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ABSTRACT
Hybrid materials consisting of oxygen plasma-treated multiwalled carbon nanotubes decorated with metal nanoparticles (e.g., Rh, Pd, Au or Ni) can be tailored for the recognition of benzene vapors with high sensitivity and selectivity. Metal nanoparticles donate or accept a significant amount of charge upon adsorption of a target molecule, so as to affect electron transport in the nanotube. The plasma treatment enables the cleaning, activation, functionalization and metal decoration of carbon nanotubes in a single step, which offers enormous flexibility for tuning the interfacial properties of the resulting hybrid materials. When combined in a microsensor array operating at room temperature, the use of benzene-sensitive and benzene-insensitive metal-decorated multiwalled carbon nanotubes can provide selective detection of benzene at trace levels with a detection limit below 50 ppb.

1. Introduction
Long term exposure to relatively low concentrations of benzene over months or years leads to severe haemotoxic effects such as aplastic anaemia and pancytopenia and to acute non-lymphocytic leukaemia [1–5]. This is why the permissible exposure limit has been lowered from 10 ppm to 100 ppb in the last 10 years [6]. Occupational exposure to benzene occurs in the petrochemical industry, land reclamation, coke/oven operators, petrol stations, motor vehicle repair and roadside works [1,3,5]. An effective and accurate monitoring of benzene needs the use of simple, affordable and widespread sensing systems. Two paramount features of such sensing systems should be their sensitivity, since the concentration of benzene must be detected in the ppb range [6], and their selectivity. The reference methods for the detection of benzene imply pumped sampling and subsequent analysis for chromatographic determination, the use of colorimetric detector tubes and photoionization detectors (PID), which are not selective for benzene and give a total reading for volatile organic compounds. Therefore, a very sensitive, selective and affordable benzene sensor/monitor that can be used in industrial and transport environments is not yet available.

In the last few years, different studies have shown the excellent potential of carbon nanotubes (CNTs) as sensitive material for detecting biological and chemical molecules [7,8]. Via a functionalization of CNT sidewalls, a better chemical bonding between a specific chemical species and the nanotube can be reached and the selectivity of the adsorption process can be enhanced [7,8]. Some properties of CNTs make them very attractive to produce small, wearable sensors for industrial and transport environments:

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Their intrinsic strength makes them suited for miniaturized sensors and usable on flexible substrates [9]. They respond even when operated at room temperature, which is optimal for ultra-low power, wearable, battery-operated devices. Such devices could easily meet the requirements of intrinsically safe operation, needed in industrial environments where the occurrence of flammable/explosive atmospheres is possible. The adsorption of a small quantity of chemical species can result in a dramatic change of the CNT conductivity. Therefore, CNT are suited to detect species at low concentrations (e.g. low ppb level). A sensor can be built using a simple transducer (comb electrodes) to monitor the electrical resistance of a CNT-based film.

Carbon nanotubes are known to weakly interact with molecular benzene. Ab initio calculations have shown that the electronic properties of CNTs remain almost unchanged upon benzene adsorption [10]. There is only a small hybridization between the CNT states and those of the benzene molecule. The total electronic density of states (DOS) corresponds to the simple superposition of that of the two separate systems. This reaction involves weak π-stacking interactions and is an example of noncovalent functionalization of CNTs [10]. The calculated binding energy is around 0.2 eV per benzene molecule and the molecule–tube surface distance (around 3.2 Å) is of the same order as the usual separation between two sp²-like systems. Under these circumstances, it is not surprising that no journal papers have been published on benzene detection employing pristine carbon nanotubes.

As an alternative to the usual functionalization techniques, CNT can be decorated with metal nanoparticles. For example, Pd-coated CNT become sensitive to H₂ [11]. Metal clusters have a broad range of diverse structures and can provide a wide range of reactivity with different species. The concept of using CNT-metal cluster hybrids, as the sensitive material of a device where the metal cluster surfaces act as reactive sites for the adsorption of the target molecules, has been introduced recently in a theoretical study. In this study CNT–Al clusters are considered and it is shown that such a system displays initial specificity towards ammonia [12]. The adsorption of ammonia produces a substantial polarization and accumulation of charge in the region between the Al cluster and the nanotube. This charge transfer provides important information regarding the system’s electronic response. It affects the ionic component of the bonding, alters the position of the Fermi level and the band alignment. Therefore, the variations in the electrical conductance of the CNT–Al system are a measure of the sensitivity of chemical sensors based on this material [12].

According to these preliminary theoretical results, CNT-metal cluster hybrids could be tailored for the recognition of chemical species with high sensitivity and selectivity. The key concept is to use nano-clusters (small size is essential to maximize the effect of adsorbates on metal clusters) that donate or accept a significant amount of charge upon adsorption of a target molecule, so as to affect electron transport in the nanotube. This concept was first applied by different research groups in 2006 and 2007. Kumar and co-workers employed a wet chemistry route to obtain Pt-decorated carbon nanotubes highly sensitive to hydrogen [13]. Star and co-workers decorated CNT by selective electroplating either with Pt, Pd, Au or Rh for detecting CO, NO₂, CH₄, H₂S, NH₃ and H₂ [14]. Espinosa and co-workers decorated CNT with Au or Ag by evaporation for detecting NO₂ at room temperature [15]. Penza and co-workers decorated CNT with Au and Pt by using sputtering for enhancing response towards NO₂ and NH₃ [16]. Finally, Guo and co-workers oxidized nanotubes in nitrosulfuric acid and decorated them with Pd by a reduction method for detecting benzene [17]. Also Lu and co-workers employed Pd-coated CNT for discriminating NO₂, HCN, HCl, Cl₂, acetone and benzene [18]. The sensors from these two groups showed small benzene sensitivity [17,18] at concentrations three orders of magnitude higher than the required detection threshold for ambient safety applications.

2. Experimental

2.1. Synthesis of hybrid nanomaterials

The MWCNTs used in our experiments were provided by Nanocyl S.A. They were grown by CVD (Chemical Vapor Deposition) with purity higher than 95%. Nanotubes were up to 50 μm in length and their outer and inner diameters ranged from 3 to 15 nm and 3 to 7 nm, respectively. To decorate these nanotubes with Rh and Pt nanoparticles, two colloid solutions were employed for 5 min into a methanol solution. Surface treatment and metal decoration were conducted using plasma post-discharge at atmospheric pressure. The plasma was generated with a RF torch (Atomflo-250, from Surfx Technologies LLC), powered at 80 W and working for an argon flow of 30 L/min. To improve the deposition of metal nanoparticles, oxygen was mixed to the argon gas at the rate of 30 mL/min. The MWCNTs, placed 10 mm away from the RF torch, were exposed to the plasma post-discharge for 2 min to activate their surface. Then, during 30 s, a metallic colloid solution (rhodium or platinum) was sprayed onto the MWCNTs. These treated MWCNTs had to be exposed 3 more minutes before switching off the RF torch. In the final step, they were introduced for 5 min into a methanol solution and submitted to ultrasonication. The plasma activation and deposition processes are further explained in [21]. As a result of this treatment, either metal particles are immobilized at oxygenated vacancies present in CNT sidewalls or the capping agent is activated and helps forming a bridge between C and Rh [21].

The process of decoration with Au, Pd or Ni nanoparticles was as follows. In the first step MWNTs from Nanocyl S.A. were treated using an inductively coupled plasma at an RF frequency of 13.56 MHz. The treatment was performed at a pressure of 0.1 Torr, using a power of 15 W, during 60 s. In the second step either Au, Pd or Ni were evaporated on the oxygen plasma-treated CNTs. A quartz crystal microbalance
was employed to monitor metal coverage. At low metal coverage (1 nm), small and well dispersed Au, Pd or Ni clusters are formed (cluster size was 10 ± 2 nm), suggesting that plasma treatment induces reactive sites where gold, palladium or nickel atoms are easily trapped. The decoration of MWCNT by evaporated metals such as Au, Pd or Ni, involves first the adsorption of metal atoms onto the surface, followed by diffusion of these adatoms across the surface until nucleation of islands occurs when diffusing adatoms form a stable nucleus. After the formation of stable nuclei at nucleation centres, the next incoming adatoms can either attach to an existing nucleus or diffuse on the surface until they encounter another adatom to form a new stable nucleus. The density of nucleation centres depends on the interaction between adatoms and the substrate. Considering the strong adsorption bond between metal atoms and C vacancies or oxygenated C vacancies, such defects will be the principal nucleation sites [22,23].

2.2. Sensor fabrication

Sensor substrates were fabricated by Microsystems technology on a silicon substrate. Devices consisted of an integrated array of four inert micro-hotplate substrates, each one comprising a polysilicon heating resistor sandwiched between two thin silicon nitride layers and a pair of interdigitated Pt electrodes on top (electrode gap was 50 μm). The membrane thickness was about 0.6 μm and the active (hot) area of 500 μm × 500 μm. The micro-hotplate structure provides milliwatt power consumption required for hand-held detectors [24]. Plasma-treated metal-decorated MWCNT were dispersed in dimethyl formamide (DMF) by ultrasonication at room temperature to form uniform suspensions. The suspensions were airbrushed onto the interdigitated electrodes so each 4-element sensor array was coated with Rh, Ni, Pd and Au decorated CNTs. After DMF evaporated at room temperature, a mat of metal decorated CNTs spanned across neighboring fingers. DMF was chosen since it enables the formation of uniform suspensions of plasma-treated CNTs and easily evaporates at room temperature [25]. The coverage density of metal decorated CNTs on the electrode area was easily varied by selecting the airbrushing pressure. Finally, sensors were annealed at 250 °C for 4 h. in air flow to completely remove the remnant DMF and improve the nanotube-electrode contact.

2.3. Sensor characterization

The gas sensing properties at room temperature of the different active materials produced were tested in the presence of benzene and NO₂. To perform the measurements, the gas sensors were placed in a 2 × 10⁻⁵ m³ volume Teflon/stainless steel test chamber. The desired concentrations of each species were obtained using a computer controlled measurement rig that employed mass flow meters and calibrated gas bottles. Dry air was used as carrier gas. The concentrations tested were as follows: 50, 100, 200 and 500 ppb for benzene vapors and 50, 100 and 500 ppb for NO₂. To assess the reproducibility of results, each measurement was replicated four times. An Agilent 34970A multimeter was used for continuously monitoring the electrical resistance of the sensors. The measurement process was as follows (identical for all species tested): Air flow was set to 100 sccm and kept constant. Data acquisition started 20 min before injecting the desired concentration of a given species into the measurement chamber. 20 min after the injection, the sensors were flushed with dry air and their temperature was raised to 150 °C for promoting the cleaning of their surface. 20 min after heating had been switched off, another measurement was performed.

3. Results and discussion

Here we report on a reversible and selective sensing platform based on hybrid nanostructures consisting of discrete metal nanoparticles distributed on the surface of plasma-treated multiwalled CNTs (MWCNTs). These hybrid nanostructures show high sensitivity to very low concentrations of harmful species at room temperature (e.g., benzene or nitrogen dioxide at ppb levels). Metal nanoparticles are an integral active part of the sensing platform, whose detection capability is mainly based on the reactivity of cluster surfaces. Sensing devices show quantum-mechanical attributes by taking advantage of the electron transfer between the metal nanoparticles and the CNTs upon gas adsorption. The plasma treatment provides an opportunity to engineer the interfacial properties of hybrid nanostructures in a single step, not only by enabling the cleaning, activation, functionalization and metal decoration of CNTs, but also by allowing the control of metal nanoparticle shape, size, (under)coordination and diffusion. For the different preparation methods carried out, the nanoparticles have an almost spherical shape and a well controlled size. For example, grafted nanoparticles have the same size and size distribution than in colloidal solutions. Furthermore, the dispersion of nanoparticles is homogeneous. This is illustrated in Fig. 1, which shows that the plasma treatment allows a homogeneous decoration of CNT sidewalls with metal nanoparticles. On the other hand, Fig. 1 also shows that this is not the case for pristine CNTs, where the occurrence of cluster diffusion and coalescence is clearly revealed. Metal atoms are mobile and diffuse at the “pure” CNT surface until they find a nucleation centre and there are significantly more nucleation centres for the O₂ plasma-treated CNTs. All these aspects and the possibility of using different metals offer tremendous flexibility for tuning the sensitivity of individual sensing elements (i.e., nanotubes decorated with nanoparticles of a given metal with particular shape, size and density on the CNT sidewalls) [26]. The resulting nanohybrid sensing elements are potentially superior to either of its constituent components (e.g. they detect gases that are normally undetectable by pristine or plasma-treated bare CNTs). This can be further exploited in parallel sensor arrays to obtain selectivity for the molecular recognition of a target species.

Electrical conductance in CNTs is ballistic even at room temperature [27,28], which enables the rapid detection of electron transport through CNTs. Oxidative treatments affect the DOS of valence bands and increase the work function of purified MWCNTs (4.3 eV) [29]. The work function of oxygen plasma treated MWCNTs ranges from 4.9 to 5.1 eV [29]. These values are very close to that of metals such as Pt (4.8 eV) [30],
Au (4.9 eV) [31], Pd (4.95 eV) [32], Ni (5.04 eV) [33] or Rh (5.0 eV) [34], making it easy for electrons to travel between the metal nanoparticles and the CNT, with the direction of charge transfer depending on the gaseous environment. The effective electronic interaction between metal nanoparticles and the CNT facilitates the detection of gases through the change in the electrical conductivity of mats formed by these hybrid nanomaterials.

Two possible benzene sensing mechanisms can be expected for the hybrid nanomaterials: (1) benzene directly adsorbs onto an oxygenated defect located at the CNT sidewall created by the oxygen plasma treatment, inducing electron transfer and changing the electrical conductivity of the hybrid nanomaterial; or (2) benzene adsorbs onto a metal nanoparticle and this results in a significant charge transfer between the nanoparticle and the CNT, which eventually changes the electrical conductivity of the hybrid nanomaterial. This second mechanism corresponds to what is theoretically described in [12].

The hybrid nanomaterials were synthesized by employing commercially available MWCNTs and either atmospheric plasma with different reagents (colloidal metal solutions) injected in the post-discharge during plasma treatment or low pressure plasma followed by metal evaporation. Four-element integrated micromachined sensor arrays, which comprised interdigitated Pt electrodes were coated with different hybrid nanomaterials by air brushing. Fig. 2 summarizes these results. SEM imaging shows that a very thin MWCNT mats coat the electrode area (electrodes are clearly visible in Fig. 2b) and that MWCNTs bridge electrode gap. TEM and HR-TEM images show that a good dispersion of metal nanoparticles attached to MWCNT sidewalls is achieved. Metal particle size is about 5 nm. The preserved structural characteristics of the graphene layer under the Pd layer (see Fig. 2d) suggest the absence of a Pd-C phase formation. XPS analyses performed on sensor chips confirm the presence of metal nanoparticles on the carbon nanotube sidewalls after the coating procedure (see Fig. 3). According to XPS results, metal concentrations were estimated to range between 1% and 2.5%.

Sensors based on Au-MWCNT hybrids were responsive to NO2 but not to benzene. NO2 response is in good agreement with previous experimental results [15,16]. Additionally, ab initio calculations performed on CNTs decorated with Au metal clusters indicate that there is no significant charge transfer between gold clusters and nanotubes upon benzene adsorption.1 This could explain the lack of response towards benzene vapors for our Au-decorated carbon nanotube sensors. On the other hand, Rh, Pd and Ni based hybrids were responsive both to NO2 and to benzene when operated at room temperature. The sign of sensor response changes when benzene (an electron donor) or NO2 (an electron acceptor) are detected (see Figs. 4 and 5). Sensor resistance increases with increasing concentrations of benzene. This suggests that, upon benzene adsorption, a significant amount of electronic charge is transferred from the metal clusters towards the CNT. On the other hand, sensor resistance decreases with increasing concentrations of NO2. Upon NO2 adsorption, electronic charge is transferred from the CNT towards metal clusters [35]. According to these results, our mats of plasma-treated, metal-decorated MWCNTs behave as p-type semiconductors [36]. Although MWCNTs tend to show a metallic behavior at room temperature due to the fact that band gap decreases when tube diameter increases [37], the semiconducting behavior observed here can be attributed to the presence of oxygen species adsorbed on CNTs [38] promoted by the oxygen plasma treatment. These results reveal

Fig. 1 – TEM images of Pd decorated MWCNTs without oxygen plasma treatment (a), and with oxygen plasma treatment (b), TEM images of Au-decorated MWCNTs without oxygen plasma treatment (c), and with oxygen plasma treatment (d).

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the possibility of designing a benzene selective detector by exploiting the different responses towards benzene obtained by using an array of CNTs decorated with different metal nanoclusters. Such a sensor array would make use of a benzene-insensitive sensor (e.g., an Au-MWCNT sensor is sensitive to the background but not to benzene) and some benzene-sensitive sensors (e.g., Rh-MWCNT, Pd-MWCNT, etc. show different benzene sensitivities). By applying well established pattern recognition techniques often employed with sensor arrays showing overlapping sensitivities, it would
be possible to discriminate the presence of benzene in a gaseous background [39].

Benzene detection is performed at room temperature and the detection limit is well below 50 ppb. The $t_{90}$ response time is about 60 s for 500 ppb of benzene. Although some sensors are subject to baseline drift, the sensing platform is reversible because sensors tend to regain their baseline resistance after removing the pollutant gas and heating at 150°C. This is especially true for Rh-MWCNT sensors, which show excellent baseline recovery (see Fig. 5). Although baseline drift is often experienced with CNT based chemo-resistive sensors [40], their effects can be minimized in a benzene detector by employing simple baseline correction techniques [41].

The effect of the amount of metal nanoparticles grafted to the MWCNT surface on benzene sensitivity is under investigation. Preliminary results show that a 4% increase in the content of Rh nanoparticles decorating CNT sidewalls leads to an increase in benzene response by a factor of 2.5. This result indicates that the second mechanism of detection considered (i.e. benzene adsorption onto metal nanoparticles results in charge transfer between particles and CNTs [12]) could explain the response observed. Further work is needed to optimize the amount of nanoparticles because if metal content was increased until the complete wetting of MWCNTs, this would decrease sensitivity.

4. Conclusions

A miniaturized integrated gas sensor array employing hybrid nanomaterials consisting of metal nanoclusters (Rh, Pd, Ni or Au) decorating MWCNTs has been demonstrated. In contrast to the lack of benzene sensitivity for bare and Au-decorated carbon nanotubes, Rh, Pd or Ni decorated MWCNTs show room temperature benzene sensing capability. When combined in a microsensor array, the use of benzene-sensitive and benzene-insensitive metal-decorated MWCNTs can provide selective detection of benzene at trace levels (ppb concentration). The sensing performance of the hybrid nanomaterials could be mainly attributed to the different effectiveness of electron transfer between different metal nanoclusters and MWCNTs, to specific reactivities of metal cluster surfaces and, finally, to an increase in the specific surface area of our hybrid nanomaterials. The plasma treatment enables the cleaning, activation, functionalization and metal decoration of CNTs, which offers enormous flexibility for tuning the sensitivity of individual sensing elements. The methods employed for fabricating the hybrid nanomaterials and the integrated sensor arrays are simple and compatible with Microsystems technology. Additionally, plasma treatments are greener than conventional wet chemistry routes employed in CNT functionalization and decoration. The former
can be run at atmospheric pressure, which facilitates scaling up the process for mass production. Therefore, this new platform will pave the way for the development of innovative portable/wearable gas sensing applications.

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