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Role of Defects in Single-Walled Carbon Nanotube Chemical Sensors

**Joshua A. Robinson, Eric S. Snow,* Ştefan C. Bădescu,
Thomas L. Reinecke, and F. Keith Perkins**

*The Naval Research Laboratory, Electronic Science and Technology Division,
4555 Overlook Avenue, Washington, D.C. 20375*

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ABSTRACT

We explore the electronic response of single-walled carbon nanotubes (SWNT) to trace levels of chemical vapors. We find adsorption at defect sites produces a large electronic response that dominates the SWNT capacitance and conductance sensitivity. This large response results from increased adsorbate binding energy and charge transfer at defect sites. Finally, we demonstrate controlled introduction of oxidation defects can be used to enhance sensitivity of a SWNT network sensor to a variety of chemical vapors.

The use of single-walled carbon nanotubes and nanotube random networks for chemical detection of gases and chemical vapors has been a subject of active research for several years. During this time, advances have been made in the understanding of how molecules interact with single walled nanotubes (SWNT) and how the presence of a given analyte is detected. Kong et al.,[1] first reported the utility of SWNTs as chemical sensors for sensing NH_3 and NO_2 based on a charge transduction mechanism. This study subsequently led to additional research on the use of SWNTs as sensors for various other chemical vapors. Snow et al.[2,3] later report the use of random networks of carbon nanotubes as chemical sensors utilizing charge and polarization-based transduction mechanisms.

The observed response in previous research was attributed to the adsorption of analyte molecules on the pristine SWNT sidewall,[1−3] and many molecules have been calculated to bind to the sidewalls of SWNTs with a range of energies, charge transfer, and polarizability.[4−9] Molecules such as acetone, NH_3, and CH_4 have been calculated to interact weakly with minimal charge transfer when in contact with the nanotube sidewall.[4,9] However, recent experimental work and theoretical calculations of the interaction between SWNTs and molecules such as acetone and NH_3 have called this simple representation into question.[10−14] Experiments indicate NH_3 exhibits significant charge transfer (based on threshold voltage shifts)[1] and desorption energies of ∼1 eV/molecule that are attributed to topological defects along the SWNT sidewall.[15] Consequently, it is important to consider the possibility that defect sites might affect the sorption properties of other chemical vapors as well.

In this Letter, we establish that SWNT defect sites play an important role in the electrical response for a broad spectrum of chemical vapors, and the controlled introduction of defects can be used to increase the sensitivity and chemical selectivity of both the conductance and capacitance responses. We use a combination of electronic calculations and experimental data to establish that nanotube defects form low-energy sorption sites, which also serve as nucleation sites for additional condensation of analyte vapor. We controllably introduce carboxylic acid sites on the SWNTs (<2% of the total sites),[16,17] which produces an increase in both the capacitance and conductance response for a broad spectrum of analytes. These results have important implications both for the fundamental understanding of SWNT/molecular interactions and for the development of functionalization schemes to modify the sensitivity and selectivity of SWNT sensors.

Test structures consisted of a pair of interdigitated Ti/Au electrodes deposited on a SWNT network.[18] A capacitively coupled back gate is used to measure the network capacitance and to calibrate the charge response by using $Q_{\mathrm{CNT}} = C_{\mathrm{CNT}}V_{\mathrm{g}}$. Both the conductance and capacitance measurements are accurate to better than 10^{-4}, which corresponds to a charge sensitivity of $\sim 10^{-2}$ e^-/μm of SWNT. Details of the growth, fabrication, and device characterization can be found in refs 2 and 3.

Oxidation defects were introduced into the SWNTs by exposure to ultraviolet light (UV)/ozone followed by a soak in peroxide solution. Samples were placed on a hot plate at 120 °C and were subsequently bombarded by UV/ozone formed by an ozone generator. Ozonation continued until the conductance (G) of the sample was reduced to a predetermined value (either $0.8G_o$ or $0.4G_o$). Following

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* Corresponding author. E-mail: snow@bloch.nrl.navy.mil.

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14. ABSTRACT

We explore the electronic response of single-walled carbon nanotubes (SWNT) to trace levels of chemical vapors. We find adsorption at defect sites produces a large electronic response that dominates the SWNT capacitance and conductance sensitivity. This large response results from increased adsorbate binding energy and charge transfer at defect sites. Finally, we demonstrate controlled introduction of oxidation defects can be used to enhance sensitivity of a SWNT network sensor to a variety of chemical vapors.

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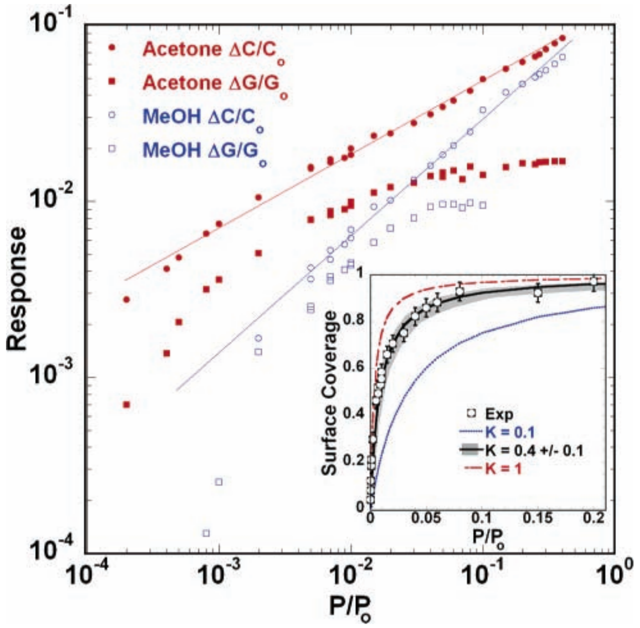

Figure 1. Capacitance and conductance response to sequential doses of acetone or methanol. Inset: Langmuir surface coverage of acetone as a function of acetone partial pressure.

ozonation, the samples were soaked in a mixture of 30% H_2O_2 (aq) and methanol (7:75) for 1 min at 60 °C to break the C−C bonds on the SWNT sidewall and produce C−O groups.[19] This process resulted in a further reduction of the conductance by approximately 30−50%. Future reference to the oxidized samples are in the form of $0.8G_o$ or $0.4G_o$.

We have also made ab initio calculations of the electronic and structural properties of analyte/nanotube interactions using a two-layer ONIOM technique.[20] Here, the chemically active region involving the adsorbate, the functional group and the neighboring C atoms is treated with the B3LYP hybrid functional using a large 6-31++G(d,p) basis set, whereas the surrounding cluster is treated with a PM3 semiempirical potential. These techniques have well established capabilities for accurately predicting structures, adsorption energies, and charge transfers.[21,22]

The influence of defect sites on the interaction between chemical vapors and SWNTs may be illuminated by correlating the electrical response of SWNT network sensors with the results of calculations. Figure 1 shows the concentration dependence of both the conductance and the capacitance response to acetone and methanol vapors. We observe that the conductance response ($\Delta G/G_o$) to both acetone and methanol vapors saturates at $P \sim 0.05P_o$ (see Figure 1). This saturation behavior indicates the adsorption sites responsible for the conductance response are fully occupied. From experimental data the binding energy is estimated using a Langmuir isotherm fit. (NOTE: The conductance response to acetone and methanol is actually negative. For comparison and calculation, only the magnitude is presented.)

In the Langmuir model the occupation probability, θ, of an adsorption site is given by $\theta = KP_o(P/P_o)/[1 + KP_o(P/P_o)]$,[23] where K is an adjustable fit parameter called the Langmuir constant. Using $\theta = \Delta G/\Delta G_{sat}$ where ΔG_{sat} is the saturated value of ΔG, we use a best fit of the data to extract K.[24] The Figure 1 inset is a plot of the Langmuir isotherm for various K values for acetone. Also plotted is the experimental value $\Delta G/\Delta G_{sat}$. The best fit of the data occurs when $K = 0.4$ (± 0.1) mbar^{-1} (see Figure 1 inset).

The binding energy (E_b) to a SWNT is calculated using the best-fit Langmuir constant. K is related to E_b by $K = \sigma_A\tau_o/[\mathrm{SQRT}(2\pi m k_B T)]\exp(E_b/k_BT)$, where σ_A is the molecular cross section ($\sim 10^{-19}$ m^2), τ_o is the molecular resonance time ($\sim 10^{-13}$ s), and m is the molecular mass.[23] Using $K_{acetone} = 0.4$ (± 0.1) mbar^{-1} yields $E_b = 430$ (± 7) meV for acetone. A similar analysis yields $E_b = 420$ (± 10) meV for methanol.

For comparison, we have calculated the adsorption properties of acetone and methanol adsorption on a pristine (8,8) SWNT. We find that acetone and methanol physisorb on a pristine nanotube with $E_b < 50$ meV/molecule, below the accuracy of these calculations. The resulting charge transfer (ΔQ_{mol}) is also negligible ($\Delta Q_{mol} < 0.01$ e$^-$/molecule). No bound state and negligible charge transfer for acetone at a Stone−Wales defect on a (8,8) SWNT are also calculated. Clearly, the experimental data indicate a much stronger interaction than given by theory.

A second interesting feature of the data in Figure 1 is that, in contrast to the conductance data, the capacitance response ($\Delta C/C_o$) does not saturate. Evidently, at high concentrations the capacitance and conductance responses originate from two different adsorption sites. Therefore, a model of the SWNT/adsorbate interaction has to account not only for the large binding energies and charge transfer but also for the lack of saturation of the capacitance response.

We propose a model whereby defect sites serve both as low-energy adsorption sites and as nucleation sites for additional condensation of the analyte on the SWNT surface. In this model, charge transfer (i.e., the conductance response) occurs primarily when an adsorbate binds to a defect site. At low concentrations, $P \ll 0.05\ P_o$ for acetone and methanol, population of the defect sites accounts for both the conductance and the capacitance response. At high concentrations, the defect sites are fully populated and the conductance response saturates. However, vapor condensation caused by analyte−analyte interactions still occurs. This condensation does not contribute additional charge because every charge transfer (i.e., defect) site is occupied. However, the electric-field polarization of the condensed molecules continues to contribute additional capacitance response.

Our calculations for acetone and methanol indicate adsorption to oxidation defect sites (carboxylic acid) produces binding energies comparable to that measured experimentally. Figure 2 is a calculated model of the (a) binding and (b) clustering of acetone on a (8,8) nanotube sidewall containing a carboxylic acid defect. The calculated binding energy (charge transfer) of acetone and methanol to a carboxylic acid group is 353 meV (0.033 e$^-$) and 302 meV (0.018 e$^-$), respectively. These calculations indicate hydrogen bonding between the acetone and −COOH group on the nanotube sidewall. The similarity between experimental and

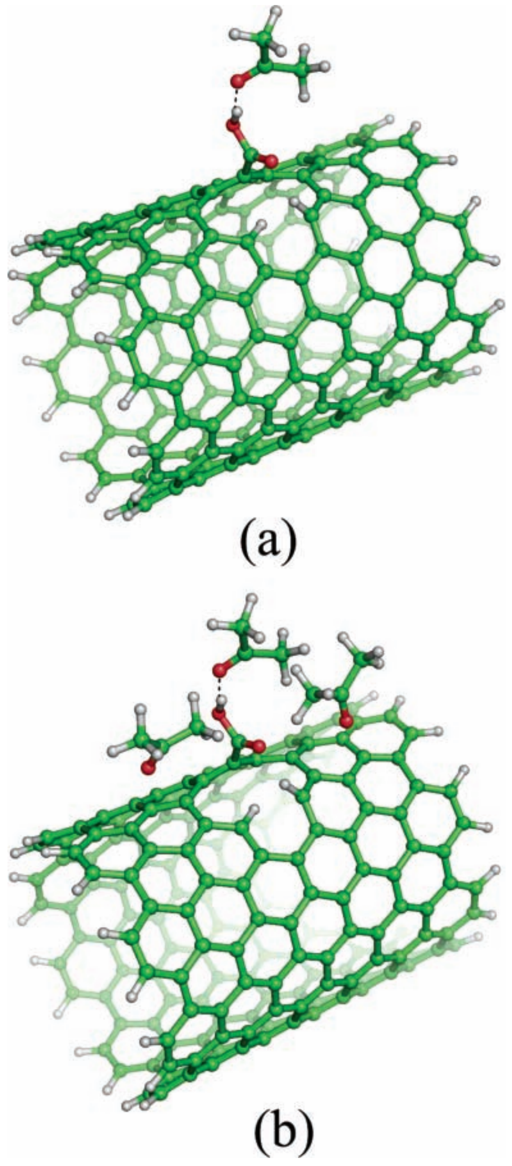

Figure 2. (a) Binding of acetone to a carboxylic acid defect on a SWNT sidewall. (b) Clustering of acetone around the defect via intermolecular bonding.

theoretical binding energies provides evidence that defects are a dominant part of measurable binding events.[25]

According to our theoretical results, additional acetone molecules can adsorb in the vicinity of the initial acetone−carboxyl complex with energies of ∼120 meV/molecule, without further charge transfer to the nanotube. This value is similar to intermolecular bonding for acetone and methanol in a vacuum,[26,27] which suggests that analyte clusters may form around a defect site on the nanotube sidewall. We note that the adsorption energies and charge transfers for both acetone and methanol adsorption on oxidized defects on nanotubes are typical of H bonding in organic systems.[28]

As a test of this model, we introduced additional defect sites into the SWNTs using a UV/ozone/H_2O_2 process and measured the resulting change in charge transfer and capacitance response. For this oxidation process, approximately 53% of the sites are −COOH (carboxylic acid), 37% are −COH (alcohol), and the balance consist of ketones.[17]

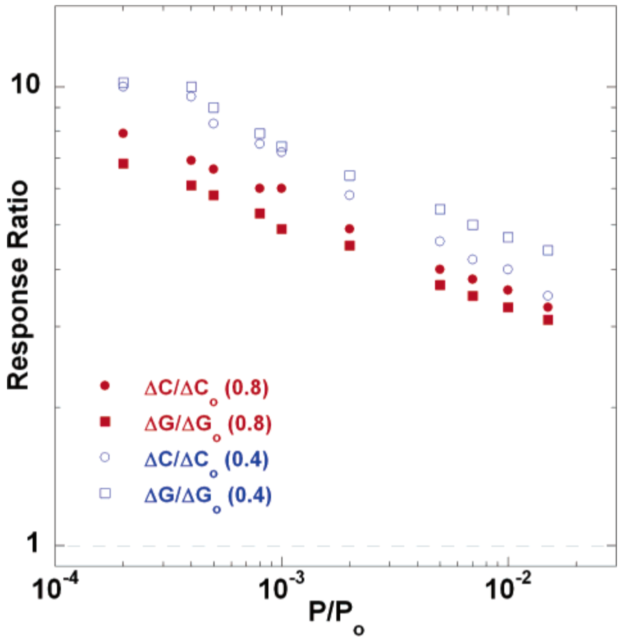

Figure 3. Response ratio of SWNT network sensors to acetone following oxidation. Samples that were more heavily oxidized show greater increases in the ΔC and ΔG.

Following oxidation of the SWNT network sensors, there is a measurable increase in both the conductance and capacitance response to acetone and methanol. This increase is especially evident at the lowest concentrations tested. In Figure 3 we present average response ratios to acetone for each oxidation process. In this case the response ratio is defined by the ratio of response before and after oxidation ($\Delta C/\Delta C_o$ and $\Delta G/\Delta G_o$). It is evident that the oxidation greatly improves the sensitivity to acetone.

For a given dose of analyte, the charge transfer per unit length of SWNT can be extracted from the measured values of ΔG and dG/dQ ($=1/C_o\, dG/dV_g$, where C_o is the capacitance per unit length calculated for SWNTs in a network).[29] From this analysis, acetone produces a saturated charge transfer of 15 (22) $e^-/\mu m$ for the $0.8G/G_o$ ($0.4G/G_o$) samples, which compares to 3 $e^-/\mu m$ before oxidation (positive $e^-/\mu m$ indicates e^- donation to the SWNT).

The percentage of carbon atoms that are converted to oxidation defects can be estimated from the saturated charge values listed above and using the charge transfer of 0.03 e^-/defect estimated by theory. This estimate produces ∼455 (636) defect sites/μm of SWNT for the $0.8G/G_o$ ($0.4G/G_o$) samples. In this case, the number of defects rises in proportion to the ozone exposure, 90 and 120 s for $0.8G/G_o$ and $0.4G/G_o$, respectively.

The above analysis indicates only a small fraction (∼2%) of the carbon atoms are oxidized in the ozone process. However, the amount of measured charge transfer is increased by ∼1000%. Thus, the oxidation sites produce a highly disproportionate electrical response, which indicates a small number of defect sites along the sidewall can be used to control the chemical sensor properties of SWNTs.[30]

To assess the generality of this effect, we measured the amount of charge transfer before and after oxidation for

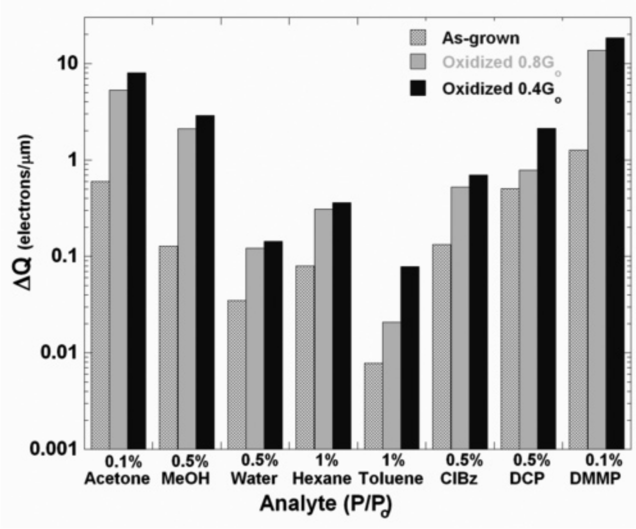

Figure 4. Charge transfer ($\Delta Q/\mu$m) between various analytes and the SWNT network as a function of oxidation.

several different classes of chemical vapors. The averaged results for four devices are shown in Figure 4. The data indicate that increased defect density (resulting from oxidation) produces additional charge sensitivity to all chemical vapors tested. These results suggest defects play an important role in the electronic response for many chemical vapors and may be responsible for much of the observed behavior noted in the literature.

An important implication of the analyte/defect interaction is that the chemical selectivity of SWNT sensors can be affected by the chemical functionalization of only a small fraction of the SWNT surface. Oxidation of ∼2% of the carbon atoms produces a significant decrease in the electrical conductivity, which limits the level of covalent functionalization possible while maintaining electrical continuity. However, the disproportionately large contribution of defect sites to the chemical sensitivity indicates that chemical selectivity through defect chemistry may readily be achieved with less than 1% of the sidewall atoms.

We have explored the electrical response of SWNTs to the presence of chemical vapors. We find that adsorption on defect sites, such as those created during the purification process of SWNTs (oxidation) can dominate the electrical response. The defect sites form low-energy adsorption sites that also serve as nucleation sites for analyte condensation at high vapor concentrations. In addition, we find that the chemical sensitivity of SWNTs can be increased significantly by controllably introducing a low density of defects along the nanotube sidewall. This result suggests the sensitivity and chemical selectivity of SWNT sensors can be controlled via the introduction of a few chemically functionalized adsorption sites. Efforts to establish such control are underway.

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(30) In addition to the response from sidewall defects, it is possible that part of the sensor response comes from modulation of the inter-SWNT junctions. Although the network conductance is heavily dependent on the transport properties of the inter-SWNT junctions, the capacitance is primarily determined by the fractional surface coverage and is not sensitive to the network transport properties. There is no direct measure of the relative importance of the junctions; however, we find that the oxidation produces similar increases in sensitivity for both capacitive and conductive sensing. This suggests that both responses originate from common sites, i.e., the regions between the junctions.

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