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Effects of adsorption of alcohol and water on the electrical transport of carbon nanotube bundles

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Abstract

In situ studies on the effects of physisorption of various alcohol molecules ($C_nH_{2n+1}OH$; $n = 1-4$) on the transport properties of thin films of bundled single-walled carbon nanotubes reveal large increases in the thermoelectric power (TEP) S ($\sim 1-4 \mu V K^{-1}$) and four-probe resistance R ($\sim 4-8\%$) at $40^\circ C$. Interestingly, exposure to water causes virtually no change in the TEP, although the electrical resistance shows a change of $\sim 4\%$, typical for the alcohols. We observe a simple exponential response of $S(t)$ and $R(t)$ to a sudden change in the molecular pressure. The characteristic time constants ($\tau \sim 10$ min) for S and R are found to be essentially the same for a given molecule, indicating that the changes in these transport properties track each other. In fact, plots of S versus ΔR are linear, the slopes depending on the specific molecule. The transport results are interpreted in terms of a Boltzmann model and the introduction of a new scattering channel for charge carriers in *metallic* tubes due to weak interactions with physisorbed molecules. The trends in the changes in S and R with adsorption of these polar molecules can be explained on the basis of the interplay between the adsorption energy and the molecular coverage on the nanotube surfaces.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Single-walled carbon nanotubes (SWNTs) exhibit extremely interesting and unique chemical and physical properties [1, 2]. The electronic structures, and consequently the transport properties of SWNTs, are expected to be susceptible to influence by the presence of adsorbates due to the fact that every atom in a SWNT can be considered a surface atom and is exposed

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to the environment. Much attention has been focused in recent years on the interactions of nanotubes with their environment, in part due to the possibility of using nanotube bundles in practical applications, such as in gas storage [3] and in chemical and gas sensing [4, 5].

Recently, it has been demonstrated experimentally that very small concentrations of gas molecules (NO_2 and NH_3) can substantially change the electrical transconductance of individual field-effect transistors based on *semiconducting* nanotubes, and this property can be used for the design of high sensitivity chemical sensors [5]. In these cases, charge transfer is suspected to amplify the effect of adsorption. Other experimental investigations have shown that O_2 adsorption has a significant effect on the electrical transport of carbon nanotubes and induces a change in sign of the TEP [6–8]. Charge transfer [9] and the presence of defects [10, 11] have been identified as important to the O_2 –SWNT system. Interestingly, small systematic changes in the resistivity and the TEP of SWNTs were also observed on physisorption of six-membered ring molecules (C_6H_{2n} ; $n = 3$ –6) [12], and also due to collisions with non-reactive gases and small molecules (He, Ne, Ar, Kr, Xe, N_2 , CH_4 and H_2) [4, 6, 13, 14]. In such cases, the changes in S and R upon gas exposure were identified as resulting from weak interactions between the gas and the metallic nanotubes that induce changes in the electron and hole free carrier lifetimes. These results also suggested that even gas collisions with the nanotube walls at a few hundred degrees celsius and 1 atm affect the transport properties of SWNTs [14].

In this paper, we present the results of a systematic study of the changes in the TEP and four-probe resistance of vacuum-degassed thin films of nanotube bundles induced by the adsorption of polar alcohols ($\text{C}_n\text{H}_{2n+1}\text{OH}$; $n = 1$ –4) and water. Someya *et al* [15] have reported on the influence of alcohols on the characteristics of field-effect transistors (FET) fabricated from individual carbon nanotubes. They observed significant, reversible changes in the FET drain current when the device is exposed to various kinds of alcoholic vapours.

2. Experimental details

The SWNT material studied here was obtained from CarboLex, Inc., and consisted of ~50–70 vol% carbon as SWNTs produced by the arc discharge method using a Ni–Y catalyst. Typical high resolution scanning electron microscope images showed that the nanotubes are present in long bundles, with bundle diameters in the range 10–15 nm, i.e., containing ~100–200 tubes. The material was also found to exhibit the characteristic $T = 300$ K Raman spectra (514 nm excitation) published previously [16], including the radial breathing mode band at 186 cm^{-1} and the stronger tangential mode band at 1593 cm^{-1} . The radial band frequency observed indicates that the average diameter of these tubes is close to that of a (10, 10) tube (~1.4 nm). Chemical purification of the arc-derived material was carried out in a two-step process: (1) oxidation in dry air for 30 min at 350°C followed by (2) refluxing in 4 M HCl at 120°C for 4 h. Step (1) is designed to oxidize the amorphous carbon (by conversion to CO_2) and to weaken the carbon passivation coating over the Ni–Y catalyst particles. Step (2) is designed to remove the Ni–Y while minimizing damage to the nanotube walls. The metal (Ni–Y) content of the purified sample was determined by oxidizing the sample in flowing dry air (100 sccm) in a thermogravimetric analyser (Hiden, Inc.) and heating the sample slowly to 1000°C . Typical values for the residual Ni–Y content in purified material were found to be less than ~1 at.%. The purified SWNT material was then finally subjected to a $\sim 10^{-7}$ Torr vacuum-degassing process at 1000°C for 24 h. SWNT samples were in the form of thin films of tangled ropes deposited from an ethanol suspension onto a warm ($\sim 50^\circ\text{C}$) quartz substrate. Approximately 20 mg of purified SWNTs were dispersed in 50 ml of ethanol and agitated in an ultrasonic bath for 2–4 h.

Table 1. Comparison of the $T = 40^\circ\text{C}$ thermoelectric and resistive responses of a SWNT thin film to adsorbed water and $\text{C}_n\text{H}_{2n+1}\text{OH}$; $n = 1-4$. The vapour pressure p at 24°C , the molecular area A , the static dipole moment μ and the adsorption energy E_a of the corresponding molecule (measured on graphitic surfaces) are also listed. S_0 and R_0 refer to the degassed film before exposure to water and alcohols. An increase in vapour pressure did not change the values of ΔS_{max} or ΔR_{max} ; see the text.

Molecule	ΔS_{max} ($\mu\text{V K}^{-1}$) ^a	$(\Delta R/R_0)_{\text{max}}$ (%) ^b	M (g mol^{-1})	p (kPa) ^c	A (\AA^2) ^d	E_a (eV) ^d	μ (D) ^c
CH_3OH	3.7	8.2	32.04	16.9	16.0	0.43	1.70
$\text{C}_2\text{H}_5\text{OH}$	2.7	7.5	46.04	7.8	22.0	0.49	1.69
$\text{C}_3\text{H}_7\text{OH}$	2.1	6.8	60.09	5.8	29.0	0.56	1.68
$\text{C}_4\text{H}_9\text{OH}$	1.8	5.4	74.12	2.3	36.0	0.62	1.66
H_2O	~ 0	4.4	18.02	3.2	10.8	0.04	1.85

^a $\Delta S_{\text{max}} = S_{\text{max}} - S_0$.

^b $\Delta R_{\text{max}} = R_{\text{max}} - R_0$.

^c Data from [18].

^d Data from [19, 20].

Two chromel–Au/7 at.% Fe thermocouples and two additional Cu leads (all 0.003'' diameter wires) were attached with small amounts of silver epoxy to four corners of the 2 mm \times 2 mm sample to measure the TEP and the DC four-probe electrical resistance simultaneously. The TEP (i.e., Seebeck coefficient) data were collected using a heat pulse technique described previously [17]. Further details of the transport measurements are available elsewhere [4, 6, 13]. The $T = 300\text{ K}$ resistance of the sample was $\sim 300\ \Omega$. This 300 K sample resistance is also typical for our earlier studies with other gases and molecular vapours [6, 12, 13]. The nanotube sample was also vacuum-degassed *in situ* in the TEP apparatus at 500 K before water or various $\text{C}_n\text{H}_{2n+1}\text{OH}$ molecular vapours were introduced. A glass bulb containing the water or alcohol was connected via a valve to the TEP apparatus (see the inset to figure 2). All the alcohols were spectral grade (Sigma-Aldrich, Co.) and had been previously vacuum-degassed. The water was de-ionized and had a resistivity of $\sim 18\ \text{M}\Omega\ \text{cm}$. The vapour pressure p above the SWNTs for each $\text{C}_n\text{H}_{2n+1}\text{OH}$ or H_2O was that known to be in equilibrium with the liquid in the bulb at 24°C (table 1). After the thermoelectric and resistive responses to a particular molecular vapour were recorded, the sample was then degassed *in situ* at 500 K again until the TEP and four-probe resistance of the sample returned to the original ‘degassed’ values (S_0 , R_0). Then the same film was exposed to the next molecular vapour and so on. Data are presented here from one such film; other SWNT films, prepared in the same way, showed similar behaviour.

3. Results

Exposed to room air for several days under ambient conditions, *purified* and annealed bundles of SWNTs have been found to exhibit a positive large TEP $S \sim +10\ \mu\text{V K}^{-1}$ at room temperature [14, 21]. During *in situ* degassing of our SWNT films at $T = 500\text{ K}$ for $\sim 15\text{ h}$ in a vacuum of 10^{-7} Torr, S was first noticed to decrease, then change sign and asymptotically approach a negative value of $S_0 = -2.7\ \mu\text{V K}^{-1}$, representative of the degassed state⁵.

⁵ The ‘swing’ in S upon the initial vacuum-degassing of the SWNT sample at 500 K is smaller in this study than that previously reported by our group. This reduction in the magnitude of the TEP swing is related to the sample history (e.g., post-synthesis purification, thermal treatment) and may be due to the presence of impurity and wall damage states in the nanotubes that can pin the Fermi level [21]. The SWNT material used in the present study has a lower residual metal content (growth catalyst) and has been vacuum-annealed at 1000°C . However, independently of this initial TEP swing, all SWNT samples show similar behaviours on exposure to chemicals after the initial vacuum-degassing.

This behaviour is in agreement with previous results on similar bundled SWNT mats or film samples [6, 7, 14, 21]. However, very recently, Goldoni *et al* [11] have used high resolution core-level photoemission spectroscopy to study the interaction between O₂ and SWNTs at low temperature (150 K). A strong interaction with O₂ was found for contaminated samples with traces of Na (mainly chemical residues of the purification, dispersion and filtration processes) due to charge transfer from the tube to the Na–O complex, whereas weak interaction with O₂ was observed when dosing the Na-free sample. Thus, Goldoni *et al* [11] suggested that O₂ has no effect at all on the transport properties of SWNTs if impurities (i.e., catalyst particles, contaminants and defects coming from the chemical treatments) are carefully removed from the nanotube samples. Note that in our purification procedure, we do not use surfactants or NaOH, which might leave residual Na in the SWNTs. Besides, as mentioned in [11], the high temperature annealing at ultrahigh vacuum completely removes any Na contamination and strongly reduces the number of defects introduced by the purification treatments, restoring the nanotube structure and the bundle network. Our samples were annealed at ~1000 °C in a 10⁻⁷ Torr vacuum for 24 h. We also note that the experiments in [11] were carried out by exposing nanotubes to O₂ at 150 K. At this low temperature, we expect O₂ to interact weakly with SWNTs through a physisorption process only. Due to the negligible charge transfer between physisorbed oxygen and SWNTs, such species are not expected to facilitate the doping responsible for the observed change in the transport properties of SWNTs [10]. As suggested by Ulbricht *et al* [10], it seems likely that the observed effect of O₂ on the transport properties of SWNTs is due to charge transfer by a minority oxygen species, weakly bound either at defect sites on the SWNT bundles [21] or at tube–metal contacts in electronic devices [22–24]. Further work in our laboratory is under way aiming to resolve these issues.

We have shown that exposure of SWNTs to ambient air leads to *reversible* changes in the electrical properties [21]. On the other hand, exposure of our degassed films to O₂ at 500 K leads to *irreversible* change in the electrical properties, i.e., vacuum-degassing at 500 K does not reverse the chemical changes in the system induced by high *T* exposure to O₂, as seen from TEP and *R* measurements [21]. The long equilibrium time that we observed for reaching *S*₀ in purified SWNT films exposed to ambient air suggests that some of the O₂ must reside in the interstitial channels and/or within the central pores of opened SWNTs. Fujiwara *et al* [25] have used adsorption isotherms and x-ray diffraction at 77 K to investigate the gas adsorption properties of bundled carbon nanotubes and have concluded that O₂ molecules are adsorbed preferentially inside the bundles, and then mostly in the interstitial channels. Single-file diffusion would be necessary to empty the interstitial channels. After extensive degassing of ambient O₂-loaded SWNTs at 500 K, we cooled the sample to 40 °C and admitted the vapours of either water or a particular alcohol (C_{*n*}H_{2*n*+1}OH; *n* = 1–4). A sample temperature of 40 °C was chosen to avoid condensation of liquid on the nanotube bundles, i.e., the liquid in the bulb was maintained at 24 °C. Later measurements indicated that the SWNT bundles were saturated under these conditions.

Figures 1 and 2 show, respectively, the *in situ* TEP and the four-probe resistance responses with time *t* to the vapours of methanol (CH₃OH), ethanol (C₂H₅OH), isopropanol (C₃H₇OH), butanol (C₄H₉OH) and H₂O. Dashed curves in figures 1 and 2 are fits to the data using a simple exponential function,

$$S = S_0 + \Delta S_{\max}(1 - e^{-t/\tau_S}), \quad (1)$$

where *S*₀ is the initial or degassed TEP, Δ*S*_{max} is the maximum response to physisorption (*t* → ∞) and τ_S is the time constant for the response. The same function is used for the resistive response, but *R*₀, Δ*R*_{max} and τ_R replace their counterparts in equation (1).

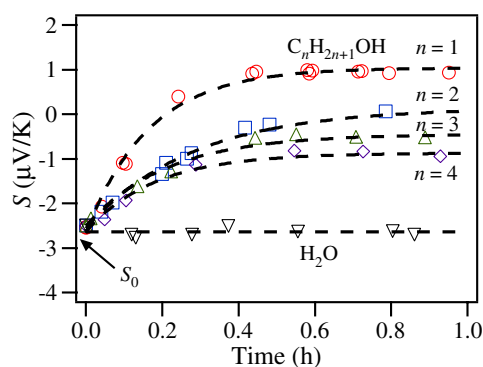


Figure 1. The time dependence of the TEP response of a SWNT thin film to successive exposure to vapours of water and alcohol molecules ($C_nH_{2n+1}OH$; $n = 1-4$) at 40°C . Dashed curves are fits to $S(t)$ data using an exponential function. Comments regarding the measurement can also be found in the caption to figure 2.

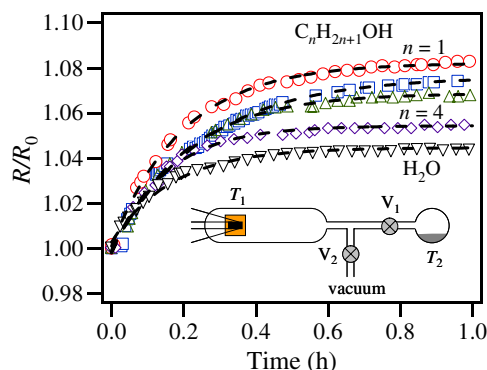


Figure 2. The time dependence of the normalized four-probe resistance response of a SWNT thin film to successive exposure to vapours of water and alcohol molecules ($C_nH_{2n+1}OH$; $n = 1-4$) at 40°C . The dashed curves are fits to the $R(t)$ data using an exponential function. The inset shows a simple schematic diagram of the measurement apparatus. The liquid temperature T_2 establishes the vapour pressure in the sample chamber which is at a temperature $T_1 > T_2$. The system is evacuated through V_2 . After degassing, V_2 is closed and V_1 is opened. The responses of S and R are then measured simultaneously.

After each set of curves in figures 1 and 2 was collected for a specific adsorbate, the sample was then heated again *in situ* under vacuum (10^{-7} Torr) to 500 K to remove the molecules. After a few hours at 500 K, the sample was found to fully recover the original degassed values S_0 and R_0 . In figure 1, it is seen that for methanol, ethanol, isopropanol and butanol the TEP also rises exponentially with time from the degassed value $S_0 \sim -2.7 \mu\text{V K}^{-1}$ to a higher plateau after ~ 1 h. For methanol and ethanol, S is even driven positive, saturating at $S_{\text{max}} \sim +1.1$ and $+0.1 \mu\text{V K}^{-1}$, respectively. Exposure to larger alcohol molecules, i.e., isopropanol and butanol, is found to lead to smaller changes in S and saturation at $S_{\text{max}} \sim -0.5$ and $-1.0 \mu\text{V K}^{-1}$, respectively. Interestingly, exposure to water vapour (another small, but very polar molecule) induces virtually no change in the TEP. Bradley *et al* [8] have also found very weak or no response of the TEP of mats of bundled SWNTs to water vapour. This lack of sensitivity of the TEP to water is very interesting and will be discussed later. Table 1 shows some relevant parameters of the molecules studied here including molecular weight, projection area and dipole moment.

Table 2. Adsorption time constants for thermoelectric (τ_S) and resistive (τ_R) responses of a SWNT thin film to adsorbed water and $C_nH_{2n+1}OH$; $n = 1-4$; see equation (1).

Molecule	τ_R (min)	τ_S (min)	$\tau = \frac{\tau_R + \tau_S}{2}$	$\sqrt{\frac{M_{\text{alcohol}}}{M_{\text{water}}}}$	$\frac{\tau_{\text{alcohol}}}{\tau_{\text{water}}}$
CH ₃ OH	11.7	10.1	10.9 ± 0.8	1.33	1.10 ± 0.08
C ₂ H ₅ OH	15.1	16.0	15.6 ± 0.5	1.56	1.59 ± 0.05
C ₃ H ₇ OH	11.3	12.6	12.0 ± 0.6	1.83	1.22 ± 0.06
C ₄ H ₉ OH	9.1	10.5	9.8 ± 0.7	2.03	1.00 ± 0.07
H ₂ O	9.8	—	9.8	1	1

In a separate study, we have investigated the effect of an *increase* in molecular vapour pressure on S_{max} and R_{max} for each alcohol. After the values S_{max} and R_{max} were observed from exposure to vapour pressure in equilibrium with the liquid at 24 °C, and before any vacuum-degassing, the bulb containing the alcohol (inset to figure 2) was heated from 24 °C to a higher temperature (~60 °C) to increase the vapour pressure. After ~30 min of exposure to the higher vapour pressure, no further changes in S and R were observed. This suggests that the values of ΔS_{max} and ΔR_{max} that we observed in earlier experiments correspond to the response of a maximum molecular coverage attainable for our bundled SWNT sample at 40 °C. In effect, our experiments suggest that the surface was saturated at 40 °C. Also, we should mention that we have no direct evidence as to what extent the nanotubes are ‘open’ or ‘closed’ at their ends, although step (1) in the nanotube purification process is expected to open the tubes. Furthermore, all the molecules investigated in this work satisfy the inequality $D_K > d_1$, where D_K is the kinetic diameter of the molecule and d_1 is the diameter of a typical interstitial channel ($d_1 \sim 0.21$ nm for (10, 10) tube bundles). This suggests that the molecule cannot easily enter the channel, unless the bundles swell to accommodate these molecules. However, they are all small enough to enter an internal pore of a (10, 10) or larger tube if the tube end is open or if a large hole is present in the tube wall.

Figure 2 shows the time evolution of the normalized four-probe resistance. The data for each molecule type were taken concurrently with the TEP data in figure 1. The trends for ΔR_{max} versus n for the alcohols ($C_nH_{2n+1}OH$; $n = 1-4$) match those observed for ΔS_{max} (figure 1), i.e., exposure to methanol shows the largest change in R , with an increase of ~8.2%. Ethanol, isopropanol, butanol and water induce an increase in R , with $\Delta R/R_0$ saturating at 7.5%, 6.8%, 5.4% and 4.4%, respectively. As can be seen from the fits in figures 1 and 2, both $R(t)$ and $S(t)$ exhibit simple exponential behaviour, as described by equation (1). The time constants obtained from the fits to $R(t)$ are all in excellent agreement with those obtained from the fits to $S(t)$ (table 2). According to simple molecular kinetic theory, the diffusion time should be proportional to the square root of the molecular mass, i.e., $\tau \sim \sqrt{M}$.⁶ However, the time constants obtained in our study do not exhibit any systematic dependence. This result indicates that the rate limiting step may not be ordinary diffusion, but perhaps the rate of success for entering the tube pore through an open end. In a computational study of molecular diffusion through carbon nanotubes, Mao and Sinnott [26] have shown that the intermolecular and molecule–nanotube interactions strongly affect the molecular diffusion ranging from normal mode (individual molecules can pass each other within the pore) to single-file diffusion (individual molecules cannot pass each other in the pore due to their large size relative to the pore diameter).

⁶ We assumed that the rate limiting step in the equilibration of the bundle with the alcohol molecules is the surface diffusion into the bundle, although one might expect the pressure of the background gas that supplies molecules to the surface to be an important issue which has been omitted in the present analysis.

The increase in ΔR_{\max} is identified with an additional impurity scattering of the conduction electrons in metallic tubes within the bundles due to physisorbed molecules. This will be discussed in detail later. Interestingly, when they are exposed to water vapour, the resistances of the SWNT films increased by $\sim 4.4\%$, even though the TEP was constant and equal to its initial degassed value. Although we see no change in the TEP ($\Delta S_{\max} = 0$) for H_2O , in agreement with Bradley *et al* [8], we do see a strong response and saturation in R for the same exposure to H_2O . This result is in contrast to the results of Zahab *et al* [27], who have reported an initial increase of resistance of the SWNTs when exposed to water vapour, with an eventual crossover to a decrease of resistance for increasing exposure, reaching a resistance value lower than the starting value. We have not observed this crossover in three separate studies of $\text{H}_2\text{O}/\text{SWNT}$ systems. Furthermore, Zahab *et al* [27] have interpreted their results on the basis that the outgassed SWNTs are p-type *semiconductors* and water molecules act as compensating donors. It is difficult to speculate about the different behaviour of $R(t)$ observed in our samples with respect to the Zahab *et al* samples. We do note, however, that they initially degassed their sample at 220°C in a vacuum of 3×10^{-6} mbar for only 5 h. According to our experiments, this may not be sufficient time to remove all the weakly chemisorbed oxygen. We also do not know whether they have annealed their samples at 1000°C as we have done. In our work, we have monitored S and R versus t during vacuum-degassing and have waited for an exponential approach to a lower plateau in $S(t)$ and $R(t)$ before exposing the sample to a particular vapour for study.

4. Discussion

Previous studies on the TEP behaviour of SWNT films have been found to be consistent with a diffusion TEP dominated by *metallic* tubes in a rope [21]. This can be understood by considering the TEP of a rope as the sum of the conductance-weighted contributions from all tubes connected in parallel in the rope [21]. The TEP or Seebeck coefficient S for a metallic system can be described by the Mott relation [28]

$$S = -\frac{\pi^2 k_B^2 T}{3|e|} \left(\frac{d \ln \sigma(E)}{dE} \right)_{E_F}, \quad (2)$$

where σ is the electrical conductivity, e is the electronic charge, k_B is the Boltzmann's constant and T is the temperature. The logarithmic derivative of σ is evaluated at the Fermi energy E_F . As predicted by equation (2), S for our purified, annealed and degassed SWNT films is observed to be approximately linear in temperature [21]. Recently, a broad peak in $S(T)$, observed below 100 K and superimposed on a linear T background, has been attributed to an additional contribution from phonon drag [21, 29]. As our measurements in this study were made at $T = 40^\circ\text{C}$, we ignore a phonon drag contribution which is a low temperature effect. For our purpose here, it is convenient to separate two contributions that limit the conductivity:

- (1) carrier scattering intrinsic to the degassed metallic tubes (identified with phonons and permanent tube wall defects) and
- (2) additional carrier scattering in the metallic tubes associated with the perturbation in the local tube wall potential due to adsorbed gas molecules or collisions with gas molecules.

We assume that the scattering contributions (1) and (2) follow Mathiessen's rule [30]. That is, the respective resistivities in each nanotube are additive, i.e.,

$$\rho = \rho_0 + \rho_1, \quad (3)$$

where ρ_0 is identified with the resistivity of the degassed metallic tubes and ρ_1 is identified with the *extra* impurity scattering due to gas molecules interacting with the tube wall.

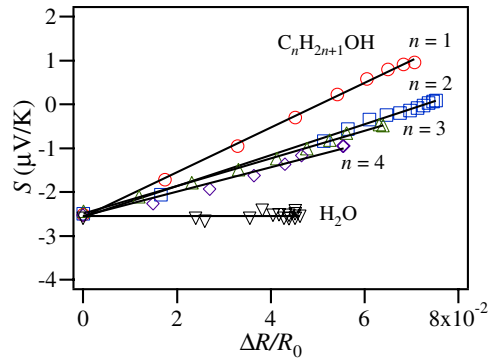


Figure 3. S versus $\Delta R/R_0$ plots during exposure of degassed SWNT bundles to water and $C_nH_{2n+1}OH$ ($n = 1-4$). The solid lines are linear fits to the data until saturation is established.

Using the well known expression for $\sigma(E) = 1/\rho(E)$ given by

$$\sigma(E) = e^2 v(E)^2 D(E) \tau(E), \quad (4)$$

where v , D and τ are, respectively, the free carrier velocity, the density of states and the carrier lifetime, we find the result [13],

$$S = S_0 - \frac{\pi^2 k_B^2 T}{3|e|} \left(\frac{\rho_l}{\rho_0 + \rho_l} \right) \left[\frac{1}{\tau_l} \frac{d\tau_l}{dE} - \frac{1}{\tau_0} \frac{d\tau_0}{dE} \right]_{E_F}. \quad (5)$$

Thus, depending on the signs and magnitudes of the terms $1/\tau_l(d\tau_l/dE)$ in equation (5), we can anticipate a positive or negative slope to the S versus ρ_l data collected at fixed temperature T . Furthermore, we consider a simple form for the scattering rate $1/\tau_l \sim \xi \alpha g(E)$, where ξ is the number of molecules adsorbed on the nanotube wall, E is the carrier energy and $\alpha g(E)$ is the scattering cross section. We note that in this form $1/\tau_l(d\tau_l/dE)$ is independent of the molecular coverage ξ and the constant prefactor α of the scattering cross section. Therefore, $1/\tau_l(d\tau_l/dE)$ (and hence $\Delta S/\Delta R$) depends only on $g(E)$; only the energy dependent factor $g(E)$ survives in the logarithmic derivative. For example, if $g(E) \sim E^m$, then $1/\tau(d\tau/dE) = m$, and the bracket in equation (5) is replaced by the difference in exponents.

Figure 3 displays the evolution of the thermopower versus the fractional change in the four-probe resistance ($\Delta R/R_0$) at fixed temperature (40°C). As the coverage of the molecules on the SWNTs increases with increasing time of exposure to the respective molecular vapour, both S and $\Delta R/R_0$ increase. It is very important to note that the data for all the alcohols show linear behaviour for S versus $\Delta R/R_0$, consistent with equation (5) (i.e., $S \sim \rho_l$ for $\rho_l \ll \rho_0$) [4]. It should also be noted that E_F is considered as a constant in the derivation of equation (5). Therefore, this result (equation (5)) is appropriate for physisorption and not for a chemisorption process involving significant charge transfer. Thus, the linearity of S versus $\Delta R/R_0$ implies that little or no charge transfer is taking place between the adsorbed molecules and the SWNTs; i.e., H_2O and the alcohols that are physisorbed onto high T annealed films do not chemically dope the SWNTs. In our previous study on the effects of physisorption of six-membered ring molecules (C_6H_{2n} ; $n = 3-6$) on SWNTs, we have found a slightly non-linear behaviour of S versus $\Delta R/R_0$ data [12]. This non-linear character in the C_6H_{2n} /SWNT system is not well understood, and we have tentatively identified it with a multiple-electron-scattering process [12].

From figures 1 and 2, it seems that the physisorption behaviour of water on the surface of carbon nanotubes is markedly different from that of the alcohols. Adsorption of strongly polar molecules such as water vapour is thought to occur by hydrogen bonding on graphitic surfaces and on carbon nanotubes [20], but it appears that the predominant interaction for all alcohols is the relative dispersion (i.e., van der Waals) contribution from the alkyl chains, which increases with alkyl chain length [31]. In fact, H₂O has a behaviour different from all the molecules we have studied, i.e., a zero response of the TEP and yet a normal resistive response. At this time, all we can conclude is that equation (5) may hold the answer for our observation (i.e., $\Delta S_{\max} \sim 0$), although we do not have a microscopic model for the scattering mechanism required to apply equation (5).

From a similar study on the effects of physisorption of the C₆H_{2n} family of molecules on *S* and *R* for bundled SWNTs, we were able to correlate the strengths of the TEP and resistive responses to the energy of molecular adsorption on graphitic surfaces [12]. In this former case [12], all the C₆H_{2n} molecules have adsorption energy E_a that is related to the number of π electrons on the molecule and is therefore a measure of the coupling of the molecule to the nanotube surface. E_a was then presumed to be a measure of the perturbative interaction of the gas molecules on the nanotube wall potential, responsible for the enhanced electron scattering rate [12]. In the present study, all the molecules share a dipolar character, but have different projection area A . Furthermore, we have found that the surface appears saturated. We presume that the scattering rate w , and thus ρ_I in equation (5), is related to the product of the molecular coverage ξ and the adsorption energy, i.e.,

$$w \sim E_a \xi, \quad (6)$$

where ξ is the areal density of physisorbed molecules on the nanotube surfaces. We furthermore expect that $\xi \sim 1/A_j$, where A_j is the projection area of the particular molecule j . Thus, from equations (5) and (6) we expect that $\Delta S_{\max} \sim \beta \rho_I \sim \beta E_a/A$ (β is the slope of the *S* versus $\Delta R/R_0$ straight lines in figure 3), i.e., the maximum change in *S* is proportional to the adsorption energy and inversely proportional to the projection area of the molecule. The projection areas A for the molecules studied here are also given in table 1. Yang *et al* [32] have recently studied the adsorption of butanol and methanol on HiPCo SWNTs at 30 °C, and have found that the number of adsorbed moles of molecules of butanol per unit weight is smaller than that for methanol. This result has been identified with the difference in molecular volumes [32]. The explanation should be equivalent to one involving projection molecular areas.

Thus, in an attempt to explain the systematics of ΔS_{\max} against the molecular properties, we have plotted ΔS_{\max} versus the quantity $\beta E_a/A$ in figure 4. Interestingly, all the data fall on a quasi-linear curve, motivating suggestion of the concept that the *extra* electron scattering in the nanotube wall due to physisorption is proportional to the product of the adsorption energy and the molecular coverage. The curvature of this quasi-linear curve at high $\beta E_a/A$ could be an indication of the saturation of the thermoelectric and resistive responses. On the other hand, methanol might be too small to be expected to follow the linear trend established for butanol, isopropanol and ethanol in figure 4 (dashed line).

5. Conclusions

In conclusion, we have utilized *in situ* measurements of TEP and resistivity to investigate the adsorption of various polar molecules (alcohols and water) in bundled SWNTs. We observe a strong effect on both the TEP and resistivity for methanol, ethanol, isopropanol and butanol. Surprisingly, water vapour does not have any effect on the TEP, i.e., $\Delta S_{\max} \sim 0$, but has a

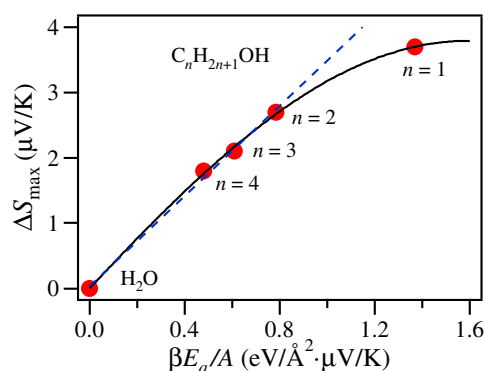


Figure 4. Maximum TEP change ΔS_{\max} of a SWNT thin film successively exposed to vapours of water and alcohol molecules ($C_nH_{2n+1}OH$; $n = 1-4$) as a function of the quantity $\beta E_a/A$, where E_a is the adsorption energy per molecule, A is the projection molecular area and β is the slope of the corresponding S versus $\Delta R/R_0$ straight line in figure 3. Solid and dashed lines are guides to the eye.

significant impact on the resistance, i.e., $(\Delta R/R_0)_{\max} \sim 4.4\%$. The fact that $\Delta S_{\max} \sim 0$ may be due to a fortuitous cancellation of scattering terms in equation (5). We have also observed that S exhibits a linear relationship with $\Delta R/R_0$, consistent with the creation of a new impurity scattering channel via physisorption, and that the slopes of the S versus $\Delta R/R_0$ data are specific to the particular molecules. In an effort to correlate what we have observed with molecular properties, we have found that, for water and the C_1 – C_4 alcohols, the maximum change in the TEP is proportional to the product of the molecular adsorption energy (measured on graphitic carbons) and the molecular coverage $\sim 1/A$, where A is the molecular projection area on the host surface.

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