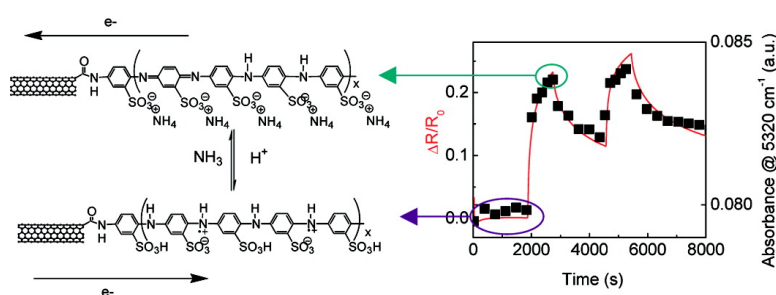Article

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Mechanism of Ammonia Detection by Chemically Functionalized Single-Walled Carbon Nanotubes: *In Situ* Electrical and Optical Study of Gas Analyte Detection

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Abstract: We provide definitive evidence for the mechanism of electronic detection of ammonia by monitoring *in situ* changes in the electrical resistance and optical spectra of films of poly(*m*-aminobenzenesulfonic acid)-functionalized SWNTs (SWNT-PABS). The increase of resistance during exposure to ammonia is associated with deprotonation of the PABS side chain that in turn induces electron transfer between the oligomer and the valence band of the semiconducting SWNTs. Near IR spectroscopy is used to demonstrate that the charge transfer is a weakly driven process, and this accounts for the high reversibility of the sensor. We show that the sensitivity of the chemiresistors increases as the film thickness is reduced to the percolation threshold and that the SWNT-PABS film thickness provides a simple means to enhance the electronic response.

Introduction

As a result of their excellent electrical conductivity, one-dimensional nanoscale form factor, and well developed chemistry, single-walled carbon nanotubes (SWNTs) are ideal materials for the development of a broad spectrum of low-power, portable sensors in an extremely compact device architecture.[1–10] Current SWNT films consist of a mixture of metals and semiconductors, but in previous work it has been shown that treatment of such SWNT mixtures with oxidizing agents leads to a strong decrease in the resistivity of the films.[11] We have shown that this may be attributed to the introduction of holes into the valence band of the semiconducting SWNTs which is observable as a decrease in intensity of the first semiconducting

interband transition (S_{11}) that occurs in the near-infrared (NIR) region of the spectrum (Figure 1).[12,13] Thus, the model for oxidative doping of SWNT films that consist of a mixture of metallic and semiconducting SWNTs is clear: the metallic SWNTs undergo a shift in the position of the Fermi level, but because the conduction band density of states (DOS) is quite flat there is little change in conductivity,[9] whereas the Fermi level of the semiconducting SWNTs shifts from the middle of the energy gap into the valence band which generates free carriers that contribute strongly to the conductivity (Figure 1).[14] The extreme sensitivity of the electronic structure of semiconducting SWNTs to dopants[1,2] can be further modulated by the introduction of chemical receptors so as to provide selective and sensitive response to a wide range of toxic chemicals.[6,15,16]

Most previous studies of chemically modified SWNTs as chemical and biological sensors have utilized noncovalent functionalization approaches[15–17] that present serious obstacles in the fabrication of devices with reproducible characteristics because of difficulties in the control of the material composition. The preparation of well-defined materials through covalent bond

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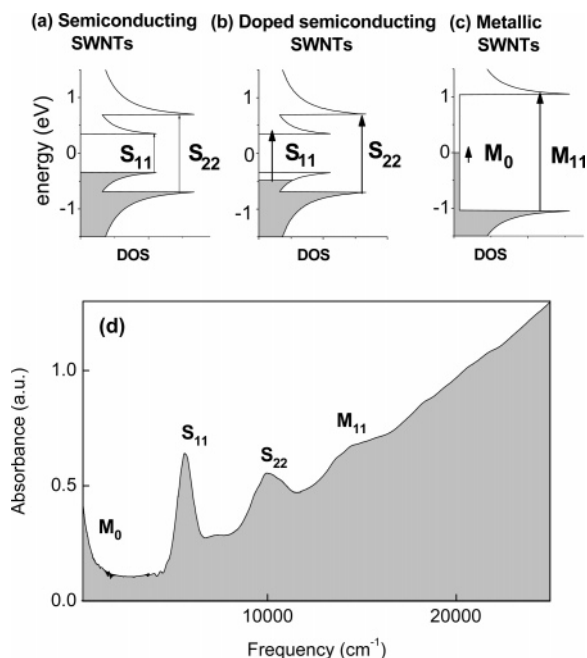
Figure 1. Schematic representation of the density of states (DOS) of (a) semiconducting SWNTs, where S_{11} and S_{22} correspond to the first and second interband transitions, (b) hole doped semiconducting SWNTs, illustrating the reduced intensity of the first interband transition, S_{11}, due to depletion of the valence band, and (c) metallic SWNTs, where M_0 and M_{11} correspond to the Fermi level and first interband transitions, respectively. (d) Electronic spectrum of electric arc produced SWNTs.

formation constitutes the only controlled route for the introduction of chemical receptors into SWNTs that allows the isolation and characterization of specific compounds of known electrical conductivity.[14] The well-defined composition and properties of covalently functionalized SWNTs provide an opportunity to dynamically characterize the nanotube electronic structure and electrical conductivity in the presence of analyte molecules.

In the present study we explore the sensing mechanism of the graft copolymer, SWNT-poly(*m*-aminobenzenesulfonic acid), SWNT-PABS.[18,19] Apart from the fact that this material offers superior performance as an ammonia sensor,[6] we have demonstrated that this is the first functionalized SWNT material with a hybrid electronic structure which is not a simple sum of the individual components.[19]

Such materials offer great promise as sensors because the attached functionality may be tailored for specific analytes while the influence of the chemistry on the oligomer side-chain is detected via a change in the electronic conductivity due to a modulation of the joint density of states of the SWNT graft-copolymer. Below we offer definitive evidence for this picture of the electronic response of the material by *in situ* spectroscopic and electrical measurements and thereby provide a definitive answer to the mechanism of ammonia sensing (change in electrical resistance) by SWNT−PABS films. By dynamically observing the spectroscopic changes and conductivity of the material on exposure to analyte, we show that the sensor action is associated with the refilling of the depleted valence band of the semiconducting SWNTs (Figure 1), due to charge transfer from the ammonia molecule via the attached PABS. Thus

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Scheme 1. Mechanism of Interaction of SWNT-PABS with NH_3. The Arrows Indicate Charge Transfer between SWNT and PABS
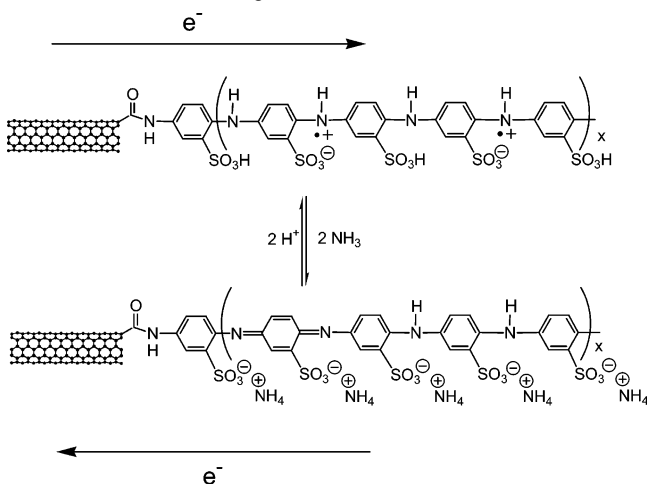
ammonia sensing occurs by deprotonation of the side-chain oligomers that in turn induces electron transfer between the side-chain and the SWNTs (Scheme 1), thereby decreasing the conductivity because addition of electrons to the semiconducting SWNTs refills the valence band (Figure 1).[6] We show that the sensitivity of these sensor devices is enhanced when the films operate in the vicinity of the percolation threshold.

Experimental Section

The poly(*m*-aminobenzenesulfonic acid)-functionalized SWNT material (SWNT-PABS)[18,19] was obtained from Carbon Solutions Inc. (www.carbonsolution.com), and it is also available from Sigma-Aldrich. Aqueous dispersions of SWNT-PABS with a concentration of ∼0.5 mg/mL at pH 5 were prepared by ultrasonication (bath sonicatior Aquasonic 50HT, VWR Scientific, sonic power 75 W) for 1 h and sprayed with an airbrush on a glass substrate held at 160 °C in order to allow the fabrication of films of reproducible and uniform thickness. The spraying was performed using an airbrush with a 0.3 mm nozzle; a chromatography sprayer from Fisher Scientific has been used with similar success in previous studies. The sprayer was operated at ∼1 psi air pressure (0.07 kg/cm²) without applying sonication to the dispersions during spraying. The spraying was performed in a fume hood and use of a facial mask is recommended in order to protect the operator from the sprayed aerosol. The thickness of the SWNT-PABS films was estimated from the intensity of the absorbance at the second pair of singularities in the DOS of semiconducting SWNTs (S_{22} with a maximum at 9750 cm^{-1}) and the extinction coefficient ($\epsilon = 7.3$ L g^{-1} cm^{-1}),[19] assuming a bulk density of 1.45 g cm^{-3};[14] we have previously shown by NIR and AFM measurements that this technique is capable of providing the SWNT film thicknesses with a standard deviation of ∼20%.[14]

In this study we used glass substrates prepatterned with five sets of gold contacts, thereby leading to the preparation of four devices with interdigitated contacts separated by 100 µm and one device with contacts separated by 4 mm (Figure 2a). The contacts are prepared by sputtering a 100 ± 20 nm gold layer on a glass substrate and a 20−40 nm chromium layer is used for improved adhesion. For the *in situ* optical and electrical measurements the substrates were loaded in a stainless steel chamber with a sapphire window. The desired analyte concen-
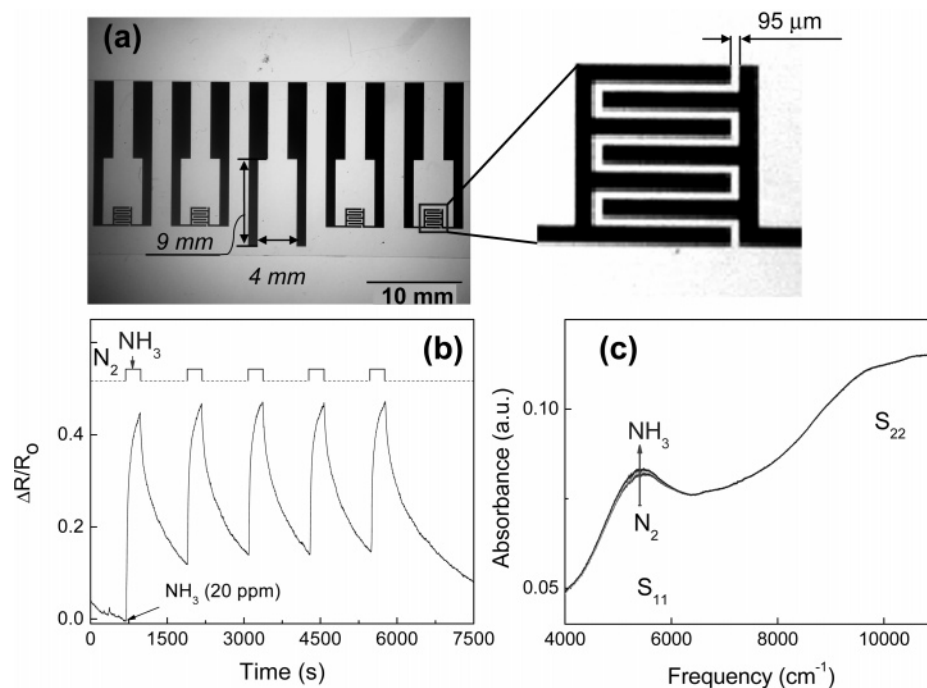
Figure 2. (a) Optical image of a glass substrate with five sensors for simultaneous measurement of the electrical resistance and film spectra. (b) Change of resistance of SWNT-PABS films (thickness, 20 nm) in response to 20 ppm NH_3. (c) Optical spectra of the SWNT-PABS film recorded in nitrogen and during exposure to 20 ppm of ammonia. The arrow indicates the evolution of the S_{11} transition upon exposure to ammonia.

trations were obtained by dilution with nitrogen using a computerized gas dilution system (Environics Inc., Tolland, CT). The experiments were performed at room temperature and a flow rate of 1000 cm^3 min^{-1}, and nitrogen was used as a balance gas. The resistance of the films was measured in a two-probe configuration using a Kethley 236 source measure unit controlled by custom LabVIEW software. The measurements were performed at 0.5 V unless otherwise stated. The near-IR (NIR) spectra were recorded on a Varian CARY 500 UV−vis-NIR spectrophotometer between 4000 cm^{-1} and 20 000 cm^{-1} in order to capture the interband transitions of semiconducting SWNTs.

Results and Discussion

Electrical and Spectroscopic Measurements of SWNT-PABS upon Exposure to Ammonia. Figure 2b shows the typical electrical response of a SWNT-PABS film to ammonia; in this experiment the sensor (film thickness $t = 20$ nm) was purged in nitrogen for 15 min and then exposed to 20 ppm ammonia for 5 min. The resistance of the sensor was recorded continuously during five successive cycles of analyte exposure (15 min N_2, 5 min NH_3) and the response ($\Delta R/R_o$) calculated as a change of resistance ($\Delta R = R_i - R_o$) normalized by the initial resistance of the device R_o. The resistance of the film increases by ∼45% upon exposure to ammonia in the first cycle, and the replacement of ammonia with nitrogen recovers ∼80% of the initial resistance. The response becomes reproducible after the first exposure to ammonia; the resistance of the film increases by 30% during successive injections of 20 ppm NH_3 and reaches its asymptotic resistance after purging with nitrogen for ∼15 min.

As discussed above, we suggested that the resistance change is due to a charge-transfer process between the SWNTs and the PABS oligomer that is sensitive to the presence of ammonia (Scheme 1).[6] If this mechanism is correct, we reasoned that it

might be possible to dynamically observe the charge-transfer process by using optical spectroscopy to measure the change of the carrier concentration in the valence band of SWNTs, and that if Scheme 1 is correct, the presence of ammonia should serve to (partially) refill the valence band and thereby increase the intensity of the S_{11} transition in accord with the previous understanding of the effect of doping on the interband transitions in SWNTs.[9,12,20−22] This premise is born out by Figure 2c, where the near-IR (NIR) intensity of the first interband transition (S_{11}) of the semiconducting SWNTs progressively increases during exposure of the film to ammonia and supports the idea that this process leads to dedoping of the semiconducting SWNTs (refilling of the valence band).

In order to analyze the changes in film resistance as a function of the band filling we performed dynamic *in situ* experiments in which the resistance and NIR spectra were recorded simultaneously as a function of time and analyte dosage. In these experiments the measurements were performed using a 100 nm thick film of SWNT-PABS exposed to 20 ppm of ammonia in two cycles (N_2 for 30 min, NH_3 for 15 min, Figure 3). Figure 3a shows the baseline-corrected absorption spectra in the spectral range between 4000 cm^{-1} and 12 000 cm^{-1}, which captures the first (S_{11}) and second (S_{22}) semiconducting interband transitions. The absorbance intensity at the maximum of the first interband transition (5320 cm^{-1}) continuously increases upon exposure to 20 ppm ammonia for a total change of ∼3% (Figure 3b), whereas the second interband transition S_{22} remains unmodified (Figure 3a). Clearly the increase of the intensity of the S_{11} transition is correlated with the increase of the electrical

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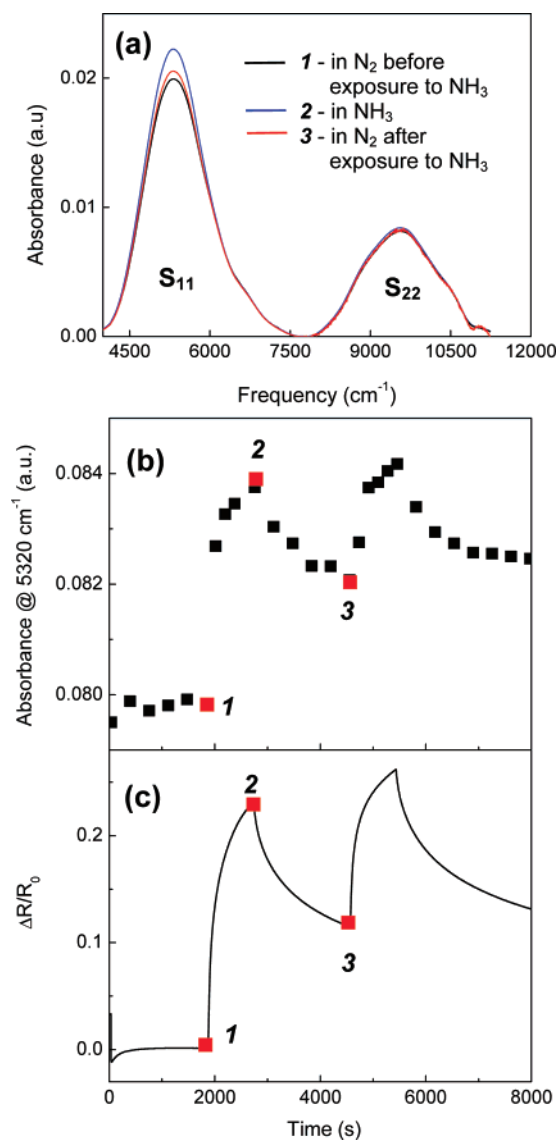
Figure 3. (a) Baseline corrected NIR spectra of a 100 nm thick SWNT-PABS film recorded in N_2 (black and red lines) and NH_3 (blue line). (b) Change of the absorbance intensity of the SWNT-PABS film at 5320 cm^{-1} (maximum of S_{11} transition) in response to 20 ppm ammonia: **1**, **2**, and **3** correspond to the change in the chamber environment: **1**, **3** (N_2 to 20 ppm NH_3) and **2** (20 ppm NH_3 to N_2). (c) Resistance change of the film in response to 20 ppm ammonia.

resistance of the SWNT-PABS film measured simultaneously and shown in Figure 3c.

This supports the proposed transduction mechanism, which relies on dedoping of the SWNTs due to electron charge transfer from the deprotonated PABS side-chain to the nanotube, as shown in Scheme 1. The S_{11} transition decreased when NH_3 is replaced with N_2 (Figure 3a,b); however, the intensity does not reach the initial level in accord with the resistance measurements. The first exposure to ammonia results in a change of resistance by ~25%, and the second exposure to ammonia increases the resistance by ~16% (Figure 3c). Thus we conclude that the presence of the PABS functionality provides acid–base sites in the side-chain of the material that mediate the electron density on the semiconducting SWNTs and thereby produces observable changes in the electrical resistance and the intensity of the S_{11} interband transition of the film in accord with the mechanism detailed in Scheme 1 and Figure 1.

Further evidence for the mechanism proposed in Scheme 1 and for the pivotal role of the PABS oligomer is provided by *in situ* measurements of the resistance and optical behavior of nonfunctionalized SWNTs in response to exposure to ammonia. For these measurements we selected purified SWNTs with a chemical and physical nature that closely resemble pristine SWNTs (P2-SWNT, www.carbonsolution.com). Films of non-functionallized SWNTs show a relatively small change of resistance when exposed to 20 ppm ammonia (Figure S1)[6] and recover only ~20% of their initial resistance after purging with nitrogen. The fact that the purified SWNTs do not exhibit the sensitivity of SWNT-PABS to ammonia confirms that the modulation of the electronic properties of SWNTs depends on the presence of the PABS side chains.

The distinction discussed above is supported by the role of water in the sensing behavior of the two materials. It has been previously reported for SWNT-FET devices that the presence of adsorbed water is essential for the electrical response to ammonia and that devices degassed in vacuum are insensitive to NH_3.[4] In accord with this observation we found that films of pristine SWNTs (P2-SWNT) showed significantly reduced response to ammonia after heat treatment in vacuum (Supporting Information, Figure S1). In order to test the effect of adsorbed water on the sensitivity of SWNT-PABS film chemiresistors we degassed devices in vacuum (3×10^{-6} Torr, 110 °C, 2 h); it was found that the degassed devices operated in an identical manner to the as-prepared SWNT-PABS films, which presumably contain adsorbed water molecules (see Supporting Information, Figure S2). It is worth noting that PABS strongly binds water through the formation of H-bonds, and the complete desorption of water cannot be accomplished without decomposition of the polymer.[23] Thus, we conclude that while water may be present as a constituent of the PABS oligomer, its presence is immaterial to the response of SWNT-PABS to ammonia. The measurements of the SWNT-PABS film response to ammonia at temperatures below the freezing point of water provides further evidence that water molecules are not involved in the charge-transfer mechanism. For this experiment the stainless steel chamber was enclosed in a sealed container purged with nitrogen and immersed in an ethanol–dry ice bath. The temperature was measured using a calibrated thermistor that was incorporated into the substrate of the SWNT-PABS film. The response curve of a SWNT-PABS film to 20 ppm of ammonia was recorded at 20 °C, the film temperature was lowered to −20 °C, and the response of the film was recorded again (Figure 4).

The absolute value of the film resistance increased as the device was cooled down to −20 °C, but the response ($\Delta R/R_o$) to NH_3 was essentially unchanged. The data indicate that the change of resistance of the SWNT-PABS film on exposure to ammonia occurs much faster at high temperature (Figure 4, inset), which is in accord with the increase in the reaction rate between the PABS side chains and ammonia molecules. Thus, we conclude that the presence of physically adsorbed water is not involved in the interaction between the SWNT-PABS and ammonia molecules and it does not mediate the change transfer process.

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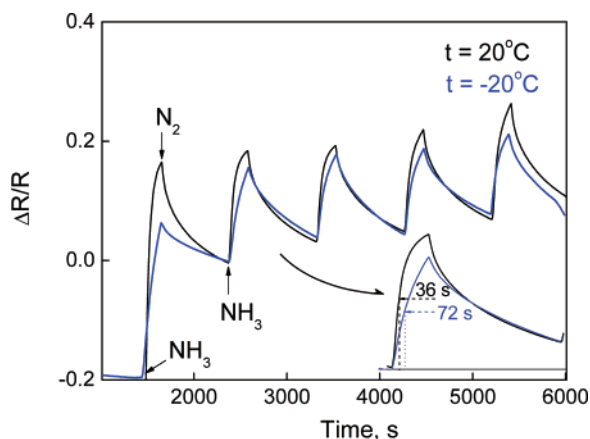
Figure 4. Response curves of a SWNT-PABS film to 20 ppm ammonia at 20 °C (black curves) and −20 °C (blue curves). The resistance was calculated from the current at 0.1 V. The gas flow rate in these experiments was 400 cm³ min⁻¹. The inset shows the delay in the response at lower temperature.
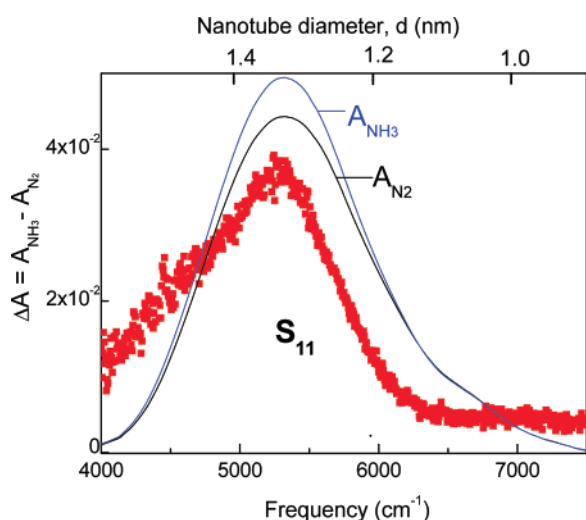

Figure 5. Difference of the absorption spectra of SWNT-PABS film (ΔA, red squares), before (A_{N2}) and after (A_{NH3}) exposure to 20 ppm ammonia in the spectral region of the first interband transition of the semiconducting SWNTs (S_{11}). The baseline corrected S_{11} spectra of SWNT-PABS in nitrogen and ammonia are given as black and blue solid lines, respectively. The SWNT diameter, d, is calculated using the relationship $S_{11} = 2a\beta/d$.[24]

In order to further understand the modulation of the electronic structure of SWNT-PABS by ammonia, the absorbance change of the first semiconducting interband transition (S_{11}) is plotted as a function of frequency in Figure 5 (see also Figure S3 in Supporting Information).

The frequency or energy of the optical transitions between the van Hove singularities is related to the band gap energy of SWNTs; for semiconducting nanotubes the energy of the first interband transition (S_{11},eV) is inversely proportional to the nanotube diameter (d, nm), $S_{11} = 2a\beta/d$,[24] where a is the carbon−carbon bond length (0.142 nm) and β is the transfer or resonance integral between the π-orbitals ($\beta = 2.9$ eV). On the basis of this equation, it is clear from Figure 5 that the maximum intensity change occurs at a SWNT diameter $d \sim 1.3$ nm, which is close to the mean diameter of arc-produced SWNTs ($d = 1.37$ nm ± 0.1 nm).[25−27]

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The absorbance change ($\Delta A = A_{NH3} - A_{N2}$) plotted in Figure 5 (see also Figure S3 in Supporting Information), suggests that the modulation of the electronic structure of the SWNTs by ammonia is sensitive to the nanotube diameter, and that the charge-transfer process is mainly associated with SWNTs with $d > 1.3$ nm (energy gap <0.63 eV), whereas there are no changes in the optical spectra of nanotubes of diameter, $d < 1.1$ nm (energy gap > 0.75 eV). While the spectroscopically observed band gap in Figure 5 provides information on the population of SWNT diameters that are associated with the charge-transfer process, it is not the band gap itself that is important in governing the charge-transfer process but rather the ionization potential of the valence band. Thus, SWNT-PABS acts as a sensitive and reversible sensor toward ammonia because of the dynamic alignment of the Fermi level with various electronic energy levels of the protonated forms of the PABS oligomer and the valence band of some fraction of the SWNT population.

The fact that the spectra of SWNTs of a diameter less than a particular threshold value ($d \sim 1.1$ nm) are unaffected by the presence of ammonia provides insight into the mechanism and effectiveness of the SWNT-PABS material as an ammonia sensor. The lack of an ammonia response by semiconducting SWNT populations of diameter $d < 1.1$ nm has two possible explanations: *first* that this cohort of SWNTs was not doped in the first place by functionalization with PABS, or *second* that ammonia is ineffective in dedoping this group of SWNTs by deprotonation of the side chain functionalities. It seems quite unreasonable that ammonia would not be an effective base for the sulfonic acid groups, and thus it is likely that not all of the SWNTs are able to undergo charge transfer to the PABS side chain, and that the SWNTs of diameter $d < 1.1$ nm are too difficult to oxidize to undergo doping in the parent SWNT-PABS material.

This provides an important piece of information which helps to explain the effectiveness and reversibility of SWNT-PABS as an ammonia sensor when compared to unfunctionalized SWNTs (above). The data suggests that the charge-transfer process from the semiconducting SWNTs to PABS is a weakly driven reaction and that the ammonia binding process is in turn a very weakly exergonic process such that the replacement of the ammonia atmosphere with nitrogen is able to reverse the process.[28] In order to test this hypothesis we investigated the effect of a strong protic acid (HCl) on the electronic structure of SWNT-PABS.

Electrical and Spectroscopic Measurements of SWNT-PABS Films upon Exposure to Hydrogen Chloride (HCl). A SWNT-PABS film of thickness 100 nm was exposed to 20 ppm anhydrous HCl (Figure 6); exposure to HCl for 15 min decreases the resistance of SWNT-PABS film, but the resistance does not recover after the hydrogen chloride is replaced with nitrogen for 30 min (Figure 6a). The exposure to HCl suppresses the S_{11} interband transition (Figure 6b), which is indicative of

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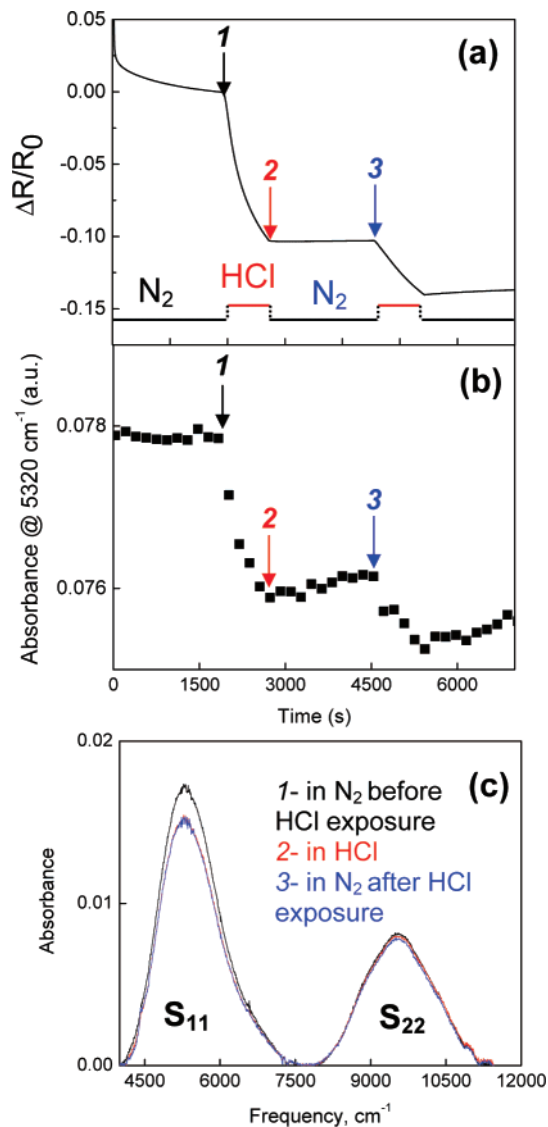
Figure 6. (a) Resistance change of a SWNT-PABS film upon exposure to 20 ppm HCl; **1**, **2**, and **3** correspond to the change of the environment: **1**, **3** (N_2 to HCl) and **2** (HCl to N_2). (b) Intensity change of the absorbance at 5320 cm^{-1} (maximum of S_{11}) in response to 20 ppm HCl. (c) Baseline corrected NIR spectra of the SWNT-PABS film: **1**, in nitrogen; **2**, at maximum change of resistance in presence of HCl for 15 min; **3**, in nitrogen after the exposure to HCl and purging for 30 min.

charge transfer from the nanotube to the protonated side chain due to depletion of the valence band, and the reduction of the S_{11} intensity follows the decrease in resistance of the SWNT-PABS film upon exposure to HCl (Figure 6c). Thus, it seems likely that the interaction of SWNT-PABS with HCl is the converse of the behavior discussed above with ammonia, perhaps with additional protonation of the side chain (Scheme 2), but in this case the protonation reaction is irreversible because HCl is a very strong acid. This behavior is anticipated in the chemistry of polyaniline (PANI), where it has been shown that hydrochloric acid is an efficient dopant of PANI[29−31] and leads to the emeraldine salt of PANI. The additional protonation

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Scheme 2. Schematic of the Protonation/Deprotonation of SWNT-PABS upon Interaction with HCl and NH$_3$, Respectively
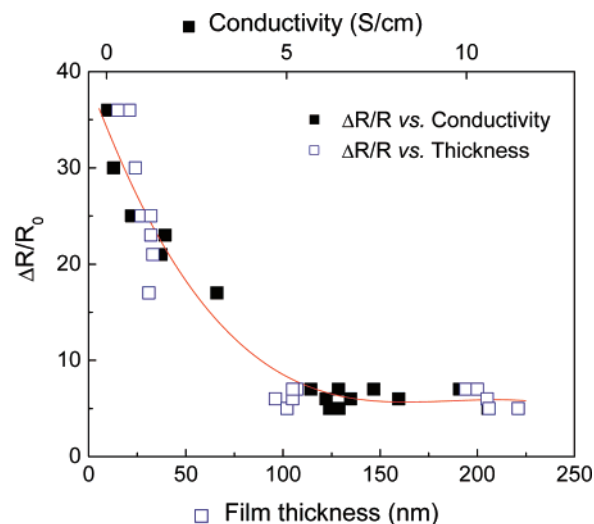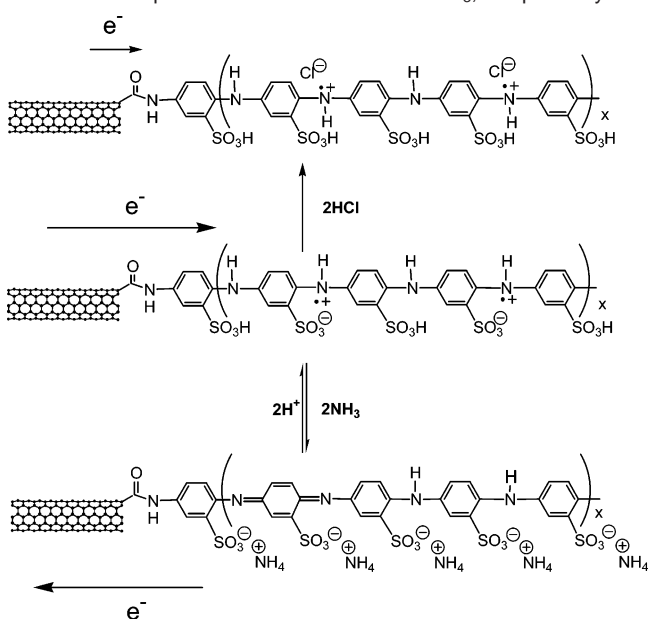

Figure 7. Response ($\Delta R/R_o$) of SWNT-PABS film to 20 ppm ammonia as a function of film thickness and conductivity.

of the PABS side chain is expected to have a smaller effect on the SWNT-PABS conductivity, as the PABS backbone itself is not directly involved in this reaction and the induced charge-transfer process will be relatively weak.

Furthermore, analysis of the data shows that there is now no discrimination based on the diameter of the SWNTs, and it is apparent that the electron transfer and protonation processes are strongly exergonic and thus largely irreversible (Supporting Information, Figure S4). The HCl effectively dopes the entire population of semiconducting SWNTs independent of their diameter (and ionization potential and band gap).

Film Response as a Function of Thickness. Figure 7 shows that the resistance change of SWNT-PABS films on exposure to ammonia falls on a universal curve as a function of both the film thickness and conductivity, and the observed behavior suggests that thin films operate as a percolating network in their sensor response.

In our previous analysis of the absolute conductivity of SWNT films as a function of film thickness, we showed that

the films operate as percolating networks, and such a model is supported by the data in Figure 7, where it may be seen that the thin films are the most sensitive.[14] The response of the film resistance, ($\Delta R/R_0$), shows a weaker dependence on thickness than the absolute conductivity but reaches an asymptotic value at about the same thickness ($t \sim 200$ nm),[14] which is to be expected because the change in total conductivity of the sensor is small (Figure 7) compared to the variations seen in the film conductivity as a function of thickness, which cover 4 orders of magnitude.[14]

The increased sensitivity of very thin films is due to the fact that these films are in the vicinity of the percolation threshold and therefore depend more critically on the presence of (doped) semiconducting SWNTs in order to maintain conducting channels through the network. The response of the film ($\Delta R/R_0$ value) shows a weaker dependence on thickness than the absolute conductivity,[14] because the dedoping of SWNT-PABS decreases the conductivity of the pathways involving semiconducting SWNTs in the percolating channels but does not affect the concentration of pathways involving metallic SWNTs.

As noted in the introduction, the change in conductivity of the SWNT networks on doping is dominated by changes in the conductivity of the semiconducting SWNTs, which normally limit the conductivity of the film and force the mobile electrons to traverse the metallic SWNTs. The sensor functions by activating a population of the semiconducting SWNTs which introduces new pathways into the percolating network and thus yields a dependence of the sensor action on thickness similar to that which was seen in the parent functionalized SWNTs.

Supporting Information Available: Response of annealed nonfunctionalized SWNT and SWNT-PABS films upon exposure to ammonia; change of the optical spectra of SWNT-PABS in response to ammonia and anhydrous hydrogen chloride. This material is available free of charge via the Internet at http://pubs.acs.org.

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