

INFLUENCE OF SURFACE FUNCTIONAL GROUPS ON MOLECULAR ADSORPTION BY SINGLE WALLED CARBON NANOTUBES (SWNTs)

Xue Feng^{1,2}, Seokjoon Kwon³, Radisav Vidic², Eric Borguet¹

1 Chemistry Department and Surface Science Center, University of Pittsburgh

2 Department of Civil and Environmental Engineering, University of Pittsburgh

3 Connecticut Agricultural Experiment Station, New Haven, CT

Introduction

Functional groups (defect sites) on single walled carbon nanotubes (SWNTs) affect their properties. Changing the quantity and/or type of functional groups modifies the solubility[1] and adsorption behavior [2] of SWNTs as well as their ability to work as catalysts [3], capacitors [4], materials for electrolytic transport [5] and biosensors[6].

Experimental

A stainless steel ultra high vacuum (UHV) chamber, pumped by a turbo molecular pump backed by a mechanical pump, providing a base pressure of 5×10^{-10} torr after bake out, was used for temperature programmed desorption (TPD) experiments with a typical heating rate of 2.5 K/s. Samples could be cooled below 100 K via a liquid nitrogen dewar and heated up to 1300 K via resistive heating. A detailed description was provided previously [7]. Infrared studies were performed in another high vacuum chamber with base pressure of 2×10^{-9} torr. Samples could be cooled to 90 K via a liquid nitrogen dewar and heated up to 1400 K via resistive heating. Molecules were purified and dosed into both chambers through a leak valve. Exposure was reported in Langmuir units ($1L = 10^{-6}$ torr·s).

The solid, as-received HiPco SWNTs were provided by Carbon Nanotechnologies Incorporated (Houston, TX). HiPco SWNTs were purified by flowing moist air (0.2 L/min) through as-received nanotubes at 150 °C, followed by acid (HCl) extraction. 40% of the nanotubes were lost during the purification process. 90% of the iron catalyst was removed according to TGA measurement. The purified HiPco SWNTs were dispersed in hexane. The nanotube sample for TPD was made by depositing nanotubes on a 10X10X0.25 mm, highly oriented pyrolytic graphite (HOPG, grade SPI-1, SPI supplies) plate using a drop and dry method. Control experiments were performed on a clean HOPG plate. The purified nanotube sample for infrared experiments was deposited directly on a W grid using a drop and dry method.

Results and discussion

The objective of our study was to understand the effect of functional groups on the adsorption of small molecules on nanotubes. We selected polar molecules (acetone and pyridine) and non-polar molecules (hexane and propane) as the probe molecules.

It is reported that heat treatment effectively removes oxygen containing functional groups from nanotube surfaces [8]. Heating the nanotubes led to desorption of 16, 18, 28 and 44 m/e containing species. In order to completely remove all the functional

groups from HOPG, the sample needs to be heated over 1000 K [9].- The TPD spectra, showing the gas evolution as a function of heating temperature, are shown in Figure 1d. At 500 K, gases began to desorb from the surface due to the decomposition of functional groups. The purpose of 473 K treatment is to remove physisorbed impurities from the surface without affecting the functional groups.

TPD spectra for 473 K-treated and 1273 K-treated samples exposed to pyridine at 95 K are shown in Figures 1a and 1b, respectively. The Quadrupole Mass Spectrometer (QMS) signal (ion current for $m/e=52$) was plotted as a function of sample temperature. The area under each TPD curve represents relative coverage of pyridine molecules on the surface. The relative coverage as a function of exposure, Figure 1c, is related to the uptake efficiency of the nanotubes. The uptake of both samples increased linearly with exposure (reported as Langmuir) and there is no evidence of saturation up to 25 L. The uptake rate of nanotube samples decreased by a third after 1273 K treatment. For the three other molecules studied, i.e. acetone, hexane and propane, the uptake also showed no evidence of saturation. After 1273 K thermal treatment, the acetone adsorption rate decreased while the rate of hexane and propane uptake increased.

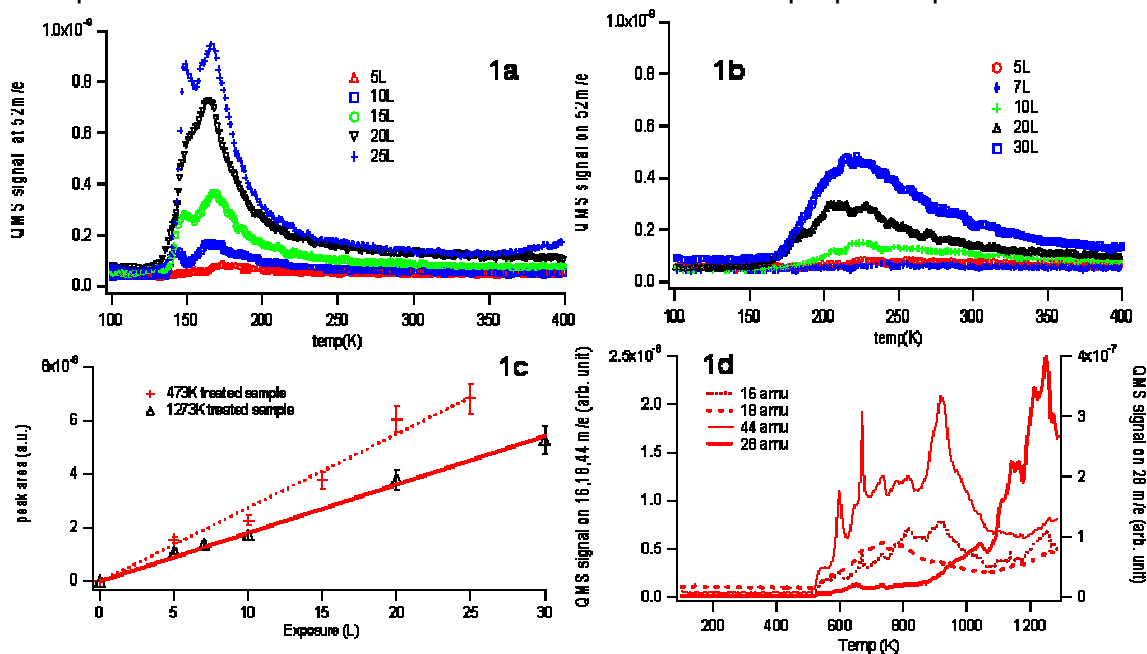


Figure 1. TPD data for pyridine desorption from SWNTs after 473 K (a) and 1273 K (b) treatment. Total uptake of nanotubes for pyridine after 473 K and 1273 K treatment (c) and evolution of surface functional groups from nanotubes (d). Dosing temperature ~ 95 K.

The transmission infrared spectra, shown in Figure 2, clearly reveal the changes in the spectra of adsorbed species on nanotubes after 1373 K treatment. All the FTIR spectra were recorded at 90 K. The spectra of molecules adsorbed on 473 K treated sample were compared with 1373 K treated sample for the same exposure. The IR results are consistent with the TPD results. For the same exposure level, pyridine and acetone uptake decreased following thermal treatment. However, hexane and propane show the opposite behavior as the uptake rate increased after heating SWNTs to 1373 K.

The carbonyl peak of the acetone molecule and the CH₂/CH₃ peak of the propane molecule red-shift (peak position was determined by fitting the experiment data with one Lorentzian) after thermal treatment to 1373 K. The thermal treatment changes not only the uptake rate but also the nanotube structure and hence the interaction with adsorbed species as suggested by IR frequency shifts.

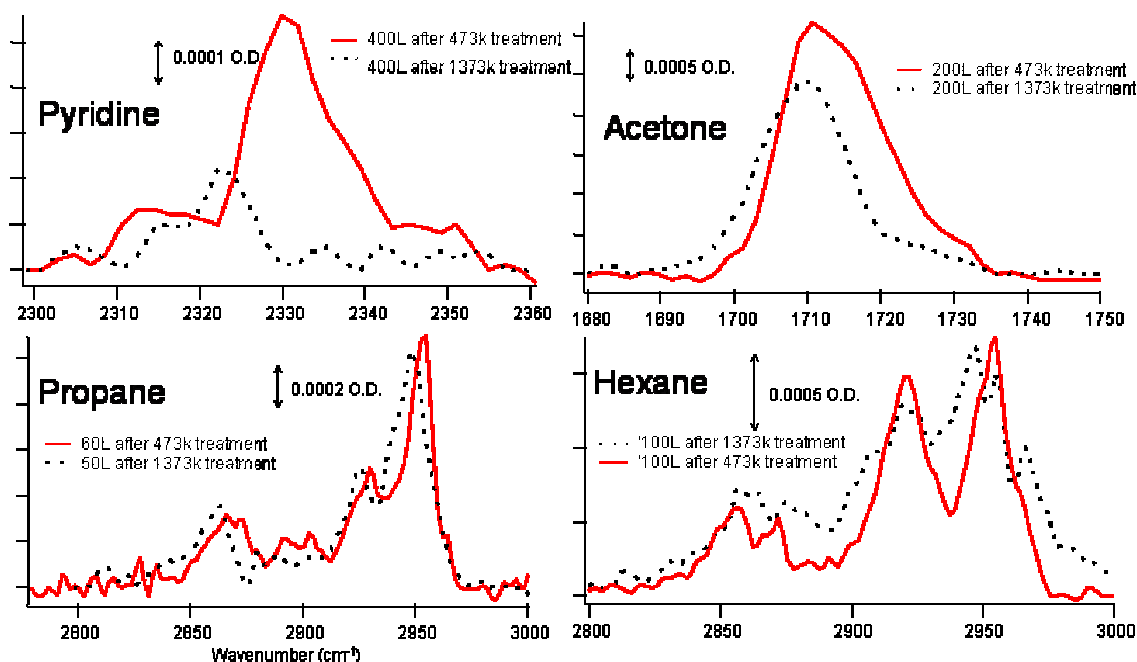


Figure2. Infrared spectra of pyridine, acetone, propane and hexane adsorption on nanotube after 473 K and 1373 K treatment

The TPD and FTIR results suggest that acetone and pyridine, which are polar molecules, have favorable interactions with the functional groups on nanotube surfaces. In our experiment, we found that the as-received HiPco nanotubes easily dissolve into non-polar solvents (e.g., hexane). However, after purification (oxidation), SWNTs dissolve more readily into polar solvents (e.g., toluene or acetone) than non-polar solvents. This suggests that the functional groups on the nanotube surface are polar and their removal apparently diminishes the uptake rate of nanotubes for polar molecules. Qualitatively similar behavior was reported previously, i.e. the purification by oxidation, which increased the concentration of functional groups, greatly enhanced the adsorption for CH₃OH and C₂H₅OH vapors at 303 K under a low relative pressure[10]. The authors associated the increased uptake with the enhanced micro porosity and the presence of oxygen-based functional groups introduced on the surface by the purification. Our previous study on the adsorption of acetone on HOPG also showed that the presence of polar functional groups on HOPG results in more favorably adsorbed polar molecules.[9] The opposite appears to be true for the non-polar molecules studied here. Functional groups on the nanotube surface reduced the uptake rate, possibly by blocking the entrance to the endohedral sites. After all the functional groups are removed, higher energy sites, probably on the insides of the nanotubes, are opened for non-polar molecules.

Conclusions

Oxygen- and hydrogen-containing functional groups, that exist on HiPco nanotube surfaces, influence nanotube adsorption properties as revealed by both TPD and IR study. These groups decompose during thermal treatment (>1000 K) under vacuum with evolution of carbon dioxide, carbon monoxide and other gases as revealed by TPD. Removal of these groups presumably opens the entry ports for adsorption on the inner surface of SWNTs and leads to increasing adsorption for non-polar molecules (propane and hexane). However, the uptake rate of SWNTs for polar species (pyridine and acetone) decreased after thermal treatment. Removal of those polar functional groups appears to decrease the affinity of the surface for polar molecules. The behavior of polar and non-polar adsorbates reveals distinct molecular interactions with SWNTs exterior, interior and surface functional groups.

Acknowledgement

The authors thank Dr. Christopher Matranga, Dr. Milton Smith and Dr. Bradley Bockrath from the National Energy Technology Laboratory for supplying the nanotubes.

References

- [1]. Zhou, B., Y. Lin, H.P. Li, W.J. Huang, J.W. Connell, L.F. Allard, and Y.P. Sun, Absorptivity of functionalized single-walled carbon nanotubes in solution. *Journal of Physical Chemistry B*, 2003. 107(49): p. 13588-13592.
- [2]. Wang, S.G., Y.H. Li, X.Y. Gong, H.Z. Zhao, Z.K. Luan, C.L. Xu, and D.H. Wu, Surface characteristics of modified carbon nanotubes and its application in lead adsorption from aqueous solution. *Chinese Science Bulletin*, 2003. 48(5): p. 441-443.
- [3]. Li, C.H., K.F. Yao, and J. Liang, Influence of acid treatments on the activity of carbon nanotube-supported catalysts. *Carbon*, 2003. 41(4): p. 858-860.
- [4]. Li, C.S., D.Z. Wang, J.J. Wu, W.Z. Lu, and J. Liang, Effect of inorganic acid treatment on ultrahigh capacitor made of carbon nanotubes. *Journal of Inorganic Materials*, 2003. 18(5): p. 1010-1016.
- [5]. Joseph, S., R.J. Mashl, E. Jakobsson, and N.R. Aluru, Electrolytic transport in modified carbon nanotubes. *Nano Letters*, 2003. 3(10): p. 1399-1403.
- [6]. Nguyen, C.V., L. Delzeit, A.M. Cassell, J. Li, J. Han, and M. Meyyappan, Preparation of nucleic acid functionalized carbon nanotube Arrays. *Nano Letters*, 2002. 2(10): p. 1079-1081.
- [7]. Kwon, S., E. Borguet, and R.D. Vidic, Impact of surface heterogeneity on mercury uptake by carbonaceous sorbents under UHV and atmospheric pressure. *Environmental Science & Technology*, 2002. 36(19): p. 4162-4169.
- [8]. Kuznetsova, A., D.B. Mawhinney, V. Naumenko, J.T. Yates, J. Liu, and R.E. Smalley, Enhancement of adsorption inside of single-walled nanotubes: opening the entry ports. *Chemical Physics Letters*, 2000. 321(3-4): p. 292-296.
- [9]. Kwon, S., R. Vidic, and E. Borguet, The effect of surface chemical functional groups on the adsorption and desorption of a polar molecule, acetone, from a model carbonaceous surface, graphite. *Surface Science*, 2003. 522(1-3): p. 17-26.
- [10]. Yang, C.M., H. Kanoh, K. Kaneko, M. Yudasaka, and S. Iijima, Adsorption behaviors of HiPco single-walled carbon nanotube aggregates for alcohol vapors. *Journal of Physical Chemistry B*, 2002. 106(35): p. 8994-8999.