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High sensitivity, moisture selective, ammonia gas sensors based on single-walled carbon nanotubes functionalized with indium tin oxide nanoparticles

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ABSTRACT

An effective monitoring of the air quality in an urban environment requires the capability to measure polluting gas concentrations in the low-ppb range, a limit so far virtually neglected in most of the novel carbon nanotube (CNT)-based sensors, as they are usually tested against pollutant concentrations in the ppm range. We present low-cost gas sensors based on single-walled CNT (SWCNT) layers prepared on plastic substrates and operating at room temperature, displaying a high sensitivity to [NH_3]. Once combined with the low noise, the high sensitivity allowed us to reach an ammonia detection limit of 13 ppb. This matches the requirements for ammonia monitoring in the environment, disclosing the possibility to access the ppt detection limit. Furthermore, a blend of SWCNT bundle layers with indium-tin oxide (ITO) nanoparticles resulted in a threefold sensitivity increase with respect to pristine CNT for concentrations above 200 ppb. Finally, the peculiar response of the ITO-SWCNT blend to water vapor provides a way to tailor the sensor selectivity with respect to the relevant interfering effects of humidity expected in outdoor environmental monitoring.

1. Introduction

Novel perspectives in the development of chemiresistor gas sensors (CGS) are determined by the capability to meet the requirements of environmental monitoring, in particular (i) the sensitivity in the low ppb range and (ii) the capability to monitor the polluting molecules on a background of water molecules brought about by the humidity conditions. Among the chemiresistor gas sensors, devices based on nanostructured materials have become one of the most explored alternatives to thin films, due to the high surface/volume ratio and to the manifold of morphologies that are expected to offer several alternatives for the improvement of sensitivity and selectivity. As nanostructured materials, carbon nanotubes (CNT) play a central role in the development of novel devices aimed to monitor the environmental conditions. So far, CNTs have been tested against many polluting gases, as they are known to interact with many gas molecules that, depending on their reducing or oxidizing properties, may inject or extract electrons from the CNTs, resulting in a

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detectable electrical signal. Indeed, a large body of studies reports the response of CNTs to many gases, in particular to ammonia and nitrogen dioxide [1], as prototypes of reducing and oxidizing gas, respectively. Many CNT-based gas sensors devices have been tested so far, showing that CNTs are a promising class of materials for the development of gas sensors [2–13].

In gas sensing devices, CNTs can provide a high physical and chemical stability, an efficient transport of charge to the electrodes and a wide range of possible architectures [14] and operational features, that make them a unique system for gas detection.

In this framework we investigate the possibility to use low-cost CNT-based gas sensors prepared on plastic substrates to monitor the presence of ammonia in the environment, where NH_3 concentrations ([NH_3]) in the low-ppb range are expected. A systematic monitoring of ammonia concentrations [15] 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 determine severe environmental problems, as the acidification of soils and the formation of fine particulate matter in the atmosphere [16–23].

In spite of this urgency, the detection of ammonia atmospheric concentrations in urban areas has been so far widely overlooked, since its average levels are usually low, i.e. in the 20–30 ppb range [24], while novel ammonia CGS are not usually tested at these low levels.

So far, many CNT-based architectures have been proposed (from FET to CNT bundles, and from aligned CNT layers to CNTs decorated or functionalized with single molecules and nanoparticles [4,11,12,25]), following a systematic investigation in testing chambers. However, little attention has been paid to the capability of these sensors to measure sub-ppm [NH_3] in air. In fact, ppt sensitivity of pristine CNTs to ammonia has been demonstrated, though in inert Ar atmosphere under UV irradiation [26], and a detection limit (DL) of 50 ppb has been achieved for ammonia diluted in Ar using CNTs functionalized with polyaniline [27]. Though results so far reported 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, i.e. not inside a testing chamber, which is much closer to the final destination of the CNT sensors.

Finally, the control over interfering effects is also mandatory when monitoring the [NH_3] in the environment. In particular, the presence of humidity can dramatically alter the working conditions of the gas sensors, biasing the expected signal at a determinate ammonia concentration [24].

In this study, we present the results obtained from low-cost gas sensors, based on single walled carbon nanotubes (SWCNT) layers deposited on plastic substrates and operating at room temperature. Ammonia concentrations in air as low as 25 ppb have been measured and a detection limit of 13 ppb is demonstrated, which fully meets the range of the average NH_3 concentration in urban environments. The present results are well below the sensitivities so far reported for CGS based on pristine CNT layers deposited on plastic substrates, operating in air at room temperature [25]. For ammonia concentrations above 200 ppb a 3-fold sensitivity increase is obtained through functionalization with indium-tin oxide (ITO) nanoparticles. Furthermore, the peculiar response of ITO-SWCNT blend to water provides a way to tailor the sensor selectivity with respect to humidity effects expected in outdoor environmental monitoring. A discussion of sensing mechanisms is provided, with focus on hole compensation effects introduced by high concentrations of water molecules. Finally, the use of cheap flexible plastic substrates discloses possible production for ink-jet printing process, or application in flexible integrated circuits [28,29].

2. Experimental

2.1. *Device preparation and electrical measurements*

The pristine sample (SWCNT) was prepared starting from a SWCNTs dispersed in a solution containing water, sodium hydroxide and sodium lauryl sulfate (CarboLex Inc.) and deposited by drop casting onto a plastic substrate. The functionalized sample (ITO-SWCNT) was prepared by adding 5% wt Indium Tin Oxide nanoparticles (average diameter < 50 nm, purity grade 99.99%, IoLiTec Gmbh) to the CNT dispersion prior to the deposition on the plastic substrate. The CNT + ITO nanoparticles mixture was sonicated for 1 h and then deposited on the flexible plastic substrate. In both cases, the sample is a rectangle with a sensitive area of about 75 mm^2. Two strips of Ag paste were deposited on the sides of the sample. An image of the samples is shown in Fig. 1(a and b).

All sensors, including humidity and temperature sensors, were mounted on a specifically designed circuit board connected to a personal computer through a National Instrument PCIe-6251 data acquisition board. 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

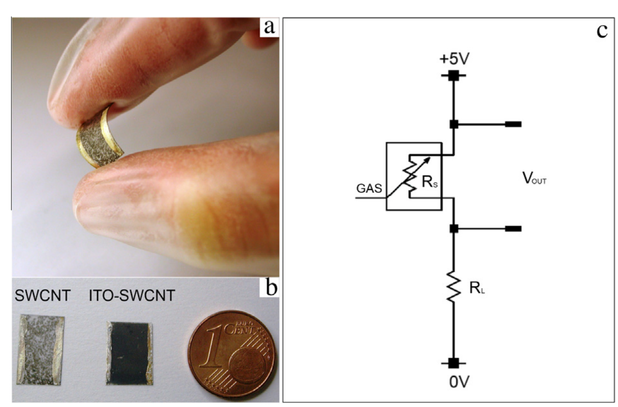

Fig. 1 – (a and b) CGS based on single-wall carbon nanotubes onto a flexible plastic substrate. (c) Scheme of the circuit for the electrical measurements: a constant voltage V_C = 5V is applied across the CGS, connected in series with a load resistor R_L = 33 kΩ. By monitoring the voltage V_{out} across the sensor, its resistance is measured. (A color version of this figure can be viewed online.)