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TOPICAL REVIEW

Sensing gases with carbon nanotubes: a review of the actual situation

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Abstract

Here we review the possible application of carbon nanotubes (CNTs) as chemiresistor and field-effect transistor chemical sensors. The endeavor of this paper is to understand the key facts emerging from the literature that seem to demonstrate the high sensitivity of CNTs to several molecular species, with the effort to catch the results in a correct manner.

(Some figures in this article are in colour only in the electronic version)

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1. Introduction

The development of sensors that can detect gas molecules in the environment with good sensing performance will significantly impact our lives. Indeed, the ability to detect chemical molecules and biological entities in the atmosphere by means of miniature and portable sensors is of great importance for environmental pollution analysis, public security, industrial emission monitoring and control, medical diagnosis, and agriculture.

Carbon nanotubes (CNTs) have attracted a great deal of attention as model systems for nanoscience and for various potential applications, including composite materials [1], battery electrode materials [2], field emitters [2, 3], nanoelectronics [2, 4] and, obviously, nanoscale sensors [5–7]. In particular there are two main characteristics that suggest carbon nanotubes as promising candidates for extremely sensitive gas sensors. First, as one-dimensional systems,

their 'quantum nature' makes the intrinsic properties highly sensitive to very tiny external perturbations. Second, the active surface area is huge.

When chemicals in the surrounding environment bond to the tube, the adsorbed molecules may act as dopants, shifting the Fermi energy of the nanotube, or may change the band structure of the tube due to the orbital hybridizations for bond formation, possibly influencing the conducting properties [6]. A typical example is shown in figure 1. Since such changes can be easily detected when the nanotubes are embedded in electronic devices, CNTs appear extremely promising candidates for miniaturized sensors having high sensitivity and a fast response time to the chemical environment. This is especially advantageous in fields such as pollution monitoring, space exploration, agricultural and medical diagnostics and hazardous gas detection. Therefore, CNT-based chemical and biological sensors are the objectives of a significant research endeavor [8–81].

In this paper we discuss chemiresistor and field-effect transistor (FET) sensors, while CNTs can also be exploited as chemical sensors using the capacitor [82, 83] and field emission [84–86] properties. The efforts to study the chemiresistor and FET CNT sensors can be roughly divided into two classes: one that exploits a certain property of the pure nanotube (such as a change in conductivity and/or electronic properties with gas adsorption) and the second that relies on the ability to functionalize the nanotube (tip and/or side wall) with metals or molecular groups that serve as sensing elements.

Much experimental evidence seems to demonstrate the high sensitivity of CNTs to several molecular species, both



Figure 1. (Top panel) Calculated contour plot of electron density (slice in the (100) direction and passing through the NO₂ molecule) for the top nine valence bands of (10, 0) SWCNTs interacting with a NO₂ molecule. (Bottom panels) Density of states for a (10, 0) SWCNT (middle), NO₂ (bottom) and NH₃ (top) interacting with a (10, 0) SWCNT. Modification of the SWCNT density of states caused by band splitting is more pronounced in NO₂ than NH₃. Due to the existence of the molecule level near the valence band edge, hybridization between the SWCNT and NO₂ shifts the Fermi level into the valence band, making the SWCNT a p-type conductor. This figure is a composition reproduced with permission from [33]. Copyright 2002 IOP Publishing.

organic and inorganic, in the gas phase [8–81]. Although most of the experimental reports must be taken *cum grano salis* and a number of technical problems must be deeply investigated and solved, there is the effective possibility to produce a sensor technology based on CNTs. In this paper the results of these efforts are summarized.

2. 'Pure pristine' carbon nanotubes

Starting with the chemical sensitivity of pure nanotubes, many papers found that single-wall carbon nanotubes (SWCNTs) and multi-wall carbon nanotubes (MWCNTs) may be used to detect O_2 [8] or for miniature chemical sensors to detect small concentrations of toxic gas molecules with high sensitivity [8-36]. Chemical sensors based on individual or ensembles of pure CNTs can detect hazardous chemicals such as NO₂ [8, 13, 14, 16, 20], ammonia (NH₃) [8, 13, 14, 18], SO₂ and NO [13, 14]. In fact the electrical properties of CNTs are extremely sensitive to charge transfer and chemical doping effects. A major role in understanding and optimizing the gas-sensing behavior of nanotubes is played by computational investigations, which should precisely define the chemical reactivity, the bond geometry and predict the effect of gasphase chemisorption [29-36] on the electronic characteristics First-principles calculations investigating the of CNTs. interaction of several representative molecules (NO₂, CO, NH₃, O₂, H₂ and H₂O) with SWCNTs have been performed using density functional theory. Many theoretical papers [29-36] indicate that when electron-withdrawing molecules (e.g. NO2, O2) or electron-donating molecules (e.g. NH₃) interact with the p-type semiconducting CNTs, they will change the density of the main charge carriers (i.e. holes) in the 'bulk' of the nanotube, which changes the conductance of CNTs. By measuring the change in the conductance of nanotubes the presence of gases could be precisely monitored. It was seen that the response times of nanotube sensors are at least one order of magnitude faster (a few seconds for a resistance change of one order of magnitude) than those based on presently available solid-state sensors [87–90]. Gas sensors dedicated to toxic gases typically use semiconducting metal oxides (SnO_2 for example) and conducting polymers. As a general comparison, conventional solid-state sensors for NO2 and NH3 operate at temperatures over 700 K, while conducting polymers provide only limited sensitivity [87-90]. SWCNT and MWCNT sensors apparently operate at room temperature and have response times of about 10 s to a detection level of sub-ppm (part-per-million) by using the CNT in a fieldeffect transistor configuration, or simply by contacting the two ends of a nanotube and measuring the resistance [8-36]. This is an advantage over metal-oxide sensors [87, 90], which require high temperatures, and polymer sensors which have poor sensitivities and slow (10 min) response times [89].

Therefore, according to literature, several works apparently demonstrate the sensitivity of 'intrinsic and clean' carbon nanotubes to diverse gases at room temperature induced through the charge transfer from or to the adsorbed gas molecules. For a semiconducting single-walled nanotube exposed to 200 ppm of NO₂, it was found that the electrical conductance increases by up to three orders of magnitude in a few seconds [9]. On the other hand, exposure to 2% NH₃ caused the conductance to decrease by up to two orders of magnitude [9]. The adsorption of oxygen molecules on an individual semiconducting SWCNT in a FET device, or in a mat of SWCNTs at ambient conditions, seems to decreases the resistance from 10 to 15% [8, 86] up to approximately two orders of magnitude [91].



Figure 2. Behavior of photoemission intensity for the C 1s and N 1s peaks in clean SWCNTs (a) and graphite (b) as a function of the NO_2 exposure at 150 K. The arrows indicate the exposure at which the N1s peak and the C1s peak have the same intensity. Corresponding C1s ((c), (d)) and N1s ((e), (f)) spectra measured after the above indicated NO_2 exposure for SWCNTs and graphite. C1s (g) and N1s (inset) spectra after an exposure of 6000 L of NO_2 for SWCNTs at room temperature: it is clear that there is no variation of the electronic properties of SWCNTs and adsorption of NO_2 .

A gas and organic vapor sensor, fabricated by the simple casting of SWCNTs on an interdigitated electrode, with detection limits of a few hundred of ppb (part-per-billion) at room temperature has been proposed by Li *et al* [17]. Kordas *et al* [20] developed potentially cost-effective inkjet printing for generating conductive MWCNT patterns on paper and polymer surfaces. They used a commercial desktop inkjet printer to form a conductive pattern that was found to be sensitive to very high concentrations of various gases or vapors such as H_2O , NH_3 and alcohols. A similar detector was fabricated by Dua *et al* [28] who used a desktop inkjet printer to print a film of SWCNTs dissolved in water and Triton X-100 on PET.

On the other hand, as shown in figure 2, Larciprete *et al* [45], using the interaction with NO₂ as a prototypical case, demonstrate that intrinsic clean SWCNTs practically behave like graphite and at room temperature, in the case of several gases, they are refractory to adsorption. Moreover, while clean SWCNTs in the form of bucky paper kept at 150 K are sensitive to ppb amounts of environmentally significant toxic gases such as NO₂, NH₃ and SO₂, with the formation of several chemisorbed species on the SWCNT surface [13, 14], Goldoni *et al* [13] have also seen that at the same temperature O₂, N₂ and CO₂ do not physisorb and do not influence the intrinsic

electronic spectra of SWCNTs. A similar result was obtained for the case of O_2 at room temperature by Barberio *et al* [65]. These authors observed that only the exposure to O_2^+ assures the attachment to SWCNTs.

It appears, therefore, that the formation of chemisorbed species is important for the chemical sensitivity of clean SWCNTs. In particular for the case of NO₂ the chemisorbed species are mainly NO₃, and in minor amount NO. The formation of such chemisorbed species via chemical reaction between NO₂ molecules, once NO₂ is allowed to physisorb on the nanotube surface, has been confirmed by Peng *et al*'s [37] calculations.

Considering that at room temperature the presence of chemisorbed species is quite unusual (like in graphite), the sensitivity of CNTs is therefore related to the presence of contaminants or defects on the CNT itself, which allow the occurrence of chemisorption. Because CNTs are usually grown in the presence of a variety of carbon species, catalyst particles, and other unwanted constituents, much attention has been given to CNTs purification. However, after purification a lot of defects induced by the acid treatments and other molecules due to the washing may be trapped between the bundles or attached to the nanotube. Valentini *et al* [25] fabricated CNT thin film sensors based on defective and defect-free nanotube structures. The transition from defect-free to

defective CNTs can be induced through high temperature exposure to reactive plasma. Chemiresistors made with defective CNTs exhibited a greater sensitivity toward NO₂ compared to defect-free sensors [25]. This observation was consistent with theoretical calculations indicating that the defect sites on the CNTs resulted in a strong chemisorption of NO₂ and a large charge transfer interaction. In a similar way, MWCNTs chemically oxidized and full of defects can detect a few ppm of NO₂ and NH₃ while there is almost no response in pristine (not acid treated) nanotubes [66].

A diverse interpretation, which probably harmonizes this matter, has been envisaged after new and specific experiments, whose results strongly indicate that molecular adsorption on the metal contacts, which are much more reactive than the inert tube walls, cannot be neglected when explaining the undoubted sensitivity of the CNT-based sensors [38-44, 67]. NO₂ detection by CNT field-effect transistors was related by Zhang et al [44] to the changes at the interface between the nanotubes and the electrodes and not to molecules adsorbed on the CNT surface. By masking the CNT/electrode contacts the authors measured only a delayed response compatible with the diffusion through the passivation layer, which excluded any measurable effect due to charge transfer from CNTs to NO₂. Moreover, additional proof that the Schottky contact resistance between CNT and metal plays a strong role in the observed sensitivity to NO2 was obtained by revealing a strong dependence of the sensor response on the electrode (Pd, Cr, Al, Au, Ti, Pt) material [44, 67]. These results reveal that probably other elements present in the sensor device besides CNTs, that is residual contaminants, defects, metal catalyzer particles even forming caps which decorate the CNT tips, or metal contacts, can be responsible for a major contribution to the sensor response, which becomes dramatically dominant in a thermal regime where the low adsorption energy hampers the direct interaction between gases and CNTs.

In general a bottleneck for a wide diffusion of CNT-based sensors is the recovery time to the pristine CNT properties. In the experiment of Kong et al [9], it took about 12 h for the conductivity of the CNTs to go back to the original value after the exposure to gas. To desorb strongly adsorbed analytes and accelerate the recovery process an external energy source may be implemented to lower the adsorption energy barrier. Heating the sensor to 465-500 K reduced the recovery time to about 1 h [16, 24, 25] and at 700 K the recovery time is a few tens of seconds [14]. Illuminating the SWCNTs with ultraviolet light (250 nm) at a low photon flux [17, 24], causes rapid desorption of adsorbed species at room temperature and the recovery is <20 min. A shorter recovery time of about 3 min was measured in the experiment of Dua et al [28] and was probably attributed to the very small thickness of the inkjet printed sensor. A similar recovery time using back gate bias was observed by Chang et al [15] who found that a negative back gate voltage was required to refresh a SWCNT FET exposed to NH₃ and that a positive voltage was required to refresh sensors exposed to NO2. They also suggested that this mechanism could be used to circumvent the low sensing specificity of pristine SWCNT sensors, allowing for a good identification of the molecular species.

Finally for O_2 sensors, despite the controversy on the adsorption or not of O_2 molecules on CNTs [8, 13, 34, 91], the experimental evidence shows that O_2 desorption in chemiresistors or FET, even under high vacuum, is considerably too slow for sensor applications [38, 39].

3. Functionalized carbon nanotubes

The gas sensing with functionalized CNTs was mainly directed toward nanostructures with either organic polymers, biomolecules or catalytic metal, metal-oxide and nanoparticles attached to the CNT sidewalls. These nanoparticles and molecular groups serve as sensing elements, exhibiting a broad range of electronic, chemical, physical and biological recognition properties that are often highly sensitive to changes in their chemical environment. CNTs are the support that is physically responsive to stimuli from the molecular world around these functionalizations.

3.1. Metallic and metal-oxide clusters

Theoretical works [46, 60, 68] and experimental investigations [45, 47–57, 64, 69–73] indicate that metallic clusters strongly interact with CNTs producing significant charge reorganization. Therefore, another way to exploit the high sensitivity of CNTs to detect molecules that have a weak or repulsive interaction with them is the creation of nanotube–metal cluster (atoms) assemblies. Moreover, these clusters can be mechanically and chemically robust and stable, and hence, compared to polymer-based sensors, metal-based sensors can operate at higher temperatures and in harsher environments.

In [45] the sensitivity to ppb amounts of NO₂ is switched on at room temperature by coating SWCNTs with Rh particles (see figure 3). While the behavior of the coated SWCNT electronic properties (measured by following the C1s) mirrors what is observed at 150 K on clean SWCNTs, photoemission spectroscopy indicates that the sensing behavior is induced through the NO₂ interaction with Rh particles, since there is evidence of NO₂ absorption on the metallic particle surface only and not on the metal-free SWCNT surface [64]. Rh was chosen because the catalytic activity of Rh versus NO₂ is well known, but other metals can be used, as suggested by Zhao et al [46], tuning in such a way the sensitivity of the metal-coated/SWCNT system to different chemical species. Using NH₃ as a prototypical gas species and Al clusters, Zhao et al [46] have performed first-principles quantum transport calculations predicting that gas adsorption onto the metal clusters drastically changes the electronic properties, for both metallic and semiconducting nanotubes. The electrical resistance of a metallic CNT-Al cluster assembly increases dramatically after the adsorption of NH₃ on the cluster, while the opposite occurs for a semiconducting assembly. The observed behavior can be understood in terms of interactions between the molecular species and the nanotube-cluster system, where successive charge transfers between components tailor the electronic and transport properties.

Several groups demonstrated room temperature H_2 sensors based on Pd nanoparticles deposited at the surface



Binding Energy (eV)

Figure 3. C 1s, Rh $3d_{5/2}$, O 1s and N 1s core level spectra measured on the clean SWCNTs (black, top spectrum) and on the Rh/SWCNTs before (red, middle spectrum) and after (light blue, bottom spectra) the exposure to 1 L of NO₂ at room temperature. In each panel the curves were normalized to have the same height. The Rh $3d_{5/2}$ shows two components attributed to Rh adatoms located below (B) and at the surface sites (S) in the metallic clusters. Upon adsorption of NO₂ the surface component is washed out and the spectrum is broadened by the contributions of Rh atoms bonded to NO and NO₂ molecules. The two N 1s components correspond to chemisorbed NO₂ and NO; in the O 1s spectrum the main peak includes the contributions of both NO and NO₂ oxides and the shoulder on the low energy side is due to O atoms resulting from the NO₂ dissociation. The inset displays the SEM image of the SWCNT bucky paper decorated by the Rh-nanoclusters.

of SWCNTs [47–52, 69]. Pd-functionalized SWCNTs were shown to be highly sensitive toward H₂ with a response time of 5–10 s, and a time for recovery between 30 and 400 s. Both the response time and the sensitivity decreased with increasing temperature. The Pd–CNTs are also sensitive to CH₄ with enhanced sensitivity, reduced size and power consumption compared to conventional metal-oxide sensors [53]. A charge transfer sensing mechanism was proposed in both cases related to the ability of Pd to interact with hydrogen.

Surface coatings with Pt-, Ru- and Ag-nanoclusters of vertically aligned CNT networks, obtained by radiofrequency plasma enhanced chemical vapor deposition onto alumina substrates covered by nanosized Fe-catalyst, provide higher sensitivity for NO₂, H₂, ethanol and toluene up to a low limit of sub-ppm level [70].

Young et al [54] fabricated NO₂ sensors based on SWCNT-Au nanoparticle composite films. A SWCNT mesh was doped with alkanethiol-monolayer-protected gold clusters (MPCs) resulting in a composite film that was then used for the chemiresistive sensing of low concentrations of NO₂ under ambient conditions. The sensitivity of the sensors was dependent on the loading of MPCs, which decreased the detection limit for NO₂ approximately tenfold, to 4.6 ppb, compared with that obtained with uncoated SWCNT sensors. Illumination with ultraviolet radiation accelerated the recovery after exposure to the target analyte. A similar sensor of Aumodified CNTs was fabricated by the group of Penza [71] showing a decrease in electrical resistance upon exposure to oxidizing NO₂ gas and an increase in resistance upon exposure to reducing gases (NH₃, CO, N₂O, H₂S, SO₂) up to a lowpressure limit of sub-ppm level. Negligible response has been found in Au-modified CNTs sensors exposed to CO, N_2O , SO_2 . Hydrogen sulfide was also detected by Fam *et al* [72] using silver nanoparticle decorated SWCNTs at room temperature.

It seems therefore that the presence of different metallic particles functionalizing the CNT walls make the CNTs sensitive to several gases at room temperature. This must be compared to unmodified clean CNTs at room temperature, which like graphite are not sensitive to any gases [45]. As a consequence, multiple sensor elements consisting of isolated networks of SWCNTs integrated into Si chips were prepared by Star et al [55]. For chemical selectivity, SWCNTs were decorated with metal nanoparticles. The differences in the catalytic activity of 18 catalytic metals for detection of H₂, CH₄, CO, and H₂S gases were observed. Furthermore, a sensor array was fabricated by site-selective electroplating of Pd, Pt, Rh, and Au metals on isolated SWCNT networks located on a single chip. The resulting electronic sensor array, which was comprised of several functional SWCNT network sensors, was exposed to a randomized series of toxic/combustible gases and demonstrates that the employment of metal/metaloxide nanoparticles as gas recognition layers makes the carbon nanotube sensor arrays more robust and suitable to real life applications.

Male *et al* [56] used the combination of nanoparticles and CNTs to modify glassy carbon electrodes to improve the electroactivity and selectivity for glucose, while Penza *et al* [57] demonstrated a chemiresistor with one order of magnitude improved sensitivity made of MWCNTs functionalized with Au and Pt clusters sensing at high temperature (400–550 K) NO_2 and NH_3 . For the same gases, a relatively simple horizontally aligned CNT film on a titanium/gold-coated glass plate sensor was made by Jung *et al* [73]. This sensor exhibited low noise and thus high sensitivity to the NH_3 and NO_2 molecules and the response times were relatively short. The recovery time was within 40 s when a dc voltage of 5 V was applied for less than 30 s [73].

Novel hybrid gas-sensitive materials were fabricated by means of CNTs and metal-decorated CNTs dispersed with nanoparticle metal oxides $(SnO_2, WO_3 \text{ or } TiO_2)$, which could be potentially applied as gas sensors for detecting indoor air pollutants emitted from building and decoration materials [74-78]. The CNT materials can be used as a guide for the nanoparticle metal-oxide film growing and this allows the coating of the inner and outer surface of the tubes with a highly conformal film of controllable thickness and hence, the production of high surface area hybrid materials. Systems such as Au/CNT/SnO₂, Nb-Pt co-doped/CNT/TiO₂, Sb/CNT/SnO₂ etc were applied to the identification of CO, NH₃, ethanol, formaldehyde, toluene, NO₂, C₆H₆ and O₂. The hybrid material sensors improved the gas-sensing performance by factors of 2-5 compared to that of the sensor without CNT inclusion. Moreover, all hybrid sensors can operate with high sensitivity and stability at a relatively low operating temperature (<335 °C). For example, hybrid layers based on titania and CNTs [79] possess an unprecedented responsiveness towards oxygen (i.e. more than four times higher than that shown by optimized Nb-TiO₂ films [90, 92]) and significantly lower operating temperatures [92]. These new hybrid sensors show good potential for monitoring traces of oxygen (i.e. <10 ppm) in a flow of CO₂, which is of interest for the beverage industry.

Finally, electrical and sensing properties of resistive gas sensors based on hybrid vanadium oxide-coated carbon nanotubes (V_2O_4 -CNTs) were studied by Willinger *et al* [80] for the detection of NO₂. The strict contacts between V_2O_4 coating and CNTs contribute to the improvement of sensing performance.

3.2. Coating with polymers and molecules

Functionalized carbon nanotubes are believed to be very promising for the preparation of functional and composite materials and biological technologies. Immobilization of nanotubes with specific recognition biosystems indeed provides ideal miniaturized biosensor.

Polymer functionalization is used to impart high sensitivity and selectivity to the CNT sensors. Polyethyleneimine coating affords n-type nanotube devices to be capable of detecting NO₂ concentrations lower than 1 ppb, while being insensitive to NH₃. On the contrary, Nafion (a polymeric perfluorinated sulfonic acid ionomer) coating on nanotubes blocks NO₂ and allows for selective sensing of NH₃ [40]. A good sensitivity to NH₃ was also obtained by SWCNTs and MWCNTs functionalized with polyaniline [58, 81]. The results show a superior sensitivity $\partial R/R \sim 2.44\%$ per ppm of NH₃, a detection limit as low as 50 ppb and good reproducibility upon repeated exposure to 10 ppm of NH₃. The typical response time of the sensors at room temperature is on the order of minutes and the recovery time is a few hours.

Gao *et al* [59] demonstrated that the use of aligned MWCNTs coated with inherently conducting polymers provides a novel electrode platform for biosensors. These three-dimensional electrodes offer advantages in terms of large enzyme loadings within an ultra-thin layer, sensitivity and selective sensing.

An electrochemical DNA biosensor with a favorable performance for rapid detection of specific hybridization has been obtained by functionalizing CNTs with a carboxylic acid group (COOH) [60].

In the past several years, there has been a steady increase in activities that incorporate nanotubes into biological systems, including proteins, DNA, and living cells. This is an interesting and relatively new area that can be categorized as the 'wet' side of nanotube science and technology. A prerequisite in this field is the development of chemical methods to immobilize biomolecules onto carbon nanotubes in a reliable manner. The sp² hybridization and the outstanding electronic properties of the nanotubes coupled with the specific recognition properties of the immobilized system indeed make CNTs an ideal biosensor.

One possibility is DNA immobilization on CNTs, which is considered a fundamental methodology for the construction of DNA biosensors [61]. A DNA sensor was obtained by adding surface-bound double-strained DNA chains on a plasma-treated aligned carbon nanotube electrode [63]. Experiments carried out with the non-complementary singlestrained DNA chains pre-labeled demonstrated that the electrode possess a high sensitivity, with capabilities of selectively recognizing single-strained DNA sequences. Thus, DNA functionalization of CNTs holds interesting prospects in various fields including solubilization in aqueous media, nucleic acid sensing, gene-therapy and controlled deposition on conducting or semiconducting substrates. Most of the recent results on the DNA functionalization of CNTs and the use as a bio-chemical sensor have been reviewed by Daniel et al [61]. Exciting results and discoveries have already been achieved in this CNT sensor field, and much more can be expected in the next few years.

4. Conclusions

Purified and clean CNTs at room temperature behave like graphite and are refractory to the absorption of gases. When CNTs are decorated by metal and/or metal-oxide particles, polymer layers or functionalized with substances that selectively bind to specific chemical or biological molecules they can be used as extremely sensitive sensors. Possible applications of these small-size and low-power sensors are in the detection and identification of toxic, biological and combustible gases for personal safety and air pollution monitoring.

Despite the great achievements in this field, several critical issues remain to be addressed for a deeper understanding of tube–molecule interaction and practical applications. From the theoretical point of view, some accurate calculations on functionalized tube–molecule interaction and electronic band structure of gas-adsorbed functionalized nanotubes are essential. On the experimental side, it is important to develop efficient ways to distinguish among the different gaseous molecules in a mixture, further improving the results achieved by recent multiplex functionalizations of nanoparticle-CNT sensor arrays, and to really understand why CNT sensors may have a slow recovery time to the initial state or why in some cases the recovery process is instead accelerated.

The above works indicate that excellent steps were performed toward a commercialization of chemical sensors made of CNTs. However, these new results need to be reproduced and really understood before these sensors become a reality.

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