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Gas sensors based on nanostructured materials

Giselle Jiménez-Cadena, Jordi Riu* and F. Xavier Rius

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Gas detection is important for controlling industrial and vehicle emissions, household security and environmental monitoring. In recent decades many devices have been developed for detecting CO₂, CO, SO₂, O₂, O₃, H₂, Ar, N₂, NH₃, H₂O and several organic vapours. However, the low selectivity or the high operation temperatures required when most gas sensors are used have prompted the study of new materials and the new properties that come about from using traditional materials in a nanostructured mode. In this paper, we have reviewed the main research studies that have been made of gas sensors that use nanomaterials. The main quality characteristics of these new sensing devices have enabled us to make a critical review of the possible advantages and drawbacks of these nanostructured material-based sensors.

Introduction

Interest in detecting gases and determining their composition has constantly been on the increase in recent years. Detection is important because it is necessary in many different fields (for example, industrial emission control, household security, vehicle emission control and environmental monitoring).^{1–4} Most studies have focused on detecting CO₂, CO, SO₂, O₂, O₃, H₂, Ar, N₂, NH₃ and H₂O, because of their toxicity, their relation with atmospheric composition or the fact that they can be

found at high levels in some environments. Organic vapours such as methanol, ethanol, isopropanol, benzene and some amines, among others, have also been detected. Most studies have been made in simple matrices, generally of a single component in Ar, N₂, or in synthetic air. Therefore, the selectivity required for a particular gas to be determined in the presence of complex samples and matrices still has to be evaluated in most cases. What is more, because they are in such wide demand, devices need to be developed that are not only robust but which also have high sensitivity, selectivity and reversibility in favourable temperature conditions. From the operative point of view, among other characteristics, they need to be compact and manufacturing costs need to be low.

Gas detection using semiconducting oxides⁵ has had considerable impact to date. However, the need to operate at high temperatures often limits the use of this type of detection. For these reasons, proposals have been made to modify some of the structural parameters: for example, crystal shape and orientation.⁶ Nanostructured materials (nanomaterials) can also be used to reduce working temperatures and they consume less power and are safer to operate.

One of the characteristics of nanometric materials is their high surface area/volume ratio. This favours the adsorption of gases on the sensor and can increase the sensitivity of the device because the interaction between the analytes and the sensing part is higher. Many studies, then, have focused on

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reducing the size of the metal oxides in the form of nanoparticles and nanowires. Thin films of some organic polymers, metal nanoparticles and, more recently, carbon nanotubes, have been used too. All of these are materials change their electrical properties (e.g. conductivity or impedance) and optical properties (e.g. coefficient of molar absorptivity or refractive index), among others, when they receive the stimulus of the sensing layer after the molecular- or ion-recognition event. The mechanisms for recognizing the gases to be determined include absorption processes, particularly in metal oxides and carbon nanotubes, and specific recognition for the formation of supramolecules or covalent bonds between the sensor and the analyte, as occurs with some metal complexes.

It is difficult to compare quality parameters such as the sensitivity and selectivity of nanometric sensors with larger-scale sensors because most of the new studies on nanometric sensors are qualitative and the results are expressed in many different forms. However, some studies suggest that sensitivity increases or response time decreases as the film thickness or the particle size of metal oxides^{6–8} or organic polymers^{9,10} decreases.

This paper describes the research made on gas sensors that contain nanomaterials and the main quality parameters of these sensing devices. The review, then, does not aim to be a compendium of all the bibliography available on the subject; rather, it selects some representative examples of the various mechanisms involved in nanostructure-based sensors and it highlights the new properties that

appear when these materials are used. Our goal is not to promote the use of sensors based on nanostructured materials but to make a critical review of the state-of-the art of these promising materials applied to gas sensing, with particular attention to the quality parameters of these sensors, and their weaknesses and strengths. One of the features of nanosensors is that they have a transducer system that consists of nanometric materials. On this basis, in some devices the sensor and the transducer are different components. In other devices, the sensor also functions as the transducer (for example, in semiconducting oxides and other systems).

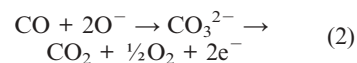
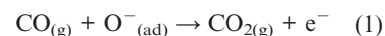
The article has been structured around the composition of the materials that determine the nanometric character of the devices. We start with metal oxides, and then move on to the materials developed in recent years as an alternative to sensors with a lower working temperature, such as some metals, organic polymers and organometallic complexes. Finally, we discuss carbon nanotubes, widely used and even functionalized with other compounds to increase their selectivity to particular analytes. In this case, the nanotubes function as the transducer while the material with which they have been functionalized is the sensing part.

Nanosensors with metal oxides

Nanostructured metal oxides are one of the main types of material used to fabricate gas sensors. The semiconducting nature of some of these compounds makes

it possible for the electrical conductivity of the material to change when the composition of the surrounding atmosphere changes. This means that most of these devices can be classified as conductimetric nanosensors. Nano-sized materials have a very favourable area/volume ratio. Therefore, for the same chemical composition, the smaller the nanomaterials are, the more sensitive the sensor is.

They are based on the same principles as standard metal oxide sensors.^{11,12} Between 200 and 500 °C (the normal working range for metal oxides) charged species^{13–15} such as O₂[–], O[–] and O^{2–} are adsorbed on the metal oxide, charging it negatively. Other gases adsorbing on the surface can give rise to a charge-transfer reaction. If a reducing species such as CO is present, it oxidizes and releases a negative charge, which increases the conductivity of the material. For example:



In the presence of an electronegative species such as NO₂, the charges are attracted to the adsorbed molecule, which decreases the conductivity⁵ of the material:



Given that these mechanisms involve an adsorption process, the physical properties and the shape of the material determine the response of the nanosensor. Higher area/volume ratios favour gas adsorption (and a change in conductivity), decrease the response time and increase the sensitivity of the device. Because of the advantages they have over the same sensor built with bulk material, nanoparticles and thin films of metal oxides (less than 1000 nm thick) have been used to detect a wide variety of gases.

To increase the surface area of the sensor layer, and therefore the sensitivity, several techniques have been developed for depositing oxides. Martinelli *et al.*¹⁶ used screen-printed technology to deposit La, Fe and Sm oxides in the form of nano-sized powders, free of intragranular pores, which are very suitable for making thick films. This technique mixes the oxides with agglom-



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erate and an organic compound (ethyl cellulose and α -terpineol) to make a paste that is subsequently printed on an aluminium substrate. The technique reported by Martinelli was used by Traversa *et al.*¹⁷ with Ti oxide doped with Ta and Nb, on aluminium substrates for detecting CO. They also carried out annealing on the sensor film with temperatures between 650 and 1050 °C in an attempt to reduce the response time and increase the reversibility of the device. When they evaluated the change in conductance of sensors exposed to 100 ppm of CO, they found that the sensitivity increases considerably above 380 °C, with films whose annealing temperature is 850 °C. These sensors were also used in field tests. They were positioned beside a conventional station for monitoring atmospheric pollution and they reliably detected CO concentrations above 0.5 ppm. Hong and Han¹⁸ also used screen-printing to deposit nanoparticles of SnO₂ doped with Pd and Pt on aluminium substrates. The electrical resistance of the film decreased when it was exposed to methane, the response time was short – approximately 20 s – and it was reversible. This sensor was used to detect methane concentrations between 500 and 10 000 ppm.

Another technique is the sol-gel methodology, which Shukla *et al.*¹⁹ used to deposit films of MgO nanoparticles. The precursor solution of magnesium acetate was obtained from the pure metal and acetic acid by evaporation of the solvent and oxidation of the metal on a Pyrex substrate. With this device, the response to humidity can be evaluated from the change in the electronic or optical properties of the sensor material. The process of water molecule adsorption can lead to H⁺ transfer, which can not only change the electrical resistance but also the refractive index. The change in this latter property was used to detect water vapour in the range between 10 and 90% of relative humidity. Ling and Tsai²⁰ used radio frequency magnetron sputtering to deposit films of SnO₂ doped with Pt, SiO₂ or CaO. This technique was carried out in a vacuum chamber which contained the substrate and a blank made of the material to be deposited. The blank was subjected to an electrical discharge that emitted electrons, ions and neutral species of the material. The

deposition, by gravity, randomly distributed the particles over the whole surface, and ensured high stability and sensitivity to the gaseous atmosphere. Au electrodes and a RuO₂ resistor were used to control the working temperature (Fig. 1). The electrical resistance was reduced by three orders of magnitude (from 10¹⁰ to 10⁷ Ω) when in contact with 3000 ppm of ethanol in air for short periods, and the process was reversible in doped films but not in pure SnO₂. Unlike most sensors based on metal oxide nanoparticles, in which the change in electrical conductivity is monitored in the presence or absence of the analyte of interest, in this case a sensor equipped with an optical fibre is used. The ratio between the transmitted intensity and the initial intensity, I/I_0 , of the light beam is determined by the refractive index of the material that coats the fibre. The results show that when the percentage of relative humidity increases, the I/I_0 ratio also increases, although the mechanism has not been elucidated. Martucci *et al.*²¹ also used the sol-gel technique to obtain nanocrystals of NiO on SiO₂. They found that the higher the deposition temperature, the greater the absorption in the IR spectrum of the film on the bands at 1070, 800 and 450 cm⁻¹. They attributed this change to the increase in size of the NiO crystals when the deposition temperature increased (they found a mean

size of 2.5 nm at 500 °C and a size between 6 and 10 nm at 1000 °C). Experiments to evaluate the sensitivity of the nanocomposite material to CO (because of the decrease in the anionic density of oxygen on the NiO surface during the catalytic oxidation of CO) are in progress.

Another way of increasing the surface area of the sensing part is to obtain different geometries for the sensor materials. For example, Elibol *et al.*²² used confined lateral selective epitaxial growth to obtain Si nanowires. A layer of SiO₂ was deposited, on top of which was deposited a layer of Si and finally another layer of SiO₂. The Si layer was then removed to form a cavity that was to serve as a mould for the nanowires. When the nanowires were exposed to a gas containing 20% of O₂ in argon, the conductance of the material decreased by 9%. Although the response time was short, the desorption process was favoured by increasing the temperature (80–90 °C under vacuum). Kolmakov *et al.*²³ synthesized SnO₂ nanowires by using porous anodic alumina templates: starting from β -Sn that was electrochemically deposited on the template, SnO was obtained and subsequently SnO₂. The nanowires were deposited on a Si/SiO₂ substrate with Au and Ti electrodes and their conductance increased when the CO concentration was changed. The

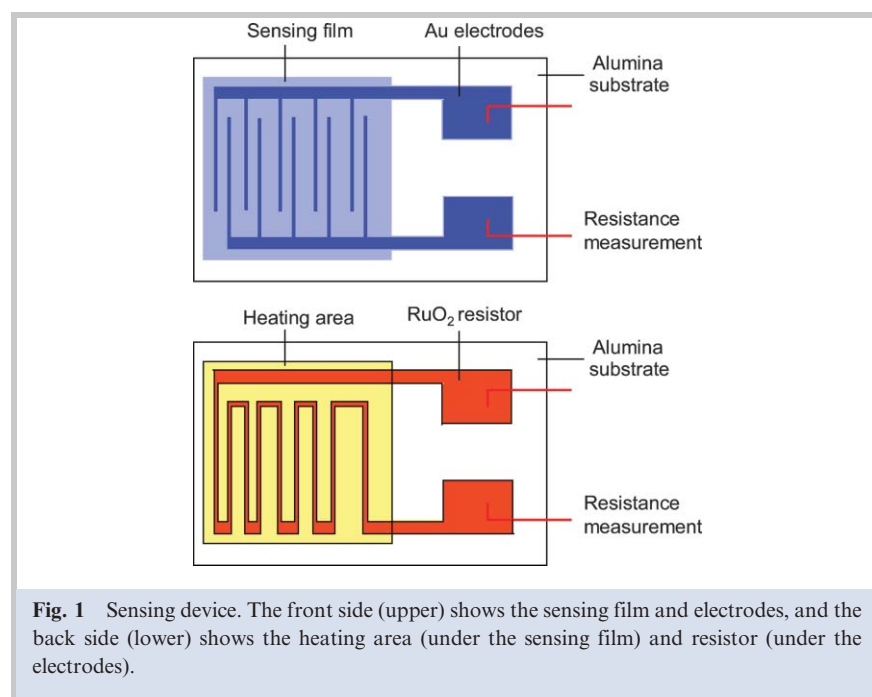


Fig. 1 Sensing device. The front side (upper) shows the sensing film and electrodes, and the back side (lower) shows the heating area (under the sensing film) and resistor (under the electrodes).

detection mechanism proposed is based on reaction (1) mentioned above. In this case, $O^-_{(ad)}$ corresponds to ionosorbed species when SnO_2 is annealed at high temperatures. As in most sensors, a change in the electric current was detected when CO was introduced into the sensor. When sensors consisted of a single nanowire, the electric current changed for CO concentrations lower than 1%.

Chen *et al.*²⁴ synthesized α - Fe_2O_3 nanotubes by impregnating an aluminium substrate with an iron nitrate solution. The solvent was evaporated and the nitrate was oxidized thermally. The change in conductivity was evaluated in contact with independent samples of ethanol and H_2 and was seen to increase when the concentration of ethanol and hydrogen increased (studies between 10 and 40 ppm). The nanotubes were also more sensitive than Fe_2O_3 films. Xiangfeng *et al.*²⁵ used ZnO nano-tetrapods,²⁶ chemical structures with four 'arms', to detect ethanol, methane and isopropanol (in independent samples and concentrations between 50 and 1000 ppm) on an aluminium substrate with Au electrodes. The authors hypothesized that the sensor could be selective to ethanol at 300 °C. The response and recovery times were approximately 20 s.

Jitianu *et al.*²⁷ obtained porous networks of SnO_2 nanoparticles by the sol-gel method using an organically modified Sn precursor. In this case, the reflectance of crystalline SnO_2 changed at 620 nm when exposed to CO and O_2 (10% in argon in both cases) at 400 °C (the CO decreased the reflectance which then increased on re-oxidation with O_2). The authors suggest that, in the presence of a reducing gas, some oxygen atoms belonging to the network react with the gas and generate oxygen vacancies and a decrease in the reflectance of the SnO_2 nanoparticles.

In other studies, doping the oxides increased the stability and sensitivity to the analytes studied. Many authors have found that the change in electrical conductance is greater when small amounts of oxides or transition metals are added to the sensing part. Tan *et al.* used nano-sized solid solutions of TiO_2 and Fe_2O_3 ,²⁸ and ZrO_2 and Fe_2O_3 ,²⁹ obtained by mixing hematite, anatase

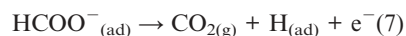
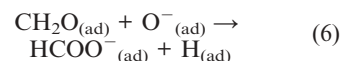
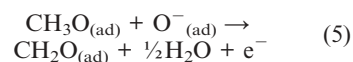
and zinc oxide. These solutions, doped with SnO_2 , $SrTiO_3$, Sn, Ti and ZrO_2 , were deposited on ceramic substrates, thus making their sensitivity to ethanol (100 ppm in air) better than that of pure oxides. The response mechanism selected was still the change in the resistance of the sensing material. Liu *et al.*³⁰ deposited crystalline $CdSnO_3$ doped with Pt (between 0.1 and 2 wt%) on an aluminium and ceramic substrate, and obtained a maximum sensitivity at 200 °C for a concentration of 50 ppm of ethanol. They also obtained a response to other organic vapours such as CO, methane, butane and LPG (liquefied petroleum gas) in concentrations of 500 ppm, and to gasoline in concentrations of 50 ppm. On the basis of these results, the authors stated that the sensor is selective for the detection of ethanol.

Han *et al.*³¹ constructed a MEMS-type sensor (micro-electro mechanical system) using SiO_2 doped with F nanocrystals starting from an organic precursor. They obtained greater sensitivity and selectivity than a commercial sensor for hydrogen (they managed to detect 100 ppm of H_2) and a response to propane, methane, and CO (also at concentrations of 100 ppm of each of the gases, but with less sensitivity). Cerdà *et al.*³² developed a micromachined twin sensor, the sensing layer of which consisted of SnO_2 nanoparticles modified with Pd on a dielectric membrane, for detecting changes in conductivity in the presence of CO and O_2 . The sensor consists of two parallel membranes, each of which works independently of the other and contains a different amount of Pd so that it can be more sensitive to CO or O_2 . A relation was found between the measured resistance and the concentrations of CO and O_2 . This model makes it possible to predict the concentration of these two analytes in mixtures. The authors point out that when the mixture contains a new gas (e.g. N_2), the system must be recalibrated. Similar results to these nanoparticles have been obtained with CeO_2 and ZrO_2 mixed with C for detecting O_2 . Sensitivity was good at oxygen partial pressures between 10^{-17} and 10^5 Pa.³³ Steffes *et al.* used $In_xO_yN_z$ with Au nanoparticles to detect 500 ppm of H_2 ,³⁴ with the added advantage that the gold-nano-dots, which are randomly distributed on and inside the $In_xO_yN_z$ layer,

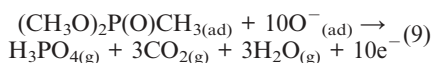
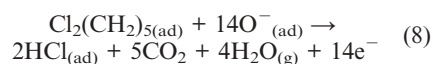
showed not only electrical but also optical gas sensitivity (with an optimal detection wavelength of 619 nm).

Doping has also been used in electro-nic noses. A device with nine nano ZnO thick film gas sensors doped with different amounts of TiO_2 , MnO_2 , V_2O_5 , Bi_2O_3 , Ag and W was used for detecting and clustering 17 Chinese vinegars.³⁵ The study used conductimetric detection, principal component analysis (PCA) and cluster analysis (CA) to interpret the results.

Neri *et al.*³⁶ used thin films of Fe_2O_3 doped with CeO_2 to detect methanol. They used aluminium substrates and Pt electrodes at working temperatures below 350 °C. Neri suggests increasing the number of current-carrying electrons on the basis of the following reactions:



With these sensors they obtained detection limits between 1 and 3 ppm. This same mechanism was proposed by Tomchenko *et al.*³⁷ who used thin films, prepared from a mixture of metal oxide nanocrystals with a glass frit and an organic binder to detect hexane, diesel oil vapour, methanol, 1,5-dichloropentane (DCP) and dimethyl methylphosphonate (DMMP) in air. These substances are interesting for vehicle emissions and because they can act as simulants (DCP and DMMP) of mustard gas and nerve agents. The oxides used were SnO_2 , WO_3 , In_2O_3 , CuO and Y_2O_3 , with which the limits of detection were 10 ppb at temperatures of 400 °C. The detection mechanisms considered for DCP and DMMP are given in eqn (8) and eqn (9):



The responses obtained were studied by principal component analysis in order to

determine how the films responded to the different analytes. This procedure is an alternative for the specific detection of analytes in mixtures.

Mädler *et al.*³⁸ used SnO₂ nanoparticles doped with Pt on aluminium substrates and Pt interdigitated electrodes (Fig. 2). The nanosensor they obtained had a linear relation between conductance and CO concentration between 8 and 50 ppm, in dry air at 350 °C, and the detection limit was 1 ppm. The mechanism that explains the increase in conductivity is similar to the one reported by Kolmakov in eqn (1). Ruiz *et al.*³⁹ used WO₃-Cr, SnO₂-Pd and TiO₂-Cr as sensor materials for NH₃. The nanopowders were mixed with propanediol and deposited on a micromachined hot plate substrate. This type of substrate allows rapid changes in temperature which activate the metal oxide surface and decrease the response time of the sensor. A linear relation was found between the sensor response, defined as $R_{\text{air}}/R_{\text{gas}}$ for WO₃-Cr and SnO₂-Pd (because they behave like n-type semiconductors) and as $R_{\text{gas}}/R_{\text{air}}$ for TiO₂-Cr (which behave like p-type semiconductors), and the NH₃ concentration between 100 and 1000 ppm. Jiang *et al.*⁴⁰ used ZnFe₂O₄ and ZnFe₂O₄ nanoparticles doped with V as a sensor material. The addition of V to the oxide decreases the electrical resistance of the device. This is thought to happen because the Zn²⁺ or Fe³⁺ ions are replaced by V⁵⁺. The increase in the positive charge increases the number of oxygen atoms with a negative charge in the structure and, therefore, the number of electrons in the network. In comparison with the pure oxide, the doped device is more sensitive to benzene, xylene and toluene, and less sensitive to ethanol and acetone. This may be due to

V₂O₅ acting as a catalyst in the oxidation of aromatic compounds, although the detection mechanism has not been elucidated.

Both the annealing temperatures and the working temperatures of the devices have been studied to evaluate the sensitivity of metal-oxide-based nanomaterials. Maffei *et al.*⁴¹ used SnO₂ to obtain greater sensitivity at 250 °C for O₂ and CH₄. Gong *et al.*⁴² worked with ZnO nanocrystals doped with Cu and Cu₂O and they evaluated the conductimetric response of the sensor in the presence of CO. They found optimal values for 350 °C and detected 20 ppm of CO. Another of the materials stabilized by an annealing at 650 °C is indium tin oxide (ITO),⁴³ which was used to construct an H₂ sensor. With this oxide, the capacity of the response can be varied by changing the proportions of the precursors, SnO₂ and In₂O₃. With this sensor the conductivity of the material changes upon exposure to H₂ and to a lesser extent upon exposure to CH₄ and C₃H₈, so the authors speak of its good selectivity. Hu *et al.*⁴⁴ studied the effect of the annealing temperature for SrTiO₃ films on an aluminium substrate. At a working temperature of 40 °C, much lower than conventional working temperatures for gas sensors based on metal oxide semiconductors, and an annealing temperature of 400 °C, the sensitivity was maximum for O₂. Chu *et al.*⁴⁵ presented a thermal treatment for nanoparticles of ZnFe₂O₄, and obtained a material sensitive to 100 ppm of ethanol.

The results obtained for gas sensors based on metal oxides suggest an improvement in several performance parameters with respect to bulk materials. Because the interaction between gases and the sensing layer is easier due

to the higher area/volume ratio, sensitivities are higher, response times are lower and, in some cases, the working temperatures are also lower. However, specific studies of nano- and bulk-materials would have to be carried out under the same conditions to check this. Annealing processes can give rise to more stable particles and films and the particle size can be controlled after heating at high temperatures. Selectivity can be increased by doping with metal nanoparticles.

However, nanosensors are more expensive than bulk materials because of the use of advanced techniques for depositing the nanoparticles or the films (see Table 1 showing the main performance parameters and fabrication techniques of the sensors described in this paper). Moreover, post-treatments such as calcinations or annealing may be required to improve the stability of the materials and advanced microscopes need to be used as characterization techniques. In summary, once the use of these (somewhat complicated or expensive) techniques for depositing, post-treating or characterizing are in routine use, the fabrication of these kinds of device can be evaluated as a feasible option for improving the sensing characteristics of the metal oxides.

Nanosensors based on metal nanoparticles

Metal nanoparticles are dispersed on the surface of a substrate to increase the area/volume ratio and favour the adsorption of gases. When they are in contact with the analyte, they change their electronic properties or the properties of the substrate because the gas molecules adsorb on the metal. Generally, the deposition is made by vapourizing the metal precursor, which provides the nanoparticles or films for a subsequent annealing. For example, Kimura and Goto⁴⁶ presented an electrode to measure the electromotive force (emf) values in an oxygen concentration cell built from a nanocompound of iridium, yttrium and zirconium with iridium nanoparticles between 5 and 10 nm in diameter. The films were prepared from precursors of diacetyl-monoxime-β-pyridyl(2)-methyl-imine, dpm: Ir(dpm)₃, Zr(dpm)₄ and Y(dpm)₃, by heating in the presence of oxygen. In the presence of only oxygen



Fig. 2 Interdigitated electrodes. This type of geometry increases the contact area between the electrodes connected by the sensing film.

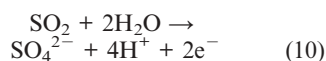
Table 1 Quality performance parameters and fabrication processes for sensors based on nanostructured materials

Nanomaterial	Detection limit/analyte	Working temperature	Reversibility	Response time	Dynamic range	Other parameters	Fabrication techniques
Metallic oxides	0.5 ppm CO; ¹⁷ 10 ppm H ₂ ; ²⁴ 50 ppm EtOH, CH ₄ , IPA; ²⁵ 1 ppm CH ₃ OH; ³⁶	Up to 200 °C; ^{17,26,30,38} 40 °C ⁴⁴	O ₂ ; ^{22,27} CO ^{27,42}	20 s ¹⁸	5000–10 000 ppm CH ₄ ; ¹⁸ 10–90% H ₂ O; ¹⁹ 8–50 ppm CO; ³⁸ 100–1000 ppm NH ₃ ; ³⁹	Selectivity: ethanol; ^{26,30} CO, O ₂ ; ³² H ₂ ⁴³	Screen-printing; ^{17,18,21} annealing; ^{17,44,47} sol-gel; ^{19,27} sputtering; ²⁰ confined lateral selective epitaxial growth ²²
Metal nanoparticles	2.6 ppm SO ₂ ⁴⁸	650 °C; ⁴⁶ room temperature ⁴⁷	None reported	10–20 s; ⁴⁶ 2 s ⁴⁷	5–500 ppm SO ₂ ⁴⁸	Sensitivity: 5.4 × 10 ^{−10} A ppm ^{−1} 48 to SO ₂ Selectivity: SO ₂ ⁴⁸	Annealing; ⁴⁷ electrochemical etching ⁴⁷
Metal complexes	40 mM IPA; ⁴⁹ 5% CO ₂ ⁵⁰	Room temperature	MeOH, EtOH, IPA; ⁴⁹ CO ₂ ⁵⁰	300–1300 s ⁵⁰	21.5–86 mM EtOH, 31–125 mM for MeOH; ⁴⁹ 0–20% CO ₂ ⁵⁰	Stability: 3 months ⁴⁹ Recovery time: 2000–4000 s ⁵⁰	Electrostatic self-assembly method ⁴⁹
Organic polymers	20% H ₂ O; ⁵⁸ 400 ppm acetone, THF, EtOH, MeOH ⁵⁷	Room temperature	CO; ⁵⁴ CO ₂ ⁵⁶	10–30 s; ⁵² 15–27 s; ⁵³ 100 s ^{54,57}	700–2000 ppm CO ₂ ; ⁵⁶ 400–2000 ppm acetone, THF, MeOH, toluene ⁵⁷	Analysis of mixtures ⁵⁷ Recovery time: 60 s; ⁵³ 100 s ⁵⁴	Layer by layer nanoassembly; ⁵³ spin coating; ⁹ spray pyrolysis ⁵⁸
Unfunctionalized CNTs	2 ppm NO ₂ ; 0.1% NH ₃ ; ⁶³ 44 ppb NO ₂ ; 262 ppb nitrotoluene; ⁶⁵ 1 ppb NO ₂ ; 125 ppb NH ₃ ; ⁶⁶ 100 ppb NH ₃ ; NO ₂ ; ⁷⁰ SO ₂ ; ⁶⁷ 10 ppb NO ₂	Room temperature; ⁶⁶ 25–215 °C ^{68–70,72,73}	NO ₂ ; ^{63,67–70,75} NH ₃ ; ^{63,67} SO ₂ ; ⁶⁷ CO ^{68,69}	1.2 min; ^{63,67,68,73} 5 min; ⁷⁵ 10 min ^{65,66}	10–100 ppb NO ₂ ⁷⁰	Recovery time: few min; ⁷⁰ 10 min; ⁶⁵ 8–12 h ⁷⁰	Chemical vapour deposition (CVD); ^{63,66} photolithography; ⁶⁵ high- pressure carbon monoxide disproportionation process; ⁶⁵ acid purification, ⁶⁵ thermal purification; ⁶⁵ microwave plasma CVD ⁶⁸
CNTs – polymers	500 ppm NO ₂ ; ⁸⁴ 33% H ₂ O ⁸⁵	Room temperature	Pyridine, benzene; ⁸¹ MeOH, NH ₃ ; ⁸⁶ SO ₂ ⁸⁸	100 s; ⁸⁷ 2000 s ⁸⁶	0–3000 ppm NO ₂ ; ⁸⁴ 33–98% H ₂ O ⁸⁵	Reproducibility for CO ₂ ⁸³ Selectivity: NO ₂ ; ⁸² SO ₂ ; ⁸⁸ Recovery time: 2–4 s ⁸⁶	Spin coating ⁸⁴
CNTs – metal nanoparticles	500 ppb NO ₂ ; ⁹⁴ 10 ppm CO	180 °C; ⁹⁰ 25–350 °C; ⁹¹ 50–150 °C; ⁹² room temperature ^{93,94}	CH ₄ ⁹²	1–20 min; ^{92,94} 9 min ⁹³	0.1–4% H ₂ ; ⁹¹ 202–1010 ppm NO ₂ ⁹³	Stability: 1 year ⁹¹ Recovery time: 1.5 min ⁹³ Sensitivity: 1.8–81 × 10 ^{−3} Δ(R _{NO2} /R _{air}) ppm ^{−1} 93	Microwave plasma CVD; ⁹⁰ sputter-deposition; ⁹⁰ magnetron sputtering; ⁹⁰ heating; ⁹¹ spin coating ⁹³
Other CNTs – sensors	0.5 ppb dimethyl methylphosphonate, 0.5 ppm acetone ¹⁰²	Room temperature, 25–150 °C ⁹⁵	O ₂ ; ^{95,103} CO ₂ ¹⁰³	2–3 min; ^{97,98} 4 min (O ₂), 45 s (CO ₂), 2 min (NH ₃); ¹⁰³ 15 min ⁹⁶	0–100% H ₂ O; 0–70% NH ₃ ⁹⁷	Lower power consumption, low cost, small size and higher sensitivity with respect to bulk materials ^{99,100} Recovery time: several hours; ⁹⁷ 370 s (DMMP), 4 s (acetone); ¹⁰² 50 min ⁹⁶	Photolithography ¹⁰¹

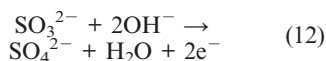
at a working temperature of 650 °C, the conductivity of the sensor changed with response times between 10 and 20 s. The sensor response can be explained by the oxidizing action of the O₂. Also, the iridium nanoparticles allow greater interaction between the molecules and the substrate, which provides greater contact area with the analyte. Similarly, a hydrogen sensor has been developed.⁴⁷ In this case, the sensing part consists of nanoparticles of Pd deposited on a Si p-type substrate. The substrate was submitted to an electrochemical etching with HF/ethanol/H₂O, which led to the formation of nanopores (average diameter about 10 nm) on the surface. Subsequently, the Pd film (approximately 4 nm) was deposited and then stabilized with an annealing at 900 °C for one hour, during which SiO₂ and PdO formed. This process increased the contact surface area of the sensor, and the electrical resistance also increased because vacancies were generated in the silicon. This porous silicon–Pd sensor was used in a custom testing chamber with a four-point probe configuration. The conductivity of the device increased under nitrogen and with hydrogen concentrations of 0–1.5%. In this case, the Pd acted as the catalyst for the dissociation of hydrogen, which transferred electrons to the silicon substrate, thus decreasing the resistance. Because the PdO formed during the annealing can be reduced at temperatures of 100 °C or above, which affects detection, the device is operated at ambient temperature.

As well as the measurements in the gas phase, studies have also been made to detect sulfur dioxide in acidic and basic solutions. Li *et al.*⁴⁸ used a Pt electrode with Au nanoparticles on its surface (with a Ag/AgCl reference electrode). The Au nanoparticles were attached to a cysteine-modified Pt electrode by dipping this electrode into a Au colloid for 24 h. The amperometric detection was carried out in HCl 0.1 M, H₂SO₄ 1 M, HClO₄ 0.1 M and NaOH 1 M, as internal electrolytes. Results were best in 1 M NaOH: other gases in the system such as CO, NO, NH₃ and CO₂ did not interfere, the linear response was between 5 and 500 ppm of SO₂ and the sensitivity was 5.4×10^{-10} A ppm⁻¹ with a detection limit of 2.6 ppm (calculated at a signal-to-noise ratio of 3).

The anodic oxidation of SO₂ was expressed in acidic solution as:



while the following reactions are proposed for basic solutions:



The greater sensitivity in NaOH is explained by the fact that SO₂ is extremely soluble in basic solutions.

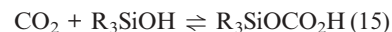
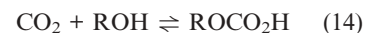
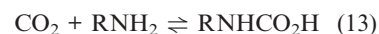
The use of metal nanoparticles as a sensing layer allows such analytes as H₂ and SO₂ to be selectively detected with smaller amounts of material. Some of these devices can also work at low temperatures. However, most of the studies reported use metal oxides as the substrate. The use of metal nanoparticles on inert substrates should be studied in greater depth.

Nanosensors with metal complexes

Because transition metals are capable of establishing reversible interactions with other atoms, some metal complexes may act as receptors for different types of molecules. This behaviour can be exploited to form complex-analyte supramolecules and to increase the selectivity of several sensor types. This was done by Elosúa *et al.*⁴⁹ who reported an optical fibre sensor coated with a complex of Au and Ag {[Au₂Ag₂(C₆F₅)₄(C₆H₅N)₂]} for detecting volatile alcoholic compounds. The recognition layer of the sensor is a nanometer-scale Fizeau interferometer, doped with the complex which, in the presence of methanol, ethanol and isopropanol vapours, has vapochromic behaviour. The vapochromism is manifested by a change in the colour and the refractive index. The solvents coordinate with the Ag metal centres and break the Ag–Ag and Ag–Au bonds, which give the complex its initial colour (orange to red). The sensing part is deposited on an optical fibre using the ESA method (electrostatic self-assembly method). The complex is incorporated in the last layer of the cationic polymer. The detection mechanism follows a process of total internal reflection through the optical

fibre (see section ‘Other types of carbon nanotube-based sensors’). The concentration range was 21.5–86 mM for ethanol and 31–125 mM for methanol. For isopropanol, the response was evaluated at 40 mM, with reversible detection processes. The authors claim that the sensor was used for at least three months in their laboratory and that it was not seen to degrade in the slightest.

Brousseau *et al.*⁵⁰ worked on the detection of carbon dioxide using CO₂ reactions with amines, alcohols and hydroxysilanes under ambient temperature and pressure conditions. They used three bifunctional receptors for the gas: *p*-xylylenediamine (*p*XDA), 3-aminopropanol (APA) and (3-aminopropyl)methyldihydroxysilane (APMDHS). These are bifunctional molecules that have an amine group to coordinate the metal ion of a thin film of copper octanedylbis(phosphonate), which is on a quartz crystal microbalance. The other functional group reacts reversibly with the CO₂. In this case, covalent bonds are formed, leading to the formation of carbonates and carbamates by the following reactions (one for each of the three bifunctional receptors):



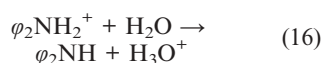
The concentration range evaluated was between 0 and 20% of CO₂ in Ar, and a linear relation was found between the change in frequency of the quartz crystal microbalance (QCM) and the analyte concentration for the devices with *p*XDA and APA. For APMDHS, the behaviour was linear as from 5% CO₂. The reaction between the analyte and the sensing part was reversible at ambient temperature, although the response and stabilization time was between 300 and 1300 s and recovery took between 2000 and 4000 s, depending on the CO₂ concentration and the receptor used (data obtained from the Δf vs. *t* curves).

The principal advantage of using metal complexes as the sensing layer is the reversible interactions between the analytes and the devices. The coordination bonds formed during the detection process can be broken by increasing the

temperature or changing the chemical environment of the sensor. Moreover, each receptor can be designed to interact with a specific analyte, hence increasing the selectivity. Since synthesizing these complexes can be expensive, one of their potential applications is as specific receptors in functionalization processes that use other nanostructured materials as transducers (for instance, see section 'Carbon nanotubes functionalized with organic polymers').

Nanosensors for gases with organic polymers

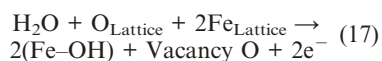
In recent years numerous sensors with polymeric materials have been developed, most of which have been reviewed by Adhikari and Majumdar.⁵¹ These materials have been used in different types of sensors for detecting many analytes, among which are aromatic compounds, amines, medicines, surfactants, herbicides, ionic species, organic vapours and gases.⁵² Generally, polymers are deposited in the form of thin films, the main objective of which is to increase the sensitivity of the sensing device, which is determined by the thickness and the sensing area of the material. Nohria *et al.*⁵³ used thin films of poly(anilinesulfonic acid) (SPANI) to construct a humidity sensor. Films were deposited by spin coating, from a solution of the polymer, leading to a film 90 nm thick, or by the layer-by-layer (LbL) nanoassembly technique, which negatively charges the substrate to couple the layers of a polycation [poly(allylamine hydrochloride)] (PAH), and a polyanion [poly(styrene sulfonate)] (PSS). Once the layers have been deposited, the PSS is replaced by the SPANI to give a 26 nm-thick film. When the sensor is exposed to air, its resistance decreases as the relative humidity increases, with response times of 15 s (LbL) and 27 s (spin coating). The sensor's detection mechanism is explained by the following acid-base reaction:



When the number of protons on the polymer surface decreases, the number of electron pairs available for charge transport increases, which in turn increases the electrical conductivity of the

material. The shorter response time obtained for the LbL sensor is attributed to the thinner polymer layer. The results also show that the reproducibility of this sensor is higher.

Other studies describe the formation of nanostructures from anionic or cationic polymers and metal oxides. Ram *et al.*⁵⁴ reported a nanosensor for carbon monoxide constructed from nanolayers of compounds of polyaniline-SnO₂ and polyaniline-TiO₂ on a glass substrate coated with indium tin oxide. The electrical resistance of the device decreased when in contact with the CO because it acted as an oxidant, increasing the number of holes responsible for the conductivity of the material. The presence of metal oxide nanoparticles maintained the PANI (polyaniline) as a reduced species, which converted it into an easily oxidized substrate and favoured electronic transfer with the analyte. A saturation concentration of 1000 ppm of CO was obtained for PANI-SnO₂ and 800 ppm for PANI-TiO₂. The behaviour in the presence of 1000 ppm of SO₂ was also evaluated. There was a slight change, which indicates that at relatively high concentrations this gas can interfere with the process of detection. Tandon *et al.*⁵⁵ worked on a humidity sensor with a polymer based on polypyrrole and nanoparticles of Fe₃O₄. They found that the conductivity of the material increased when the percentage of relative humidity was increased, which is explained by the following reaction:



O and Fe atoms in the crystalline network react with water, leave an oxygen vacancy and release two electrons, thus increasing the number of charge transporters.

Luoh and Thomas⁵⁶ used polyacrylonitrile (PAN) fibres with nanoparticles (diameters between 10 and 70 nm) of Fe₂O₃, ZnO and Sb₃O₄-SnO₂ (1 : 9). A total of 2000 ppm of CO₂ was detected by measuring the absorbance at 2356 cm⁻¹ in the IR region. The results show that adding Fe₂O₃ nanoparticles increases the sensitivity and that the adsorption processes are reversible. The relationship between absorbance intensity and concentration is roughly linear (with only

four experimental points) between 700–800 and 2000 ppm of CO₂.

As well as metal oxides, other materials such as carbon nanoparticles or fibres have been used to increase the sensitivity of polymer-based sensors. Quercia *et al.*⁹ described a sensor based on poly(methyl methacrylate) (PMMA) and carbon nanoparticles (CN) deposited by spin coating on a glass substrate. Sensitivity (defined as the ratio between the change in electrical resistance and initial resistance, $\Delta R/R_0$) was greater with PMMA-CN than with thin films obtained with commercial carbon blacks (without nanostructure) and by exposing the sensor to acetone vapours. This was attributed to the increase in the surface area of the polymer with the presence of the nanoparticles. Zhang *et al.*¹⁰ worked on the detection of tetrahydrofuran, benzene, toluene, cyclohexane, n-hexane, carbon tetrachloride, chloroform, ethyl acetate, diethyl ether, acetone, methanol, ethanol, propanol and isopropanol vapours. They used a polystyrene film with carbon nanofibres (cylinders consisting of tightly rolled graphite sheets that have diameters of 70–200 nm and lengths of 1–100 μm) to obtain sensors that were more stable than those obtained with carbon black. The vapours were detected by means of the change in electrical resistance shown by the device. The fact that the material is in the form of fibres gives higher stability because, when the gas is adsorbed, the nanoparticles increase in size and tend to join together again, destroying the nanostructure of the material and giving less reproducible results. Xie *et al.*⁵⁷ used poly(4-vinylphenol) (PVPH), poly(ethylene oxide) (PEO) and polycaprolactone (PCL), each mixed with carbon black on a substrate of Si₃N₄/SiO₂/Si and electrodes of Au. They analyzed acetone, tetrahydrofuran, methanol, ethanol and toluene in concentrations of 400–2000 ppm on a simple matrix of nitrogen, with the three types of devices simultaneously. As the thickness of the polymers decreased so did the response times and, at different concentrations, the electrical resistance of the analytes studied was clearly different. This can be seen by the way in which principal components analysis classifies the responses. The only analytes that have similar behaviour are tetrahydrofuran

and toluene at 400 ppm, so they were differentiated using pattern recognition analysis. As well as the simple matrix, they analysed mixtures of toluene–methanol and ethanol–acetone. The responses obtained with the three sensors enable the two types of mixtures to be differentiated by means of a pattern recognition analysis. Chemometric analysis and the chemical analysis made with the three sensors have made it possible to differentiate between the behaviours of several substances and even their mixtures, so it is to be expected that other mixtures can also be differentiated and even mixtures of more than two analytes.

Lukaszewicz and Skompska⁵⁸ used furfuryl alcohol as the precursor to obtain thin films of carbon sensitive to water vapour in the atmosphere. The films were obtained by spraying the precursor on a hot glass plate. In this way, the alcohol polymerizes and is then carbonized (spray pyrolysis) to obtain Na₂CO₃–carbon films. The films are p-type semiconductors. The main precursor was furfuryl alcohol, which was mixed with Na₂CO₃, a hydrophilic compound, in an attempt to increase the sensitivity to humidity. The result is a sensor based on a carbon thin film with nanocrystals of Na₂CO₃, the electrical resistance of which changes above 20% of relative humidity. The results suggest that the formation of the polymer during the spray pyrolysis procedure is necessary if the nanocrystals are to form, and if they are to be stable and evenly distributed, thus increasing the hydrophilicity of the sensor.

Organic polymers are cheap and very sensitive to several analytes. The deposition techniques used to obtain the thin films are relatively simple and cheap. For these reasons, polymers are a quick way of building gas sensors. The main problems with these materials are their lack of selectivity and their lower stability regarding time and temperature. The use of carbon nanoparticles and fibres has been studied for improving selectivity and stability but some problems still remain to be solved.

Carbon nanotube-based gas sensors

Ever since they were discovered,⁵⁹ carbon nanotubes (CNTs) have aroused

considerable interest because of their structure, properties and possible applications. Single-walled carbon nanotubes (SWNTs) are cylinders consisting of a single layer of rolled graphite, which can be between less than 1 and 3 nm in diameter, and in the order of micrometers long. Multi-walled carbon nanotubes (MWNTs) are made of concentric SWNTs and can also be of different diameters. Because of their physical and electronic properties, both SWNTs and MWNTs have been used in several types of sensors.

Because of the arrangement of the atoms on the surface of the SWNTs and their high area/volume ratio, adsorption processes are highly favoured, which increases their sensitivity to the surrounding atmosphere. As far as electrical conductivity is concerned, nanotubes can be metals or semiconductors, depending on the chirality of their structure.⁶⁰ Semiconducting nanotubes can be used (as metal oxides are) to construct devices such as field effect transistors (FETs). These devices are designed to detect analytes by means of a change in the electrical conductivity of the CNTs caused by the effect of the analyte on their surface. This effect can have two consequences: they may promote a charge transfer from the analyte to the nanotube, or the analyte may act as a scattering potential. The charge transfer increases the conductivity when the analyte adsorbed is an electron attractor (hole donation). If the analyte is an electron donor, the number of holes on the nanotubes will decrease, which leads to a decrease in the electrical conductivity. This effect can be used to modulate FET-type devices with a third gate

electrode (Fig. 3). On the other hand, if the analyte acts as a scattering centre, the current will decrease without shifting the characteristics.⁶¹ However, one of their most notable characteristics – sensitivity to the surrounding chemical environment – is at the same time a drawback because it means a lack of selectivity. So several functionalization processes have been implemented to incorporate specific sensing elements. Among the functionalization processes that we have reviewed are coating with different polymeric materials and the doping or deposition of oxides and metal particles. As a result, not only will the selectivity of the carbon nanotube FET (CNTFET) sensors be higher than that of the same systems made of metal oxides, but the sensitivity will also be higher and the working temperatures lower.

Unfunctionalized carbon nanotubes

As we have mentioned above, carbon nanotubes can be used as the sensor/transducer in a gas detection device, because their electrical properties (basically their conductivity) are affected by interaction with the molecules adsorbed on their surface. Therefore, studies have been made of how they behave when exposed to gases such as NO₂, NH₃, CO, H₂O, N₂ or organic vapours. It is important to point out that nanotubes respond differently to different gases, which add or remove electron density from the surface of the nanotubes. This property in itself is not very selective, so mechanisms need to be developed to increase the selectivity of the detectors that consist of unfunctionalized nanotubes.

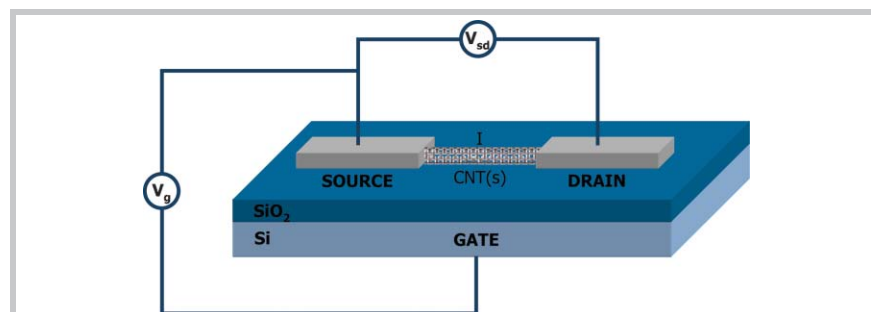


Fig. 3 Schematic diagram of a FET device based on a single CNT (SWNT or MWNT) or a network of CNTs. The current intensity between these electrodes is modulated by the voltage applied between the source and gate electrodes.

The electrical characterization of semi-conducting SWNTs integrated in CNTFETs, before being exposed to gases, was reported by Zhou *et al.*⁶² They described how electrical currents were measured by varying the potential between Ni/Au electrodes connected through individual SWNTs of different diameters obtained by chemical vapour deposition (CVD) on Si/SiO₂ supports. The silicon substrate was used as a back gate electrode. At ambient temperature, the SWNTs showed linear behaviour on an *I*-*V* graph with a resistance of approximately 340 k Ω at $V_{\text{gate}} = 0$ V. At positive V_{gate} , the conductance of the sample decreased, which indicates p-type semiconductor behaviour and their potential application in the construction of electrochemical sensors. In general, the resistance of SWNTs with diameters of more than 2 nm was in the range 160–500 k Ω . For SWNTs with smaller diameters, resistance was in the order of megaohms. Kong *et al.*⁶³ were the first researchers to report the behaviour of SWNTs in contact with ammonia and nitrogen dioxide. They found that the conductance of SWNTs synthesized by CVD on substrates of Si/SiO₂ changes by about three orders of magnitude when exposed to NO₂ and NH₃. The process is reversible after cleaning with Ar at high temperatures for one hour. The limits of detection obtained are 2 ppm for NO₂ and 0.1% for NH₃, with response times of between 1 and 2 min. This change in conductivity can be explained by a direct process of charge transfer between the molecule adsorbed and the SWNT⁶⁴ leading to the modulation of the Fermi level in the semiconducting tubes. The adsorption of an electron-donor molecule, such as NH₃, on a p-type semiconductor neutralizes the positive holes and this decreases the conductance of the material and the intensity of the electrical current. The opposite process takes place with electron-attracting molecules such as NO₂. In this case, the intensity signal increases, which may make it easier to measure and explain the lower limit of detection obtained by Kong's group for NO₂. This mechanism requires a favourable process of adsorption of the analytes on the SWNTs, so Andzelm *et al.*⁶⁴ have made a theoretical study of the role that some SWNT defects can have in the adsorption of NH₃.

Li *et al.*⁶⁵ developed a sensor based on SWNTs and used it to detect NO₂ and organic vapours. In this sensor, the SWNTs form a network that covers the interdigitated electrodes (IDEs) used. This network provides electrical contact between the electrodes and increases the area in contact with the gas. The IDEs, with a finger width of 10 μm and a gap size of 8 μm , were fabricated using a photolithographic method which deposited Au on a substrate of Si/SiO₂. These resistive-type devices can detect the change in electrical conductivity when the potential is modified, without using a third electrode as back gate as in the FETs. The SWNTs were treated with acid, which removed the metal impurities, and heat, which removed the graphite particles. Subsequently they were suspended in dimethylformamide and deposited on the substrate. The change in the conductance of the system presented a linear relation with the concentration of NO₂ and nitrotoluene, with limits of detection of 44 and 262 ppb, respectively. To find these limits, samples were used in each case that contained only the gas of interest diluted in N₂, which means that the only thing left to check was the selectivity of the sensor. The authors explain that non-polar molecules were detected by a hopping mechanism of adsorption that takes place in the interstitial space between the SWNTs. In this way, SWNT–molecule–SWNT junctions are formed, leading to an intertube charge transfer between SWNTs and an intertube modulation of the SWNT network instead of a change in conductivity. This mechanism does not depend on the polar character of the molecules, and provides a non-linear response and high sensitivity at low concentrations. From the practical point of view, the authors also describe how exposure to UV radiation decreases the desorption-energy barrier and facilitates NO₂ desorption, thus decreasing the time it takes to return to baseline to about 10 min.

The same research group⁶⁶ subsequently reported a similar sensor based on a p-type substrate of Si/SiO₂ with interdigitated Pt and Ti electrodes which are in contact by means of a network of SWNTs synthesized by CVD. The sensor was exposed independently to NO₂ and NH₃ and the limits of

detection found were 1 and 125 ppb, respectively.

Goldoni *et al.*⁶⁷ evaluated the effect of impurities caused by the synthesis and purification on the sensitivity of SWNTs to some gases. When contaminants such as Na and Ni were removed by thermal treatment, the response to O₂, CO, H₂O and N₂ was suppressed but sensitivity to NH₃, NO₂ and SO₂ was maintained with limits of detection of 100 ppb. The desorption processes can be reversed by heating at 800 K in an ultra high vacuum. On the basis of these results, the authors suggest that some molecules (for example, O₂, H₂O and N₂) interact with the nanotubes only by dispersion forces and not by charge-transfer reaction, so the impurities mentioned above determine the adsorption process.

Cantalini *et al.*^{68–70} presented resistive gas sensors sensitive to NO₂ with limits of detection of 100 ppb in dry air. The type of substrate used was a wafer of Si/Si₃N₄ on which the electrodes (Pt) were deposited and the nanotubes were synthesized by microwave plasma enhanced chemical vapour deposition (MPECVD) using Ni as the catalyst. When the thickness of the Ni film was modified, two sensors were obtained: A and B. In sensor A, the nanotubes have different orientations and form aggregates, which generates a wide range of differently sized pores. The authors assume that this increases the surface area that interacts with the gas, and therefore increases the sensitivity in comparison to that of sensor B, which is compact and has aligned nanotubes. They also assume that these structural differences are responsible for the suppression of a forbidden band in the nanotubes of sensor B, because the resistance does not depend on temperature whereas it does in sensor A. The sensor was tested in the temperature range between 25 and 215 $^{\circ}\text{C}$, and the sensitivity was maximum at 165 $^{\circ}\text{C}$. Their study also includes some theoretical calculations of the adsorption processes for NO₂ and CO. Other studies on the detection of NH₃,⁷¹ NO₂,^{72–77} CH₄ and CO⁷⁸ have been made in recent years and the mechanism that governs adsorption processes has been studied theoretically.⁷⁹

Carbon nanotubes are a very sensitive material because they can easily interact with many gases and change their con-

ductivity in the presence of several analytes at room temperature, even if these analytes have different chemical behaviours. Carbon nanotubes are relatively cheap and easy to synthesize and deposit. Therefore, several substrates can be used that require only a small amount of the material. However, their high sensitivity means that they are non-selective, which limits their use for sensing purposes in real samples. To achieve selectivity, carbon nanotubes need to be functionalized, as we will show below.

Carbon nanotubes functionalized with organic polymers

We have seen that the electrochemical sensors based on raw carbon nanotubes are devices that operate at ambient temperature and are highly sensitive to different types of gases, although they are not very selective. With the aim of increasing this selectivity, several functionalization methods have been developed. These include doping, or inserting atoms or functional groups in the nanotube structures, which constitutes a type of covalent functionalization. This is the case of the sensor reported by Villalpando-Páez *et al.*,⁸⁰ a resistive gas sensor, the sensing part of which consists of aligned nanotubes⁸¹ synthesized by thermolyzing benzylamine/ferrocene [$\text{PhCH}_2\text{NH}_2/\text{Fe}(\text{C}_5\text{H}_5)_2$] solutions. This method provides nanotubes doped with N (CN_x) atoms: that is to say, with pyridine-type sites on their surface. They evaluated their sensor with two types of device: pellets and films. The results show that the pellets are sensitive to acetone, ethanol, chloroform and gasoline, despite the fact that the increase in resistance is irreversible: that is to say, chemisorption takes place on the surface of the CNTs. The films are sensitive to the same substances as pellets and ammonia, and the processes are also irreversible. However, the films are much more sensitive than the pellets because a greater surface area is in contact with the gas. All the devices had response times of milliseconds and saturation times of 2–3 s. The resistance of the system increased because of the contact with molecules which, according to DFT (density functional theory) theoretical calculations, have an affinity for pyridine sites, such

as ethanol, acetone and ammonia. Pyridine and benzene showed reversible behaviours, which indicates physisorption and weak interactions with CN_x .

Functionalization can also be non-covalent. This consists of depositing particles or coating the surface of the CNT with a material that interacts with the analyte of interest. In the latter case, the nanotubes still act as a transducer system, while the material deposited on the surface becomes the sensing part of the device. In this section, we describe those nanotube-based sensors that have been functionalized by coating with organic polymers, and although the response of the devices is determined by the electron-donor character or the polarity of the gases, in most cases selectivity is not complete for just one analyte.

Qi *et al.*⁸² used Nafion and polyethylenimine (PEI) to functionalize nanotubes in FET-type sensors. Their results indicate that Nafion has a selective response for ammonia, caused by an acid–base reaction between the gas and the sulfonic acid groups of the polymer, and which increases the electrical resistance of the sensor. With PEI they obtained a response to NO_2 with no appreciable reaction with other gases such as ammonia, carbon dioxide, carbon monoxide, methane, hydrogen and oxygen. This is because there is a charge-transfer reaction between the amino groups of the PEI and the NO_2 . The result is a decrease in the number of charge-carrying electrons in the polymer and, therefore, an increase in the electrical resistance of the device. The authors do not mention the possible interference of the reaction between the amine groups of the PEI and acid gases such as CO or CO_2 .

Star *et al.*⁸³ proposed some nanofets for detecting CO_2 in which the SWNTs are non-covalently functionalized with a mixture of PEI and starch. The basic detection mechanism is based on the acid–base reaction between CO_2 and the amine groups of the PEI. This reaction lowers the total pH of the polymer layer and modifies the chemical gating effect on the semiconducting nanotubes, resulting in a change in their electrical conductance. The starch facilitates the reaction because the gas is adsorbed on the polymer layer and then

an equilibrium is established between the amino groups of the PEI and the water molecules contained in the starch. The authors indicate that the response is rapid and reproducible at low concentrations of CO_2 .

An *et al.*⁸⁴ proposed a resistive-type device for detecting nitrogen dioxide, the sensing part of which was the product of the copolymerization of the pyrrole with carbon nanotubes. The chemical polymerization was followed by spin-casting the samples onto two Au/Ti electrodes, separated by 500 μm , which had been previously patterned on top of the substrates made of silicon wafers with 500 nm-thick thermally grown oxide on the surface. The electrical resistance increased when the NO_2 concentration was in the range 500–3000 ppm. When the two materials were combined to form the nanocomposite, sensitivity (defined as $\Delta R/R_0$) was approximately ten times greater than that of polypyrrole and unfunctionalized nanotubes.

Li *et al.*⁸⁵ also proposed a resistive-type sensor for detecting humidity. Nanocomposite films of SWNTs or MWNTs and a silicone-type material containing polyelectrolytes were used as the sensing materials. The presence of the electrolyte increases the hygroscopic character of the nanotubes, which favours their interaction with water. The range of relative humidity to which the sensor is subjected is between 33 and 98%, and the conductance of the device increases. The presence of CNTs in the sensing film considerably decreases the impedance of the sensor but does not affect its sensitivity or linearity. Likewise, studies have been made of CNT functionalization processes with poly(methyl methacrylate) for the detection of ammonia and methanol,⁸⁶ and with polystyrene⁸⁷ for the detection of organic compounds (among others, tetrahydrofuran, benzene, toluene, cyclohexane, carbon tetrachloride, chloroform, ethyl acetate, diethyl ether, acetone and ethanol).

Jiménez-Cadena *et al.*⁸⁸ have developed a field effect transistor (FET) based on SWNTs functionalized with a platinum(II) complex $[\text{Pt}(\text{H}_4\text{C}_4\text{O}_2\text{NOCO})-2,6-\{\text{CH}_2\text{N}(\text{CH}_3)_2\}_2-\text{C}_6\text{H}_2]$ ⁸⁹ for the selective detection of SO_2 in air at room temperature. The functionalization process consists of coating the carbon nanotubes with polyethyleneimine

(PEI) and subsequently binding the platinum(II) complex to PEI. The metal complex (the sensing part) acts as a selective and reversible pincer for SO₂, binding the molecule by coordination bonds. The specific detection is improved by using a blocking molecule (*N*-acryloxysuccinimide), which prevents interferences from reaching the surface of the SWNTs.

Non-covalent functionalization with polymers does not usually require expensive materials or fabrication techniques. The polymers can act as the sensing layer because they are more selective (although selectivity is not complete) than the raw carbon nanotubes, which then act as the transducer part. If selectivity has to be complete, then a specific receptor for the target analyte has to be attached to the polymer. As in the sensor based on organic polymers, stability is still a problem.

Carbon nanotubes and metal particles

In an attempt to decrease the working temperature of some materials that can be used as the sensing part and to increase the sensitivity of the devices, several studies have combined CNTs with oxides or metal particles. The functionalization is not covalent, since the CNT structure is not modified: the process incorporates nanoparticles or films on the surface of the nanotubes, thus changing the adsorption mechanism of the analytes with respect to the unmodified nanotubes. CNTs, then, play the role of the transducer in this type of sensors.

One of the first studies was made by Wong *et al.*⁹⁰ who used MWNTs obtained by microwave plasma enhanced chemical vapor deposition (MPECVD) on silicon substrates to construct nano-FETs. The top part of the MWNTs is coated with a sputter-deposited thin layer of palladium (1000 Å), which also serves as the gate electrode. The Pd layer acts as a catalyst for the dissociation of the H₂ molecules in its atoms. The atomic hydrogen, adsorbed on the Pd nanoparticles, transfers electrons to the CNTs, which decreases the number of hole carriers and, therefore, the conductivity of the device. The authors monitored the change in the electric current by sub-

stituting air for a flow of H₂ and checking the effect of temperature. They found that there was a significant increase in detection sensitivity at higher operating temperatures (180 °C). The same mechanism was used by Sayago *et al.*⁹¹ to explain the behaviour of their sensor, this time by airbrushing SWNT dispersions onto aluminium substrates. Two strategies were used to incorporate Pd into the CNTs: refluxing SWNT-containing toluene solutions of a Pd complex salt, and direct magnetron sputtering of Pd. In this study, they also observed changes in the sensor resistance when they changed the hydrogen concentrations between 0.1 and 4% in the presence of air and nitrogen. With air, they found a linear relationship between resistance and hydrogen concentration, whereas with nitrogen they found a saturation concentration. The authors considered that this was because, in the presence of air, SWNT electrons are transferred to the O₂ in the atmosphere and the number of hole carriers therefore increases. In nitrogen, there are fewer holes and, therefore, they are neutralized more quickly. The sensor also had a weak response to toluene and octane vapours, and a considerable increase in resistance in the presence of ammonia. It was also found that the sensor response decreased when the temperature increased (resistance peaks were highest between 25 and 100 °C and then decreased). The results obtained indicated that aging processes (*e.g.* storing the sensors for more than a year, which may introduce carboxylic acid functionalities due to exposure to oxygen and/or the complete removal of solvent traces) and thermal treatments (*e.g.* heating to 350 °C for some hours) were required to improve the sensor response. Lu *et al.*⁹² presented a sensor with SWNT and Pd nanoparticles (approx 1 wt%). They used interdigitated Au electrodes on a silicon substrate, between which the Pd–SWNT solution was dispensed. The device was sensitive to methane between 6 and 100 ppm at ambient temperature, and undergoes a process of reversible desorption. The detection mechanism proposed includes the formation of a weakly-bound complex Pd^{δ+}(CH₄)^{δ-}. When the Pd polarizes, it attracts electrons from the surface of the SWNTs and the number of hole carriers increases, which

produces a charge transfer to the methane, the hydrogen atoms of which tend to attract Pd electrons. In this way, the conductivity of the device increases. The authors also found an increase in response and a shorter reaction time at higher temperatures (for example, at 150 °C the relative response was three times what it was at 50 °C for a methane concentration of 15 ppm). At this temperature, the sensor also begins to recover by itself.

Other studies have focused on decreasing the working temperature of certain metal oxides. Wei *et al.*⁹³ used Al₂O₃ substrates and gold electrodes on silver and palladium wafers. They presented three types of sensors: SnO₂, SnO₂–SWNT at 0.0003 wt% and SnO₂–SWNT at 0.003 wt%. The sensors were prepared by dispersing the nanotubes with ultrasound in a solution of tin(II) 2-ethylhexanoate in 2-ethylhexanoic acid, used as a precursor of SnO₂. The dispersion was then deposited on the substrate by spin coating and sintered at 500 °C in air. The results show that NO₂ can be detected between 202 and 1010 ppm at ambient temperature when the SnO₂ is doped with SWNTs, because the resistance of the device increases in the presence of the analyte. What is more, when the concentration of SWNTs increases, the response and sensitivity of the device also increase. The response mechanism of the sensor is based on the electronic transfer that takes place from the metal oxide to the NO₂ (an electron-attracting molecule), which explains the increase in resistance. The amplification of the response in the hybrid sensor is due to the formation of a depletion layer between the SnO₂ (n-type semiconductor) and the SWNTs (p-type semiconductor). This zone is free of charge carriers because there is an electronic transfer from the n-type semiconductor to the holes in the p-type semiconductor. Although the two materials, as a whole, are neutral, the presence of the SWNTs produces an additional positive charge on the SnO₂, which further increases the resistance, and therefore the sensitivity of the device. This same mechanism was used by Bittencourt *et al.*⁹⁴ The n-type semiconductor was WO₃, which they used in integrated micro-hotplates with arrays of four microsensors, and drop-coating

double-side polished p-type Si substrates (300 μm thick). In this way, four types of sensors were obtained. It was determined experimentally that two of them were p-type (their resistance decreased in the presence of oxidizing species such as NO_2), based on MWNTs and MWNTs- WO_3 1 : 100 wt, and the other two were n-type, based on WO_3 and MWNTs- WO_3 1 : 1000. The gases analyzed were NO_2 (between 500 ppb and 5 ppm), NH_3 (between 1 and 100 ppm) and CO (between 10 and 100 ppm), which were detected even at ambient temperature, although when temperatures were increased to 150 and 250 $^\circ\text{C}$ lower concentrations could be used. The results indicate that hybrid sensors (MWNTs- WO_3) have lower working temperatures than the WO_3 sensor (250 $^\circ\text{C}$ or above) and increased sensitivity (limits of detection were 500 ppb for NO_2 and 10 ppm for CO at ambient temperature). A temperature of 150 $^\circ\text{C}$ is required for the detection of ammonia. No response was obtained at ambient temperature with any of the sensors constructed. The authors consider that hybrid sensors work better not only because of the formation of a depletion layer but also because the presence of the MWNTs increases the area of contact of the WO_3 .

In this kind of device small quantities of carbon nanotubes increase the area/volume ratio of the metal oxides or nanoparticles and makes it easier for the gases to interact. The final result is an increase in sensitivity and stability, and a decrease in the working temperature.

Other types of carbon nanotube-based sensors

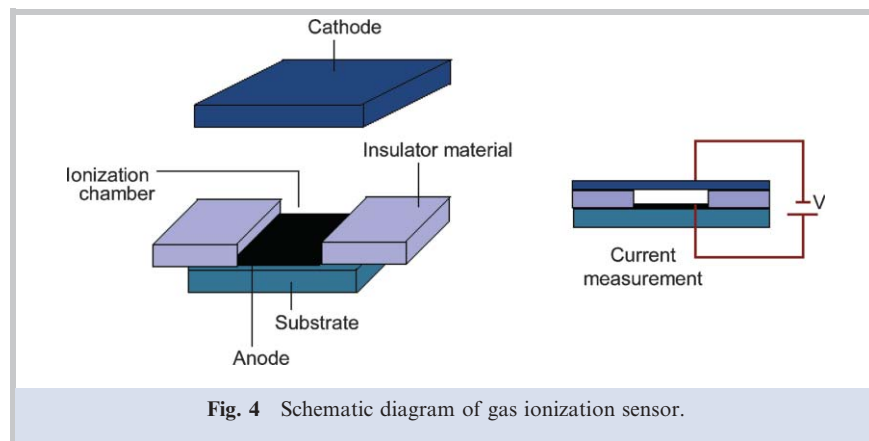
Although most of the carbon-nanotube-based devices are resistor-type, in recent years other types have been developed. Here we provide a general review of the main research reported to date.

One of the first articles to explore the possibility of using CNTs as gas sensors was by Collins *et al.*⁹⁵ They evaluated the change in electrical resistance and thermoelectrical power (TEP) of SWNT thin films and bundles. They found that the properties measured change when the substrates are exposed to air, O_2 and N_2 . Adu *et al.*⁹⁶ reported a thermoelectric nano-nose constructed from

compacted mats of SWNT bundles (mean bundle diameter around 15 nm, with bundles of about 1 mm \times 2 mm \times 0.1 mm). By clustering the nanotubes in this way, the adsorption process can take place on the surface, in the interstitial channels, inside the nanotubes (by exploiting defects in their walls) and in the grooves between the nanotubes. The authors placed a small ceramic-coated resistor near one end of the SWNT mat, and used it as a heater to introduce a small temperature difference ($\Delta T < 0.5$ K). The corresponding thermoelectric voltage (ΔV) was measured, and the thermoelectric power $S = \Delta V/\Delta T$ was calculated. The measurements show that the nanotubes respond to independent exposures of N_2 , H_2 , O_2 , NH_3 and He, all of high purity (99.999%), although neither selectivity nor different concentrations of gases were tested. Varghese *et al.*⁹⁷ used impedance spectroscopy to evaluate the capacitance and electrical resistance of the MWNT-based sensors: the first one was a MWNT- SiO_2 nanocomposite on a planar interdigital capacitor; the second one was a resistor with MWNTs deposited on a SiO_2 substrate. They were found to be sensitive to independent exposures of H_2O (response times of 2–3 min in both sensors, and recovery times of several hours), NH_3 (response time of 2–3 min in both sensors, and recovery times of several days under vacuum and at 100 $^\circ\text{C}$), CO (response only in the capacitive sensor) and CO_2 (response only in the resistive sensor). Argon was used as the carrier gas in all cases. Unlike the results found by other groups, the authors did not find sensitivity to O_2 . The

authors show that the MWNT behaviour is that of p-type MWNTs dispersed among the predominantly metallic MWNTs, in which the adsorbed water molecules or the reducing gas molecules donate electrons to the valence band, thus increasing the electrical resistance (in n-type MWNTs the chemisorption of reducing gases increases the number of conduction band electrons and hence the conductivity, but this is not observed in these sensors). The presence of a Schottky barrier also helped to increase the resistance. This barrier may arise as the result of junctions forming between metallic and semiconducting MWNTs or between the MWNTs and the catalyst. The fact that O_2 did not react might be because the O_2 was not completely de-absorbed in the annealing process before being exposed to the atmosphere (and it could not be removed by argon flushing). Hence, surface coverage might have reached a maximum value. The interdigital capacitor proved to be the most sensitive sensor.

Another of the most interesting gas sensors is the gas ionization sensor (Fig. 4). These devices have an ionization chamber with pairs of electrodes between which a potential difference is applied to ionize the gas. The cations go to the cathode and the electrons to the anode, which generates a current within the chamber. For each gas there is a single voltage at which ionization occurs – the breakdown voltage – by which the substance can be identified. The intensity of the current produced will be proportional to the concentration of gas in the chamber. These sensors enable mixtures



to be analyzed and detection does not depend on adsorption processes. However, bulky sensors require high voltages and operation temperatures between 200 and 500 °C (when SnO₂, ZnO or TiO₂ are used on the surface of the electrodes), which increases energy consumption and makes them more difficult to use. In an attempt to decrease the ionization voltages, Modi *et al.*⁹⁸ used an Al cathode and a MWNT anode (with an electrode separation of 150 µm), which allowed them to create high electrical fields near the electrodes and facilitate the gas breakdown process. For example, the results show that, for air, currents of 460 µA are obtained at a voltage of 346 V when MWNTs are used, while currents of 69 µA are obtained at a voltage of 960 V with metal electrodes. This means that the breakdown value decreases by almost 65%: that is to say, energy consumption is lower, operational risk is lower and the current obtained, and therefore the sensitivity of the device, is about six times greater. What is more, the relations between the discharge current and the logarithm of concentration for air, argon, nitrogen, ammonia and oxygen were linear, and concentrations in the order of µM were detected. Likewise, Li *et al.*⁹⁹ also used a discharge gas sensor with four different types of electrode tips in the cathode: metal, tungsten, metal-coated nanotubes and tungsten-coated nanotubes (in all cases with a copper plate on the anode). The results indicate that the electrode tips with nanotubes give a higher signal (the current values increase three-fold) than pure metal or tungsten. Kim¹⁰⁰ made a similar study using MWNTs on the cathode as electron emitters and a Si p⁺-type anode. The ionization of air and argon was evaluated, both at independent concentrations, between 10⁻⁷ and 10⁻⁴ M. The breakdown voltage in argon was lower than in air (minimum breakdown voltage around 230 V, less than in air, which was around 340 V) because of the relatively low electronegativity of argon. Some of the quality parameters of these sensors are their small size, low cost and low power consumption.

Penza *et al.*¹⁰¹ presented three sensors constructed of Langmuir–Blodgett films (defect-free, molecularly ordered ultra-thin films with controlled thickness and orientation) formed by tangled bundles

of SWNTs and used them to detect volatile organic compounds (VOCs). The transduction mechanisms used included transmitting surface acoustic waves (SAWs), measuring the change in mass of a quartz crystal microbalance (QCM) and the intensity of light transmitted through a standard silica optical fibre (SOF). The authors claim that the integration of different chemical detectors with complementary transducing principles can increase the amount of information extracted. In both the SAW sensor and the QCM, the nanotubes favour the process of adsorbing several organic substances and the sensitivity was greater than that of the same device without SWNTs. The presence of nanotubes on the surface of the fibre in the SOF sensor means that the refractive index of the top layer varies because several analytes are adsorbed. This modifies the intensity of light transmitted and, therefore, provides a response to the change in concentration of the substances. The vapours analyzed individually include ethanol, methanol, isopropanol, acetone, ethyl acetate and toluene, and their sensitivity values increased in all cases.

Other studies used capacitors coated with nanotubes. Snow *et al.*¹⁰² developed a SWNT chemicapacitor coated with chemoselective materials (a chemoselective acidic strong-hydrogen-bonding polycarbosilane polymer, and a self-assembled monolayer of allyltrichlorosilane). The capacitor was built by photolithography with a 2 mm × 2 mm interdigitated array of Pd electrodes being placed on top of a SWNT network. The capacitance was measured by applying an AC bias between the top surface and the underlying conducting Si substrate. The sensor was tested with a wide variety of chemical vapours, which were prepared by mixing saturated vapours of the analyte with dry air at 25 °C. Among other results, the authors obtained a minimum detectable level of 0.5 ppb for DMMP, with an approximate recovery time of 370 s, and a minimum detectable level of 0.5 ppm for acetone, with a recovery time of less than 4 s. It should be pointed out that the chemoselective materials are not selective to a single analyte. The authors claim that since the transduction mechanism in SWNT chemicapacitors is the polarization of surface

adsorbates, the capacitance response is more sensitive, recovers much faster and can be applied to a wider range of analytes than SWNT chemiresistors, in which the detection is due to charge transfer from analytes to the SWNTs. Ong *et al.*¹⁰³ made a planar inductor–capacitor resonant circuit covered with a gas sensing layer of a MWNT–SiO₂ composite (made by dispersing MWNTs in a solution of 20 wt% SiO₂ nanoparticles in water). The property measured is the resonant frequency of the sensor (which changes as the permittivity and/or the conductivity of the MWNT–SiO₂ changes), monitored through a loop antenna, which makes the sensor attractive for wireless monitoring applications. So the frequency spectrum makes it possible to calculate the relative permittivity and the conductivity. Because of the strong chemisorption of NH₃, this sensor provides responses to independent exposures of O₂ (in 4 min) and CO₂ (in 45 s) and irreversible responses to NH₃ (in 2 min). Since NH₃ and CO₂ are reducing agents that give electrons to the p-type MWNTs, conductivity decreases in their presence. The opposite result is found with O₂, an oxidizing agent. To remove the effect of temperature and humidity, the CO₂ sensor was prepared using three sensor elements (a SiO₂-coated sensor, an uncoated sensor and a MWNT–SiO₂-coated sensor) which enables a humidity–temperature calibration to be made by independently measuring humidity and temperature with the two first sensor elements. Chopra *et al.*¹⁰⁴ used a circular disk resonator (resonating at 4 GHz) coated with bundles of SWNTs (several microns long). The resonant frequency was calculated using the return loss spectrum of the resonator. Before any measurements were made, the SWNTs were degassed by heating at high vacuum, because previous experiments showed that the resonant frequency did not change when non-degassed SWNTs were exposed to inert gases. When the sensor was exposed to *ca.* 1500 ppm of He, the resonant frequency decreased by 0.8 MHz. Results were similar for *ca.* 1500 ppm of NH₃ (although previous studies by the same authors showed that 100 ppm can be detected), with a decrease in the resonant frequency

of 3.55 MHz. Exposure to other gases (Ar, N₂, O₂, CO) resulted in different decreases in the resonant frequency, which prompted the authors to claim that the sensor is selective (although no tests were made with mixtures of gases). The shifts in the resonant frequencies are higher for polar gases (NH₃ and CO). As in other studies¹⁰⁴ the authors also find that a percentage of NH₃ chemisorbs onto the CNT walls, but in this case the sensor can be fully recovered after the degassing process mentioned above.

The carbon nanotube-based sensors reviewed in this section have proved to be very sensitive but, again, not very selective. Functionalization processes are required in order to improve their selectivity. Other performance parameters, such as low power consumption, low cost or small size are achieved by using gas ionization sensors with carbon nanotubes as the electrodes. The detection process of these gas ionization sensors does not use CNTs in the sensing layer so their operational parameters could be improved by incorporating CNTs.

An overview of the main quality parameters of all the sensors discussed here and the main fabrication techniques can be found in Table 1. Table 2 shows the main advantages and disadvantages of the nanostructured materials used for sensing purposes. In most cases the comparison between the different types of sensors is not straightforward since not all of the quality parameters have been tested and described for all the sensors. CNT-based sensors seem to have the lowest detection limits. While most of the sensors can detect in the ppm range, the sensors based on carbon nanotubes (raw and functionalized) can detect in the ppb range. This is a consequence of the high sensitivity of carbon nanotubes, which also results in low detection limits. Most of the sensors reviewed can work at room temperature. However, metal oxides require relatively high temperatures: one way of decreasing these temperatures may be to use them with such other materials as metal nanoparticles or CNTs. Most of the references on reversible behaviour use high temperatures, UV light or gas cleaning. However, some devices behave irreversibly to specific analytes such as NH₃ or some organic compounds. This behaviour depends on the material and the analyte. Time parameters, dynamic range and other

Table 2 Main advantages and disadvantages of nanostructured materials used for sensing purposes

Nanomaterial	Advantages	Disadvantages
Metal oxides	<ul style="list-style-type: none"> • High area/volume ratio. Low response times and high sensitivity • Doping processes with metal nanoparticles increase the sensitivity and the stability of the sensors • Lower working temperatures (than bulk materials) • The results can be improved using annealing processes 	<ul style="list-style-type: none"> • The nanostructures require post-treatments, such as calcination and annealing, and the use of high temperatures and advanced techniques for film deposition • Additional characterization processes are required to obtain information about the size and form of the materials
Metal nanoparticles	<ul style="list-style-type: none"> • The sensing layer does not require so much material. Some nanoparticles act as catalysts and increase the speed of the detection process • Specific interactions with biomolecules can be used to immobilize the sensing layer (<i>e.g.</i> Au–cysteine) 	<ul style="list-style-type: none"> • Nanoparticles require annealing and advanced techniques for deposition • The characterization techniques are expensive
Metal complexes	<ul style="list-style-type: none"> • The detection is based on specific reactions. These devices are therefore selective and, in many cases, reversible 	<ul style="list-style-type: none"> • Synthesizing the complexes is expensive
Polymers	<ul style="list-style-type: none"> • With a thin polymer layer, response times are short and reproducibility is high 	<ul style="list-style-type: none"> • Stability and selectivity are low
Carbon nanotubes (CNTs)	<ul style="list-style-type: none"> • Shorter response and recovery times, high sensitivity, reversibility and stability for raw CNTs • Several techniques can be used to obtain CNTs (synthesis or deposition) • Responses at room temperature • Aging and thermal processes increase the sensitivity of the sensors • When metal oxides are deposited as nanoparticles on the surface of the CNTs, working temperatures are lower • Gas ionization sensors are small and have lower ionization voltages. Therefore, power consumption, cost and operational risk are lower 	<ul style="list-style-type: none"> • Additional purification processes are required • Lack of selectivity for raw CNTs • CNTs are relatively expensive in comparison with other materials • Networks of CNTs decrease the repeatability of the sensors
In summary	<ul style="list-style-type: none"> • High sensitivity, small size, smaller amounts of sensing material, short response and recovery times, low working temperatures and power consumption 	<ul style="list-style-type: none"> • Post-treatments, expensive characterization techniques, advanced and expensive techniques for depositing the materials, low repeatability and reproducibility of the signals, and functionalization processes are required to increase the selectivity

characteristics are less reported and have been defined in so many ways that it is difficult to compare them.

The increase in cost of nanosensors is in most cases directly related to how they are fabricated. Therefore, costly and/or time-consuming processes such as techniques for depositing the nanoparticles or films (e.g. sputtering), characterization techniques at the nano-scale (e.g. microscopies), or lithographic processes for introducing microelectrodes into some of the devices can significantly increase their cost.

Conclusions

This review focuses on the main aspects of nanostructures that are part of sensor devices for detecting gases: from nanostructured metal oxides to organic polymers, carbon nanotubes and mixtures of a variety of materials. The objective of these nanostructures is to obtain better quality parameters for nanosensors. The results in the original papers are presented in different ways, so it is difficult to compare the performance characteristics of gas sensors based on nanostructured materials (nanosensors) and the same devices based on the bulk material. Although nanosensors are expected to be more sensitive because nanoparticles and thin films favour gas adsorption, the results suggest that this may not always be the case. Functionalization processes are being used to modify the very structure of the carbon nanotubes or the surface of the nanostructures by means of some type of coating in an attempt to increase the selectivity. However, selectivity has been suitably checked only very rarely in nanosensors and most of the tests involve only the analyte of interest in a simple matrix (Ar, N₂ or synthetic air). So the problem of obtaining specific sensors has not been fully solved yet. Other parameters of quality such as limits of detection, limits of quantification, dynamic range, linearity, response and recovery times and lifetime have not always been checked in nanosensors, and they should be studied in similar devices built with bulk material for purposes of comparison. Other operational parameters such as the cost, portability and reusability of the nanosensors have seldom been evaluated since the main goals and expectations

nowadays are the improvement of selectivity and sensitivity.

The results discussed show that it may be possible to use nanostructured materials to efficiently detect various types of gases: e.g. nitrogen oxides, sulfur and carbon oxides, acids and bases, and some organic vapours. However, the samples analyzed generally contain only the target analyte in a simple matrix, so the analysis should be extended to more complex matrices and real samples, and possible interferences should be evaluated. One future possibility, linked to the miniaturization of the devices, is to use a series of selective sensors with subsequent chemometric treatment to differentiate between the concentrations of different analytes in a mixture.

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