CARBON NANOTUBES: A THERMOELECTRIC NANO-NOSE

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Single-wall carbon nanotubes are now under active investigation for a variety of fundamental reasons, as well as potential new technologies [1,2]. Both the electric arc and the laser produce well-ordered, tightly packed bundles of tubes containing tens to hundreds of SWNTs. Within a bundle, the tubes are bound together by a weak van der Waals force.

The samples studied in this work were made on lightly compacted mats of tangled SWNT bundles (~ 1mm x 2mm x 0.1 mm). The material was obtained from Carbolex, Inc., and consists of ~ 50-70 vol.% carbon as SWNTs. Gas adsorption effects on thermoelectric power and resistivity were studied using high purity (99.999%) gases (He, N_2, H_2, NH_3, O_2).

After *in situ* vacuum degassing at T = 500 K for ~ 10 hr in a vacuum of 10^{-8} Torr to remove O_2, the initial thermoelectric power S_0 of the mat is large and negative at room temperature ($-45\ \mu V/K < S_0 < -40\ \mu V/K$) [3,4]. The thermoelectric response (S, ρ) of a bundle of SWNTs to a variety of gases (He, N_2, H_2, O_2 and NH_3) can be understood in terms of the change in the thermoelectric power of the metallic tubes due to either a charge-transfer-induced change of Fermi energy (i.e., molecule donates an electron to the conduction band)[5] or to the creation of an additional scattering channel for conduction electrons in the tube wall. The thermoelectric power associated with the diffusion of free carriers in a metal can be written compactly as a logarithmic energy derivative of the electrical resistivity (ρ) [6]

$$S_d = C\,T\,d/dE\,\{\ln \rho(E)\}_{E_F} \qquad (1)$$

where $C = (\pi^2 k_B^{\,2}/ 3|e|)$, ρ(E) is the energy-dependent resistivity. Since the total bundle resistivity is due to (1) the scattering mechanisms pre-existing in the bundle before gas adsorption (ρ_0), e.g., from phonons and wall defects, and (2) the extra impurity scattering due to the adsorbed gas (ρ_a):

$$\rho = \rho_0 + \rho_a \qquad (2)$$

It is usually understood that $\rho_0 >> \rho_a$, i.e., the intrinsic resistivity is much greater than the additional resistivity due to impurities. Substituting (2) into (1), and approximating $1/\rho \sim \rho_0^{-1}(1 - \rho_a/\rho_0)$, we find

$$S_d = S_0 + (\rho_a / \rho_o)\,(S_o - S_a)\ , \qquad (3)$$

Where $S_j = CTd/dE(\ln \rho_j)_{E_F}$ for j=(0,a), S_0 and S_a are, respectively, the contributions to the thermopower from the host resistivity $\rho_0(E)$ and the additional impurity resistivity $\rho_a(E)$ associated in the adsorbed gas. If the particular molecules under study are physisorbed, i.e., van der Waals bonded to the tube walls, they will induce only a small perturbation on the SWNT band structure, and an almost linear N-G plot (S vs ρ_a) should be obtained. If, on the other hand, the N-G plot for a particular adsorbed gas on SWNTs is strongly curved, this non-linearity would indicate that the molecules are chemisorbed onto the tube walls. Chemisorption, of course, has a much more profound effect on the host band structure and/or the value of E_F, and thus $(S_j - S_0)$ must then depend on gas coverage or storage. N-G plots, therefore, should be very valuable in identifying the nature of the gas adsorption process in SWNTs.

In Fig. 1, we display the N-G plots for isothermal adsorption of He, N_2, and H_2 in SWNTs at 500 K. As can be seen in the figure, the data are linear for these three gases, indicating that these molecules physisorb on the SWNT surface. In the inset to Fig. 1, we display N-G plots for NH_3 and O_2; these are strongly curved, indicating, as discussed above, that these molecules must chemisorb on the tube walls. From past experience in carbons and polymers, NH_3 and O_2 act, respectively, like an electron donor and acceptor. Large changes in S and ρ and FET channel conductance have recently been reported for SWNTs exposed to O_2, and this has been identified with chemisorption. Our N-G plot in Fig. 1 (inset) certainly confirms this point of view. Furthermore, recent theoretical calculations by Louie and co-workers for O_2 on semiconducting SWNTs finds significant electron transfer from the tube wall to the O_2 molecule (0.1 e per O_2), depressing E_F and rendering the material p-type [7].

Indeed, it is the sensitivity of the N-G plots at fixed temperature to different molecules that can be the basis for the utility of a SWNT thermoelectric "nanonose". The sensitivity of S and r to coverage must be related to the quasi one-dimensional nature of the transport in SWNTs, and the fact that almost all carbon atoms are associated with one adsorption site or another.

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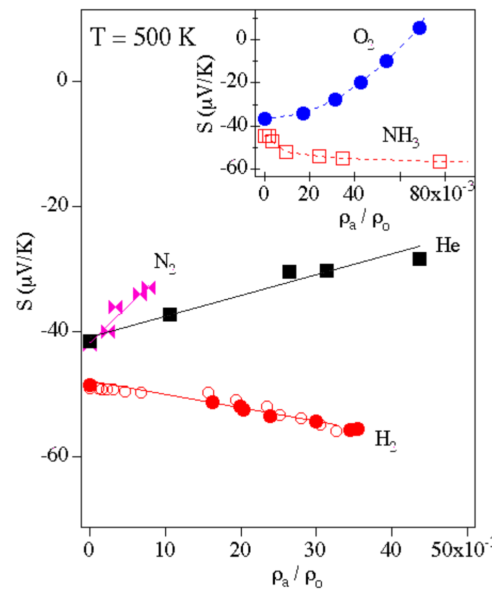

Figure 1. Nordheim-Gorter (N-G) plots (S vs ρ) showing the effect of gas adsorption on the electrical properties of the mat. A linear N-G plot indicates that physisorption (For N_2, He, and H_2). The inset shows the N-G plots for O_2 (electron acceptor) and NH_3 (electron donor). The data in the inset are strongly curved indicating chemisorption is taking place.