

## Full Paper

# Electrochemically Functionalized Single-Walled Carbon Nanotube Gas Sensor

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## Abstract

We demonstrate a facile fabrication method to make chemical gas sensors using single-walled carbon nanotubes (SWNT) electrochemically functionalized with polyaniline (PANI). The potential advantage of this method is to enable targeted functionalization with different materials to allow for creation of high-density individually addressable nanosensor arrays. PANI-SWNT network based sensors were tested for on-line monitoring of ammonia gas. The results show a superior sensitivity of 2.44%  $\Delta R/R$  per ppm<sub>v</sub> NH<sub>3</sub> (which is more than 60 times higher than intrinsic SWNT based sensors), a detection limit as low as 50 ppb<sub>v</sub>, and good reproducibility upon repeated exposure to 10 ppm<sub>v</sub> NH<sub>3</sub>. The typical response time of the sensors at room temperature is on the order of minutes and the recovery time is a few hours. Higher sensitivities were observed at lower temperatures. These results indicate that electrochemical functionalization of SWNTs provides a promising new method of creating highly advanced nanosensors with improved sensitivity, detection limit, and reproducibility.

**Keywords:** Single-walled carbon nanotubes, Conducting polymer, Polyaniline, Electrochemical functionalization, Gas sensor, Nanosensor

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## 1. Introduction

One-dimensional (1-D) nanostructures, including semiconducting single-walled carbon nanotubes (SWNTs), have been demonstrated as effective ultrasensitive chemical and biological sensors because of their high surface-to-volume ratio and their unique electrical properties. These features may enable a high enough sensitivity to charged analytes that single molecule detection becomes possible [1, 2]. In addition, the direct conversion of chemical information into an electrical signal can take advantage of existing low-power microelectronic technology and lead to miniaturized sensor devices.

Unfunctionalized semiconducting SWNT based sensors have been demonstrated for the detection of small molecules such as NH<sub>3</sub> and NO<sub>2</sub> under ambient conditions [3, 4]. The sensing mechanism is based on a charge transfer between the electron-donating/electron-withdrawing molecules and the semiconducting SWNTs, which changes the conductivity of the SWNTs [3]. However, the less than ideal sensitivity and lack of selectivity limit SWNTs in practical applications to detect various types of analytes such as volatile organic compounds (VOCs) and H<sub>2</sub>. Many researchers are currently investigating ways to develop a simple and versatile functionalization technique which enables fabrication of SWNT-based nanosensor arrays with improved sensitivity and selectivity [5–11].

Several approaches have been developed to functionalize SWNTs, including covalent and noncovalent chemical functionalization, and in studies these have shown improved performance as gas sensors. Some examples follow. SWNTs, noncovalently coated with polyethyleneimine (PEI) and Nafion, showed a certain degree of selectivity and showed enhanced sensitivity to NO<sub>2</sub> [5]. Chemically functionalized SWNTs with covalently attached poly-(*m*-aminobenzene sulfonic acid) (PABS) have shown significantly improved performance when exposed to NH<sub>3</sub> [6]. The functionalization is based on the acyl chloride-activated amidation of nanotube-bound carboxylic acids with the amine-rich PABS [7]. Pd decorated SWNTs created by electron-beam evaporation of Pd particles over SWNTs performed as a highly sensitive H<sub>2</sub> sensor based on a catalytic reaction mechanism [8]. SWNT-polypyrrole (PPY) nanocomposites formed by in-situ chemical polymerization of pyrrole in an SWNT mixture demonstrated enhanced sensitivity to NO<sub>2</sub> gas [9]. Nanotube field effect transistors (NTFETs), created by noncovalently coating SWNTs with Nafion membranes, have been evaluated as a very sensitive humidity sensor [10]. Also, sensors fabricated via the noncovalent functionalization of SWNTs with PEI and starch polymers showed a highly sensitive response to low concentrations of CO<sub>2</sub> [11]. Although they have produced marked achievements in sensor performance, these functionalization methods to modify the properties of pristine SWNTs usually require

highly reactive reagents and high temperatures, due to the inert properties of SWNTs toward most chemicals at room temperature. In addition, long fabrication time and complicated fabrication steps are needed during functionalization, which makes the process complex and costly. These functionalization techniques also have limited spatial resolution, which makes the creation of high density sensor arrays difficult.

Electrochemical functionalization is a simple and cost-effective technique which offers spatially-tailored functionalization. Because the whole process is electrochemically initiated, driven, and terminated, the functionalization is spatially localized at the electrode surface and the thickness and morphology of the coating layer can be precisely controlled by adjusting deposition time and applied potential. The electrical and other physical properties can be tailored by controlling solution compositions (metal ion or monomer concentration, supporting electrolytes, additives, complexing agents) and deposition parameters (pH, current density, applied potential, temperature, and agitation). In addition, electrochemical functionalization is able to deposit various materials including metals, metal oxides, semiconductors, and conducting polymers. Furthermore, it operates at near room-temperature without complex equipment.

In this paper, we demonstrate a facile electrochemical method to functionalize SWNTs with polyaniline (PANI) and demonstrate the good response of the resulting PANI-SWNT based sensors to ammonia gas. PANI is selected because of its tunable properties coupled with good environmental stability [12, 13]. The most promising advantage of this technique is to allow the spatial functionalization of SWNTs between a specific pair of electrodes with different sensing materials having tailored properties, enabling the possibility of creating arrays of individually addressable sensors.

## 2. Experimental

The electrochemically functionalized PANI-SWNT based sensor schematically depicted in Figure 1 was fabricated as

follows: First, interdigitated gold electrodes (IDEs) with a 5  $\mu\text{m}$  gap were microfabricated in-house using standard lithography. Using chemical vapor deposition (CVD), one micron thick  $\text{SiO}_2$  film was deposited on a (100) oriented silicon wafer to insulate the substrate. After photolithographically defining the electrode area, a Cr adhesion layer and a ca. 3000  $\text{\AA}$ -thick Au layer were e-beam evaporated. Finally, the IDE electrodes were defined using lift-off techniques.

Next, SWNTs (SWNT-COOH 80–90% purity, produced by Carbon Solution, Inc. Riverside) were dispensed across microfabricated gold IDEs by positioning a 0.5  $\mu\text{L}$  drop of aqueous solution with soluble SWNTs (1  $\mu\text{g}/\text{ml}$ ) onto the IDEs and allowing it to air dry to form an SWNT network bridging the electrodes. After formation of the SWNT network, some sensors were annealed at 300  $^\circ\text{C}$  for 30 minutes in an inert environment (i.e. 99.999% argon) to improve the contact between SWNTs and electrodes. 5  $\mu\text{L}$  of a deoxygenated aqueous solution 0.1 M aniline and 1 M HCl was then placed on top of the SWNT network for electrochemical functionalization. Two different methods were used for electropolymerization of aniline on the SWNTs. The first consisted of a two-electrode configuration and application of 1.5 VDC for 5 minutes across selected individual channels of the sensor chip to electropolymerize aniline. The second method, allowing more precise control over the electropolymerization, involved a three-electrode configuration in which the SWNT network on the IDEs, a stainless steel tip, and a Ag/AgCl wire were used as the working, counter, and reference electrodes, respectively. The polyaniline was deposited on the SWNTs potentiostatically (constant potential mode) at 0.8 V vs. wire. The coating thickness of polyaniline was adjusted by controlling the deposition time.

The morphology of PANI coated SWNTs was examined using a scanning electron microscope (Leo 1550, Germany).  $I-V$  characteristics were examined using a semiconductor parameter analyzer (Agilent 4155A) with potential sweeping from  $-1$  V to 1 V at room temperature.

For gas detection studies, the IDEs were wire bonded and each sensor was connected in series with a load resistance. The value of the load resistance was chosen to be as close as

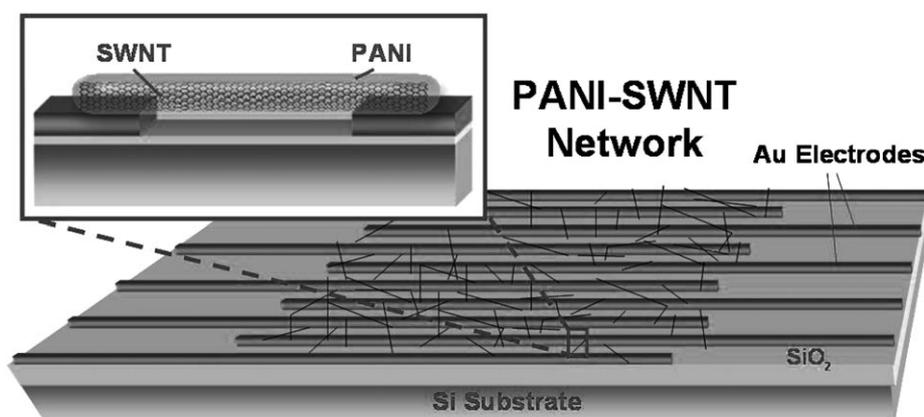


Fig. 1. Schematic of polyaniline coated single-walled carbon nanotubes (PANI-SWNTs) on interdigitated electrodes.

possible to the resistance of the sensor during gas sensing experiments to optimize the resolution obtained from measurements. The circuit was subjected to a fixed 5 VDC potential and the electrical resistance of the sensor was determined by continuously monitoring the voltage over the load resistor and applying Ohm's law. A 1.3 cm<sup>3</sup> sealed glass chamber with gas inlet and outlet ports for gas flow-through was positioned over the sensor chip. In selected experiments, the temperature of the sensor was controlled using a miniature thermoelectric module (TE technologies, Traverse City, MI) positioned below the silicon wafer. All experiments were conducted with ammonia (purity: 99.99%) diluted in argon (purity: 99.998%) at a gas flow of 200 std. cm<sup>3</sup> min<sup>-1</sup>. The ammonia and argon gas 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).

Experiments were usually conducted by exposing the sensor to the selected concentration of analyte until the sensor's response reached a steady value, followed by purging the sensor with argon until the sensor recovered its initial resistance before exposing the sensor to the next analyte concentration. Unless noted otherwise, all experiments were conducted at room temperature.

### 3. Results and Discussion

Figure 2 shows the  $I$ - $V$  characteristics (Fig. 2A) and electrical resistance (Fig. 2B) of PANI coated SWNTs as a function of PANI electrodeposition time. The electrical properties of PANI coated SWNTs were strongly dependent on deposition time, which corresponds to increasing PANI coating thickness. The  $I$ - $V$  characterization of the unfunctionalized SWNT network (inset of Fig. 2A) shows a slight "S" shape, indicating that the SWNT network behaved as a semiconductor with a small bandgap. After annealing in argon, the resistance was reduced, which indicates that annealing improved the contact between SWNTs and the electrodes. With increased electropolymerization time, the slope of the  $I$ - $V$  curve increased and appeared to be more linear. This is consistent with the increased deposition of PANI over time.

Figure 3 shows cyclic voltammograms of unfunctionalized SWNT (A) and PANI coated SWNTs (B) in 1 M HCl solution. Compared to unfunctionalized SWNT, PANI coated SWNTs exhibit two redox couples with anodic peak potential values at 0.2 V and 0.8 V vs. Ag/AgCl. These peaks have been observed by others to be characteristic of polyaniline in thin films [14–16], and thus the cyclic voltammogram of PANI-coated SWNTs indicates that polyaniline was successfully deposited on the surface of the SWNTs.

Scanning electron microscope (SEM) images of SWNTs bundle before (Fig. 4A) and after (Fig. 4B) electrochemical functionalization for 5 minutes using the two-electrode

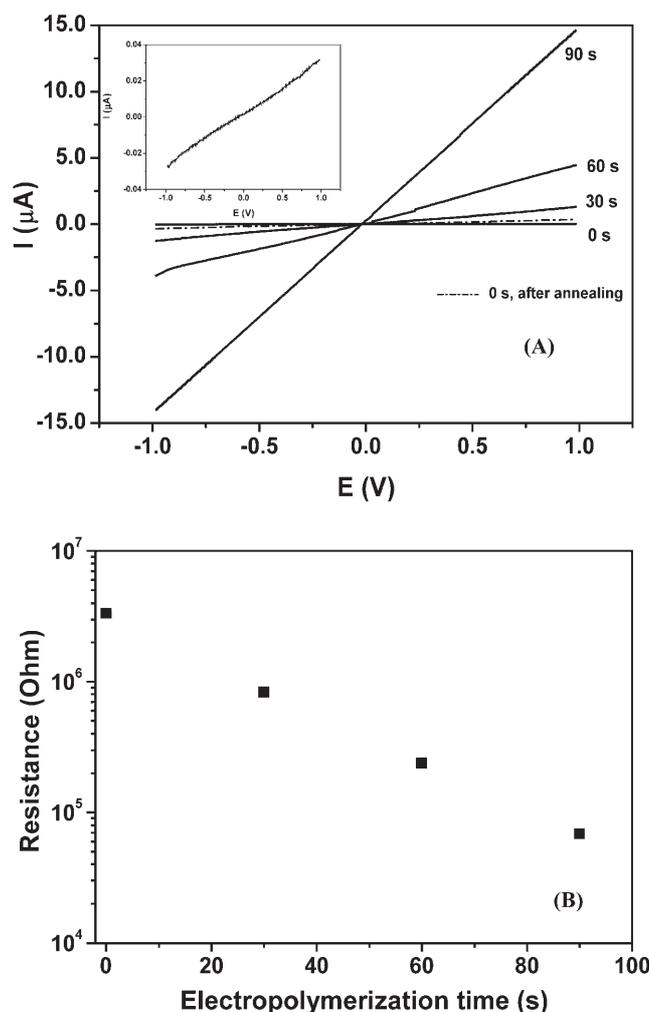


Fig. 2.  $I$ - $V$  curve (A) and electrical resistance of the sensors (B) as a function of electropolymerization time (PANI was potentiostatically polymerized at 0.8 V vs. Ag/AgCl wire in a three-electrode configuration).

configuration revealed that the mean diameter increased from  $31 \pm 2$  nm for unfunctionalized SWNTs bundle to approximately  $98 \pm 5$  nm for the polyaniline coated SWNTs bundle. The initial and final resistances depended strongly on the number of SWNTs bridging the electrodes and on the thickness of the conducting polymer coating. Both could be tuned by adjusting the concentration of SWNTs and the deposition potential and time. For gas sensing experiments, we found that the optimal sensor baseline resistance was in the kilo-ohm range, which provided greater sensitivity than sensors with lower resistance.

Figure 5 shows the sensor's response to different concentrations of  $\text{NH}_3$ , starting from an initial baseline resistance of approximately 580 k $\Omega$ . After exposure to  $\text{NH}_3$ , the resistance of the PANI-SWNT sensor dramatically increased, and then decreased upon return to pure argon gas. At room temperature, the sensor response to ammonia was completely reversible. Depending on ammonia concentration, the response time (defined as the time to reach 90% of the total resistance change) of the PANI-SWNT sensors to

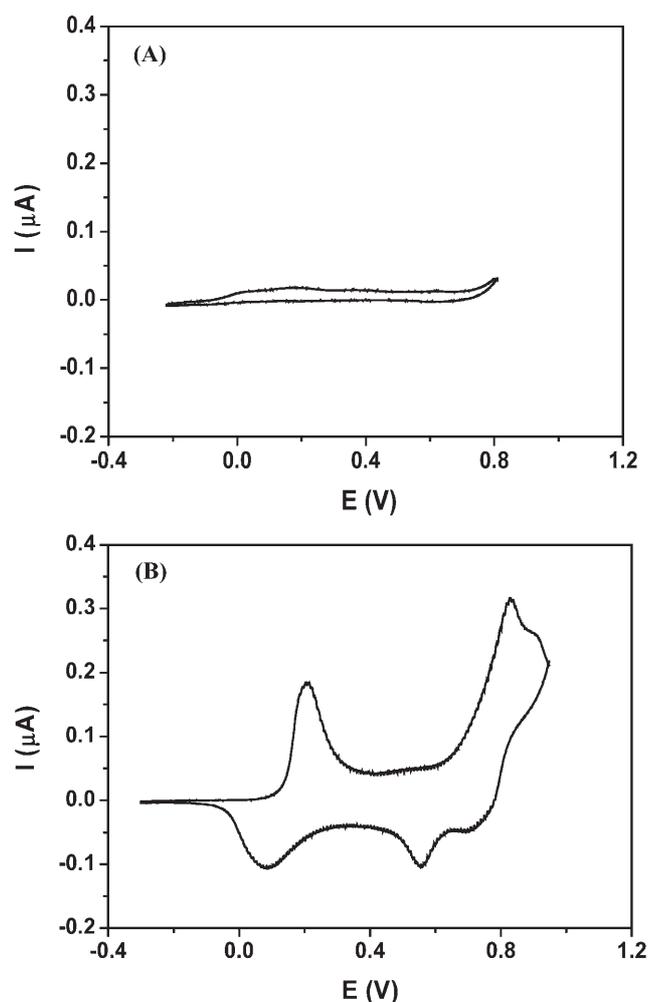


Fig. 3. Cyclic voltammograms of unfunctionalized SWNTs (A) and PANI functionalized SWNTs (B) in 1 M HCl solution with a scan rate of 50 mV/s.

ammonia exposure was on the order of a few minutes, while recovery time ranged from several minutes to a few hours. Others have found that ammonia desorption from unfunctionalized SWNT sensors is much slower, requiring more

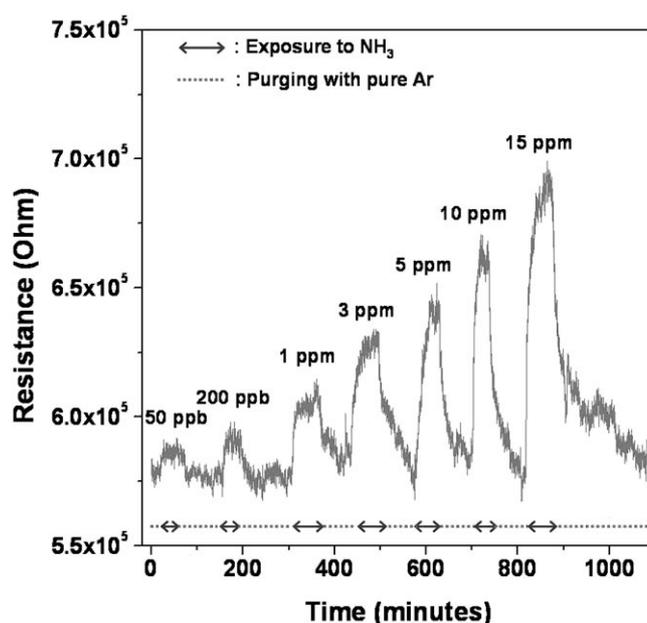


Fig. 5.  $\text{NH}_3$  gas sensing results using polyaniline coated SWNTs. The arrows show exposure times to  $\text{NH}_3$ . PANI was coated on SWNTs using a two-electrode configuration at 0.8 V for 5 minutes.

than 10 hours for the sensor to recover to its original resistance [3]. Thus, PANI functionalization appears to decrease the recovery time of SWNT-based sensors at room temperature. The detection limit (defined as the concentration providing a signal-to-noise ratio of at least 3) [17] was 50 ppb, which to our knowledge is the lowest ammonia concentration yet detected by a nanosensor at room temperature. It is one to two orders of magnitude lower than commercially available electrochemical sensors. Even lower detection limits could be possible if the electrical noise of the sensor could be reduced, e.g. by noise filtering methods and possibly improved PANI-SWNT contacts.

The sensing mechanism is complex and the possible cross-interaction between the polyaniline and the SWNT is not yet fully understood. It is known [15] that during electropolymerization, emeraldine salt is formed onto the surface of

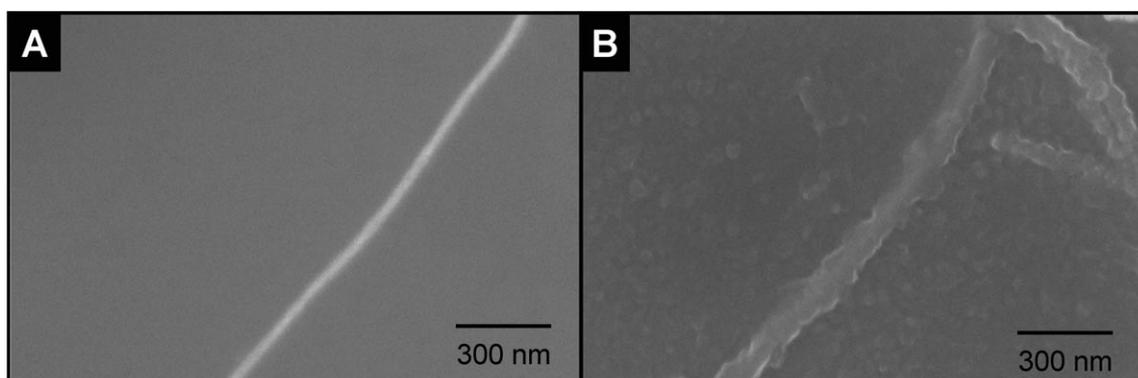


Fig. 4. SEM images of a bare SWNT before electropolymerization (A) and a coated SWNT after electropolymerization (B). PANI was coated on SWNTs using a two-electrode configuration at 0.8 V for 5 minutes.

SWNTs, making the polyaniline a p-type semiconductor with  $N^+-H$  adsorption sites. The SWNTs are also p-type semiconductors with holes as major charge carriers.

A simplistic representation of the sensor calls for the PANI-SWNT assembly to be considered as two resistances in parallel. The current will essentially flow through the lowest resistance component. For the polyaniline film, the resistance change will be modulated by the protonation–deprotonation brought by ammonia [18, 19]. As ammonia adsorbs onto or is absorbed into the polymer,  $NH_3$  molecules withdraw protons from  $N^+-H$  sites to form the energetically more favorable  $NH_4^+$ . This deprotonation process reduces polyaniline from the emeraldine salt state to the emeraldine base state, leading to reduced hole density in the polyaniline and thus an increased electrical resistance. When the sensor is purged with ammonia free gas, the process is reversed:  $NH_4^+$  decomposes to form ammonia gas and a proton, and the initial doping level and electrical resistance are restored.

In addition to the two-resistance in parallel model, PANI-SWNT network can be considered as one p-type semiconductor network. The interaction between polyaniline and SWNT may increase the  $\pi$ -electron delocalization which leads to the higher charge transfer between polyaniline and SWNT. Detailed investigations of the sensing mechanism are warranted.

The sensitivity of the PANI-SWNT network was also compared to that of unfunctionalized SWNTs. The sensitivity is defined here as the relative resistance change for a given  $NH_3$  concentration, or  $\Delta R/R_0 = (R_{eq} - R_0)/R_0$ , where  $R_{eq}$  is the steady-state resistance after exposure to  $NH_3$  and  $R_0$  is the initial resistance before exposure to  $NH_3$ . As shown in Figure 6, the PANI-SWNT sensors exhibited a linear response of 2.44% per  $ppm_v$   $NH_3$  for concentrations ranging from 50  $ppb_v$  to 3  $ppm_v$ . The response of unfunctionalized SWNTs was only 0.04% per  $ppm_v$ , or about 60 times lower than that of the PANI-SWNTs. Above 3  $ppm_v$ , the sensors displayed a nonlinear response. Saturation was observed at ammonia concentrations exceeding 300  $ppm_v$ . These results clearly demonstrate the enhanced sensitivity of the PANI functionalized SWNTs over bare SWNT sensors. The reason for the higher sensitivity lies in the great affinity of ammonia to PANI because of the coordinating roles of the nitrogen atoms of both compounds [20].

The PANI-SWNT sensor also demonstrated good reproducibility when repeatedly exposed to 10  $ppm_v$  of ammonia (Fig. 7). The resistance changes were 14.26%, 14.27%, and 14.26% for the three consecutive exposures, respectively. A simple first order adsorption–desorption kinetic model based on resistance change was developed as follows:

$$\text{Adsorption process: } dR/dt = K_a (R_{eq} - R)$$

$$\text{Desorption process: } dR/dt = K_d (R - R_0)$$

Where  $K_a$  and  $K_d$  are the adsorption and desorption rate constants, respectively.  $R_{eq}$  is the equilibrium resistance

calculated as  $R_0 + (C_g \alpha \Delta R/R_0)$ , where  $C_g$  is the gaseous concentration of the analyte and  $\alpha$  is the change in resistance per unit concentration of the analyte. Experimental data and model simulations are compared in Figure 7, which shows that simulation results were in agreement with the experimental data. The sensors followed typical first order responses with respect to concentration changes. Based on curve fitting, the first order adsorption and desorption rate constants are 0.052 and 0.015  $\text{min}^{-1}$ , respectively. Hysteresis is not uncommon in adsorption and desorption systems.

The temperature dependence of the PANI-SWNT sensor's baseline resistance and its response to  $NH_3$  was investigated by controlling the sensor temperature using a

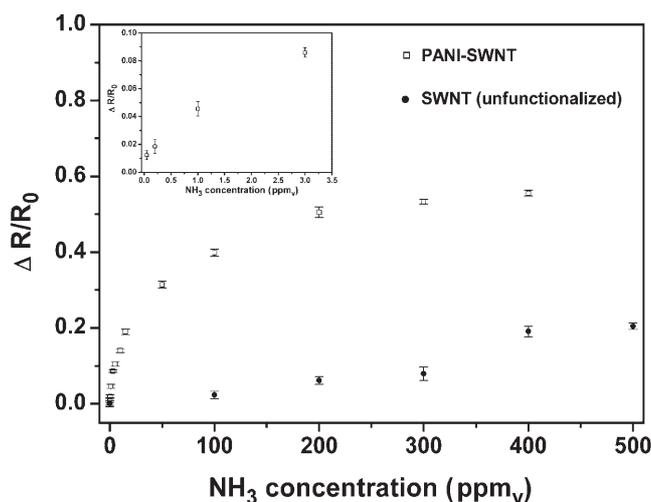


Fig. 6.  $NH_3$  sensitivity of PANI-SWNTs (PANI was coated on SWNTs using a two-electrode configuration at 0.8 V for 5 minutes) and unfunctionalized SWNTs (SWNT-COOH). The inset shows the linear range from 50  $ppb_v$  to 3  $ppm_v$ . Error bars are the standard deviations, often smaller than the symbols.

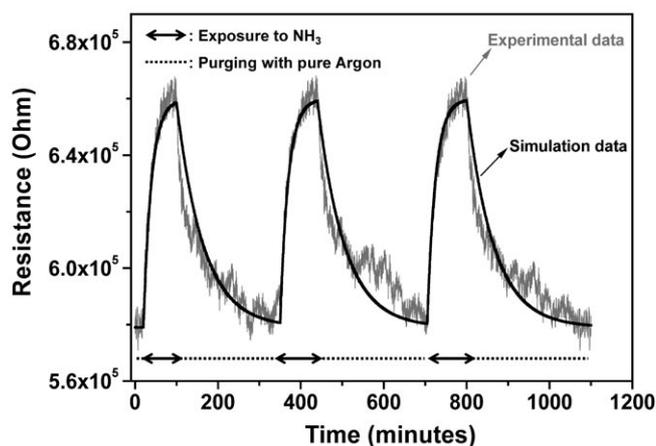


Fig. 7. Reproducibility of the PANI-SWNT sensor in response to repeated exposures of 10  $ppm_v$  ammonia. The arrows show exposure times to  $NH_3$ . The bold line is the fitted first order response. Polyaniline was coated on SWNTs using a two-electrode configuration at 0.8 V for 5 minutes.

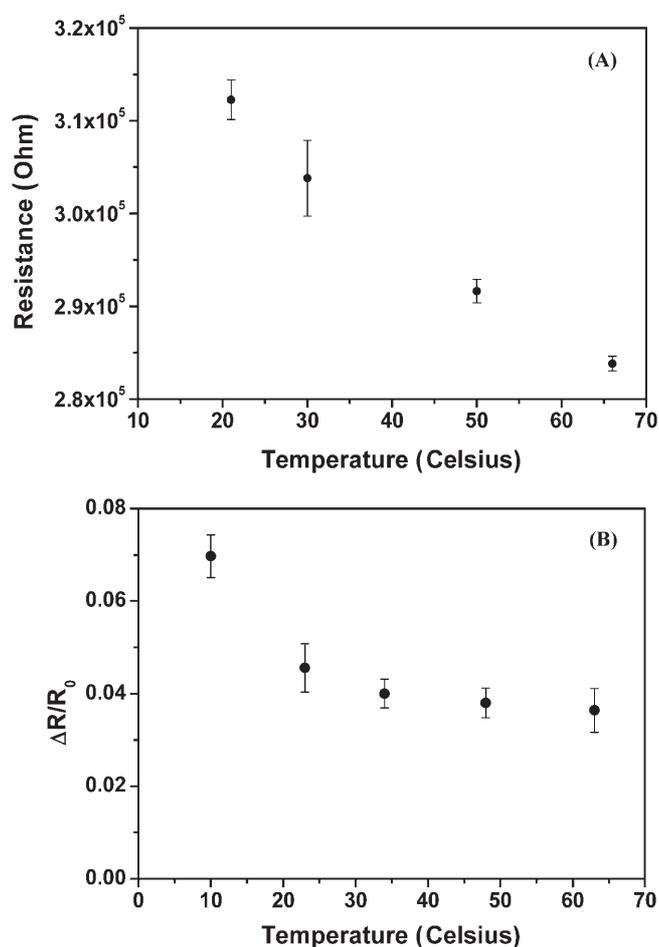


Fig. 8. Baseline electrical resistance of the PANI-SWNT sensor (A) and sensitivity to 1 ppm<sub>v</sub> NH<sub>3</sub> (B) as a function of temperature. Polyaniline was coated on SWNTs using a two-electrode configuration at 0.8 V for 5 minutes.

miniature thermoelectric module. The sensor showed a linear decrease in baseline resistance when the temperature was increased from 22 to 80 °C (Fig. 8A). This can be attributed to the semiconductor-like behavior of the PANI. Ammonia sensing experiments revealed a decreased sensitivity with increasing temperature between 10 and 63 °C, as shown in Figure 8B. The most likely explanation for this phenomenon is an increase of the gas/PANI partition of ammonia with increasing temperature, which is consistent with the explanations of Haug et al. [21].

#### 4. Conclusions

We have demonstrated a simple and efficient method to fabricate functionalized SWNT-based gas sensors and have demonstrated the outstanding sensing properties of the resulting sensors. The PANI-SWNT ammonia gas sensor produced using this method was shown to have superior sensitivity, very low detection limit, and good reproducibility compared to pure SWNT sensors and previously investigated chemically functionalized sensors. The fabrication method allows for precise control over the device's characteristics and makes possible the creation of arrays of individually addressable sensors, each functionalized with a different substance and thereby displaying different sensor characteristics. This is a promising step toward the development of miniaturized devices with extensive analytical capabilities.

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