

Hydrogen adsorption and cohesive energy of single-walled carbon nanotubes

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Hydrogen adsorption on crystalline ropes of carbon single-walled nanotubes (SWNT) was found to exceed 8 wt. %, which is the highest capacity of any carbon material. Hydrogen is first adsorbed on the outer surfaces of the crystalline ropes. At pressures higher than about 40 bar at 80 K, however, a phase transition occurs where there is a separation of the individual SWNTs, and hydrogen is physisorbed on their exposed surfaces. The pressure of this phase transition provides a tube-tube cohesive energy for much of the material of 5 meV/C atom. This small cohesive energy is affected strongly by the quality of crystalline order in the ropes. © 1999 American Institute of Physics. [S0003-6951(99)04816-0]

A few years after the report of the C₆₀ molecule by Kroto *et al.*,¹ Iijima discovered the tubular form of carbon.² Single-walled nanotubes (SWNTs) are the simplest of these structures, being but a single graphite plane rolled into a thin tube.^{3,4} Methods for the synthesis of SWNTs do not produce a monodisperse product, and the large scale purification of SWNTs has been achieved only recently.⁵ The cohesion of these molecular crystals occurs through van der Waals interactions and perhaps other effects of electron correlation,⁶⁻⁹ and it is widely observed that the individual SWNTs coalesce into rope-like strands.¹⁰ Many properties of condensed SWNTs are now topics of intensive study. The strength of the cohesive energy of crystalline SWNTs remains poorly understood, however.

There is a recent report that crystalline SWNTs have a capacity for hydrogen sorption of 5–10 wt. % at pressures less than 1 bar near room temperature.¹¹ Such a hydrogen storage capacity would be a significant advance for the use of hydrogen as a fuel when a high gravimetric density of hydrogen is a figure of merit. Until recently, the best value of hydrogen adsorption in carbon materials has been 5.3 wt. %, or 0.64 H/C, at a temperature of 77 K.^{12,13} (A recent claim that graphite nanofibers have a capacity of 24 H/C at 300 K,¹⁴ has not been corroborated.¹⁵) We were motivated to perform measurements SWNT material of high purity because the previous measurements were made on dilute SWNTs, so the analysis required a large correction for more than 99% of material that was assumed inert.¹¹

Three batches of nanotube material were prepared¹⁶ and purified.^{5,10} To cut the SWNTs and disrupt the rope structure, about 0.2 g of material was sonicated for 10 h in dimethyl formamide at a concentration of 0.1 mg/ml until the sample was completely suspended in the solvent.¹⁷ The modified SWNT material was then extracted by vacuum filtration using a ceramic filter.

Desorption and some adsorption isotherms were mea-

sured on samples of approximately 200 mg with a computer-controlled Sieverts' apparatus. After vacuum degassing at 220 °C for 10 h, the measurement temperature was attained and hydrogen gas of 99.9999% purity was admitted into the reactor to a desired maximum pressure (160 bar at 300 K, and 130, 70, 4.5 or 0.5 bar at 80 K). This pressure was maintained for 15 h to allow the adsorption to equilibrate and to check for leaks in the system. To correct for instrumental effects, we performed identical volumetric measurements on an empty reactor after each sample measurement. Surface area was measured with a Micromeritics ASAP 2000 Brunauer–Emmett–Teller (BET) surface analysis instrument using nitrogen gas. The surface areas of the as-prepared SWNT material, the material after isotherm measurement, and the material after sonication, were found to be 285 ± 5 m²/g. Phase contrast transmission electron microscopy was performed with a Philips EM430 transmission electron microscope operated at 200 kV. X-ray powder diffractometry was performed using Co K α radiation with an Inel CPS-120 position sensitive detector.

Transmission electron microscopy of the as-prepared material showed dense bundles, or "ropes" of crystallized SWNTs. Rope diameters varied from 6 to 12 nm. The high resolution image in Fig. 1 shows circular rings of approximately 1.3 nm in diameter where the tubes are parallel to the electron beam, and we interpret this as a mean diameter of the tube walls. With the hexagonal coordination seen in Fig. 1, a rope of 10 nm diameter would contain about 50 tubes, and would be 8 times the diameter of a single tube. The specific surface area of a rope would be about 6 times less than the outer surface area of a single tube (1300 m²/g). The surface area measured by BET (285 m²/g) is evidently a measure of the outer surface area of the ropes, not the total surface area of the individual tubes. The ropes perpendicular to the electron beam showed a number of sets of internal fringe spacings of 0.34 nm. Many fringe terminations were observed within the ropes, indicative of misalignments or terminations of individual tubes. The rope diameters of the sonicated material were comparable, but with a broader size distribution. The sonicated material showed a more irregular

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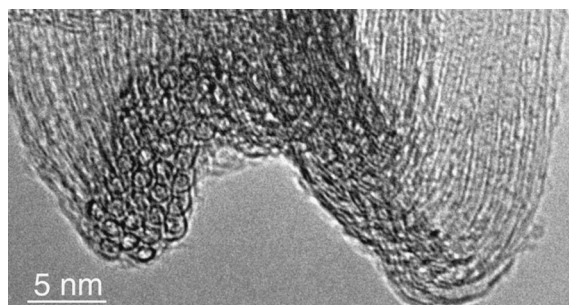


FIG. 1. High resolution transmission electron micrographs of the SWNT material as-prepared, showing cross-sections of tubes towards lower left center.

patchwork of fringes caused by more terminations of individual SWNTs within the ropes. On the other hand, x-ray diffractometry showed no differences after sonication.

For SWNTs ($285 \text{ m}^2/\text{g}$), and high surface area saran carbon ($1600 \text{ m}^2/\text{g}$),¹⁸ the hydrogen adsorptions (ratio of H atoms/C atoms) obtained at 3.2 bar at 80 K were 0.040 and 0.28, respectively. These results show a proportionality between surface area measured by BET and the hydrogen adsorption, as did the hydrogen adsorptions at 160 bar at 300 K. The low pressure composition-pressure isotherms at 80 K and the high pressure isotherms at 300 K had similar shapes for all types of carbons. They were described adequately with the Langmuir adsorption isotherm, for which the fractional coverage, f , is $f = (\exp[(\epsilon - \mu)/kT] + 1)^{-1}$. The chemical potential of a hydrogen molecule in the gas is μ , and its energy of adsorption is ϵ ($\epsilon < 0$). Using a tabulated function for chemical potential versus pressure,¹⁹ we fit the saran carbon isotherm with f . At low coverage we found $\epsilon = 38 \text{ meV}$, in excellent agreement with the results of Pace and Siebert.²⁰ The isotherm of the saran carbon material in Fig. 2 is similar in shape to isotherms from other carbons of high surface area at 80 K.^{12,13,21} Also shown in Fig. 2 is an adsorption curve calculated from the saran carbon data by reducing it in proportion to the lower surface area of the SWNT material as measured by BET. This curve, scaled by the factor $285/1600$, accounts approximately for the adsorption of the SWNT material (labeled "SWNT" in Fig. 2) at low pressures, but fails at pressures greater than about 20 bar.

At high hydrogen pressures at 80 K, the curves labeled SWNT in Fig. 2 show a ratio of hydrogen to carbon atoms of about 1.0 (8.25 wt. %), and suggest that higher concentrations may occur at pressures beyond our experimental capabilities. To our knowledge, this is the highest hydrogen storage capacity yet measured on an activated carbon material. (A coke material processed with KOH, denoted "AX-21," reaches a peak 0.64 H/C at 77 K at an optimal pressure of 30 bar.^{12,13}) Our results are inconsistent with the report of Dillon *et al.*, that such capacities are attained at 300 K and pressures well below 1 bar.¹¹ The kink at 40 bar and the steep slope of the hydrogen adsorption isotherm of the SWNT material at pressures from 40 to 100 bar is unique for hydrogen adsorption on a carbon material. This shape cannot be obtained from a sum of concave-downwards isotherms such as f even with a distribution of adsorption energies, ϵ . The shape of the SWNT isotherm is similar to isotherms of metal-hydrogen systems which form a hydride phase by a

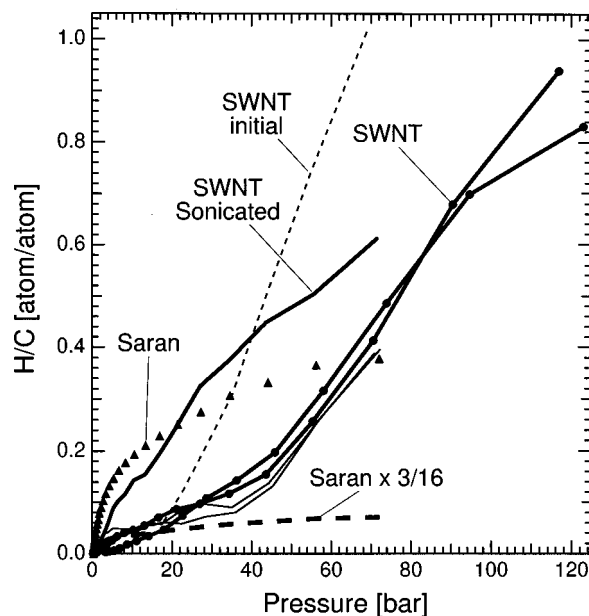


FIG. 2. Isotherms of composition vs pressure at 80 K for samples of as-prepared SWNT material, the SWNT material after sonication in dimethyl formamide, and a high surface area saran carbon. Adjacent pairs of curves (labeled SWNT) were sequential runs on the same sample. Also shown is the curve of the saran carbon scaled to lower H/C ratio by the surface area ratio of $285/1600$.

first-order phase transition,²² although the mechanism of hydrogen absorption is certainly different.

The low pressure adsorption of hydrogen on SWNT material saturates like that of the saran carbon, scaled by the surface area of the ropes. At pressures above 40 bar, however, the isotherms indicate that the SWNT material undergoes a transition to a new state of hydrogen coverage. From the large H/C ratio at high pressures, we deduce that the surface area would have to increase by about an order of magnitude. This is consistent with the hydrogen permeating into the ropes, separating them into individual SWNTs with full exposure of their outer and perhaps inner surfaces, and physisorbing onto the carbon surfaces. This high density phase must involve tube decohesion, since the hydrogen coverage is high and the attractive van der Waals and exchange forces are attenuated when the tubes are separated by short distances. The thermodynamic driving force for this tube decohesion is the high chemical potential of the hydrogen gas at high pressure. The hydrogen molecules that adsorb on the surface of the SWNTs undergo a decrease in chemical potential. The equality of chemical potential in two-phase equilibrium requires the reduction of chemical potential of hydrogen gas in the high capacity phase to be equal to the loss of van der Waals cohesive energy.²³

The data of Fig. 2 indicate an average pressure of 70 bar for the phase transition, which corresponds to a chemical potential of -11 meV per hydrogen molecule.¹⁹ This should be compared to the characteristic chemical potential for hydrogen physisorption of -38 meV , corresponding to a decrease in chemical potential upon adsorption, $\Delta\mu$, of 27 meV per hydrogen molecule. This $\Delta\mu$ can be used to determine the cohesive energy of the SWNTs in a rope. When the adsorbed hydrogen molecules are commensurate with the

carbon atoms on a graphene plane, the composition would be C_3H on one surface of the plane.^{24,25} For the measured surface area of the saran carbon of $1600 \text{ m}^2/\text{g}$, this structure would provide $H/C=0.40$, in good agreement with the saran carbon isotherm at about 70 bar. Using this same hydrogen coverage for the SWNT material at 70 bar, the $\Delta\mu$ of 27 meV/ H_2 or (13.5 meV/H) provides a cohesive energy for the SWNTs in a rope of 4.5 meV/C atom. An alternative estimate can be made by noting that the characteristic midpoint of the phase transition corresponds to a composition of $H/C=0.43$ at 70 bar, which provides a cohesive energy of 6 meV/C atom.

The slope of the SWNT isotherm in Fig. 2 is not infinite, probably because there is a distribution of cohesive energies in the material. To obtain an upper limit on cohesive energy, we note that some of the tubes separate at pressures of 100 bar at a macroscopic $H/C=0.8$. This corresponds to a cohesive energy of 14 meV/C atom for a minority of the material. Some of the change in H/C at higher pressures could be caused by additional coverage on tubes that had separated at lower pressures, however. Allowing for such a change in coverage in the majority of the material will reduce this upper limit, perhaps considerably.

Our experimental value for the cohesive energy, 5 meV for much of the material, is smaller than the 17 meV/C atom calculated by Tersoff,⁷ the 35 meV/C atom calculated by Benedict *et al.*, for large tubes with flat area of contact,⁹ or the 22 meV/C atom calculated by Cagin and Goddard.²⁶ We can account for small reductions in cohesive energy with features of the rope morphology observed by TEM. Surface energy is one contribution, but the reduced coordination at the rope surfaces will reduce the cohesive energy by only about 15%. The elastic energy of the observed tube curvature will also suppress the cohesive energy. Using an elastic modulus typical of graphite,²⁷ we obtain a typical maximum elastic energy of less than 0.5 meV per atom in the tubes.

Since there is a rapid reduction with distance of the van der Waals interaction and other electron-electron correlation effects responsible for SWNT cohesion, defects in the close-packed triangular lattice of SWNTs should cause a large reduction in the cohesive energy. The cohesive energy of SWNT crystals is expected to be reduced when the inter-tube distances are disrupted by tube terminations, misalignments, and dislocations within the crystalline rope. The following experimental evidence indicates that these defects cause a large change in cohesive energy. The curve labeled "SWNT initial" in Fig. 2 was a first run on a fresh sample, and first runs on two other samples exhibited such high reversible adsorption at lower pressures. All second and subsequent desorptions occurred at higher pressures, as shown in Fig. 2 for the group of four curves labeled SWNT. We believe that the first adsorption/desorption cycle caused the SWNTs to reorganize in structure, perhaps into a more perfect triangular lattice, causing subsequent desorptions at higher pressures. More convincing are the data on the sonicated material. The pressures of desorption for this material show a considerable breadth, indicating a distribution of cohesive energies of the tubes. Furthermore, for all hydrogen concentrations, the pressures for the sonicated material are suppressed with re-

spect to the as-prepared samples. A reduction in pressure is consistent with additional defects in the crystalline ropes of sonicated material causing a reduction in the cohesive energy of the rope structure.

Finally, we note that the first order phase transition to the SWNT high capacity phase overcomes an engineering challenge in using conventional carbons for hydrogen storage.²³ With SWNT materials, hydrogen will adsorb and desorb over a narrower range of pressure, so storage systems can be designed to operate without wide pressure excursions.

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