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Poly(m-aminobenzene sulfonic acid) functionalized single-walled carbon nanotubes based gas sensor

Ting Zhang[1,2], Syed Mubeen[1,2], Elena Bekyarova[2,3], Bong Young Yoo[1,2], Robert C Haddon[1,2,3], Nosang V Myung[1,2,4] and Marc A Deshusses[1,4]

[1] Department of Chemical and Environmental Engineering, University of California-Riverside, Riverside, CA 92521, USA
[2] Center for Nanoscale Science and Engineering, University of California-Riverside, Riverside, CA 92521, USA
[3] Department of Chemistry, University of California-Riverside, Riverside, CA 92521, USA

E-mail: myung@engr.ucr.edu and mdeshuss@engr.ucr.edu

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Abstract
We have demonstrated a NH_3, NO_2 and water vapour sensor based on poly(m-aminobenzene sulfonic acid) functionalized single-walled carbon nanotube (SWNT–PABS) networks. The SWNT–PABS based sensors were fabricated by simple dispersion of SWNT–PABS on top of pre-fabricated gold electrodes. SWNT–PABS sensors showed excellent sensitivity with ppb_v level detection limits (i.e., 100 ppb_v for NH_3 and 20 ppb_v for NO_2) at room temperature. The response time was short and the response was totally reversible. The sensitivity could be tuned by adjusting the sensor initial resistance. The sensors were also suitable for monitoring relative humidity in air.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

One-dimensional nanostructure based gas sensor arrays have attracted a great deal of attention because of their ability to detect multiple analytes with superior sensitivity, low operating temperature, real-time detection and low power consumption [1, 2]. One-dimensional nanostructures including carbon nanotubes offer significant advantages over thin films because of their ultra-high surface-to-volume ratio with unique chemical and electrical properties. For example, faster surface reactions and adsorption/desorption processes which can enhance response/recovery time and higher sensitivities are expected because most of the atoms are surface atoms.

Semiconducting pristine single-walled carbon nanotubes (SWNTs) have been demonstrated to be good sensing materials to detect some small gas molecules (e.g. NO_2, NH_3 and O_2) [2–6]. However, the number of analytes which can be detected by pristine SWNTs is limited, which restricts the usage of pristine SWNTs in practical applications. In order to further enhance the sensing performance of SWNTs, many researchers are currently investigating a variety of physical and/or chemical functionalization methods [7–12].

Chemical functionalization is a method to enhance both processibility and sensing performance of SWNTs. First, it allows the unique properties of SWNTs to be coupled to other materials, such as conducting polymers, metals and metal oxides, to create hybrid sensing materials with enhanced sensitivity, selectivity and faster response time. Second, it can improve dissolution and dispersion of SWNTs in various solvents, which opens the door to cost-effective methods to fabricate sensors by simple dispensing or printing techniques.

Conducting polymers are emerging sensing materials because their chemical and electrical properties can be tailored over a wide range to detect various gas analytes [13].

[4] Address for correspondence: Department of Chemical and Environmental Engineering, University of California-Riverside, Bourns Hall B321 and B353, 900 University Avenue, Riverside, CA 92521, USA.

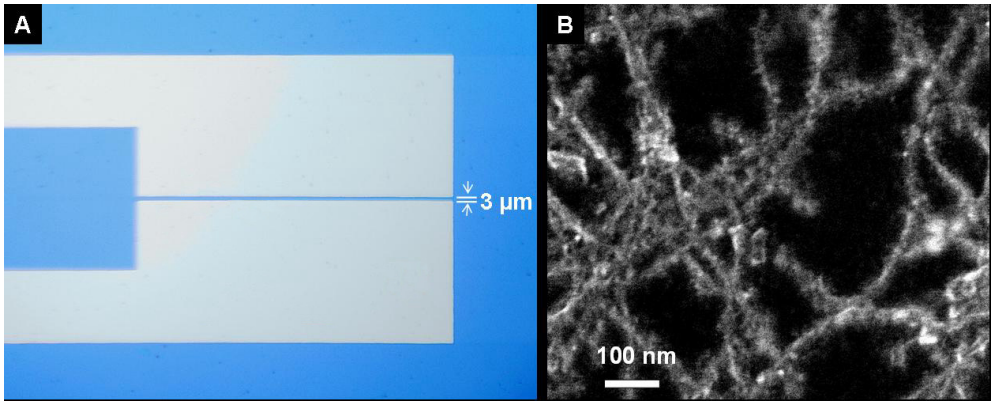

Figure 1. (A) Optical image of SWNT–PABS sensor with 3 × 200 μm gap distance between the microfabricated electrodes and (B) SEM picture of SWNT–PABS network within the gap.

Coupling of SWNTs with conducting polymer is expected to create sensing materials with improved sensing performance [12]. Recently, we developed poly(m-aminobenzene sulfonic acid) (PABS) functionalized SWNTs which show unique electroactive properties, enhanced water solubility, easy processibility and superior environmental stability [14]. The functionalization process was based on the amidation of nanotube-bound carboxylic acids groups introduced during acid treatment with the amine-rich PABS. SWNT–PABS show excellent solubility in water and improved electrical conductivity of four orders of magnitude over neat PABS. Previously, we reported that SWNT–PABS based gas sensors show better sensitivity toward NH_3 compared to pristine SWNTs based sensors [11]. In this paper, we report the systematic investigation of SWNT–PABS based sensors to detect trace amounts of NH_3 and NO_2 gas at ambient conditions. The effect of humidity on sensing and the sensing mechanisms were also investigated.

2. Experimental section

2.1. SWNT–PABS sensor fabrication and characterization

Purified SWNTs (SWNT-COOH, 80–90% purity) and SWNT–PABS, a water-soluble nanotube–polymer compound formed by poly(m-aminobenzene sulfonic acid) (PABS) covalently bonded to SWNTs via amide functionalization, were obtained from Carbon Solutions, Inc. (www.carbonsolution.com). The detailed synthesis procedure and characteristics of SWNT–PABS has been published elsewhere [14].

The electrodes for the sensor array were microfabricated on silicon substrate using standard lithographic patterning. Using chemical vapour deposition (CVD), one micron thick SiO_2 film was first deposited on a (100) oriented silicon wafer to insulate the substrate. After photolithographically defining the electrode area, a Cr adhesion layer and a ∼3000 Å-thick Au layer were e-beam evaporated. Finally, the electrodes were defined using lift-off techniques. The gap distance between electrodes was fixed at 3 μm. Figure 1(A) shows the optical images of the micro-fabricated substrate.

SWNTs–PABS were dispersed (0.05 mg ml^{-1}) in nanopure water using ultrasonic force. Then, a 0.05 μl drop of the SWNT–PABS suspension was deposited onto the electrode gap using a microsyringe. After evaporation of the solution, a network of SWNT–PABS bridged the electrode gap. The density of the SWNT–PABS network across the gap was adjusted by varying the concentration of the SWNTs in the aqueous solution and the droplet size.

The morphology of the SWNT–PABS networks bridging the electrodes was characterized using a scanning electron microscopy (Philips XL30-FEG), as shown in figure 1(B). The temperature-dependent electrical properties of SWNT–PABS networks were measured using a semiconducting parameter analyser (Agilent 4155A) and a physical property measurement system (PPMS).

2.2. Sensing apparatus and SWNT–PABS sensor integration

For gas detection studies, the sensors were wired-bonded and each sensor was connected in series with a load resistor. The value of the load resistance was chosen to be as close as possible to the resistance of the sensor during gas sensing experiments to optimize the resolution obtained from the measurements. 1 VDC potential was applied to the circuit and the electrical resistance of the sensor was determined from continuously monitoring the voltage over the load resistor using Ohm's law. A sealed glass chamber with gas inlet and outlet ports for gas flow-through was positioned over the sensor chip. All experiments were conducted with known concentrations of analyte diluted in dry air at a total gas flow of 200 std. cm^3 min^{-1}. The analytes and air flow rates were regulated by mass flow controllers (Alicat Scientific Incorporated, Tucson, AZ). A custom LabView computer program was developed to continuously control and monitor the voltage of the circuit using Fieldpoint analog input and output modules (National Instruments, Austin, TX).

2.3. Sensing procedure

Typical sensing experiments were conducted by exposing the sensor to the selected concentration of NH_3, NO_2 and relative humidity until the sensor's response reached a steady value, followed by purging the sensor with dry air until the sensor recovered its initial resistance before exposing the sensor to the next concentration. Humidity control was controlled by bubbling dry air through a water bubbler. The different

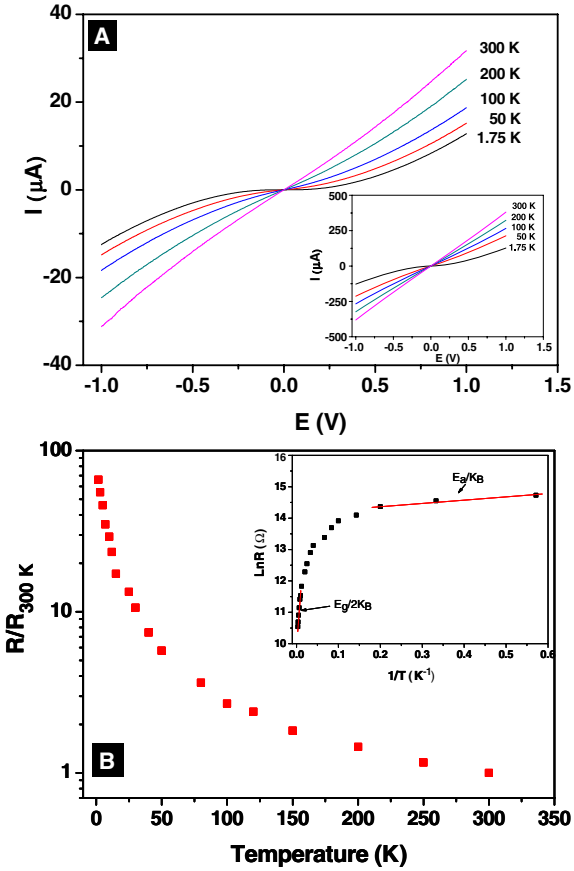

Figure 2. (A) I–V characteristics of the SWNT–PABS sensor and carboxylated SWNTs (inset) at different temperatures and (B) temperature dependence of normalized resistance of the SWNT–PABS sensor (at a bias potential of 100 mV).

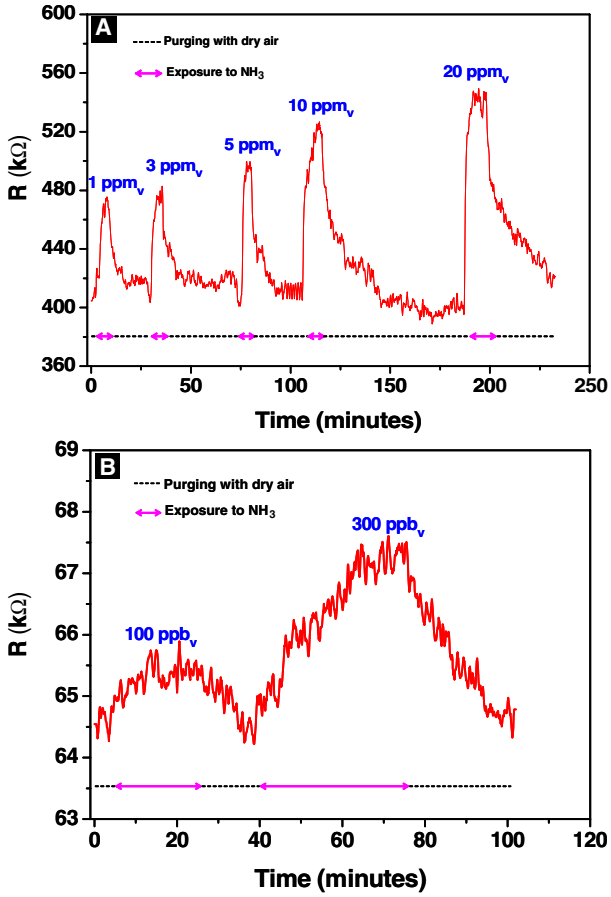

Figure 3. Real time response of the SWNT–PABS sensors to NH_3 (A) 1 to 20 ppm_v and (B) 100 and 300 ppb_v in dry air at 24 °C.

percentages of relative humidity were achieved by modulating the flow rate of dry and humid air with mass flow controllers, and the values of relative humidity were calibrated with a thermo-hygrometer (www.coleparmer.com) in the outlet of the flow cell. All experiments were conducted at room temperature.

3. Results and discussion

3.1. Electronic characteristics of SWNT–PABS sensor

I–V curves were recorded at temperatures ranging from 1.75 to 300 K which revealed nonlinearity gradually increasing with decreasing temperature (figure 2(A)). The resistance of the sensor markedly decreased with increasing temperature (figure 2(B)). This was similar to I–V curves of carboxylated SWNTs (inset to figure 2(A)). The results indicate that carboxylated and PABS functionalized SWNT networks behave as typical semiconductors. However, PABS functionalization increased the resistance by about one order of magnitude compared to carboxylated SWNTs. To calculate the bandgap energy of the SWNT–PABS, the natural log of the resistance was plotted against $1/T$ (inset figure 2(B)). The graph has two essentially linear regimes with a slope equal to $E_g/2k_B$ between 100 and 300 K and a slope E_a/k_B at lower temperature (1.75–5 K). The corresponding bandgap energy E_g was 0.031 eV, and the acceptor level energy E_a was 8.2×10^{-5} eV which indicates that the SWNT–PABS network is a doped semiconductor with a very small bandgap energy.

3.2. NH_3 sensing

Figures 3(A) and (B) show the SWNT–PABS sensor's responses to various concentrations of ammonia. After exposure to NH_3, the resistance of the sensor immediately increased and gradually approached steady state. When exposed back to dry air, the resistance decreased and slowly recovered its initial value. The sensing response was reproducible for repeated ammonia exposures (results not shown). The detection limit, defined as the concentration providing a signal-to-noise ratio of at least 3 [15], of the SWNT–PABS sensors to NH_3 was generally in the ppb_v concentration range. As shown in figure 3(B), the detection limit for this specific sensor was 100 ppb_v. This is one to two orders of magnitude lower than commercially available electrochemical sensors.

The sensitivity, S, of chemiresistive sensors can be defined as (equation (1)):

$$S = \Delta R/R_0 \times 100\% = \frac{R_{eq} - R_0}{R_0} \times 100\% \qquad (1)$$

where R_{eq} is the steady-state resistance after exposure to selected analyte, and R_0 is the initial resistance before exposure

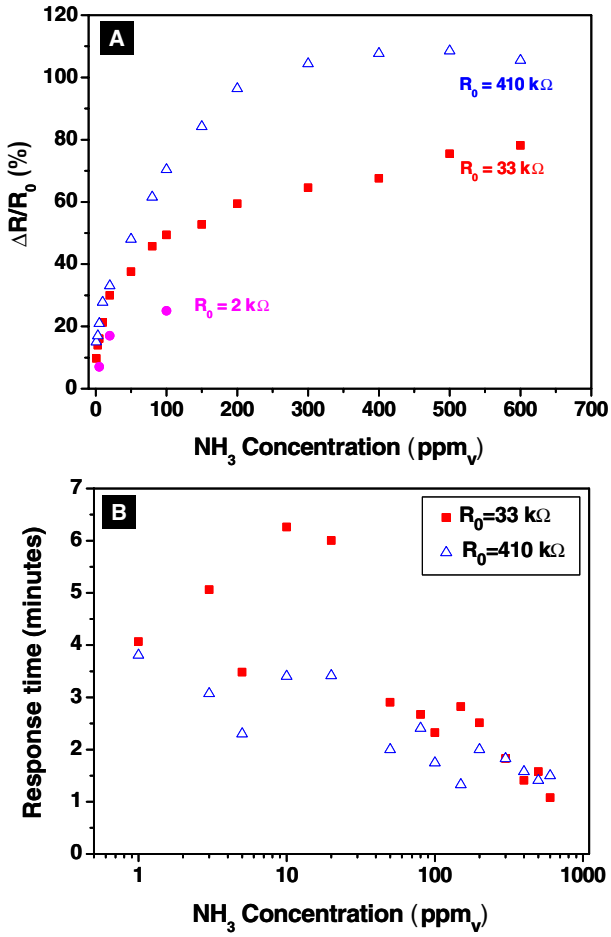

Figure 4. (A) Sensitivity and (B) response time of SWNT–PABS sensors with different initial resistance to NH_3.

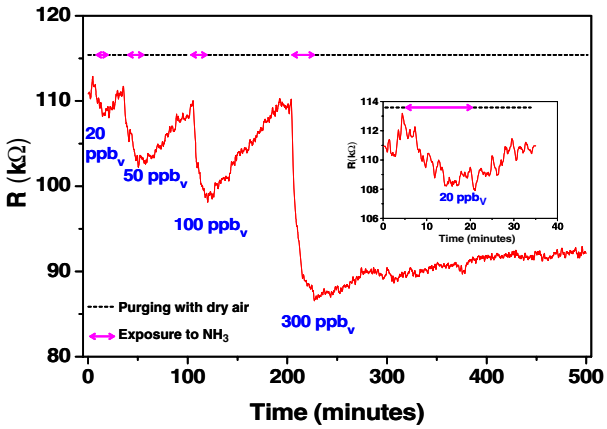

Figure 5. Real time response of SWNT–PABS sensors to different concentrations of NO_2 in dry air at 24 °C. The inset is the magnified response to 20 ppb$_v$ of NO_2.

to the analyte. The sensitivity of two SWNT–PABS sensors with R_0 of 410 and 33 kΩ to concentrations of NH_3 ranging from 1 to 600 ppm$_v$ are compared with previously published results [11] of SWNT–PABS sensors (figure 4(A)). The sensors developed in this study had a linear response at low concentration, and exhibited a typical saturation response at concentrations above 300 ppm$_v$. The sensitivity of the SWNT–PABS sensor increased when increasing the initial resistance. This result is consistent with previous findings [12, 16] and indicates that the sensitivity can be tuned by adjusting the initial resistance of the sensor. In the present case, this can be done by varying the density of the SWNT–PABS network. While some have suggested that single gas molecule detection may be possible with only one SWNT connecting the electrodes [1], we found that networks with initial resistance in the order of kiloohms were a good compromise between sensitivity and electrical noise.

The response time (defined as the time to reach 90% of the total resistance change) of the SWNT–PABS sensors is plotted against the NH_3 concentration in figure 4(B). A response time of 1–2 min was observed at high concentrations above 100 ppm$_v$. It increased significantly at ammonia concentrations below 20 ppm$_v$. The most probable reason is that the gaseous-adsorbed concentration gradient of the analyte decreases with decreasing the gaseous concentration, thereby reducing the mass transfer rate of the analyte, and increasing the time required for reaching equilibrium. However, differences between response time and sensor recovery time after exposure to the analyte suggest that other effects, yet to be identified, play an important role.

3.3. NO_2 sensing

The response of the SWNT–PABS sensors to different concentrations of NO_2 was also investigated. Figure 5 shows a sensor's response to NO_2 in air at ppb$_v$ concentration levels. During exposure to NO_2, the resistance of the sensor decreased and NO_2 concentrations as low as 20 ppb$_v$ could be detected (inset of figure 5). In figure 6(A), the sensitivity of SWNT–PABS network based sensors is compared to that of unfunctionalized SWNTs based sensors. The enhanced sensitivity of the PABS-functionalized SWNTs over pristine SWNT is evident. Similar to observations made with NH_3, the response time of SWNT–PABS sensors to NO_2 decreased with increasing the NO_2 concentration, from approximately 10 min at 20 ppb$_v$ to around 1 min at 100 ppm$_v$ (figure 6(B)). SWNT–PABS sensors regeneration after exposure to NO_2 above 300 ppb$_v$ at room temperature usually will take several hours at 20–30 °C. For faster recovery rate, UV irradiation or heat treatment has been shown to decrease the desorption-energy barrier to ease the gas molecules' desorption [2].

3.4. Relative humidity sensing

The sensor also responded to changes in air relative humidity (RH). The resistance increased with increasing the RH from 10% to 70% (figure 7). The response time to changes in RH was approximately 2–3 min, and the recovery time was usually less than 10 min. The sensitivity of two SWNT–PABS sensors to RH is reported in figure 8. A quasilinear response was obtained between 10 and 70% RH, while unstable responses were observed at values above 80%, most probably because of water condensation on the sensors' electrodes (results not shown). These results demonstrate the considerable affinity of SWNT–PABS to water vapour, consistent with previous theoretical calculations and experimental measurements on

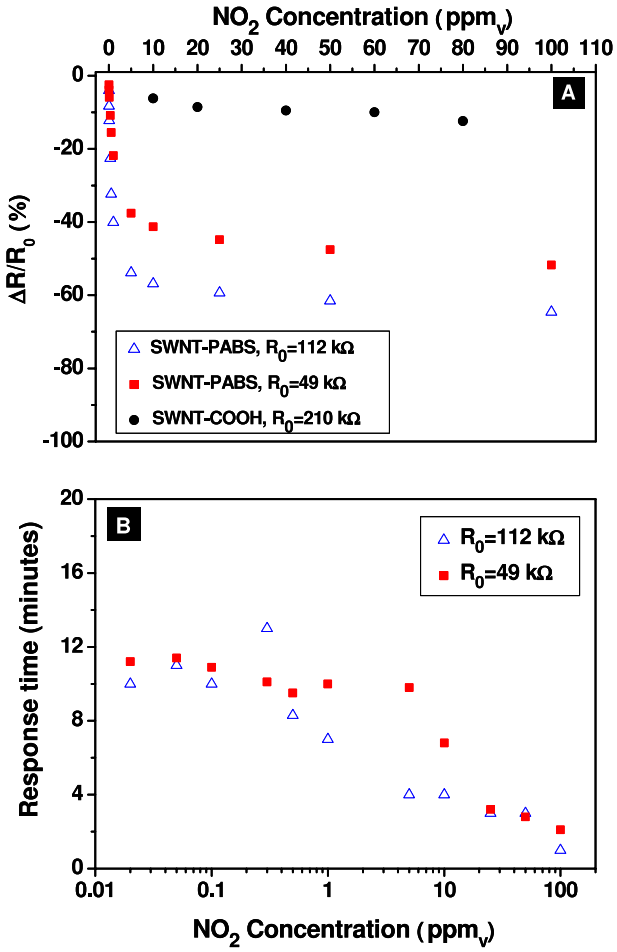

Figure 6. (A) Sensitivity and (B) response time of SWNT–PABS sensors with different initial resistance to NO_2.

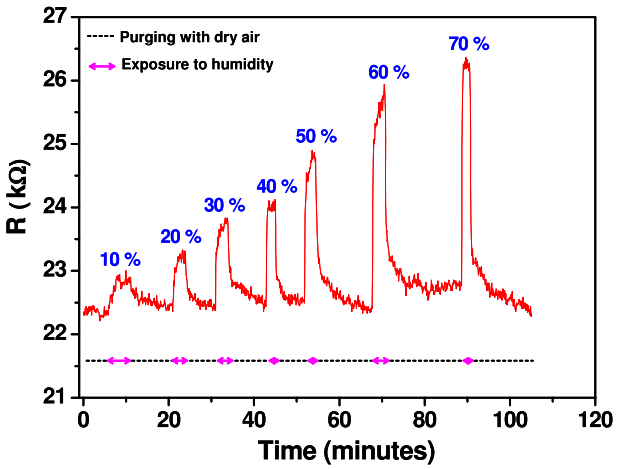

Figure 7. Real time response of a SWNT–PABS sensor to different relative humidity in air at 24 °C.

carbon nanotubes' response to humidity [17–20]. It has been proven that water molecules can adsorb on the surface of SWNTs and that there is a charge transfer of $0.03e^-$ from each water molecule to the SWNT. Thus, the hole population in SWNT is depleted [17], resulting in an increase in resistance.

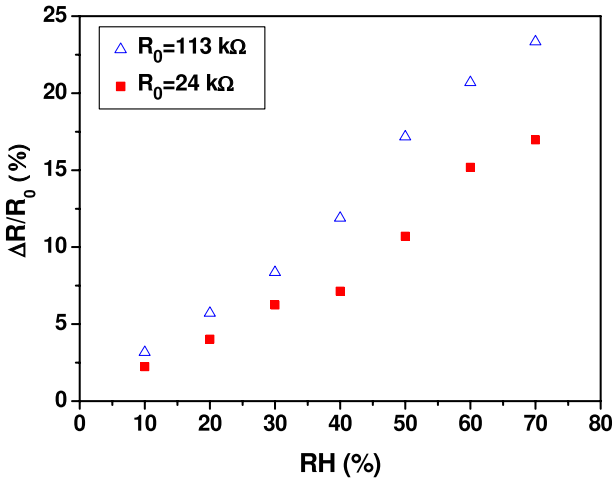

Figure 8. Sensitivity of SWNT–PABS sensors with different initial resistance to relative humidity in air.

3.5. Sensing mechanism of SWNT–PABS sensor

These promising results demonstrate that our SWNT–PABS sensor is capable of highly sensitive, fast and reversible detection of NH_3 and NO_2 at room temperature, and effective sensing of relative humidity. The sensing mechanism of the SWNT–PABS is mainly due to the protonation/deprotonation (equivalent to doping/dedoping) process of covalently attached PABS, modulating hole carriers, which dramatically changes the resistivity of SWNT–PABS [11]. PABS is a sulfonated polyaniline (PANI) derivative [11]. Sulfonated PANIs are of great interest in sensor applications due to their unique electroactive properties, easy processing and thermal stability [21, 22]. The PABS structure consists of alternated single and double bonds which leads to the formation of delocalized electronic states [22]. Sulfonic acid groups as dopants play an important role in balancing the charge distribution within the polymer [23], and they are especially attractive for introducing acid–base sensitivity [11]. When PABS is exposed to NH_3 or water vapour, the adsorbed molecules cause deprotonation of the polymer, which depletes hole carriers and therefore results in an increased electrical resistance. In contrast, exposure to NO_2 causes protonation of the polymer, which induces hole accumulation and results in a decreased resistance of the SWNT–PABS sensors. When the sensor is purged with reference gas, the process is reversed and the original electrical resistance is restored.

4. Conclusion

We have demonstrated a novel and simple approach to fabricate chemical gas sensors with poly(m-aminobenzene sulfonic acid) (PABS) covalently functionalized SWNTs. SWNT–PABS sensors showed excellent sensitivity with ppb_v level detection limit for sensing NH_3 and NO_2. The sensitivity could be tuned by adjusting the sensors initial resistance. The sensors were also suitable for monitoring relative humidity in air. In all cases, the response time was short and the response was totally reversible. SWNT–PABS based sensors could be useful for a number of applications due to their high sensitivity, very low detection limit, fast response, room temperature operation and simplicity in fabrication.

Acknowledgments

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