Giant Thermopower Effects from Molecular Physisorption on Carbon Nanotubes

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Results are presented of *in situ* studies of the thermoelectric power and four-probe resistance of single-walled carbon nanotube films during the adsorption of cyclic hydrocarbons C_6H_{2n} ($n = 3$–6). The size of the change in these transport parameters is found to be related to the π electron population of the molecule, suggesting the coupling between these π electrons and those in the nanotube wall may be responsible for the observed effects. A transport model for the SWNT film behavior is presented, incorporating the effects of a new scattering channel associated with the adsorbed molecules.

In this Letter, we report the results of a systematic study of the changes in the thermopower (S) and four-probe resistance (R) of vacuum-degassed mats of nanotube bundles induced by the adsorption of six-membered ring molecules C_6H_{2n}, where $n = 3$–6. As n increases from 3 (benzene) to 6 (cyclohexane), π electrons are removed from the molecule. For $n = 6$, cyclohexane, only σ bonds remain. Thus the C_6H_{2n}:SWNT (single-walled carbon nanotube) system is an interesting model system to study the coupling between a molecule and a nanotube, as regulated by the π-electron character of the adsorbed molecule.

The sensitivity of the electronic properties of SWNTs to environmental gases, e.g., O_2, has been well documented [1–3]. O_2-loaded bundles of SWNTs exhibit a large positive thermopower (S). However, degassing the sample at 500 K in a vacuum has been found to drive S negative as the O_2 is desorbed. Calculations by Jhi *et al.* [4] have shown that a charge transfer between the O_2 and SWNT is expected ($0.1e$ per O_2 chemisorbed). Smaller thermoelectric effects on SWNTs due to contact with H_2, He, and N_2 have also been reported and identified with a weak interaction between gas and the nanotube [5]. For these gases, the mechanism proposed behind the thermoelectric changes is the creation of an additional scattering channel for electrons in the nanotube wall created by physisorption or gas collisions with the tube wall [2].

From a broader perspective, SWNTs provide a unique opportunity to study the interaction of molecules with a conducting surface. This stems from the unique structure of the nanotube, i.e., a monolayer sheet of sp^2-bonded carbon (graphene) that is rolled into a small diameter (1–2 nm) seamless cylinder. The electron and phonon states of this unique "all-surface" solid state system are, by comparison to many other solids, relatively uncomplicated, thereby allowing fundamental calculations addressing the experimental observations presented here to be carried out. Molecular adsorbates (M) that engage in charge transfer with the nanotube wall, i.e., $M^+C_n^-$, might be expected to have a significant impact on the transport of charge and heat down the nanotube wall. However, it is indeed surprising that wide HOMO-LUMO gap organic molecules like benzene or cyclohexane can indeed be detected via the thermoelectric power or electrical resistivity of the nanotube.

The SWNT material studied here was obtained from CarboLex, Inc., and consisted of ~50–70 vol % SWNT. Their nanotubes are produced by the arc discharge method using Ni-Y catalyst. The material was found to exhibit the characteristic $T = 300$ K Raman spectrum (514 nm excitation) published previously [6], including the radial breathing mode band at 186 cm^{-1} and the stronger tangential band at 1593 cm^{-1}. The average diameter of these tubes has been shown to be close to that of a $(10, 10)$ tube. Typical high resolution scanning electron microscope images have shown that the CarboLex tubes are present in bundles, with bundle diameters in the range 10–15 nm, i.e., containing ~100–200 tubes. For this study, the as-purchased SWNT material was subjected to a post synthesis chemical purification: (1) oxidation in dry air for 30 min at 350 °C followed by (2) reflux in 4 M HCl at $T = 120$ °C for 4 h. The metal content in the purified sample was determined by oxidizing the sample in air in a thermogravimetric analyzer to be ~2 at. % (IGA, Hiden Inc.). The purified sample was then subjected to a final vacuum degassing at 1000 °C at 10^{-7} Torr for 24 h. Films used in this study were prepared by depositing ethanol-dispersed purified SWNTs onto a glass substrate under ambient conditions. Two Chromel-Au/7 at. %Fe thermocouple junctions, and two additional Cu leads (all 0.003 in. diam. wires) were attached to the edges of the film with silver paste to measure the thermoelectric power (TEP) [7,8] and four-probe electrical resistance. Details of the transport measurements are available elsewhere [9]. The sample was vacuum degassed at 500 K *in situ* in the TEP apparatus before various C_6H_{2n} molecular vapors were introduced as follows. A side arm connected to a glass bulb holding the hydrocarbon liquid was connected via a valve to the TEP apparatus. The hydrocarbon was spectral grade (Aldrich) and had been previously vacuum degassed. The vapor pressure of each C_6H_{2n} species was that in equilibrium with the liquid in the bulb at 24 °C. The vapor pressure is a very weak function of the C/H composition

[10], so by fixing the bulb temperature at 24 °C the sample was exposed to each molecular vapor at the pressure $p \sim$ 12 kPa. After the thermoelectric response to a particular C_6H_{2n} molecule was recorded, the sample was degassed at 500 K until the thermopower and four-probe resistance of the film returned to their original degassed values. Then the same film was exposed to the next molecular vapor, and so on.

Previous studies of the TEP behavior of SWNT films is consistent with a diffusion thermopower dominated by *metallic* tubes in a rope [11]. This can be understood by considering the thermopower of a rope as the sum of the conductance-weighted contributions from all tubes connected in parallel in the rope [11]. The thermoelectric power S for a metallic system can be described by the Mott relation [12]

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

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. For our purposes, it is convenient to explicitly separate contributions to the conductivity from scattering intrinsic to the degassed metallic tubes (identified with phonons and permanent tube wall defects, etc.) and additional carrier scattering associated with the perturbation in the local tube wall potential due to adsorbed gas molecules. We assume that these scattering contributions follow Matthiessen's rule [13]. That is, the respective resistivities are additive, i.e., $\rho = \rho_0 + \rho_I$, where ρ_0 is identified with the resistivity of the degassed tubes, and ρ_I with the *extra* impurity scattering due to adsorbed molecules. Incorporating this contribution to Eq. (1) and using $\sigma(E) = e^2 v(E)^2 D(E) \tau(E)$, where v, D, and τ are, respectively, the free carrier velocity, density of states, and carrier lifetime, we find the result

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

Thus, depending on the sign and magnitude of the terms $1/\tau_i(d\tau_i/dE)$ in Eq. (2), we can anticipate a positive or negative slope to the data S vs ρ_I collected at fixed temperature. Furthermore, we consider a simple form for the scattering rate $1/\tau_I \sim N \sigma_n g(E)$, where N is the number of molecules adsorbed on the wall, E is the carrier energy, and $\sigma_n g(E)$ is the scattering cross section. In this form, we note that $1/\tau_I (d\tau_I/dE)$ is independent of the molecular coverage (N) and the constant prefactor σ_n of the scattering cross section.

The experiments began with an *in situ* vacuum degassing of the SWNT film in the TEP apparatus at 500 K. After the thermopower remained constant and negative for ~8 h, we then cooled the sample to 40 °C and admitted the vapors of the particular C_6H_{2n}. The molecular vapor pressure of the C_6H_{2n} is essentially independent of

n and equal to that of the vapor in equilibrium with the liquid (vapor pressure [10] ~12 kPa at 24 °C). In Fig. 1 we show the *in situ* thermopower response with time to the vapors of benzene (C_6H_6), 1,3-cyclohexadiene (C_6H_8), cyclohexene (C_6H_{10}), cyclohexane (C_6H_{12}). The film temperature was 40 °C. After each curve in Fig. 1 was collected, the sample was heated again (*in situ*) under vacuum at 200 °C for a few hours in order to fully recover the thermopower and resistance values of the initially degassed sample. For C_6H_6 (benzene), with increasing exposure time, the thermopower is seen to increase with time from its initial (degassed) value $S = -6.4 \mu V/K$ (40 °C), eventually saturating after ~6 h at a positive value $S = +1.3 \mu V/K$. Subsequent exposure to 1,3-cyclohexadiene leads to a similar time dependence of the thermopower and a saturation at $\sim -3.6 \mu V/K$. Cyclohexene was studied and found to induce a smaller change in thermopower, saturating at $S \sim -4.6 \mu V/K$. Interestingly, cyclohexane, which has no π electrons, was found to exhibit no detectable change in the thermopower. The results are tabulated in Table I in terms of the saturated value (S_s) and the corresponding change $\Delta S = S_s - S_0$, where S_0 is the value of the degassed sample thermopower; both values S_s and S_0 refer to a sample temperature of 40 °C.

In Fig. 2 we show the concurrent time evolution of the four-probe resistance (R) for exposure to each molecular vapor at 40 °C. Exposure to benzene shows the largest change in resistance with an increase of 13% at saturation. 1,3-Cyclohexadiene and cyclohexene induce increases in resistance saturating at 10% and 7%, respectively. Consistent with the thermopower results, exposure to cyclohexane shows essentially no change in four-probe resistance. It is clear that both S and R follow similar trends with varying n in C_6H_{2n}. In Table I we also
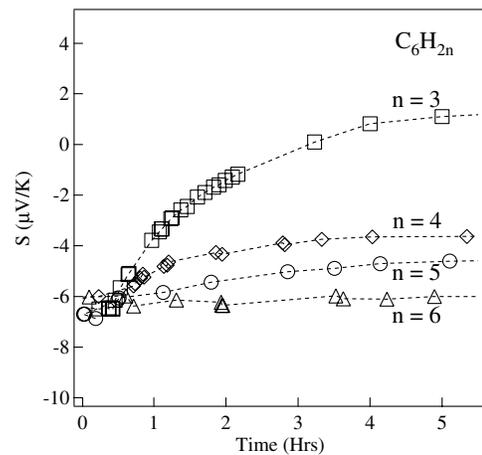

FIG. 1.   *In situ* 40 °C thermoelectric power (S) vs time (t) during successive exposure of a degassed SWNT film to vapors of six-membered ring molecules C_6H_{2n}; $n = 3$–6. The dashed lines are guides to the eye.

TABLE I. Comparison of the $T = 40\,°C$ thermoelectric and resistive response of a SWNT film to adsorbed C_6H_{2n}.

Molecule C_6H_{2n}	n	S_s (μV/K)	ΔS^* (μV/K)	$(\Delta R/R_0)^{\dagger}_{max}$ (%)	Vapor pressure [10] (kPa)	Adsorption energy (E_A)[14] (kJ mol^{-1})
Benzene	3	+1.3	7.7	13	12.7	9.42 ± 0.06
1,3-Cyclohexadiene	4	−3.6	2.8	10	13.0	8.87 ± 0.08
Cyclohexene	5	−4.6	1.8	7	11.9	8.71 ± 0.08
Cyclohexane	6	−6.4	0	0	13.0	7.59 ± 0.07

display the values of $\Delta R/R_0$, where $\Delta R = R_s - R_0$, R_s is the resistance with saturation covering of the molecules, and R_0 is the resistance of the degassed sample. We expect $\Delta R \sim \rho_I \sim 1/\tau_I \sim N\sigma_n g(E)$.

All of these C_6H_{2n} molecules are almost the same size and have approximately the same molecular weight. We therefore suggest that the observed differences in the thermopower and resistive responses should be attributed to the number of π electrons in the molecule. Adsorption of benzene ($n = 3$) induces the largest increase of the thermopower and resistance. As the number of π electrons per molecule are reduced (increasing n), the impact of the molecular adsorption on the transport coefficients (S, ρ) of the SWNT disappears. The data are therefore consistent with the idea of a new scattering channel created by the molecular adsorbate, and the size of the effect is apparently driven by the coupling of the π electrons in the molecule to π electrons in the metallic nanotube wall. It is interesting to compare the values of the TEP and resistivity at saturated coverage to the heat of adsorption E_A of C_6H_{2n} on graphitic carbons (Table I) [14]. The tabulated data show that the response ΔS and $(\Delta R/R_0)_{max}$ at $40\,°C$ correlates with the binding energy of the C_6H_{2n} molecules to a sp^2 carbon surface.

In Fig. 3, we plot the evolution of the thermopower (S) vs the fractional change in the four-probe resistance ($\Delta R/R_0$) at fixed sample temperature ($40\,°C$) and molecular vapor pressure (~ 12 kPa). As the coverage of the molecules on the SWNTs increases with increasing exposure time to the respective molecular vapor, both S and $\Delta R/R_0$ increase, as shown in Figs. 1 and 2. Data for the adsorption of three molecules C_6H_{2n} ($n = 3, 4, 5$) are shown. Cyclohexane C_6H_{12} did not produce a detectable thermoelectric response (i.e., a change in S or R). Although the maximum change in S and R observed in the same SWNT film sample after long term exposure to the various molecules is very different (Figs. 1 and 2), a universal behavior (i.e., independent of n) is observed for the dependence of the thermopower on the change in resistance $\Delta R/R_0$ (Fig. 3). We appeal to Eq. (2) for guidance in understanding this universality. First, we associate $\rho_I/(\rho_0 + \rho_I)$ in Eq. (2) with the experimental quantity $\Delta R/(R_0 + \Delta R)$ [15]. Therefore, if the lifetime factor in brackets is independent of N and σ_n, as discussed above, Eq. (2) predicts a universal relationship between S and $\Delta R/R_0$. For small $\Delta R/R_0 = \rho_I/\rho_0$, Eq. (2) also predicts a linear relationship between S and $\Delta R/R_0$. At low coverage, i.e., for $\Delta R/R_0 < 0.06$ we do observe approximately linear behavior. However, at higher values of $\Delta R/R_0$, S increases faster than a linear behavior. In fact, we can fit the data reasonably well with the quadratic relation $S = a + b(\Delta R/R_0) + c(\Delta R/R_0)^2$ over most of the range of the data. This quadratic function is plotted as the dashed line in Fig. 3. The nonlinear behavior is tentatively assigned to multiple scattering processes associated with larger molecular coverage.
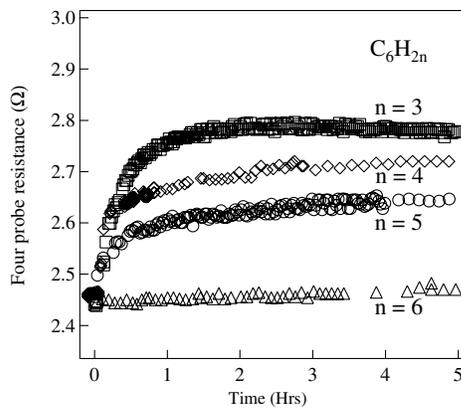

FIG. 2. *In situ* $40\,°C$ four-probe resistance (R) vs time (t) during successive exposure of a degassed SWNT film to vapors of six-membered ring molecules C_6H_{2n}; $n = 3$–6.
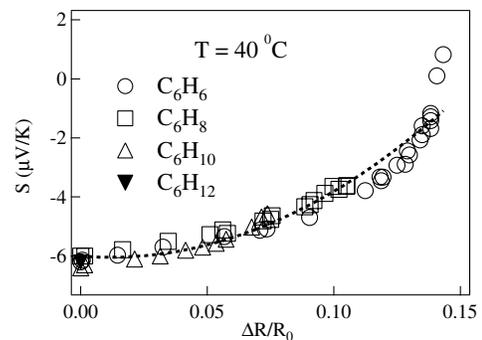

FIG. 3. S vs $\Delta R/R_0$ during exposure to C_6H_{2n} ($n = 3$–6). The dashed curve is a fit of a quadratic function $S = a + b(\Delta R/R_0) + c(\Delta R/R_0)^2$ to the data, where $a = -6.2\ \mu$V/K, $b = -8.6\ \mu$V/K, and, $c = 301\ \mu$V/K.
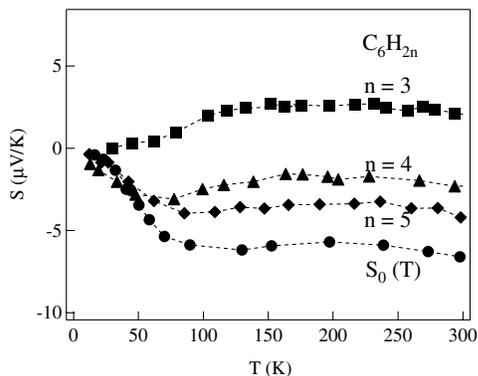
FIG. 4. Temperature dependence of the thermopower of the degassed SWNT after saturation coverage of the various C_6H_{2n} molecules. The dashed lines are guides to the eye.

In Fig. 4 we display the temperature dependence of the thermopower [16] after saturation coverage at 40 °C. Before cooling the sample to collect the data, the valve to the hydrocarbon bulb was closed. As the sample was lowered into a liquid He storage container, residual vapor in the TEP apparatus should first condense on the bottom of the sample compartment. Some of the molecules may condense on the saturated surface of the bundles forming a second monolayer over the initial primary layer. However, the effect of this overlayer on the transport properties should be small. As shown in Fig. 4, the thermopower $S_0(T)$ for the degassed film is nearly constant down to 100 K and approaches 0 quasilinearly at lower temperatures. The T dependence of thermopower for the film after being exposed to C_6H_{2n} can also be understood with the aid of Eq. (2). At high temperature, we assume the following: (1) the metallic tubes exhibit an intrinsic resistivity $\rho_0 \sim T$, and (2) the impurity resistivity ρ_I is independent of temperature. Then at high temperature, the factor $\rho_I/(\rho_0 + \rho_I) \sim 1/T$ when $\rho_I \ll \rho_0$, and the second term in Eq. (2) is a constant. Thus, the second term in Eq. (2) simply upshifts the thermopower relative to the degassed data $S_0(T)$. At low T, on the other hand, we assume that ρ_0 has a typical metallic behavior, and approaches a small constant value at the lowest temperature. Then the second term in Eq. (2) is linear in T, and S can vanish as observed in the data of Fig. 4.

In conclusion, we have used *in situ* measurements of the SWNT film four-probe resistance and thermoelectric power to investigate the coupling of six-membered ring hydrocarbons to the free carriers in metallic nanotubes. We observe strong, systematic effects on the resistance and thermopower. The effect is maximum for benzene (C_6H_6; 6 π electrons) and decreases to zero for cyclohexane (C_6H_{12}; no π electrons). A universal behavior is observed for S vs $\Delta R/R_0$. The results can be explained by the creation of a new scattering channel for electrons in the metallic tube walls associated with the molecular adsorption. The strength of the coupling increases with increasing π electron count in the adsorbed molecule.

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[15] This association assumes that the C_6H_{2n} adsorption does not change the contact resistance between bundles in the SWNT film.
[16] These data were collected on a second film successively exposed to C_6H_{2n} in the same way.