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# Novel gas sensors based on carbon nanotube networks

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**Abstract.** Novel resistive gas sensors based on single-walled carbon nanotube (SWNT) networks as the active sensing element have been investigated for gas detection. SWNTs networks were fabricated by airbrushing on alumina substrates. As-produced- and Pd-decorated SWNT materials were used as sensitive layers for the detection of $NO_2$ and $H_2$, respectively. The studied sensors provided good response to $NO_2$ and $H_2$ as well as excellent selectivities to interfering gases.

## 1. Introduction

Since their discovery in 1991 [1], carbon nanotubes (CNTs) have attracted much interest due to their unique structural and physical properties [2]. The breadth of applications for carbon nanotubes is indeed wide ranging: nanoelectronics, quantum wire interconnects, field emission devices, composites, chemical sensors, biosensors, detectors, etc [2-6]. The community is beginning to move beyond the wonderful properties that interested then in CNTs and are beginning to tackle real issues associated with converting a material into a device, a device into a system, and so on [5].

Carbon nanotubes can be considered as appropriate candidates to design high feature gas sensors due to their good conductivity, excellent mechanical properties, chemical stability, and large specific surface [2-8]. At this point, our paper focuses on using CNTs as chemical sensors for gas detection and particularly on designing, developing and optimizing nanotube-based sensors for the detection of $H_2$ and $NO_2$.

 

## 2. Experimental

SWNTs produced by the arc-discharge method [9] and by the HiPco process (Carbon Nanotechnologies, Inc.) [10] were employed in the fabrication of the sensor films. In order to improve the affinity of the samples to hydrogen, arc-produced SWNTs were chemically decorated with Pd nanoparticles [7,11,12]. The tested sensors are described in Table 1.

**Table 1.** Tested sensors

| Sensor | Sensor composition |
|---|---|
| S1 | SWNTs-Pd (1:1) |
| S2 | SWNTs-Pd (1:4) |
| S3 | Super Purified HiPco SWNTs (2% Fe) |
| S4 | HiPco SWNTs (30% Fe) |

Sensor films were fabricated by airbrushing ethanol dispersions of the employed SWNTs on two different alumina substrates (Figure 1):

1- Alumina substrates (Heraeus MSP 769) with heating element (Pt 25) and temperature sensor (Pt 1000) that allow evaluating the sensor performance as a function of temperature from 25 to 200ºC. Sensor dimensions are 6x6 mm.

2- Alumina substrates (Laser Tech Services A/S). Platinum electrical contacts were deposited by RF magnetron sputtering on the sensing element (SWNT network). These sensors were mounted on a 3-pin socket with the electrical contacts. Sensor dimensions are 25x27 mm.

Sensor devices were placed in a stainless steel test cell of 20 $cm^3$ for their characterization by dc electrical measurements. Dry air at constant flow of 200 mL/min was used as carrier gas. The employed concentrations were varied from 0.5 to 1.5% for hydrogen, and from 0.2 to 0.7 ppm for $NO_2$ (exposure time: 15 minutes). Concentrations of interfering gases were 80, 300, and 200 ppm for ammonia, toluene and octane, respectively. The gas mixtures were prepared by means of a mass flow controller into an automated gas line.

Sensor resistances were measured with a digital multimeter (DMM) connected to the personal computer through standard IEEE interface. The measurement system (multimeter and flow controller) was fully automated and controlled with a program developed in Testpoint™.

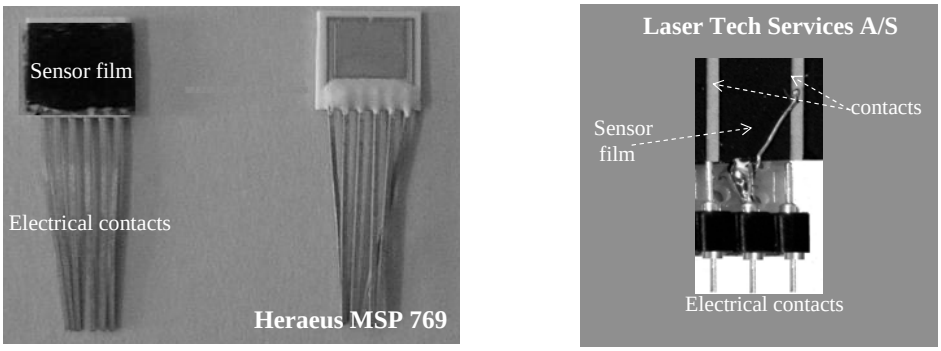


**Figure 1**: Resistive sensor devices.

Figures 2 and 3 show representative atomic force microscopy (AFM) and scanning electron microscope (SEM) images of the SWNT networks. These images indicate that networks consist of thin films of entangled, randomly distributed CNTs.

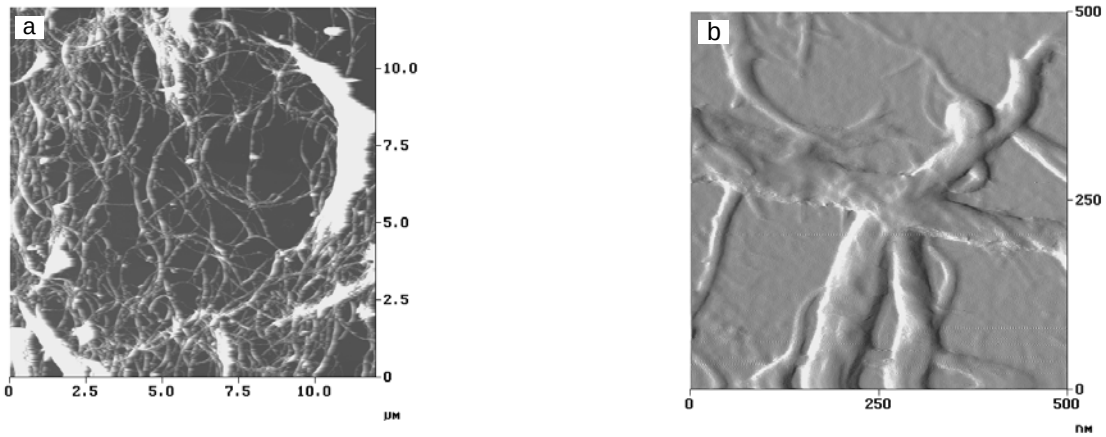


**Figure 2:** AFM images of a network of SWNT bundles (a), and SWNT bundle junctions (b).

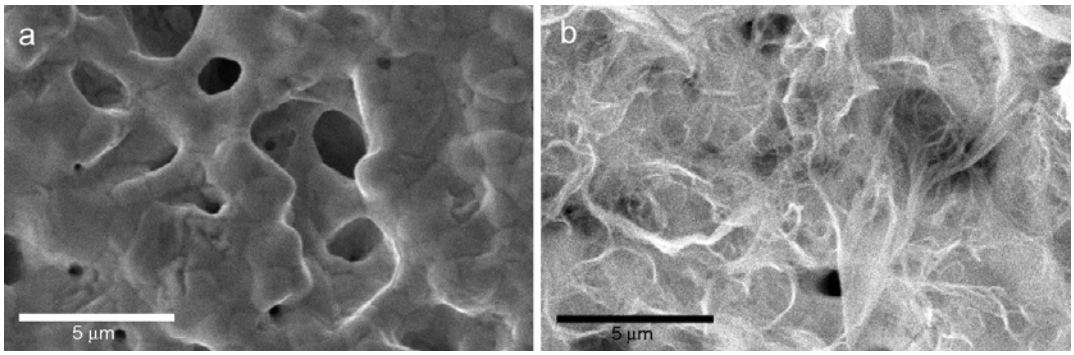


**Figure 3:** SEM micrographs of (a) a Hereaus MSP 769 sensor bare Au electrode, and (b) an airbrushed HiPco SWNT bundle network.

## 3. Results

Pd-decorated SWNT sensors exhibited good sensitivity and selectivity to $H_2$ at room temperature in reversible detection processes. The molecular hydrogen dissociation on the surface of the Pd nanoparticles results in electron transfer from these Pd nanoparticles to the SWNTs and, therefore, to the measured SWNT network resistance increase upon exposure to $H_2$ [7]. Figure 4 shows the response curves of these sensors to different gases (hydrogen, ammonia, toluene and octane). The sensor S2 provides a higher sensitivity than the sensor with a lower Pd content (S1). Sensitivity is defined as:

$S\ (\%) = 100\times(R_g-R_{air})/R_{air}$ , where $R_g$ and $R_{air}$ are the resistance values of the sensor with and without $H_2$ exposure, respectively.

The resistance variation of the studied sensors in air is proportional to the hydrogen concentration (Figure 5), following the exponential equation:

$S\ (\%) = a\ [H_2]^b$, where **S(%)** is the sensitivity, **a** and **b** are constants for each sensor and gas, $[H_2]$ is the gas concentration in ppm.

On the other hand, CNT networks prepared from unpurified, as-produced HiPco SWNTs (S4), and purified HiPco SWNTs (S3) were evaluated as $NO_2$ sensors at temperatures ranging from 25ºC to 200ºC (Figure 6). $NO_2$ concentrations as low as 0.2 ppm were detected in the tested temperature range (Table 2, Figure 6). The electron withdrawing by $NO_2$ molecules adsorbed on the CNT surface leads to the observed CNT network resistance decrease upon $NO_2$ exposure. The sensor response increased when increasing the operation temperature up to 100ºC, and then decreased at higher temperatures

(Table 2). The best sensor performance in terms of response time, sensitivity, and recovery time was achieved at 200ºC. Still, even at this temperature, long recovery times (~2 hours) were measured, therefore suggesting that $NO_2$ chemisorption processes occur during these $NO_2$ detection experiments. These sensors also provided negligible cross sensitivity to interfering gases. It is also worth mentioning that the metal impurity content significantly affect the network resistance and the sensor response (Table 2, Figure 6). Thus, networks of purified HiPco SWNTs (S3) provided higher response to $NO_2$ than as-produced HiPco SWNT networks (S4) (Figure 6). The structural modifications that result of SWNT purification processes (SWNT partial debundling and shortening, and introduction of defects and chemical functional groups) [14] might also affect the CNT-$NO_2$ interaction and, therefore, the sensor response.

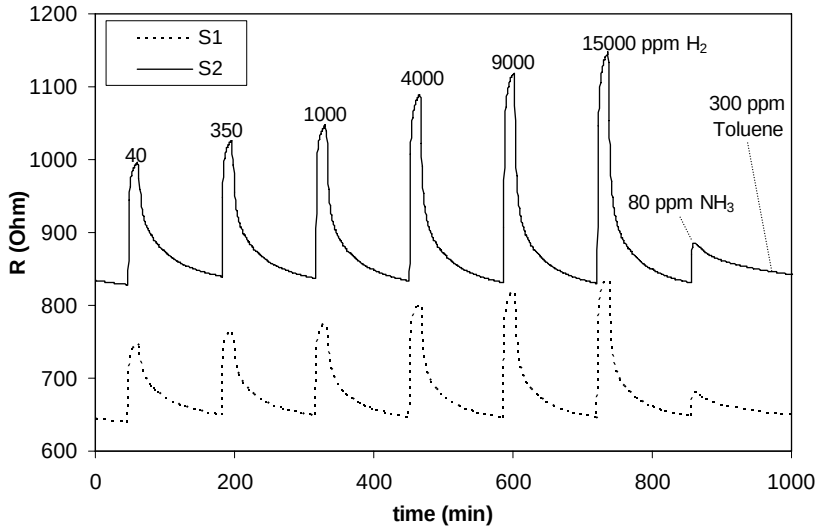


**Figure 4:** Response of the Pd-funcionalizated sensors to different gases at room temperature.

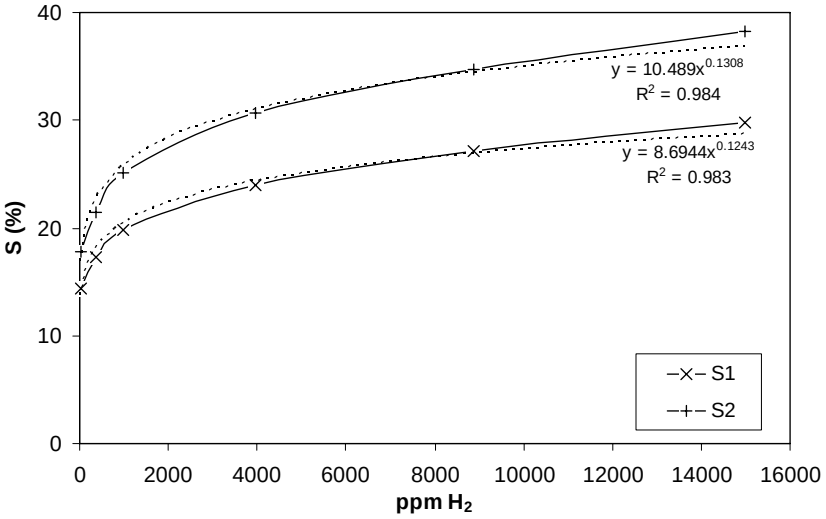


**Figure 5**: Sensitivity of the Pd-funcionalizated sensors to hydrogen at room temperature (black-dotted curves correspond to the calibration curves).

**Table 2.** Sensitivity to a 0.1 ppm $NO_2$ in air of the S3 and S4 sensor

| T (ºC) | S3 | S4 |
|---|---|---|
| 25 | 0.18 | 0.1 |
| 100 | 10.43 | 6.3 |
| 200 | 5.50 | 2.5 |

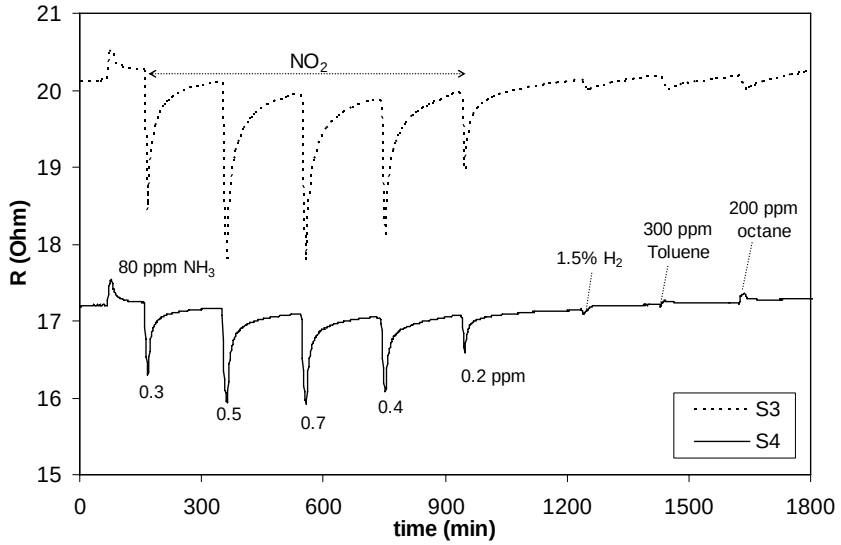


**Figure 6:** S3 and S4 response curves in air atmosphere at 200 ºC.

## 4. Conclusions

The employed Pd-decorated SWNT- and HiPco SWNT networks provided good response to $H_2$ and $NO_2$, respectively, as well as excellent selectivities to the tested interfering gases. The drawback of these CNT-based systems is the slow and incomplete recovery time that may limit their application as gas sensors. Future work will focus on improving this sensor performance and in the design of a sensor array for the simultaneous detection of $H_2$ and $NO_2$ in polluting gas mixtures.

## Acknowledgments

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