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Selective detection of benzene traces at room temperature using metal decorated carbon nanotubes

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Abstract

Hybrid materials consisting of oxygen plasma treated multiwalled carbon nanotubes (MWCNTs) decorated with four different metal nanoparticles can be tailored for the recognition of benzene vapors with high sensitivity and selectivity. The plasma treatment enables cleaning, activating, functionalizing and metal decorating carbon nanotubes in a single step. Metal nanoparticles transfer significant amount of charge upon adsorption of a target molecule, so as to affect electron transport in the nanotube. 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 (i.e., detection limit below 50 ppb

Keywords: multiwall carbon nanotube; oxygen plasma treatment; metal decoration; metal nanoparticles; benzene sensor

1. Introduction

Long term exposure to relatively low concentrations of benzene over months or years leads to severe toxic effects [1-5]. Permissible exposure limits to benzene have been lowered from 10 ppm to 100 ppb in the last 10 years [6]. Occupational exposure to benzene occurs, for example, in the petrochemical industry, petrol stations, motor vehicle repair or roadside works among others [1-3].

The industry standard for the detection of benzene at trace levels implies pumped sampling into a photo ionization detector (PID), which is not selective for benzene and gives a total reading for volatile organic compounds. Selectivity is obtained using disposable filter tubes, but these are single use and expensive. An effective and accurate monitoring of benzene needs the use of simple and affordable sensing systems. Two paramount features of such sensing systems should be their sensitivity, since the concentration of benzene must be detected in

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the ppb range [6], and their selectivity. Nowadays, a very sensitive, selective and affordable benzene detector that can be used in industrial and transport environments is not yet available.

Different studies have shown the excellent potential of carbon nanotubes (CNT) as sensitive material for detecting toxic gases [7, 8]. However, *first principles* calculations have shown that the electronic properties of CNTs remain almost unchanged upon benzene adsorption [9]. 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 in an example of noncovalent functionalization of CNTs [9]. 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 sp^2-like systems. Therefore, detecting benzene using carbon nanotubes is not straightforward.

A promising way to overcome the difficulties for detecting benzene with CNTs consists of decorating the CNT sidewalls with metal nanoparticles. The key concept behind this approach is to use nano-clusters that donate or accept a significant amount of charge upon adsorption of a target molecule (e.g. benzene), so as to affect electron transport in the nanotube. For example, Pd-coated CNTs become sensitive to H2 [10]. Indeed, electrical conductance in CNTs is ballistic even at room temperature, which enables the rapid detection of electron transport through CNTs. Oxidative treatments affect the DOS and increase the work function of purified MWCNTs (4.3 eV) [11]. The work function of oxygen plasma treated MWCNTs ranges from 4.9 to 5.1 eV. These values are very close to that of metals such as Pt (4.8 eV), Au (4.9 eV),Pd (4.95 eV), Ni (5.04 eV) or Rh (5.0 eV) [12], 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. This paper reports on the selective detection of benzene using metal decorated multiwalled carbon nanotubes.

2. Experimental

The MWCNTs were grown by CVD (Chemical Vapor Deposition) with purity higher than 95%. To decorate these nanotubes with Rh and Ni nanoparticles, two colloid solutions were used. First of all the MWCNTs were cleaned for 15 minutes in 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 and oxygen flows of 30 L/min and 30 mL/min, respectively. Nanotubes, were exposed to the plasma post-discharge for 2 minutes to activate their surface. Then, during 30 seconds, a metallic colloid solution was sprayed onto the MWCNTs. The process of decoration with Au and Pd nanoparticles was as follows. At first MWCNTs 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 or Pd were evaporated on the oxygen plasma treated CNTs. The plasma treatment induces reactive sites where metal atoms are easily trapped acting as nucleation sites for the formation of metal nanoparticles. Fig. 1 shows TEM images of MWCNTs decorated with Pd or Rh nanoparticles.

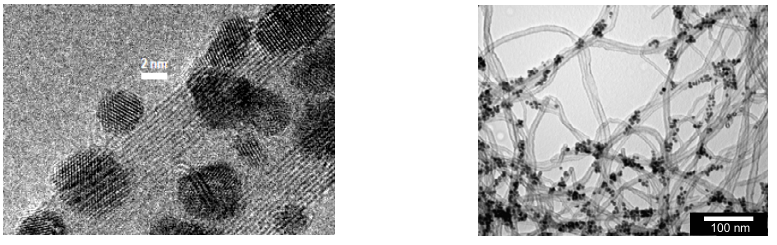

Fig. 1. (a) HR-TEM image of Pd-MWCNT; (b) TEM image of Rh-MWCNT

A micro-hotplate transducer structure (each chip is a 4-element microsensor array), which provided milliwatt power consumption was used [13]. 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. Finally, sensors were annealed at 250ºC for 4 h. in air flow to completely remove the remnant DMF and improve the nanotube-electrode contact.

The gas sensing properties at room temperature of the different active materials produced were tested in the presence of benzene (50, 100, 200 and 500 ppb), NO_2 (50, 100, 500 ppb, 1 ppm), CO (2, 5, 10, 20 ppm) and ethylene (3, 7 15, 30 ppm). Measurements were performed at 15% R.H. (20ºC).

3. Results and discussion

Sensors based on Au-MWCNT hybrids were responsive to NO_2 but not to benzene. NO_2 response is in good agreement with previous experimental results. [1, 2] Ab-initio calculations performed on CNTs decorated with Au indicate that there is no charge transfer between gold clusters and nanotubes upon benzene adsorption. This could explain the lack of response towards benzene for our Au-decorated CNT sensors. On the other hand, Rh, Pd and Ni based hybrids were responsive both to NO_2 and to benzene when operated at room temperature. The sign of sensor response changes when benzene (an electron donor) or NO_2 (an electron acceptor) are detected (see Fig. 2- Fig. 3). Upon gas adsorption, a significant amount of electronic charge is transferred from the metal clusters towards the CNT or from the CNT towards metal clusters depending on the gas. MWCNTs tend to show a metallic behavior because band gap decreases when tube diameter increases, the semiconducting behavior observed here can be attributed to the presence of oxygen species adsorbed on CNTs promoted by the oxygen plasma treatment. These results reveal 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. Benzene detection is performed at room temperature and the detection limit is well below 50 ppb. The t90 response time is about 60 s for 500 ppb of benzene.

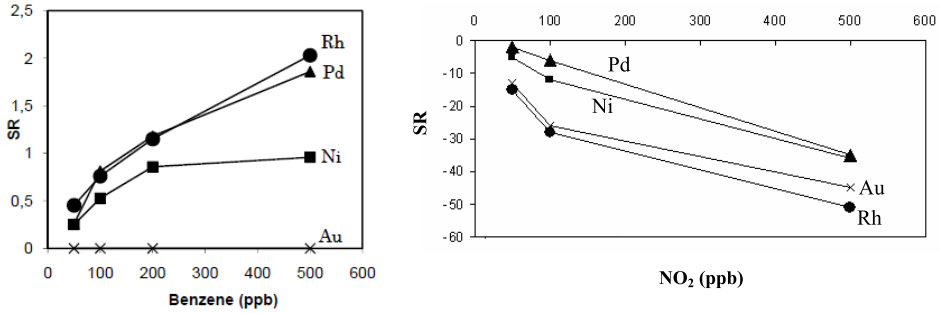

Fig. 2. Gas sensing performance characterization: Response to 50, 100, 200, and 500 ppb of benzene (left) or to 50, 100 and 500 ppb of NO_2 of the sensors based on Rh, Ni, Pd or Au-decoratedMWCNTs. Sensor response (SR) is defined as $10^2 \times$(Rg-Ro)/Ro, where Rg is sensor resistance 20 min after gas injection and Ro is sensor resistance prior to gas injection.

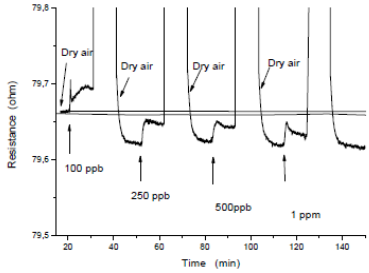

Fig. 3. Response of a sensor based on Pd-MWCNTs to increasing concentrations of benzene

A linear discriminant analysis was performed using the responses of a 4-element sensor array based on Rh, Ni, Pd and Au decorated MWCNTs. LDA was able to correctly discriminate all the species tested (see Fig. 4), which shows that the selective detection of benzene at trace levels (detection limit below 50 ppb) is possible. Within the cluster of a given species, data points are replicate measurements of different concentrations.

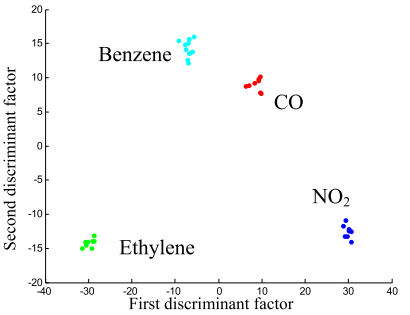

Fig. 4. LDA performed on the responses of a 4-element microsensor array coated with MWCNTs decorated with 4 different metal nanoparticles.

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