNTs have shown to greatly improve the sensitivity and selectivity of CNTs-based sensors. For instance, great improvements for room temperature detection of different gases have been reported, especially when using metal oxide/SWCNTs composites. Another subject of high interest is the development of deposition

methods and synthesis of Pd/CNTs for H₂ detection at room temperature. Interestingly, there is an increase in the tendency of combining other materials with modified CNTs. For example, CNTs decorated with metal NPs embedded in a polymer matrix or CNTs doped or CNTs doped with heteroatoms and decorated with NPs or metal oxides are some composites that have been successfully used as gas sensing materials. But not only the characteristics of the CNTs have contributed to these improvements. In fact, the reported improvements are attributed to the combination of materials and the intrinsic characteristics of the composites. This trend of combining materials demonstrates that there is a broad range of possibilities for the design of new materials to meet the requirements of an ideal sensor by showing selectivity for different gases, sensitivity at low concentrations, fast response, and room temperature operation among others.

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