

Chemically Functionalized Single-Walled Carbon Nanotubes as Ammonia Sensors[†]

E. Bekyarova,[‡] M. Davis,[§] T. Burch,[§] M. E. Itkis,[‡] B. Zhao,[‡] S. Sunshine,[§] and R. C. Haddon^{*,||}

Carbon Solutions Inc., Riverside, CA; Smiths Detection, Pasadena, California, and Center for Nanoscale Science and Engineering, Departments of Chemistry and Chemical & Environmental Engineering, University of California, Riverside, California 92521-0403

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This study demonstrates a novel approach toward development of advanced chemical sensors based on chemically functionalized single-walled carbon nanotubes (SWNTs). SWNTs with covalently attached poly(*m*-aminobenzene sulfonic acid), SWNT-PABS, have shown improved sensor performance for detection of NH₃. Compared to purified SWNTs, devices fabricated with SWNT-PABS have shown more than 2 times higher change of resistance upon exposure to NH₃. Importantly, the SWNT-PABS sensors rapidly recover their resistance when NH₃ is replaced with nitrogen. Exposure to NH₃ induces significant changes in the electronic structure of SWNT-PABS, which allow detection of NH₃ at concentrations as low as 5 ppm. Thin film deposited between interdigitated electrodes was explored as a device configuration for development of gas sensors.

Introduction

Gas sensors based on nanowires and nanotubes often rely on monitoring the direct change in their electrical properties in response to the interaction with analyte molecules.^{1–4} Single-walled carbon nanotubes (SWNTs) with their one-dimensional (1-D) structure are the ideal molecular wire with highly robust chemical structure, which provides the components necessary for large-scale integration into advanced sensor devices. Because of their delocalized electronic structure, SWNTs are very sensitive to dopants, and the semiconductors are readily doped with oxidants, even molecular oxygen.^{5–7} Exposure to NH₃ and NO₂ causes a dramatic change in the electrical resistance of SWNTs.⁶ A high sensitivity of the electronic properties of SWNTs to the presence of various gases, including nitrotoluene⁸ and nerve agents,⁹ has been observed.

While the intrinsic properties of SWNTs are a valuable platform for development of sensitive gas detectors, the modification of their electronic structure offers further scope for improving the sensor performance. Coating of the nanotubes with Nafion and polyethyleneimine has been demonstrated to impart selectivity to the nanosensors and in addition it allows for detection of molecular species at very low concentrations.¹⁰ Pd-loaded SWNTs are capable of detecting small concentrations of H₂ in air,^{11,12} whereas SnO₂/SWNTs hybrid material shows an enhanced sensitivity to NO₂.¹³ Theoretical studies predict that doping of alien atoms (B or N) into intrinsic SWNTs will widen both the molecular sensing capacity and reliability of SWNT sensors.¹⁴ Although doped SWNTs have already been prepared,^{15,16} their sensing application remains to be explored experimentally.

Here, we present a novel approach, which utilizes the chemistry of SWNTs to further improve the sensing performance of SWNTs. We demonstrate that SWNTs with covalently

attached poly(*m*-aminobenzene sulfonic acid),¹⁷ PABS, show improved reversibility and enhanced sensitivity for the detection of ammonia.

The sensor devices are based on a random network of SWNT-PABS formed between interdigitated electrodes. Our choice of the network configuration is based on the simplicity of the fabrication process, which also provides reproducibility of the sensor performance and lower electrical noise. The interest in the sensing properties of SWNTs has prompted a search for the optimal device configuration. Although devices with individual carbon nanotube can be fabricated,^{6,18–21} the individual SWNT devices face several issues limiting their practical application, such as the complex fabrication process, poor device reproducibility, and low yield. Thus, there has been an effort to develop devices based on SWNT networks.^{22,23} Such devices take advantage of the SWNT properties and in addition, the large number of carbon nanotubes in the network ensures statistical averaging, leading to similar device characteristics for devices with different local nanotube arrangements but with the same overall nanotube density.

Experimental Section

Single-walled carbon nanotubes prepared by the electric arc discharge method were produced by Carbon Solutions, Inc. (www.carbonsolution.com),²⁴ after purification (P2-SWNT). The carbonaceous purity of the P2-SWNTs as assessed by solution-phase near-IR spectroscopy²⁵ was 83%. P2-SWNTs were dispersed in dimethylformamide (DMF) by ultrasonication in a bath sonicator to obtain dispersions of 0.2 mg/mL.

SWNT-PABS¹⁷ were also produced by Carbon Solutions, Inc; aqueous solutions of SWNT-PABS (1 mg/mL) were prepared by ultrasonication.

The dispersions were deposited on an array of gold interdigitated electrodes (IDE, Figure 1), with a gap between the interdigitated fingers of ~80 μm. The deposition was performed by spraying the dispersions with an air brush in several steps until the desired resistance was obtained. The deposited material was dried in a vacuum at 80 °C for 5 min after each step.

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* Corresponding author. E-mail: haddon@ucr.edu.

[‡] Carbon Solutions Inc.

[§] Smiths Detection.

^{||} University of California.

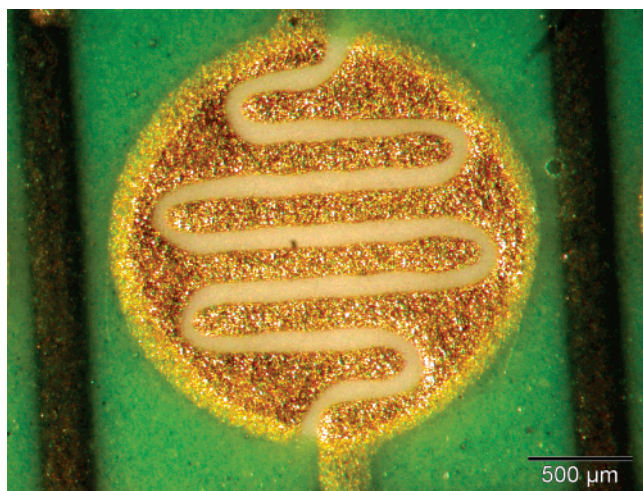


Figure 1. Optical image of an interdigitated electrode from the sensor array.

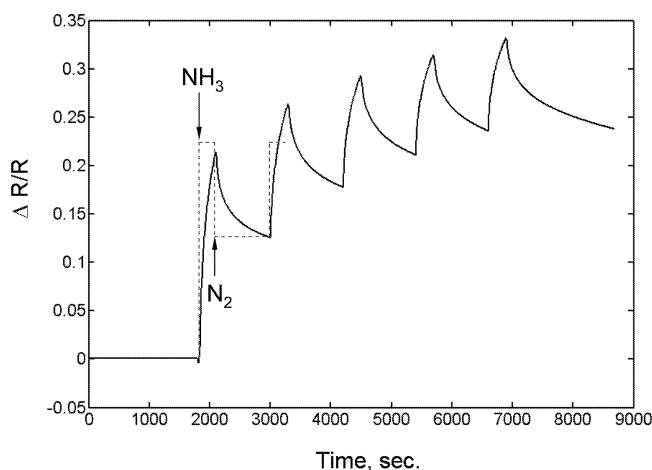


Figure 2. Response of a P2-SWNT sensor to 100 ppm NH_3 .

The response of the sensors to different concentrations of ammonia was studied in an automated gas test station. The desired ammonia concentrations were obtained by dilution with nitrogen in a computerized gas dilution system (Enviroincs Inc., Tolland, CT). In a typical experiment, the sensors were purged with nitrogen for 30 min followed by exposure to ammonia for 15 min. The ammonia gas was switched to nitrogen for 5 min between successive test experiments. The resistance of the sensors was measured at 32 °C and a gas flow rate of 400 cm^3/min .

Results and Discussion

P2-SWNTs exposed to 100 ppm NH_3 exhibit a behavior which is typical of pristine SWNTs. Representative response curves for P2-SWNT sensors are given in Figure 2. The response of the device is defined as $\Delta R/R_0 = (R - R_0)/R_0$, where R_0 is the resistance before the exposure to ammonia and R is the maximum resistance during the exposure. Exposure to ammonia rapidly increases the resistance of the SWNT network. Similar behavior has been observed with individual SWNT devices.^{6,26} Theoretical^{6,27,28} and experimental^{6,29} studies have attributed this to a charge transfer from the electron-donating ammonia molecule to the carbon nanotube. Because the semiconducting P2-SWNTs are hole-doped (p-type) from the environmental molecular oxygen,⁵ this charge transfer increases the resistance of the network by refilling the valence band of the semiconducting SWNTs.⁷ Previously published studies on the detection of

ammonia with SWNTs report a dramatic decrease of the device conductivity.^{6,26,30} Exposure to 1% NH_3 has been reported to decrease the conductance of individual SWNT devices by 2 orders of magnitudes in ~ 1 to 2 min.⁶ Large response in less than 1 min has been observed when devices consisting of few nanotubes (3–5)³¹ have been exposed to pure ammonia.²⁶ The fabricated P2-SWNTs device used in our experiments exhibits a response of $\sim 22\%$. The significantly lower response of P2-SWNTs as compared to the previously reported results can be explained by the different device configuration. The measurements reported previously were conducted on selected semiconducting SWNTs, whereas in the random network of SWNTs of our device both metallic and semiconducting nanotubes are present. Charge transfer from NH_3 to metallic nanotubes would not be expected to induce large changes in the device resistance. Furthermore, the semiconducting nanotubes are a mixture of tubes with a range of band gaps. Transport measurements have shown that modest gap semiconductors are less sensitive to doping when exposed to oxygen than small gap semiconducting SWNTs.⁵ Thus, the observed response of our device is a result of a multichannel averaging of the resistance change in semiconducting and metallic nanotubes. We attribute the relatively slower response of P2-SWNTs to the different gas diffusion and adsorption dynamics in thin film as compared to individual SWNT devices. Similar behavior has been reported for optically thick and dilute thin SWNT films after exposure to O_2 .⁵ Presumably, by engineering the thickness of the film it is possible to enhance the performance of SWNT-network devices.

In our experiments, we have observed that the replacement of NH_3 with nitrogen does not lead to the complete recovery of the initial resistance of the P2-SWNT devices in the time frame of the experiment (Figure 2). The devices recover about one-half of their initial resistance after the first exposure to ammonia. Successive exposures to NH_3 decrease the intensity of the response and the difference in the device resistance before and after exposure to NH_3 . This is not surprising as it is known that the dedoping of SWNTs occurs slowly and that the resistance recovers over a long period of time, typically more than 12 h.^{6,8} For fast recovery of the resistance, illumination with UV light or heat treatment has been utilized,^{6,8,32} however, such treatments require additional instrumentation and power, which is a practical limitation.

The chemical modification of SWNTs significantly affected the sensitivity and reversibility of the behavior of the sensors toward ammonia. PABS is a water-soluble conducting polymer,^{33,34} and the improved solubility and processability of this sulfonated polyaniline derivative, because of the presence of SO_3H groups, is especially attractive for introducing acid–base sensitivity together with a further doping response into sensor devices.

The SWNT-PABS show an enhanced sensitivity to NH_3 compared to P2-SWNTs. Figure 3 compares the response of devices fabricated with P2- and SWNT-PABS to 100 ppm NH_3 . Although the response depends on the resistance and in turn the thickness of the deposited film, Figure 3 clearly demonstrates a significantly higher response of the sensors fabricated with SWNT-PABS.

Importantly, recovery of the resistance is observed after the removal of ammonia. Figure 4 shows the response curves of SWNT-PABS for five successive exposures to 100 ppm of NH_3 . After the first exposure to NH_3 , replacement of the analyte with N_2 decreases the resistance to a level that is maintained in subsequent recoveries from exposure to NH_3 .

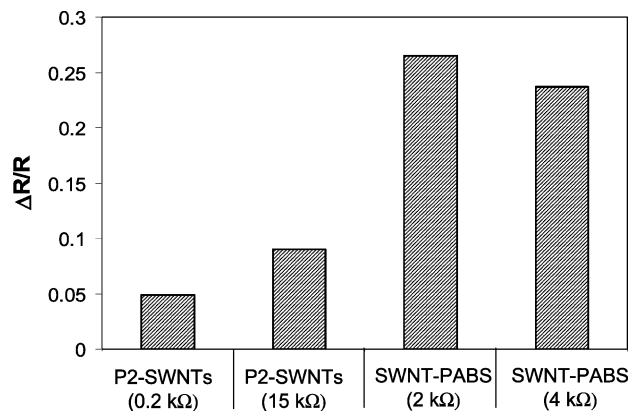


Figure 3. Response of P2- and SWNT-PABS devices to 100 ppm NH₃.

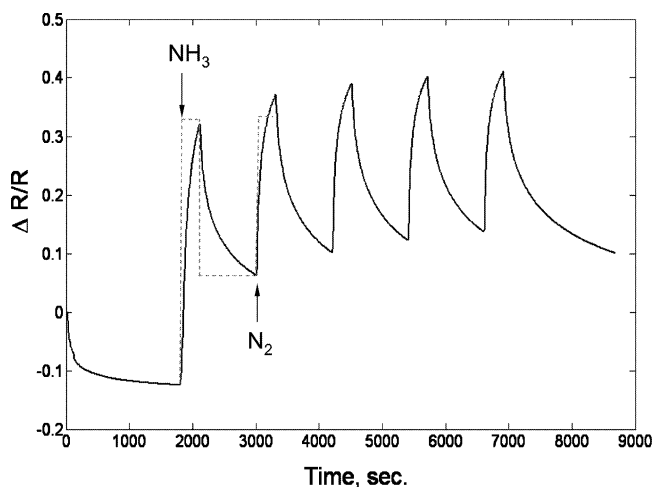


Figure 4. Response curves of SWNT-PABS to 100 ppm NH₃.

To demonstrate the performance of SWNT-PABS as a sensor for ammonia detection, we have examined the response of the sensors to different concentrations of ammonia. Because of the high toxicity of NH₃, sensors for detection of NH₃ at low concentration of the gas are desired. The limits for exposure to ammonia as set by the National Institute for Occupational Safety and Health (NIOSH) are 25 ppm for a period of 8 h or 35 ppm for 15 min.³⁵ SWNT-PABS show a significant response to concentrations as low as 5 ppm. We have also observed that devices with resistances between 2 and 7 kΩ exhibit very similar responses with a variability in the range of 10–15%. The average response of several devices with resistance between 2 and 7 kΩ, to different concentrations of ammonia is given in Figure 5.

The molecular sensing mechanism of NH₃ for the SWNT-PABS can be understood considering the chemistry of polyaniline (PANI). PANIs are appealing for sensor applications because their electronic properties can be reversibly controlled by doping/dedoping at room temperature.^{33,36–39} The doping process transforms PANI from an insulating (emeraldine base form) to a conducting (emeraldine salt) form. During the protonation, H⁺ or holes are added to the imine groups around the quinoid ring, which can be viewed as a charge delocalization of holes in the valence band. This dramatic change in the electronic properties can be easily measured. PABS is a self-doped PANI. Proton transfer from the sulfonic acid groups to the nitrogen atoms directly gives the self-doped zwitterionic form (Scheme 1). Compared to traditional PANI, PABS has lower conductivity because the electron-withdrawing sulfonic acid groups substituted on the benzene rings cause an increase of

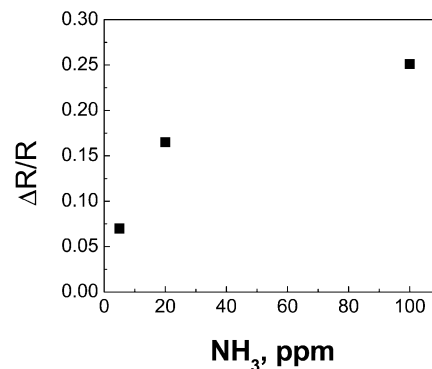
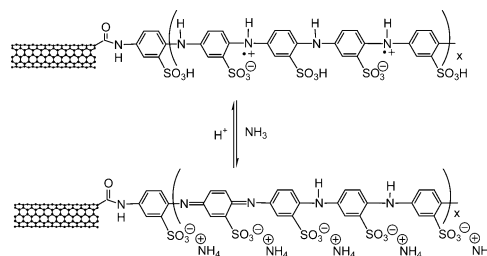


Figure 5. Response of SWNT-PABS as a function of the NH₃ concentration.

SCHEME 1: Interaction of SWNT-PABS with NH₃



the band gap. The conductance of the as-synthesized PABS is $5.4 \times 10^{-7} \text{ S.cm}^{-1}$ and SWNT-PABS has a conductance of $5.6 \times 10^{-3} \text{ S.cm}^{-1}$.¹⁷ Obviously, both the ability of PABS to undergo rapid and reversible changes in the electronic structure and the higher conductivity of SWNT-PABS material are key elements for the sensor performance. When NH₃ interacts with PABS, changes in the electronic structure of PABS are induced by the deprotonation of PABS (Scheme 1). We assume that the sensing mechanism is mediated by the PABS chemically attached to SWNTs. The deprotonation of PABS during exposure to ammonia induces hole depletion and a reduced conductance of the SWNT-PABS.

This work demonstrates a new approach for development of molecular sensors with enhanced performance by exploiting the chemistry and electron-transfer characteristics of SWNTs. Sensors fabricated from random networks of SWNT-PABS show an improved sensitivity and reversibility for detection of ammonia and offer great promise for the realization of practical devices.

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Note Added after ASAP Posting. Reference 39 was not cited in the text in the version posted ASAP October 9, 2004. Reference 39 was added in line 5 of the second-to-last paragraph of the paper, and a misspelling was also corrected in that line. The correct version was posted October 14, 2004.

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