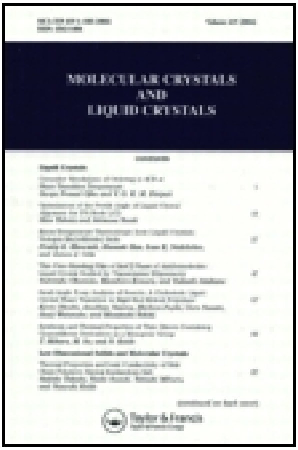

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THERMOELECTRIC CHEMICAL SENSOR BASED ON SINGLE WALL CARBON NANOTUBES

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Thermoelectric properties of single wall carbon nanotubes (SWNT) are quite sensitive to gases in contact with the tube walls. This effect makes possible a thermoelectric chemical sensor. Large, reversible swings in thermoelectric power (S), sometimes even involving sign changes in S, have been observed. Even contact of the SWNTs with He and N_2 *and* H_2 *result in easily detectable and reversible changes in S. Smaller, polar alcohol molecules stimulate a large thermoelectric response, although* H_2O *has no effect. For adsorption of six membered ring molecules* C_6H_n *in SWNTs, the large thermoelectric response observed for Benzene* ($n = 6$) *is seen to decrease as the* π *electrons in the molecule are removed, and the coupling between the molecules and the SWNT is thereby reduced. These effects are discussed in terms of the diffusion thermopower for a rope, and a new scattering channel associated with adsorbed molecules.*

Keywords: thermoelectric power; adsorption; π-electrons

INTRODUCTION

Carbon nanotubes have extremely interesting and unique chemical and physical properties [1,2]. These properties are being investigated for crucial applications such as field emission devices, actuators, nano-electronics, hydrogen storage, etc. [3]. These applications involve either individual nanotubes or mats of entangled bundles of nanotubes. Recently, several groups have reported the capability of using single wall carbon nanotubes as chemical sensors [4–6]. In particular, the thermoelectric power of mats of SWNTs has been shown to be extremely sensitive to environmental gases [5,7]. Thermopower and resistivity measurements have been interpreted as evidence that SWNTs can be easily doped by ambient exposure to O_2

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forming charge transfer complex $C_p^{+\delta} - O_2^{-\delta}$ [8,9]. These results demonstrate that the previously published large positive thermopower data are not intrinsic, but rather are the result of O_2 exposure.

EXPERIMENTAL

The SWNT samples studied in our experiments were comprised of tangled bundles of ~100's of SWNTs, either in the form of a lightly pressed mat, or as a thin film deposited on a glass substrate from an ethanol suspension. The SWNT material was obtained from Carbolex, Inc. and consisted ~50–70 vol% carbon as SWNTs produced by the arc discharge method using Ni-Y catalyst. Purification of this material was first carried out using "selective oxidation" in dry air for 30 min. at 450°C, followed by refluxing in 4 M HCl at 120°C for 24 hrs. Thermopower was measured ***in situ*** in a high vacuum apparatus using a heat pulse technique [10]. Samples were first degassed in high vacuum for 6–10 hours before the response to an adsorbed gas was recorded.

RESULTS AND DISCUSSION

Figure 1(a) shows the time evolution of TEP at T = 500 K for a typical purified thin film sample under vacuum. The sample also was previously exposed to air under ambient conditions for several days. It was then mounted in our apparatus and evacuated to 10^{-6} Torr and heated from 300 to 500 K in ~10 min.

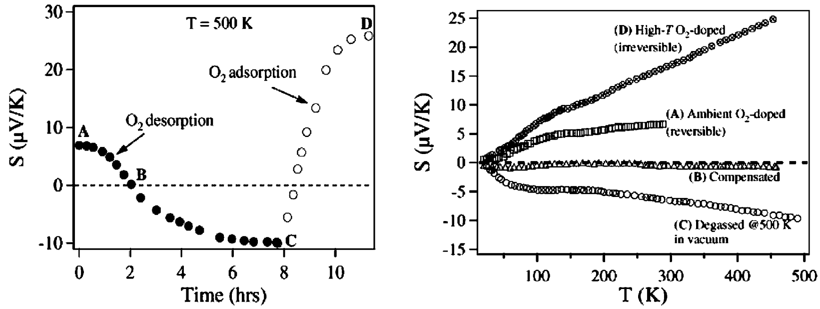
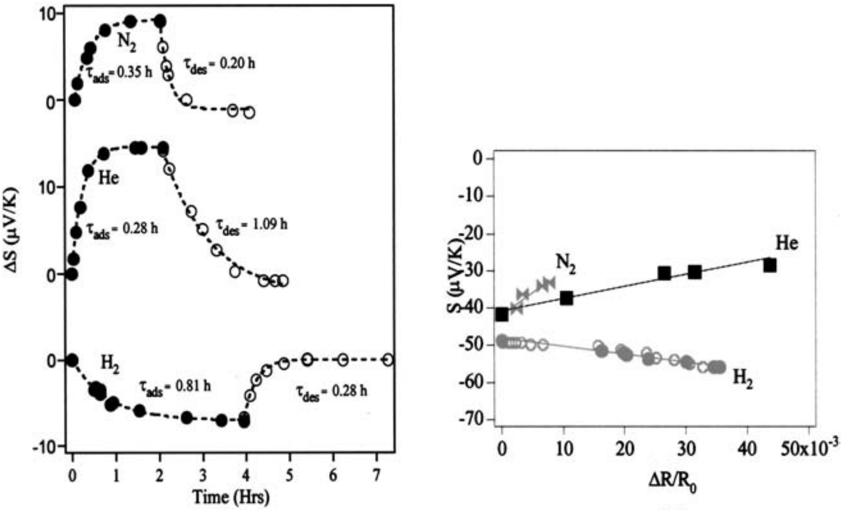


FIGURE 1 (a) Thermopower response of purified SWNT film at 500 K to vacuum and O_2 (1 atm). (b) Temperature dependence of the thermopower of the same film after successively longer period of degassing at 500 K. The letters in (b) refer to the times A, B, C, D in (a) when the sample was quickly cooled to collect the S(T) data.

As the sample is degassed at $T = 500\,K$ in vaccum the TEP was observed to decrease slowly from an initial value $S = +8\,\mu V/K$ (at "A" still air-saturated), changed sign (at "B" fully compensated) and gradually approached a saturated value of $S = -10\,\mu V/K$ (at "C" fully degassed).

When the fully degassed sample was exposed to 1 atm of pure O_2 at $T = 500\,K$ (at point "C"), we found that it irreversibly changed the TEP to a larger positive value of $S = +25\,\mu V/K$, (point "D"). By applying vacuum at "D" the TEP then remained constant, indicating possible formation of C-O bonds. Figure 1(b) displays the temperature dependence of the TEP at the points "A", "B", "C", and "D" indicated in Figure 1(a). It should be noted that any intermediate TEP between the ambient air-saturated and the fully degassed states can be reliably tuned including an almost zero TEP. In Figure 1(a), the air-saturated sample and the sample exposed to 1 atm O_2 at 500 K show positive and almost linear behavior over the entire temperature range with a positive "hump" around 120 K. The fully degassed sample shows negative and nearly linear behavior over the temperature range with a superimposed negative hump around 80 K. This low temperature hump is identified with phonon drag, which enhances the diffusion TEP. We note from the figure that it is possible to generate a sample with $S \sim 0$ over almost entire range of temperature from 4 K to 300 K [8]. We identify this behavior with a compensated sample, where the effects of acceptor and donor states cancel out. Our analysis of the data finds that the thermopower of the sample is due to the metallic tubes. Thus the sensor action is determined by changes in the thermopower of the metallic tubes. The semiconducting tubes play a role in establishing the Fermi energy of the rope. Charge transfer impurities on the semiconducting tubes will shift E_F in the rope [8].

Even gases like He and N_2, and H_2 in contact with SWNTs induce easily detectable changes in thermopower and resistivity [6]. This has been identified with a weak interaction between these gases and the nanotubes providing an additional scattering channel for electrons in the metallic tubes created by physisorption or gas collisions with the tube wall. Figure 2(a) shows the time response of thermopower for a degassed SWNT mat sample to 1 atm overpressure of N_2, He, and H_2 at 500 K (solid symbols). For each gas, the change in thermopower is plotted and offset for clarity. For N_2 and He, thermopower is seen to rise exponentially, saturating $\sim 9\,\mu V/K$ and $\sim 12\,\mu V/K$ above the degassed value (S_0) with time constants 0.35 h and 0.28 h respectively. Interestingly, for H_2, thermopower is observed to decrease exponentially saturating $\sim 7\,\mu V/K$ below S_0 with a much longer time constant of 0.81 h. By applying vacuum, N_2 and H_2 shows exponential decay (open symbols) of S with time constants of 0.20 h and 1.09 h respectively. H_2 shows an exponential rise of S with time constant of 0.28 h when the vacuum is applied. Interestingly, the adsorption and



(a) (b)

FIGURE 2 (a) The time response of thermopower for a degassed SWNT mat sample (as-prepared) to a 1 atm overpressure of N_2, He, and H_2 at 500 K (solid symbols) and to the subsequent application of a vacuum (open symbols). The dotted lines represent exponential fits to S(t). For each gas, the change in S is plotted and offset for clarity. (b) S vs R/R_0 for N_2, He, and H_2, where $\Delta R = R - R_0$, and R_0 is the initial resistance. The data are collected at $T = 500$ K as S and R evolve with time (See Color Plate II).

desorption time constants for each gas is considerably different. This may be associated with "single file" diffusion inside the long narrow tubes.

In Figure 2(b) we display plots of S vs $\Delta R/R_0$ for isothermal adsorption for N_2, He, and H_2 at 500 K, where $\Delta R = R - R_0$, and R_0 is the initial value for the 4-probe resistance.† As can be seen in the figure, data are linear for these three gases with positive slope for N_2, He and negative slope for H_2. To better understand this linear behavior and the sign of the slope, we develop the following formalism.

†In Figures 1a, 2b, 3a, b the reader may notice that different values of the initial "degassed" thermopower can be found. The values fall into two groups: small negative $S \sim -6$ to -10 μV/K and larger negative $S \sim -30$ to 50 μV/K. Samples in the former group (small neg. S) were purified and annealed in high vacuum at 1000°C for 8 hours. The residual metal catalyst was largely removed in this purification process. Samples in the latter group (large neg. S) were studied without purification, 6 at % metal remained. This residual metal strongly affects the initial values of the thermopower in the degassed state; it may be the result of the Kondo effect [11]. Nevertheless, the response ΔS to the adsorbed gas is not very sensistive to S_0 (or the metal content). This has been verified with many samples.

The thermoelectric power S for a metallic system can be described by the Mott relation.

$$S = -(\pi^2 k_B{}^2/3e)T\ d/dE\ \{\ln \sigma(E)\}_{E_F}, \tag{1}$$

where σ is the electrical conductivity, e is the magnitude of the charge on the electron, k_B is Boltzmann's constant, and T is the temperature. According to Matheissen's rule, the resistivity is the sum of contributions from separate mechanisms,

$$\rho = \rho_0 + \rho_I, \tag{2}$$

where ρ_0 is identified with the resistivity of the degassed tubes, and ρ_I with the *extra* impurity scattering due to adsorbed gas. If these contributions are incorporated into Eq. (1), and we keep only terms up to first order in ρ_I/ρ_0, we find

$$S = S_0 + (\rho_I/\rho_o)(S_I - S_0) \tag{3}$$

where, S_0 and S_I, are respectively, the thermopower of the degassed tube and the additional impurity (I) contribution from adsorbed gas. Equation (3) is the well-known Nordheim-Gorter (N-G) expression developed for metallic alloys (but for $\rho_I/\rho_0 \ll 1$). The significance of Eq. (3) is that, for fixed T, the thermopower S is linear in the extra resistance ρ_I, if $(S_I - S_0)$ is constant and not affected by the contact with the gas. This should occur if the gas contact leaves the SWNT band structure in tact and E_F unchanged, i.e., charge transfer between the adsorbed gas and the host lattice does not occur. This situation is consistent with physisorption NOT a chemisorption process. This conclusion is best seen by writing down the form of the thermopower explicitly.

We use the Mott relation (Eq. (1)) and the well known expression for σ (E) given by,

$$\sigma(E) = e^2 v(E)^2 D(E)\tau(E) \tag{4}$$

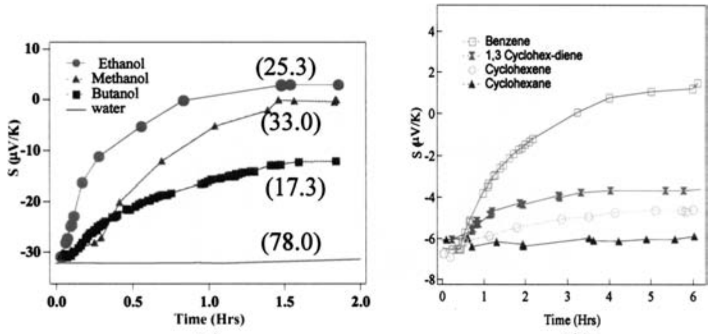
where, v, D and τ are, respectively, the free carrier velocity, density of states, and carrier lifetime. The conductivities $\sigma_0 = 1/\rho_0$ and $\sigma_I = 1/\rho_I$ are, of course, also described by Eq. (4), with $\tau(E)$ replaced by either $\tau_0(E)$ or $\tau_I(E)$. Then, for fixed E_F (no charge transfer) the Nordheim-Gorter equation (Eq. (3)) becomes,

$$\begin{aligned} S &= S_0 + (\pi^2 k_B T/3e)(\rho_I/\rho_0)[(1/\tau_I)(d\tau_I/dE) - (1/\tau_0)(d\tau_0/dE)] \\ &= S_0 + \Delta S \end{aligned} \tag{5}$$

From Eq. (5) we also note that the sign of ΔS can be greater or less than zero, depending on whether the logarithmic derivative of τ_I exceeds that of τ_0.

In Figure 3(a), we plot the time evolution of thermopower of a SWNT mat sample degassed and subsequently exposed to vapors of various alcohols in equilibrium with the liquid at 40°C. For comparison, the effect of water vapor on thermopower also plotted. Despite the fact that all these molecules are polar in nature, water vapor has virtually no effect on thermopower. However, for methanol, ethanol, and butanol the thermopower is seen to rise exponentially to a higher plateau. For methanol and ethanol, the thermopower is even driven positive from its negative degassed value. Even butanol induces a large change in thermopower. It should be noted that in this series of alcohols, the effect does not follow the molecular weight, or the polarity of the molecules. The dielectric constants of the corresponding molecular liquids are listed in parentheses above the data. The reason for this behavior is not yet understood and currently under investigation. We assume that the thermoelectric response correlates with the heat of adsorption for these molecules. We discuss this further below.

In Figure 3(b), we display the thermopower response of a purified mats of nanotube bundles induced by the adsorption of six membered ring molecules C_6H_n where $n = 6,8,19$ and 12. The vapor pressure was in equilibrium with the liquid at 40°C. All of these molecules are the same size and have approximately the same molecular weight. They differ predominantly in the number of π electrons. Adsorption of benzene ($n = 6$) at 40°C induces a giant increase of the thermopower and reverses the sign. As the number of π electrons in the molecules decrease (increasing n in C_6H_n), the effect decreases and disappears for cyclopean (no π electrons). The data are therefore consistent with the idea of a new scattering channel.



(a) (b)

FIGURE 3 (a) Time-response of the thermopower of a SWNT mat to methanol, ethanol, butane, and water. (b) Time-response of thermopower to various six-membered ring molecules introduced at 40°C. The numbers in parentheses in 9(a) are the dielectric constant of the corresponding liquids (See Color Plate III).

TABLE I Heat of Adsorption of C_6H_n on Graphitized Carbon Black and the Saturated Value of TEP

Molecule	Saturated TEP Value (μV/K)	Adsorption Energy (kJ mol^{-1}) [12]
Benzene	+2	9.42 ± 0.06
1-3 Cyclohexa-diene	−4	8.87 ± 0.08
Cyclohexene	−5	8.71 ± 0.08
Cyclohexane	−6	7.59 ± 0.07

The size of the effect is driven by the coupling of the π electrons in the molecule and the nanotube wall. It is interesting to compare the values of the TEP at saturated coverage under our experimental conditions to the heat of adsorption on graphite of the corresponding C_6H_n molecule. The results appear in Table I and show that, in effect, that the sensor activity may simply be a measure of the binding energy of the molecule, as measured by the heat of adsorption. We are currently collecting data on the alcohols to see whether this observation is universal.

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