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Environmental monitoring of low-ppb ammonia concentrations based on single-wall carbon nanotube chemiresistor gas sensors: detection limits, response dynamics, and moisture effects.

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Abstract

We present single-wall carbon nanotube (SWCNT) chemiresistor gas sensor (CGS) operating at room temperature, displaying an enhanced sensitivity to NH_3. Ammonia concentrations in the full range of the average $[NH_3]$ in a urban environment have been measured, and a detection limit of 3 ppb is demonstrated, which is well below the sensitivities so far reported for non-functionalized SWCNTs operating at room temperature. Different materials were tested as substrates, including cheap plastic flexible substrates. In addition to a careful preparation of the SWCNT layers, the low-ppb limit is also attained by revealing and properly tracking a fast dynamics during the desorption process. On the basis of these results a model of the CGS response vs time is proposed. When functionalized with indium-tin oxide nanoparticles, a sensitivity increase is detected, along with a remarkable selectivity towards moisture.

Keywords: carbon nanotubes; gas sensors; detection limit; response dynamics; ammonia; moisture selectivity.

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1. Introduction

Crucial features in gas sensors for environmental monitoring are the sensitivity in the low ppb range and the ability to discriminate variations of a certain polluting gas from other interfering gases. Monitoring of ammonia concentrations is mandatory to reduce the hazard for human health and vegetation determined by the widespread use of ammonia and its derivatives as agricultural nitrogen fertilizers, which is known to cause severe environmental problems [1]. In spite of this urgency, the detection of ammonia concentrations in urban areas with CGS has been so far widely overlooked, since the average levels are usually low, i.e. in the 20-30 ppb range while the CGSs are usually tested by exposure to ammonia in the ppm range.

Carbon nanotubes (CNT) can provide a high physical and chemical stability and a wide range of possible operational features that make them a unique system for gas detection. Several CNT-based architectures have been proposed [2] and ppt sensitivity of pristine CNTs to ammonia has been demonstrated in inert Ar atmosphere under UV irradiation [3]. Though results so far reported are encouraging, the use of inert atmosphere represents a limitation for environmental monitoring. To overcome this limitation, the present study is carried out in the lab environment, which is much closer to the final destination of the CNTs sensors. Finally, the control over interfering effects is also mandatory when monitoring the $[NH_3]$ in the environment. In particular, the presence of humidity may dramatically alter the working conditions of gas sensors. In this study, we present several strategies to increase the sensitivity to $[NH_3]$ and to lower the detection limit (DL) of low-cost SWCNT-based gas sensors operating at room temperature. Ammonia concentrations in air in the low ppb range have been measured, and a 3 ppb DL is achieved. The time dependence of the CGS response is accurately modeled by properly considering the different time-scales of the detection process. Furthermore, when functionalized with indium-tin oxide (ITO) nanoparticles, a sensitivity increase is detected, along with a remarkable selectivity towards moisture, providing a way to tailor the sensor response with respect to humidity effects expected in outdoor environmental monitoring.

2. Experimental

The CNT-based chemical resistor is prepared by drop casting 4 µl of a single-wall carbon nanotubes (SWCNT) dispersion in a solution containing water, sodium hydroxide and sodium lauryl sulphate (CarboLex Inc.) onto a ceramic substrate with interdigitated Pt electrodes. Gas exposure was carried out either in a sensor test chamber or in the lab. The testing chamber was selected mainly for the sensor calibration, while most of the $[NH_3]$ measurements were carried out in the laboratory atmosphere, which provides an environment closer to the final destination of the sensors. In the testing chamber the gas mixing system is equipped with three mass-flow controllers (MFC): two low-flow MFC for controlling the analyte flow rate (47.1±1.2 ppm for NH_3, diluted in dry air) and a high-flow MFC for further dilution in dry air.

For the electrical measurement, a constant voltage (V_c = 5V) is applied across a load resistor R_L which is connected in series with the CGS. By monitoring the voltage across the sensor (V_{out}), we can obtain the value of the resistance R_s, using the formula $R_s = V_{out} R_L / (V_c - V_{out})$. With this set-up the variation R_S/R_0 of sample resistance R_S upon gas exposure with respect to the baseline resistance value R_0 was evaluated. Details of the data acquisition system can be retrieved from Ref.[4].

Finally gas sensors based on SWCNT thin layers deposited on flexible plastic substrates and functionalized with ITO nanoparticles (IoLiTec, Gmbh) have been tested and compared to response of the pristine SWCNT layers.

3. Results and discussion

We explored several strategies in order to enhance the sensitivity of pristine SWCNTs to ammonia gas. They consist in a careful preparation of the sample, starting from a solution of pure water, NaOH, SDS, in which SWCNTs (CarboLex Inc.) are dispersed and depositing it on ceramic substrates with interdigitated Pt electrodes, following two different methods: drop-casting and sonication, dielectrophoresis method. By depositing the CNT solution only by drop-casting, without sonication process or dielectrophoresis method, the sensor response to ammonia is almost negligible (Fig.1-b). In turn the sample prepared by dielectrophoresis show a clear response to ammonia with a corresponding $\Delta R/R_0$=0.015 (Fig.1-a).
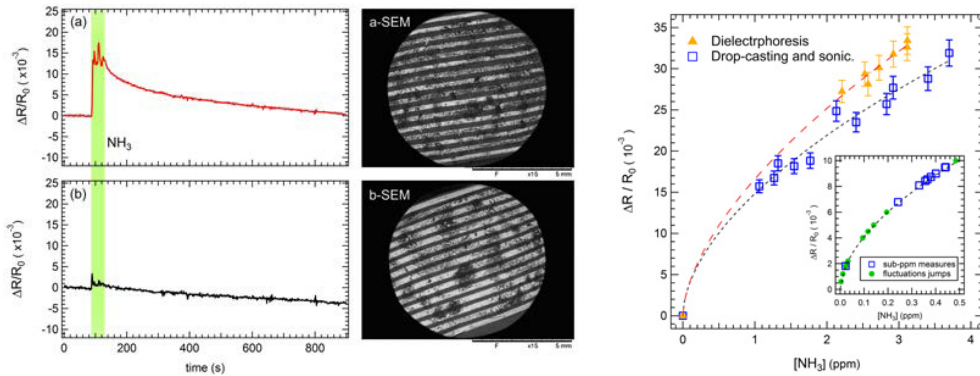
Fig. 1. Example of response to the same concentration of ammonia gas of SWCNT sample prepared by dielectrophoresis (a) and by drop-casting not sonicated (b) on alumina substrate with interdigitated Pt electrodes with the corresponding SEM images. Calibration curve of the sensors prepared by drop-casting and sonication and by dielectrophoresis (c). Inset: sub-ppm measurements.

Fig. 1-c summarizes the results obtained with the CNT-based ammonia gas sensors prepared by the two methods previously described. The response to ammonia gas of the two samples is almost the same, with a slightly better performance for the sample prepared by dielectrophoresis. By considering the noise value and the calibration curve fit parameters [4] we can obtain the detection limit (DL) that we define as the analyte concentration value corresponding to a 5σ noise fluctuation, a more restrictive than that proposed in Ref.[3], where a 3σ noise level was considered. The calibration data have been fitted by a power function $\Delta R/R = A([NH_3])^p$. The results are summarized in Table 1, where R_0 is the baseline resistance, σ is the standard deviation of R_0, A and p are fit parameters of the calibration curve. For both samples a detection limit of 3 ppb is achieved.

Table 1. Baseline resistivity (R_0), noise level, fitting parameters and detection limits of the samples prepared by drop-casting and dielectrophoresis.

Sample	R_0 (Ω)	σ (Ω)	A (10^{-3})	P	DL (ppb)
Drop-casting and sonic.	300	0.035	15±1	0.56±0.05	3
Dielectrophoresis	360	0.035	17±1	0.60±0.07	3

By comparing the sensor response to ammonia gas in the testing chamber and in laboratory air, we observed that the fluctuations during the exposure disappear when the measurement is carried out in a sealed testing gas chamber (Fig.3, left panel). These fluctuations are well above the baseline noise level and can be regarded as a signature of $[NH_3]$ fluctuations in the ambient air. From similar fluctuations the $[NH_3]$ in the ppb range reported in the inset of Fig. 1-c have been evaluated. A model is developed to interpret the resistance R(t) variation during NH_3 exposure, based on the convolution of two signals f(t) (a double-exponential function) and g(t) (combination of a step function with the first derivative of the concentration), according to the formula:

$$R(t) = \int f(\tau)\, g(t - \tau)\, d\tau \tag{1}$$

The results are shown in Fig.3, right panel. The R(t) increase upon exposure is well fitted, while a discrepancy can be found during the recovery, which might be ascribed to irreversible chemical reactions between NH_3 and CNT occurring at RT (see, e.g., Ref.[5]).

In addition, to find strategies to enhance the sensitivity in order to detect very low concentrations (in the ppb range) of NH_3, a crucial feature is the capability to discriminate the response to ammonia from the response to other interfering gases, among all water vapor, which is present in large quantities (5.000 – 20.000 ppm) in real world conditions. Chemiresistor gas sensors prepared with SWCNTs functionalized with ITO nanoparticles onto flexible

plastic substrates show high sensitivity to ammonia and an inverse response to water vapor with respect to unfunctionalized SWCNT-based sensors (Fig.4). This fact discloses the possibility to monitor ammonia gas in the environment and to control selectively humidity interfering effects.
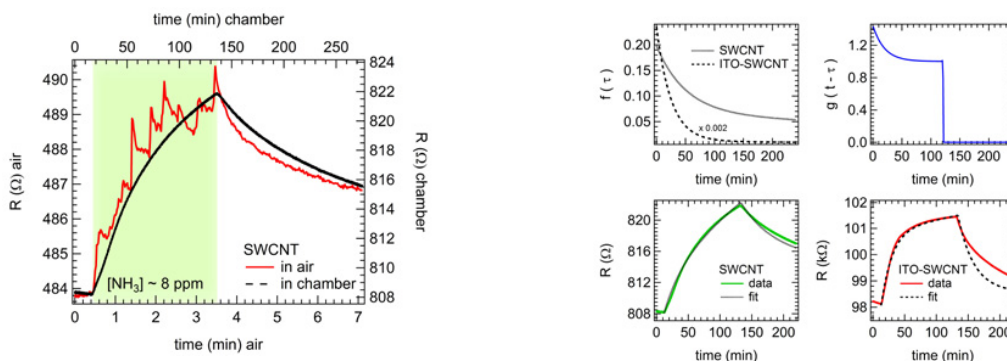

Fig. 3. Left panel: comparison of sensor response to ammonia gas in air lab and in gas testing chamber; Right panel: modeling of the CNT sensor response, seen as the convolution of the two functions f and g.
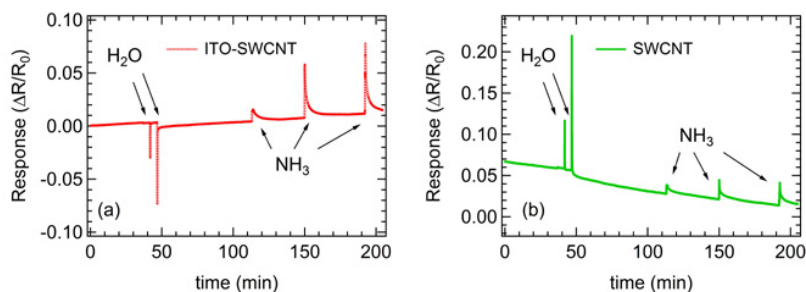

Fig. 4. Response to water vapor and ammonia gas of ITO-SWCNT (a) and pristine SWCNT (b) onto plastic substrates.

4. Conclusions

CNT-based gas sensors allowed us to measure NH_3 concentrations in air as low as 20 ppb, achieving a 3 ppb DL. And the time dependence of the CGS response has been modeled. Furthermore, when functionalized with indium-tin oxide (ITO) nanoparticles, a sensitivity increase has been detected, along with a remarkable selectivity towards moisture, which can provide a way to tailor the sensor response with respect to humidity effects expected in outdoor environmental monitoring.

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