

## SENSOR OF NITROGEN DIOXIDE BASED ON SINGLE WALL CARBON NANOTUBES AND MANGANESE-PORPHYRIN

M. POPESCU<sup>a\*</sup>, I. D. SIMANDAN<sup>a</sup>, F. SAVA<sup>a</sup>, A. VELEA<sup>a</sup>,  
E. FAGADAR-COSMA<sup>b</sup>

<sup>a</sup>*National Institute of Materials Physics, 105 bis Atomistilor Str., P.O. Box MG 7,  
077125 Măgurele, Romania*

<sup>b</sup>*Institute of Chemistry Timisoara of Romanian Academy, 24 M. Viteazul Ave,  
300223-Timisoara, Romania*

New sensors based on single wall carbon nanotubes (SWCNTs) and porphyrins have been tested for sensitivity to NO<sub>2</sub> gas. SWCNTs embedded in barium stearate multilayers were deposited with the help of Langmuir-Blodgett technique. It was demonstrated a sensitive effect of the sensor for NO<sub>2</sub> gas. The coverage of the sensor with metalloporphyrin (Mn) leads to strong enhancing of the sensitive effect to NO<sub>2</sub>, besides, the selectivity was preserved both around room temperature and at larger operating temperature (up to 200 °C). No sensitivity to CO and CH<sub>4</sub> was evidenced. The NO<sub>2</sub> sensitivity strongly increased at 100 °C but at high operation temperatures (150-200 °C) a different behaviour is observed, probably due to the structural change of porphyrin or porphyrin-SWCNT interaction. The reversibility of the sensor resistivity is reasonably good at the optimum operating temperature (100 °C).

(Received August 26, 2011; accepted August 26, 2011)

*Keywords:* single wall carbon nanotubes, manganese-porphyrin, nitrogen dioxide, sensor.

### 1. Introduction

Recently, the interest in the air pollutants and their monitoring increased tremendously. Nitrogen oxides, like nitrogen monoxide (NO) and nitrogen dioxide (NO<sub>2</sub>), are typical air pollutants that affect the environment. There are a large demand for smaller and cheaper gas sensors for NO detection in medicine. It is necessary to develop highly sensitive and not so expensive NO<sub>x</sub> gas sensors to detect low concentration of NO and NO<sub>2</sub> gases. Carbon nanotubes are expected to be a new gas sensing material, which exhibits outstanding sensitivity around room temperature, fast response and selectivity [1, 2].

The well known individual SWCNT gas sensor is based on the change of the electrical conductance of SWCNT, during absorption of gas molecules. An increase in the conductivity up to three orders of magnitude was observed within 10 s after exposing the SWCNT to 200 ppm NO<sub>2</sub> at room temperature [3]. Conventional sensors with high sensitivity for NO<sub>2</sub>, based on semiconducting metal oxides, need to operate at temperatures of up to 600 °C. However, individual SWCNT need several hours to release the analyte at room temperature. The heating speeds up the process.

The sensing mechanism of single walled carbon nanotubes (SWCNTs), which is based on the change of electrical conductance, can be explained by the fact that conductivity of the SWCNTs, which absorb oxides, is modified by the energy transfer between the SWCNT surface and the adsorbed gas molecules [4].

SWNTs functionalized, e.g. with poly(ethyleneimine), have been also used in formulation of NO<sub>2</sub> sensors [5, 6]. The NO was firstly oxidized to NO<sub>2</sub>, which was then passed

---

\* Corresponding author: mpopescu@infim.ro,

over a network of SWNTs in a field-effect transistor device, inducing changes in the conductance of the tubes.

In this paper we report the results obtained in  $\text{NO}_2$  gas detection using a sensor structure based on barium stearate films with carbon nanotubes, deposited on a ceramic ( $\text{Al}_2\text{O}_3$ ) body provided with platinum electrodes, finally covered by a manganese-porphyrin film.

## 2. Materials and methods

The multilayer films based on barium stearate molecules have been obtained from stearate powder p.a. (Sigma-Aldrich) dissolved in benzene. Carbon nanotubes have been purchased from Alfa-Aesar. The nanotubes are  $\sim 2$  micrometer long and  $\sim 1.4$  nm diameters. From the Raman spectra we have been deduced the rough composition of nanotubes in conducting and non-conducting components. The fraction of the conducting nanotubes is around 25% mol in the mixture of conducting + non-conducting nanotubes.

The synthesis of (5, 10, 15, 20-tetraphenyl) porphinato manganese (III) chloride ( $\text{MnTPP}$ )Cl was done by classical reaction of metallation using the porphyrin free ligand in ethanol at porphyrin manganese ratio of 1:20 – 1:30 and previously reported [7]. Porphyrin free ligand, tetraphenyl-porphyrin, was obtained by Adler method [8] and fully characterized [9].

The apparatus used for the preparation of the Langmuir-Blodgett multilayers is a double trough KSV 5000-3 system.

The sensitivity to gases has been tested in a Gas Mixing Station, provided with controlled water vapour in synthetic air,  $\text{CO}$ ,  $\text{CH}_4$  and  $\text{NO}_2$ .

## 3. Results

The sensing response to different gases of the new complex material with barium stearate multilayers, SWCNTs and covered by a disordered layer of manganese porphyrin is presented in the figures 1 a, b, c.

Fig. 1a shows the gas sensing properties of our samples at  $50^\circ\text{C}$ , a temperature near to the room temperature. The sensitivity ( $S$ ) at 2.5 ppm  $\text{NO}_2$  in the case of the sensor without Mn-porphyrin is  $S = 6\%$  and with Mn-porphyrin  $S = 26\%$ . A little bit sensitivity to humidity of the atmosphere, relative humidity (RH) 50 %, is exhibited by the sensor with SWCNTs ( $S = 1.5\%$ ), but without porphyrin. The material is completely insensitive to  $\text{CO}$  and  $\text{CH}_4$  toxic gases.

At  $100^\circ\text{C}$  testing temperature, the sensitivity to air humidity is smaller. In fact it seems that a significant part of water is eliminated from the sensor. In the case of the sensor without Mn-porphyrin the sensitivity at 2.5 ppm  $\text{NO}_2$  is  $S = 4\%$ . When Mn-porphyrin is applied on the body sensor, the sensitivity of the sensor even for a concentration as small as 2.5 ppm  $\text{NO}_2$  is strongly amplified (Fig. 1b). The sensitivity ( $S$ ) is 38 %.

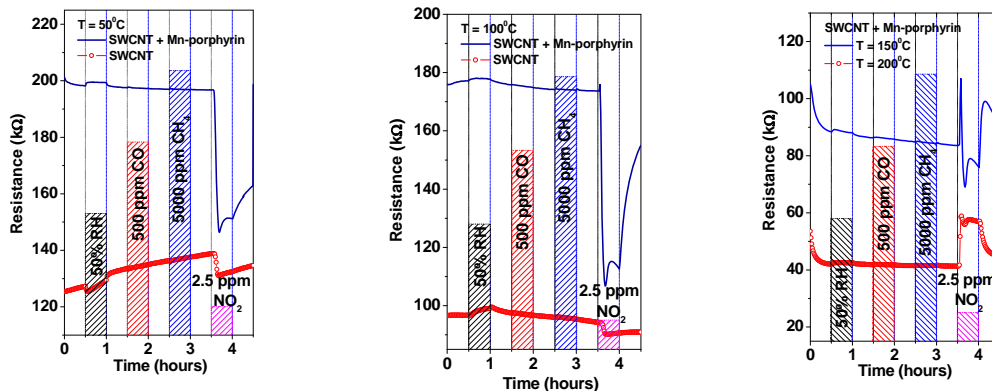


Fig. 1. Variation of the sensors resistance measured in different environments at different temperatures:

- SWCNT and SWCNT with Mn-porphyrin at  $50^\circ\text{C}$ ;
- SWCNT and SWCNT with Mn-porphyrin at  $100^\circ\text{C}$ .
- SWCNT with Mn-porphyrin at  $150^\circ\text{C}$  and  $200^\circ\text{C}$ .

The response of the sensor to NO<sub>2</sub> is maximum at 11 min after gas injection at T=50 °C and at 9 min after gas injection at 100 °C.

For the case of the sensor with Mn-porphyrin, operated at 150 °C and 200 °C (Fig. 1c), the resistive change against NO<sub>2</sub> is quite different. At 150 °C, in the first 5 minutes of gas action the resistivity increases as a narrow peak (width of the peak: 10 minutes), then a decrease of resistivity, corresponding to a maximum sensitivity of S ~ 10 % occurs. At 200 °C a completely different trend appears: during operation the resistivity increases by ~ 30 %.

One can observe that the operation at various temperatures decreases the background resistivity of the sensor with Mn-porphyrin (Fig. 2).

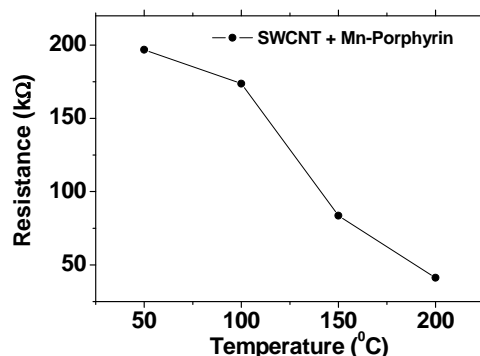


Fig. 2. The sensor resistivity as a function of temperature (50, 100, 150, 200 °C)

#### 4. Discussion

The highly selective sensor for NO<sub>2</sub> gas exhibits interesting properties. A high sensitivity seems to be provided by the porphyrin embedded in it. Regarding the sensing, a delayed detection of the NO<sub>2</sub> gas at 2.5 ppm seems to be a shortcoming in some cases. The back running of the sensor depends on the operating temperature. For 50 °C, after stopping the NO<sub>2</sub> gas the sensor reaches the background line slowly, while for 100 °C operating temperature a more rapid evolution toward the basis line occurs, after the gas is purged in the chamber.

The porphyrin layer seems to be very important for sensor sensitivity. The optimum temperature of sensing seems to be situated around 100 °C. The sensor is totally insensitive to water vapour, carbon oxide and methane, while the sensitivity to NO<sub>2</sub> is high.

The macrocyclic structure of the Mn-porphyrin is given in Fig. 3. The possible configurations of covalent functionalization of SWCNTs with manganese-porphyrin are given in Fig. 4.

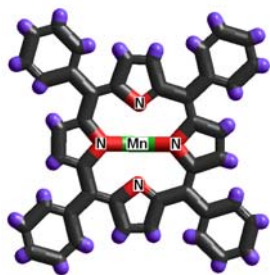


Fig. 3. The structure of manganese-porphyrin (Mn-N<sub>4</sub>C<sub>44</sub>H<sub>28</sub>). Four pyrrole groups are visible. Position of the manganese is shown.

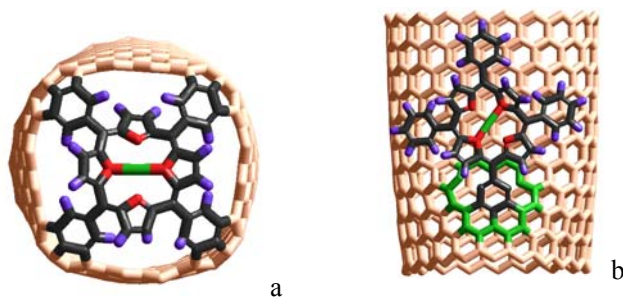


Fig. 4. Covalent functionalization of SWCNT with manganese porphyrin:  
 a. positioned at the end of a small diameter nanotube,  
 b. positioned on a vacancy in the wall

Macrocyclic molecules with extended aromaticity, such as porphyrin, are very important for gas sensing. When the porphyrin thin film is exposed to electron acceptor gases such as NO<sub>2</sub> and Cl<sub>2</sub> the charge transfer interaction between the gas molecules and porphyrin molecules takes place because the macrocycle molecules are usually considered to be electron donors or p-type semiconductors. The interaction leads to a positive charge produced and delocalized over the macrocyclic molecules, which causes the increase of the conductivity. In the presence of the carbon nanotubes, the released charge determines a strong drop of resistivity of the sensor. At high temperature (200 °C) the interaction of NO<sub>2</sub> with nanotubes and Mn-porphyrin is significantly amplified and the effect of gases on the sensor is an increase of resistivity. The porphyrin molecules can be anchored in two positions: one position is on the surface of the nanotube. The anchorage is amplified by the defects in the nanotube wall. The other position corresponds to the ends of the nanotube. In our case small diameter nanotubes fits well the size of porphyrin molecule with strong bonding (see the model from Fig. 4b). The distortion of the Mn-porphyrin molecules enhances the delocalization of the charge carriers.

## 5. Conclusions

The SWCNTs material is sensitive to NO<sub>2</sub> and totally insensitive to CO and CH<sub>4</sub> at all the operation temperatures (50 ÷ 200 °C). The use of the porphyrin coating on the complex sensor based on a background of barium stearate multilayers and carbon nanotube embedded in them, lead to the amplification of sensing effect to NO<sub>2</sub> while the selectivity against other toxic gases remains excellent.

The complex sensor with carbon nanotubes and porphyrin is a stable sensor with high sensitivity and selectivity, of interest in large scale applications. Because the structural order in the nanotubes and porphyrin molecules is not very important to the sensing effect, the sensor is simple to prepare and its cost is very low. The optimum operating temperature, which ensures a good reversibility, seems to be 100 °C.

## Acknowledgements

The authors acknowledge Dr. Adelina Stănoiu and Dr. Cristian Simion for sensor measurements.

This work was supported by CNCSIS – UEFISCDI (Romania), project number PNII - IDEI 1356 / 2009 (Contract IDEI No. 709 / 2009).

The authors thank to Dr. Nicolae Bârsan from Institute of Physical Chemistry, University of Tuebingen, Germany, for providing sensor bodies.

## References

- [1] M. Trojanovicz, Trends Anal. Chem. Vol. **25**(5), 480 (2006).
- [2] T. Ueda, M. M. H. Bhuiyan, H. Norimatsu, S. Katsuki, T. Ikegami, and F. Mitsugi, Physica E. **40**, 2272 (2008)
- [3] J. Kong, N. R. Franklin, C. Zhou, M. G. Chapline, S. Peng, K. Cho, and H. Dai, Science, **287**, 622 (2000).
- [4] S. Peng, K. Cho, P. Qi, and H. Dai, Chem. Phys. Lett. **387**, 271 (2004).
- [5] Q. F. Pengfei, O. Vermesh, M. Grecu, Ali Javey, Q. Wang, and H. Dai, Nano. Lett., **3**, 347 (2003).
- [6] O. Kuzmych, B. L. Allen, and A. Star, Nanotechnology, **18**, 375502 (2007).
- [7] E. Fagadar-Cosma, M. C. Mirica, I. Balcu, C. Bucovicean, C. Cretu, I. Armeanu, and Gh. Fagadar-Cosma, Molecules, **14**, 1370 (2009).
- [8] A. D. Adler, F. R. Longo, J. D. Finarelli, J. Goldmacher, J. Assour, and L. Korsakoff, J. Organic Chem. **32**, 476 (1967).
- [9] D. Vlascici, E. Fagadar-Cosma, O. Spiridon-Bizerea, A. Pascariu, and A. Chiriac: Rev. Chim. Bucharest, **56**, 224 (2005).