

Sensitivity of Ammonia Interaction with Single-Walled Carbon Nanotube Bundles to the Presence of Defect Sites and Functionalities

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Abstract: Ammonia adsorption on single-walled carbon nanotubes (SWNTs) was studied by means of infrared spectroscopy at both cryogenic (~94 K) and room (~300 K) temperatures. At 94 K, vacuum-annealed SWNTs showed no detectable ammonia uptake. However, the ammonia adsorption was found to be sensitive to the functionalities and defects on the nanotube surfaces. NH₃ adsorption was detected on HNO₃-treated nanotubes, characterized by significant functionalities and defects, prior to vacuum annealing. NH₃ desorbed from those nanotubes above 140 K, indicating a weak adsorbate–nanotube interaction (~30 kJ/mol). Exposure of annealed samples to ambient air, which possibly regenerated functionalities and defects on nanotube surfaces, restored partially the ammonia uptake capacity. No ammonia adsorption on SWNTs was observed by infrared spectroscopy at room temperature with up to 80 Torr dosing pressure. This work suggests the influence of functionalities and/or defect densities on the sensitivity of SWNT chemical gas sensors. Our theoretical studies on NH₃ adsorption on pristine and defective tubes, as well as oxidized tubes, corroborate these findings.

1. Introduction

Single-walled carbon nanotubes (SWNTs) have been suggested as the basis of novel monitoring technologies and devices for pollutant detection.¹ Understanding the interaction between nanotubes and small molecules, such as H₂, Xe, CO₂, NH₃, and NO₂,^{2–6} will help to reveal the mechanisms of molecular sensing. Of particular interest is ammonia, one of the first species shown to affect SWNT conductivity.⁷

The interaction of ammonia with SWNTs is somewhat controversial. Ammonia was shown to dramatically change the electrical resistance of semiconducting SWNTs by Kong et al.⁷ Recently, infrared and temperature-programmed desorption (TPD) were used to study the interaction of ammonia with heterogeneous bundles of as-received HiPco nanotubes at room temperature.⁵ The authors reported that ammonia adsorbed on

nanotubes at room temperature and could be thermally desorbed with a broad TPD peak around 430 K, indicative of a strong interaction.⁵ Valentini et al. also found an increase of the electrical resistance of SWNT sensors when exposed to a mixture of interfering gases, NH₃, ethanol, as well as 80% relative humidity, at different operating temperatures between 25 and 250 °C.⁸ Because of the presence of multiple gases, the interaction of specific molecules (e.g. ammonia) with the nanotubes was unclear. On the other hand, it is suggested that the interaction of ammonia with nanotubes is environment (humid)-sensitive.⁹

In apparent contrast, several theoretical studies showed that ammonia molecules bind to carbon nanotubes via physisorption.^{4,10,11} Only weak electron charge transfer (~0.03 electron) was reported.¹⁰

The apparent conflict about whether the interaction between ammonia and nanotubes is chemisorption or physisorption, weak or strong, as reported by different research groups motivated us to investigate the influence of sample preparation methods, purification, and oxidation processes on the properties of nanotubes. We also present new theoretical studies of ammonia adsorption on pristine, defective, and oxidized tubes.

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In this article, we report an infrared spectroscopic investigation of ammonia adsorption on SWNTs and the sensitivity to the presence of functional groups or defect sites on the nanotubes. The weak interaction between nanotubes and ammonia molecules is suggested by the observation of complete desorption above 140 K. Theoretical studies indicate very weak adsorption of ammonia to defect-free and defective nanotubes containing missing carbon atoms, but stronger interaction with oxidized tubes. No adsorption is observed by infrared spectroscopy at room temperature with up to 80 Torr ammonia dosing pressure. This work suggests that the sensitivity of nanotube gas sensors may be enhanced through functionalization (particularly oxidation) and defect generation.

2. Experimental Section

The experiments were performed in a stainless steel ultrahigh vacuum (UHV) cell with a base pressure of 2×10^{-9} Torr.¹² Solid unpurified nanotubes (as-received), produced by the HiPco process, were obtained from Carbon Nanotechnologies, Inc. (Houston, Texas). HNO₃ acid-treated HiPco samples were prepared by nitric acid refluxing as described elsewhere.⁶ Thermo gravimetric analysis (TGA) showed that the iron content decreased from 18 wt % of as-received samples to 3 wt % of purified samples. Tubes produced by laser ablation of graphite (Rice tubes) were obtained from Tubes@ Rice. Nanotubes suspended in acetone were deposited directly onto the upper part of a tungsten grid (Alfa Aesar, 100 mesh size) by a drop and dry technique. The lower part of the tungsten grid without nanotubes was used as reference. The samples were degassed at 500 K for 2 h before experiments. Ammonia exposure was recorded as Langmuir (1 Langmuir = 1 L = 10^{-6} Torr·s). A Brüker Optics Tensor 27 FTIR spectrometer was used to take transmittance mid-IR spectra with a liquid nitrogen-cooled MCT (HgCdTe) detector. A total of 500 scans were averaged for both background and sample.

3. Theoretical Studies

Computational modeling of NH₃ adsorption on nanotubes was performed with the self-consistent charge density functional tight binding method (SCC-DFTB).¹³ This method has been successfully employed, for instance, in the description of DNS strands¹⁴ and the formation mechanism of fullerene cages from randomly oriented ensembles of C₂ molecules.¹⁵ To capture weak dispersion forces occurring in physisorption, a Heitler–London term was added to the SCC-DFTB energies and gradients following the methodology described in refs 14 and 16. We also present a methodological comparison between SCC-DFTB and ab initio MP2 and CCSD(T) results of Bauschlicher et al.¹¹ for simple ammonia–benzene and ammonia–coronene systems.

4. Results and Discussions

4.1. Ammonia Adsorption on HNO₃-Treated HiPco Nanotube Surface. An infrared spectrum of ammonia adsorbed on HNO₃-treated nanotubes at 94 K (Figure 1) shows four main additional peaks overlapped on the spectrum of the nanotubes. The strong band at 3376 cm⁻¹ is assigned to the N–H asymmetric stretch.¹⁷ The symmetric stretch peak at 3290 cm⁻¹ is very weak.¹⁷ A shoulder is present on this feature at lower

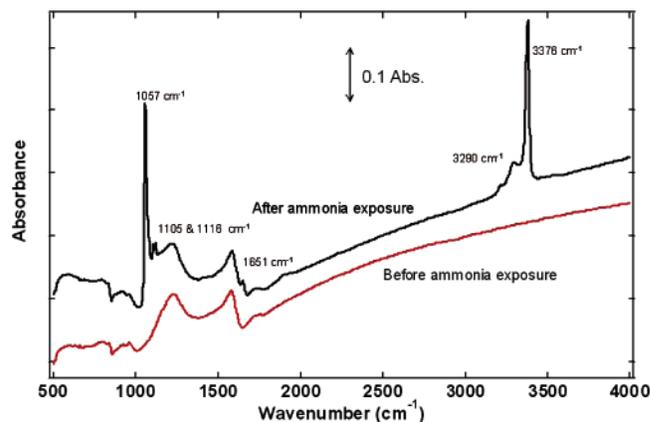


Figure 1. FTIR spectra of HNO₃-treated HiPco SWNTs before and after adsorption of ammonia at 94 K (exposure = 5000 L). Samples were subjected to 900 K thermal annealing prior to experiments.

Table 1. Vibrational Modes and Frequencies (cm⁻¹) for Ammonia Adsorbed on C₆₀¹⁷ and Nanotubes⁵ Compared with Gas-Phase¹⁷ and Condensed-Phase Ammonia¹⁸

	gas phase	condensed phase	C ₆₀ (170–180 K)	SWNTs (room temp)	SWNTs (94 K)
asymmetric stretch	3414	3378	3354	3318, 3249	3376
symmetric stretch	3337.5, 3336	3290	3222	3205, 3156	3290
bend	1627	1650	1616	1618	1651
umbrella	968, 932	1060	1132	1354, 1248	1057, 1105, 1116
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frequency. The N–H bending vibration at 1651 cm⁻¹ is weak.¹⁷ The umbrella mode (symmetric deformation)¹⁷ splits into multiple peaks (1057, 1105, and 1116 cm⁻¹), with the strongest at 1057 cm⁻¹.

The frequencies of vibrational modes of ammonia adsorbed on C₆₀ at 170–180 K,¹⁷ on carbon nanotubes at room temperature,⁵ and 94 K (present work) are compared with gas-phase¹⁷ and condensed-phase ammonia¹⁸ in Table 1. Except for the bending mode, all other modes of ammonia adsorbed on nanotubes at 94 K show similar frequencies and shift trends with ammonia adsorbed on C₆₀ compared with gas-phase modes. In the C₆₀ work,¹⁷ the authors attributed the peak shoulders to ammonia molecules adsorbed in different, less abundant sites on C₆₀. The splits (umbrella mode) and shoulder (symmetric stretch) of different bonds in Figure 1 can possibly be associated with different adsorption sites on nanotube bundles, such as interstitial and endohedral sites, as suggested for other species interacting with SWNTs.⁶

The infrared spectra of nanotube surfaces dosed with increasing ammonia exposure at 94 K are shown in Figure 2. Ammonia is detectable at 30 L exposure in this study. The reported surface areas of the HiPco nanotubes are in the range from 300 to 900 m²/g.^{19–21} One Langmuir exposure only results in at most 0.004 monolayer on the 0.09 mg sample. The larger the specific surface area, the lower the coverage will be at a given exposure.

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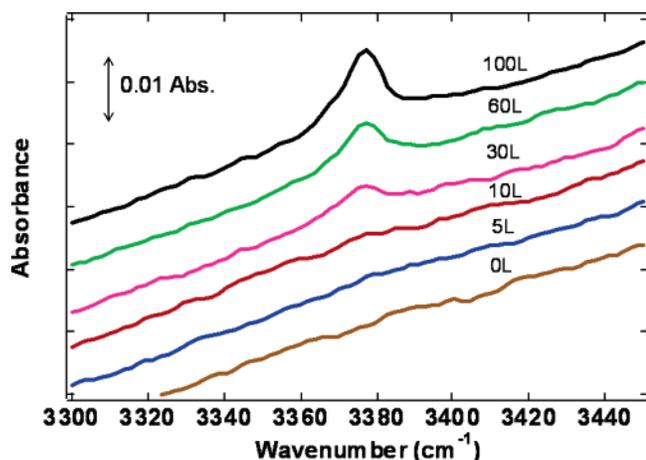


Figure 2. FTIR spectra of HNO₃-treated HiPco samples with ammonia exposure 0–100 L. The samples were heated to 500 K in vacuum before ammonia exposure at 94 K.

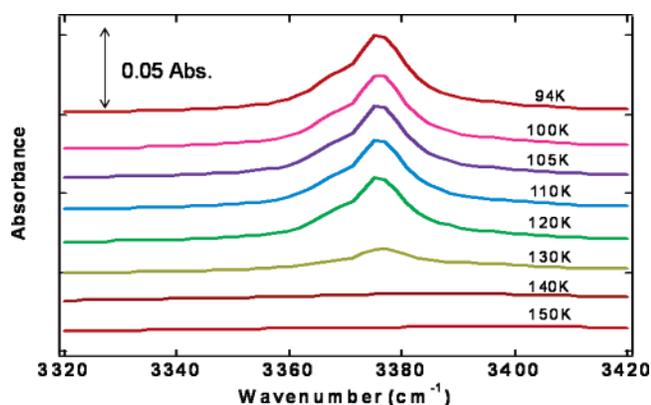


Figure 3. Ammonia desorption infrared spectra from HNO₃-treated HiPco. Spectra recorded at 94 K after flashing to successively higher temperatures indicated by label on each spectrum. The samples were heated to 500 K in vacuum before ammonia exposure at 94 K (initial ammonia exposure = 500 L).

No significant frequency shift ($<2\text{ cm}^{-1}$) is observed from the lowest detectable coverage (30 L) to highest exposure (5000 L) in this study. The frequencies are near the condensed-phase ammonia vibration mode positions,¹⁸ suggesting that the interaction energy between nanotubes and ammonia molecules is similar to the ammonia intermolecular interactions and not indicative of chemisorption. It was also reported that the NH₃–NH₃ interaction was similar in magnitude to the NH₃–graphite interaction.²²

To investigate the strength of ammonia adsorption, the following series of experiments were performed. After 500 L ammonia exposure, the sample was flash heated (at about 3 K/s) to the desired temperature and then cooled to 94 K. A FTIR spectrum was taken after every flash heating. The quantity of adsorbed ammonia, revealed by observing asymmetric stretch ($\sim 3376\text{ cm}^{-1}$) in Figure 3, remains approximately constant up to 120 K. By 140 K, however, all the ammonia appears to have desorbed. The desorption energy is estimated to be $\sim 30\text{ kJ/mol}$ according to Redhead analysis assuming the maximum desorption temperature is 120 K, a first-order process, and a pre-exponential factor of 10^{13} s^{-1} .²³ These results suggest that

the ammonia interaction with SWNTs is physisorption rather than chemisorption.^{4,9,10}

The apparent desorption of ammonia from HNO₃-treated HiPco SWNTs at $<140\text{ K}$, while revealing a physisorbed state, does not exclude the possibility of a chemisorbed state. It is possible that a chemisorbed state exists but can only be populated at higher temperature and pressure because of an activation barrier to chemisorption. To address this issue, ammonia was dosed to HNO₃-treated HiPco samples (after 500, 900, and 1300 K treatment) at pressures up to 10 Torr at room temperature. No feature associated with ammonia vibrational modes larger than 1 milli. O.D. is observed (Figure S1 in Supporting Information).

In addition to the infrared study, a TPD study of nanotube samples dosed with ammonia at room temperature was also performed. The HNO₃-treated nanotube samples were exposed to 15 L of ammonia at room temperature. There is no obvious peak of both 2 (H₂) and 17 (NH₃) amu species monitored from room temperature up to 650 K (Figure S2 in Supporting Information). We conclude, as discussed above, that no significant ammonia adsorption occurs at room temperature, consistent with a lack of chemisorption interaction between ammonia and nanotubes.

The lack of ammonia adsorption at room temperature is not inconsistent with CNT sensitivity to ammonia. A simple estimate of the equilibrium coverage, when the adsorption rate (flux of ammonia molecules from gas phase) equals the desorption rate, can be made.²⁴ At room temperature, assuming a pre-exponential factor for desorption of $10^{13}/\text{s}$, a unity sticking coefficient and a desorption energy of 30 kJ/mol, 1 ppm ammonia (0.76 mTorr) results in an equilibrium coverage of about 10^{-5} monolayer of ammonia. While this coverage is beyond the infrared detection limit, it may be sufficient to modulate CNT conductivity. If the binding energy is 12 kJ/mol, as estimated for pristine CNTs (see theory below), the surface coverage at 1 ppm ammonia is about 10^{-8} monolayer of ammonia.

In contrast to the results presented above, Ellison et al. found that ammonia adsorbed strongly on as-received HiPco at room temperature when the backfilling pressure was 50 Torr.⁵ This discrepancy could arise from the different sources of the nanotube materials, different purification methods, and differences in experimental procedures. In an attempt to address these differences, a number of additional experiments were performed. (a) Ammonia adsorption was investigated on as-received, nominally untreated HiPco SWNTs with an ammonia dosing pressure of 80 Torr, estimated from the measured decrease of ammonia in the gas line and the known volumes of the chamber and gas line. (b) The influence of water vapor (by introduction of water vapor into the chamber during ammonia adsorption), adsorption temperature (by keeping the sample at 425 K during ammonia exposure), and nanotube vacuum pretreatment temperature (373 and 725 K) were also evaluated. Under all the evaluated conditions, no peak greater than 1 milli. O.D., the noise level, appears in the infrared spectra (Figure S3 in Supporting Information). As with the HNO₃-treated HiPco tubes, no evidence of ammonia adsorption at room temperature, within the sensitivity of our experiments, is observed.

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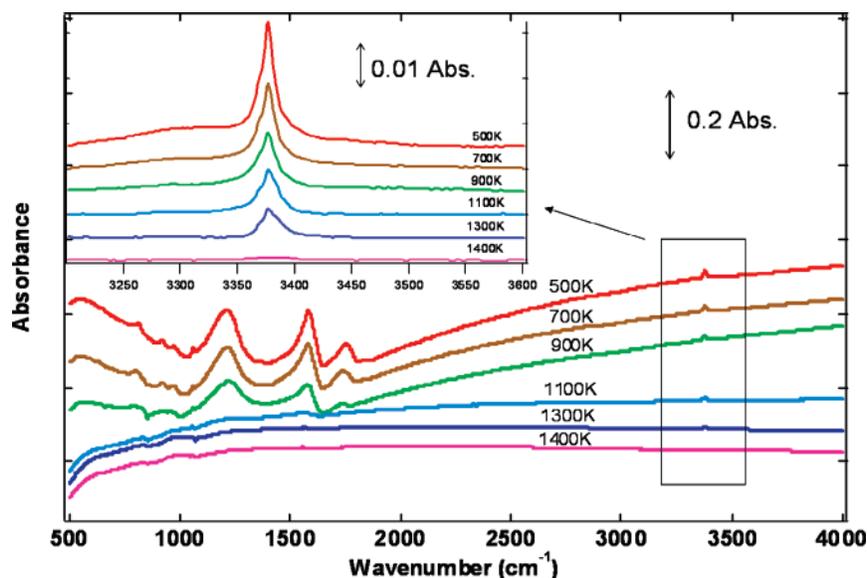


Figure 4. Infrared spectra of ammonia adsorption on HNO₃-treated HiPco at 94 K after vacuum thermal annealing of SWNTs to successively higher temperatures (ammonia exposure = 200 L).

4.2. Influence of Annealing on NH₃ Adsorption. The effect of annealing of nanotube samples, from 500 to 1400 K, on the adsorption of ammonia is shown in Figure 4. To show the results clearly, a normalized enlargement of the ammonia asymmetric stretch region is shown in the inset. The decrease in the peak intensity, for constant exposure of ammonia, reveals a decrease of ammonia sticking probability as the annealing temperature of the surface increases. The asymmetric stretch peak intensity is almost completely suppressed after 1400 K treatment.

High-temperature annealing has been reported to be an effective method to heal defect sites and recover the pristine tubes.^{12,25–27} Raman spectra showed that vacuum thermal annealing decreased the defect band (D band near 1350 cm⁻¹) intensity.¹²

Most theoretical works use pristine tubes as simulation models. So it is more reasonable to compare theoretical results with experimental values from tubes similar to pristine ones. The complete suppression of ammonia uptake by nanotubes after 1400 K treatment is consistent with the 8 ± 8 kJ/mol NH₃ binding energy estimated for “pristine” nanotubes.¹¹ Valentini and co-workers also suggested that the interaction between oxygen and defective sites may be responsible for the reported sensitivity of nanotubes to NO₂.²⁸ The control of ammonia adsorption by annealing is observed not only for HNO₃ acid-treated HiPco but also for as-received HiPco prior to purification processes and Rice tubes produced by the laser ablation technique. On each sample, ammonia adsorption decreases with increasing annealing temperature under conditions of constant ammonia exposure (Figure S4 in Supporting Information). All three kinds of nanotubes samples reveal the extreme sensitivity of ammonia adsorption to thermal annealing.

In addition to healing defect sites, annealing also causes removal of functional groups.¹² It is reported that functional groups on nanotube surfaces influence the electronic properties of SWNTs by disrupting the graphitic-like sp² network of carbon in the SWNTs.²⁹ This disruption produces local sp³ defects that can introduce an impurity state near the Fermi level²⁹ and perturb the electronic spectra of these materials.^{25,30} The electronic characteristics of nanotubes play an important role in nanotube adsorption properties.^{30,31} It is possible that removal of functional groups changes the local electronic state, and hence the affinity between ammonia and nanotubes. We suggest that the existence of functional groups and defects provides sites for ammonia to adsorb on the surface that are energetically favorable.

The role of functional groups on molecular adsorption has been reported previously.^{32–36} For example, the presence of surface functional groups changed the binding energy, while increasing the uptake kinetics, of a polar molecule (acetone)³² and decreased the uptake of a nonpolar molecule (propane)³⁶ on graphite surfaces. There is evidence that accessible functional groups rather than external surface areas were responsible for the ammonia uptake on the surfaces of organic materials.³³ These aforementioned studies, on a range of carbon materials, such as HOPG,^{32,36} activated carbon,³⁴ and activated carbon fiber,³⁵ suggest that it is not unreasonable that surface functionalities or chemistry could dramatically change the adsorption capacity of ammonia by nanotubes.

The suggested importance of functionalities does not exclude other possible impacts from annealing. Exposure of nanotube samples, thermally heated to 1400 K, to ambient laboratory air for 1 h at room temperature led to the recovery of the nanotube

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Table 2. Interaction Energies ΔE between Ammonia and Benzene/Coronene Systems^a

system	SCC-DFTB-D ΔE (kJ/mol)	ΔE ref 11 ^f (kJ/mol)
NH ₃	0.00	0.00
C ₆ H ₆	0.00	0.00
C ₆ H ₆ -NH ₃ C _{3v} ^b	-7.82	-6.74
C ₆ H ₆ -NH ₃ tilt2 ^c	-7.87	-8.41
C ₆ H ₆ -NH ₃ tilt1 ^d	-8.20	-8.45
C ₆ H ₆ -NH ₃ u/d ^e	-3.14	N/A
C ₂₄ H ₁₂	0.00	0.00
C ₂₄ H ₁₂ -NH ₃	-14.30	-6.90

^a All systems have been fully optimized at the SCC-DFTB-D level. ^b NH₃ with all three hydrogen atoms pointing toward plane of benzene. ^c NH₃ with two hydrogen atoms pointing toward plane of benzene. ^d NH₃ with one hydrogen pointing toward plane of benzene. ^e NH₃ upside-down with all hydrogen atoms pointing away from the plane of benzene. ^f Bauschlicher's MP2 calculation with largest basis set (aug-cc-pVTZ for benzene, and 6-31G(d,p) for coronene), scaled by a factor obtained using MP2/6-31G(d,p) and CCSD(T)/6-31G(d,p) for the tilt1 structure.

affinity for ammonia adsorption at 94 K. The sticking probability of ammonia on nanotubes decreased again when the nanotubes were heated to 1400 K a second time under vacuum conditions. It was reported that exposure to air or oxygen dramatically influenced the nanotube electrical resistance, thermoelectric power, and local density of states.³¹ It is possible that oxygen chemisorbed at defect sites where dangling bonds, generated by the annealing, were present.³⁷ The sample was flash-heated to 423 K to drive off physisorbed impurities (such as water) after exposure to air and before exposure of ammonia at 94 K. This excluded the possible influence of water on ammonia adsorption.⁹ We hypothesize that exposing thermally annealed nanotubes to ambient air led to the regeneration of functionality and defect sites increasing the SWNT affinity to ammonia molecules.

5. Theoretical Studies

The method of choice for our theoretical modeling of NH₃ adsorption on carbon nanotubes is the computationally cost-effective SCC-DFTB method.¹³ However, the modeling of physisorption on nanotubes in electronic structure calculations is inherently extremely difficult, since dispersion forces can only be described at the post-Hartree-Fock level of theory. An alternate way to include dispersion is to add a Heitler-London dispersion energy term to the calculated total energy as described in ref 14, which is very similar to the approaches typically used in molecular mechanics force fields. To check the accuracy of such an approach, we compared SCC-DFTB-D (-D meaning dispersion) optimized structures and energetics for the benzene and coronene C₂₄H₁₂ complexes with NH₃ to the best calculated results obtained by Bauschlicher et al.¹¹ (see Table 2). Investigated structures include complexes with one, two, and three hydrogen atoms, as well as the N lone pair, pointing toward the plane of benzene. SCC-DFTB-D predicts accurately all stationary points on the corresponding potential energy surfaces, and the differences in interaction energies between SCC-DFTB-D and the best level of theory applied by Bauschlicher are only about 1 kJ/mol for the benzene-NH₃ system. In fact, we performed SCC-DFTB-D and MP2/6-31G(d,p) frequency calculations to verify the nature of the stationary points, and the structure with all three hydrogen atoms pointing toward

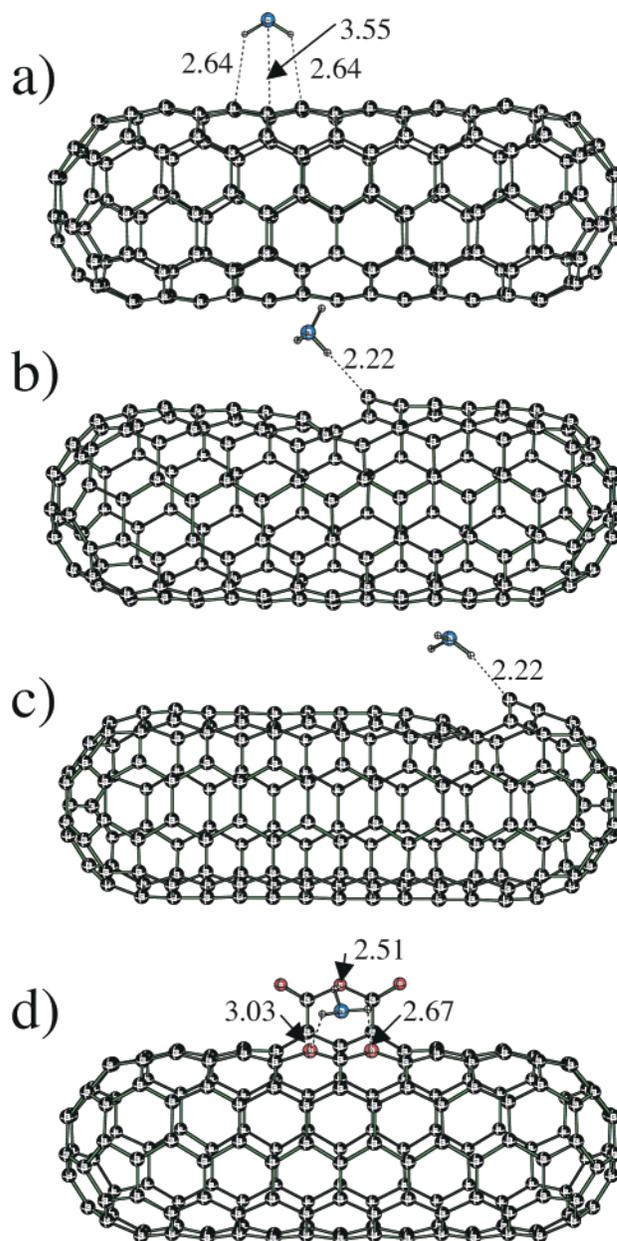


Figure 5. SCC-DFTB-D-optimized structures of a (5,5) capped 20 Å long CNT model system and one physisorbed NH₃ molecule: (a) pristine, (b) and (c) defective (one carbon atom removed), and (d) oxidized (five oxygen atoms added). H-C (panels a-c) and H-O distances are given in Å.

benzene is a transition state for the tilting motion connecting the two tilted structures. The discrepancy between SCC-DFTB-D and Bauschlicher's interaction energies is somewhat larger for the coronene system (almost 7 kJ/mol), but again, the stationary point is predicted accurately, and Bauschlicher's value for this system was actually obtained using a much smaller basis set in their MP2 calculations compared to the benzene calculations.

We therefore felt comfortable to apply the SCC-DFTB-D level of theory in the study of NH₃ adsorption on nanotubes and studied adsorption of ammonia on a pristine tube (a), defective tube (b and c), and oxidized tube (d) (see Figure 5). The model system for the nanotube was a 20 Å long (5,5) armchair tube capped at both ends with C₃₀ buckminsterfullerene half-spheres to prevent the ammonia molecule from being "sucked" inside. A defect was simulated by removing a carbon

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atom from the sidewall (at the center for system b and near the cap for system c). The defect healed in geometry optimizations to a defect site containing an opening of nine carbon atoms and a pentagon, where one carbon atom maintains an unfilled valency similar to triplet methylene. The oxidized tube model (d) was derived by adding five oxygen atoms to the (5,5) tube model to yield a tube with a cyclic anhydride group with two adjacent oxygen sites, which presumably reduces ring strain due to otherwise adjacent pentagons. This model was shown by us to be much more stable than any other combination of the tube model and five oxygen atoms in 34 different conformations.³⁸ Ammonia was placed in all calculations on top of the tube and in the vicinity of defect sites. Figure 5 shows the bond distances between the ammonia hydrogen atoms to the next-neighbored C and O atoms for a–c and d, respectively. Not unexpectedly, the interaction between a pristine tube and ammonia in (a) is very similar to the ammonia–coronene interaction with -12.1 kJ/mol. The interaction of the ammonia molecule with the unfilled valency of a defect tube is slightly increased to -15.9 kJ/mol (b and c). Yet, the presence of oxygen molecules on the tube dramatically increases this interaction energy to -40.2 kJ/mol (d), in line with the experimental observation that oxidized tubes bind ammonia significantly better than pristine tubes. Apparently ammonia forms strong hydrogen bonds with oxygen atoms in the oxidized tubes.

6. Conclusions

Several conclusions can be drawn from this study.

1. HiPco nanotubes subjected to vacuum annealing, which tends to recover pristine tubes by healing defects sites and removing functional groups, show no detectable ammonia uptake.

2. Ammonia adsorption is detected on as-received HiPco, Rice, and HNO_3 -treated HiPco nanotubes (with higher degree of functionalities and defect sites) at 94 K. Nanotube surface chemistry may dramatically influence the sensitivity of nanotube

sensors to trace ammonia from the environment. This finding is corroborated by computational modeling of ammonia adsorption of pristine, defective, and oxidized tubes.

3. Ammonia does not interact strongly with HNO_3 -treated HiPco nanotubes, as revealed by the complete desorption above 140 K (~ 30 kJ/mol desorption energy).

4. Exposing thermally annealed nanotubes to ambient air led to the recovery of ammonia uptake by nanotubes. This possibly occurs, as suggested in the literature,³⁷ through the chemisorption of oxygen at dangling bonds, leading to the regeneration of sites where NH_3 can bind.

5. Computational studies indicate that ammonia interacts more strongly with the oxidized nanotubes than with pristine or defective nanotubes, consistent with experimental observations.

6. The lack of ammonia adsorption at room temperature is not inconsistent with CNT sensitivity to ammonia, as long as conductivity is sensitive to coverage of 10^{-5} monolayer or less.

Acknowledgment. We thank Drs. C. Matranga and B. Bockrath of National Energy Technology Laboratory for useful discussions and for providing nanotube samples. This work was funded by the NSF BES 0202015. We gratefully acknowledge the computational resources provided by the DOE PNNL EMSL facility under the GC3564 grant as well as by the DURIP Grant FA9550-04-1-0321 from the AFOSR.

Supporting Information Available: Figures showing infrared spectra of ammonia adsorption on nitric acid-treated HiPco samples at room temperature, TPD spectra of nitric acid-treated HiPco nanotubes exposed to ammonia at room temperature, infrared spectra of ammonia adsorption on as-received HiPco samples at room temperature under various conditions, and infrared spectra of ammonia adsorption on as-received HiPco samples and Rice tubes at 94 K after thermal annealing of SWNT to successively higher temperatures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA042998U

(38) Irle, S.; Stanley, D. M.; Morokuma, K. To be submitted for publication.