

Reversible Intercalation of Charged Iodine Chains into Carbon Nanotube Ropes

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We report intercalation of charged polyiodide chains into the interstitial channels in a single-wall carbon nanotube (SWNT) rope lattice, suggesting a new carbon chemistry for nanotubes, distinctly different from that of graphite and C₆₀. This structural model is supported by results from Raman spectroscopy, x-ray diffraction, Z-contrast electron microscopy, and electrical transport data. Iodine-doped SWNTs are found to be air stable, permitting the use of a variety of techniques to explore the effect of charge transfer on the physical properties of these novel quantum wires. [S0031-9007(98)06385-6]

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The laser-assisted [1] or arc-assisted [2] growth of single-wall carbon nanotubes (SWNTs) has been reported to produce very long crystalline ropes of tens to hundreds of single-wall tubules with a mean tube diameter ~ 1.3 nm, close to that of a (10, 10) nanotube (for a detailed explanation of SWNT chiral indices, see Ref. [3]). More recently, it has been shown that the mean tube diameter increases with the increasing temperature in the growth zone [3]. On the basis of coherent x-ray scattering, tubules within individual ropes are thought to be nearly monodisperse, and their axes are arranged in a triangular crystal lattice [1–3] stabilized by van der Waals forces. This “rope lattice” contains interstitial channels that can accommodate foreign (dopant) atoms [4,5]. The attendant charge transfer between the nanotube and the dopant can be used as a design parameter to optimize and study quantum transport phenomena [6,7] in carbon nanotubes.

It has been previously demonstrated by Raman spectroscopy [4] and resistivity measurements [5] that SWNT bundles exhibit amphoteric behavior similar to that of graphite; that is, they can be doped with either acceptors (K, Rb) or donors (Br₂). In contrast, C₆₀ readily forms charge-transfer solids with donors (K, Rb, Cs), but not acceptors [8,9]. None of these carbon polymorph solids have been observed so far to form a charge-transfer compound with iodine, which is a weak acceptor [8–10]. However, low-dimensional organic polymers, e.g., polyacetylene, have been intercalated with charged linear-chain polyiodides (I₃)[−] or (I₅)[−] [10–12]. In these cases, electron transfer from the polymer host to polyiodide chains creates a large number of mobile hole carriers, resulting in a sharp increase in electrical conductivity, sometimes by more than 10 orders of magnitude [10–12].

In this Letter, we show that an air-stable, charge-transfer compound of SWNT with iodine can be obtained by doping SWNT mats with molten iodine. Upon iodine intercalation, the x-ray diffraction (XRD) peaks associ-

ated with the crystalline rope lattice first shift to lower angles and then disappear, indicating structural disorder in the saturated compound. These diffraction peaks are observed to recover partially upon removal of the intercalated iodine by heat treatment. We ascribe this phenomenon to a “zipperlike” effect, as the van der Waals force pulls the nanotubes back into a tightly bound rope.

Sample preparation.—Intercalation was carried out by immersing SWNT mats in molten iodine in evacuated quartz tubes at a temperature $T = 140$ °C for several hours. We obtained similar results in all measurements for both laser-produced (Rice University) and arc-produced (University of Kentucky) SWNT samples. In order to anneal the doped rope structure and to remove excess physisorbed iodine, the doped mats were heat treated *in situ* as follows. The end of the quartz tube containing the doped SWNTs was heated to 60–80 °C for 2–4 h, while the other end was submerged in liquid nitrogen where the excess iodine was collected. The resulting iodine-intercalated SWNT samples were found to be stable under ambient conditions, permitting measurements to be carried out in air, if necessary. Thermogravimetric analysis (TGA) experiments were carried out on this material by heating from 20 to 400 °C over 2 h in He gas while monitoring the weight loss. Notable weight loss commenced at $T \sim 100$ °C, and the intercalated iodine was essentially removed at $T \sim 250$ °C. The complete removal (below our detection limits) of intercalated iodine was subsequently confirmed by XRD, Raman, photoluminescence (PL), and energy-dispersive x-ray spectroscopy (EDXS). The weight uptake and TGA experiments on high purity (>90% by transmission electron microscopy) SWNT samples both suggest that an average composition for the saturation iodine-doped SWNT is close to IC₁₂.

XRD.—XRD data were collected using a Rigaku diffractometer (CuK_α radiation). Consistent with previous work [1], XRD patterns of both the laser- and

arc-produced pristine SWNT samples were dominated by a strong peak at $2\theta \sim 6^\circ$ identified as the (11) reflection from the triangular rope lattice corresponding to an average lattice spacing $d_{11} \sim 14.72 \text{ \AA}$ and a lattice constant $a \sim 16.8 \text{ \AA}$ (Fig. 1). In addition to the (11) and other higher-order features, peaks due to graphite and the metal catalyst impurities were observed at $2\theta \sim 26.8^\circ$ and $\sim 44.5^\circ$, respectively. Upon further iodine intercalation, intensities of the diffraction peaks due to the rope lattice fell below the detection limit (Fig. 1). However, in the de-intercalated samples, the (11) peak was observed to reappear near its original position at $2\theta \sim 6^\circ$. A similar result was recently reported in the case of K- and Cs-doped SWNTs [13]. The overall intensity distribution in the XRD patterns of the de-intercalated samples was different from that of the pristine samples, suggesting that although the intercalated iodine had been removed (as verified by other probes), the initial stacking of the tubes in the rope lattice did not recover entirely.

In the case of *incomplete* de-intercalation, i.e., when residual iodine was left in the sample, a broadened and weakened (11) peak was observed at $2\theta < 6^\circ$, indicating that the rope lattice was expanded and disordered. Using XRD data obtained from one of these partially de-intercalated samples, we estimate a lattice constant $a \sim 18.5 \text{ \AA}$, that is, $\sim 11\%$ larger as compared to pristine SWNTs. Work is currently underway to prepare better quality samples to assess fully the structure of the intercalated SWNT ropes from XRD data [14]. It should be noted that the (002) peak of nanoscale graphite particles coexisting with the SWNT in the sample was unshifted with doping, indicating that iodine does not intercalate into nanoscale graphite, in agreement with earlier results [10].

The x-ray data indicate that iodine acts as a “chemical wedge,” entering the interstitial channels between nanotubes, overcoming the van der Waals attraction between

the tubes to force them farther apart. At high iodine uptake levels, the rope lattice expands, and coherent placement of the tubes within the ropes is lost. However, since the tubes are very long, it is likely that the intercalated iodine chains in the interstitial channels will have voids at various points along their length, so that tubes would maintain their van der Waals contact within these voids. When iodine is removed, these voids then nucleate the restoration of coherent bundles, much like the action of a zipper. Once the tubes have zipped back into ropes, the lattice energy of the ropes will again be minimized, and the coherent x-ray scattering from the ropes is partially restored, though with some residual disorder.

Z-contrast STEM.—Z-contrast scanning transmission electron microscopy (STEM) was used to obtain information regarding the spatial distribution of the intercalated iodine within the SWNT lattice. In this technique, a focused electron beam is rastered across the sample while a large-angle annular detector collects the transmitted electrons scattered to high angles. Since the high-angle scattering is dominated by thermal diffuse scattering, the Z-contrast image intensity scales with the atomic number squared (Z^2) [15]. Large intensity differences between carbon ($Z = 6$) and iodine ($Z = 53$) are therefore observed in Z-contrast images. Z-contrast images of pristine SWNTs show almost no contrast within a rope. To our knowledge, the first direct image of an intercalated SWNT rope is shown in Fig. 2. The image exhibits stripes which we attribute to continuous, linear iodine chains located in the interstitial channels of the rope. The average spacing between the stripes was measured to be $\sim 21 \text{ \AA}$. In this moderately intercalated sample, the iodine fills only a part of all the interstitial channels in the SWNT bundle, and therefore the

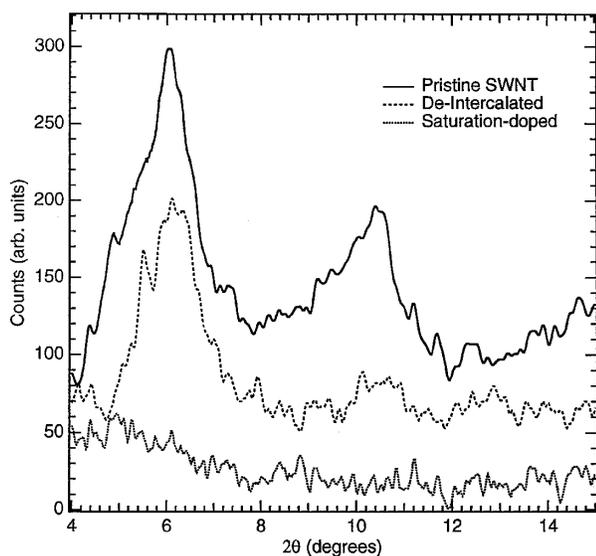


FIG. 1. Low-angle XRD data for pristine, saturation iodine-doped, and de-intercalated SWNT samples.

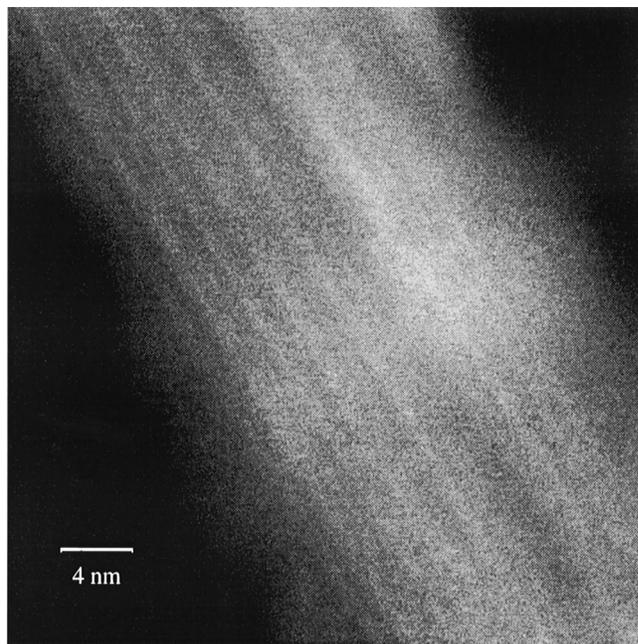


FIG. 2. Z-contrast STEM image of an iodine-doped SWNT rope.

average spacing of the iodine strips appears larger than the diameter of the tubes. Upon de-intercalation, almost all of the linear contrast disappears except for that associated with a few remnant iodine chains.

Raman scattering.—Analysis of the Raman scattering data obtained with Ar laser excitation (514.5 nm) in the backscattering geometry can be used to investigate charge transfer between the dopant and SWNTs [4] and to identify the dopant species [8,10–12,16]. We first address the Raman modes associated with intercalated iodine. In a moderately doped sample, new peaks (not associated with SWNTs) are observed at 175, 138, and 109 cm^{-1} , and a harmonic series ($2\omega_0, 3\omega_0, \dots$) of the $\omega_0 = 175$ and 109 cm^{-1} peaks also appear in the low-frequency region (Fig. 3). We attribute the strong 175 and weaker 109 cm^{-1} peaks and their overtone progressions, respectively, to resonant Raman scattering from charged $(\text{I}_5)^-$ and $(\text{I}_3)^-$ linear chain complexes. This assignment is based on comparison of our results with previous work in which resonant Raman scattering, Mossbauer spectroscopy, and x-ray diffraction were used to identify the iodine species [16]. In the saturation-doped SWNT sample, all iodine appears converted to $(\text{I}_5)^-$ (Fig. 3). This observation agrees with our preliminary x-ray photoemission spectroscopy data, which show a resolved doublet $\text{I}(3d_{5/2})$ at ~ 618 and ~ 620 eV in the moderately doped sample, while the saturation-doped sample exhibits only the ~ 620 eV peak. These peaks are assigned, respectively, to charged $(\text{I}_3)^-$ and $(\text{I}_5)^-$ polyiodide chains, according to similar studies carried out on iodine-doped polyaniline [12]. Moreover, our observation that $(\text{I}_3)^-$

forms at low iodine doping levels, and converts to $(\text{I}_5)^-$ at higher doping levels, has also been reported for several organic polymers [10–12]. It should be noted that we did not observe any Raman peaks around 215 cm^{-1} which would be expected if neutral molecular iodine $(\text{I}_2)^0$ were present in our samples [16]. The iodine-doped SWNTs also exhibited a broad PL band (cf. inset of Fig. 3) which disappeared in the de-intercalated samples, and is therefore attributable to polyiodide chains in the rope lattice.

Next we discuss doping-induced changes in the SWNT-related Raman modes. The distinctive features of the Raman spectra for pristine SWNTs (Fig. 3) include two strong, first-order bands at 186 and 1593 cm^{-1} [17]. The band at 186 cm^{-1} has been identified with the A_{1g} -type, radial “breathing” modes. The band at 1593 cm^{-1} has been assigned to an unresolved Raman triplet identified with tangential carbon atom displacement modes. These three, nearly degenerate, high-frequency tubule phonons are related to the E_{2g} ($q = 0$) symmetry intralayer mode in graphite at 1582 cm^{-1} [18]. As discussed previously, the Raman bands of SWNTs are inhomogeneously broadened due to the tube diameter distribution; the effect is most important for $\omega \leq 500$ cm^{-1} [17].

The main effect of polyiodide chain intercalation on the high-frequency Raman triplet is an up-shift of these modes by 8 cm^{-1} (Fig. 3). This sizable up-shift was observed to correlate with the doping level, and the original frequencies of these tangential modes were fully recovered after de-intercalation—clear evidence that the intercalation is reversible and that the tube walls remain intact in the process. We attribute the iodine-induced up-shift to electron transfer from the SWNTs to the iodine chains. By analogy to acceptor-intercalated graphite compounds [19], a transfer of carbon π -electrons to the intercalant is expected to induce a contraction of the hexagonal rings along the cylindrical wall of the SWNTs, up-shifting the tangential mode frequencies, as observed.

In the I-doped samples, the position of the radial SWNT mode band cannot be easily detected, perhaps because it lies very close in frequency to the strong resonantly enhanced $(\text{I}_5)^-$ mode at 175 cm^{-1} . Interestingly, in the fully de-intercalated samples, the radial mode band reappears down-shifted by ~ 2 cm^{-1} from its original position in the pristine material. We interpret this lowered frequency as an indication of a decreased van der Waals interaction between the tubes in the de-intercalated rope [20]. This result is consistent with the XRD data obtained for fully de-intercalated samples, which reveal that the original packing of the tubes in a rope is not completely restored.

Transport properties.—In Figs. 4(a) and 4(b), respectively, we display the temperature dependence of the four-probe resistance $R(T)$ and thermoelectric power $S(T)$ of pristine and I-doped SWNT mats. The arc-derived material did not exhibit a shallow resistance minimum in the range 100–250 K, as usually seen in laser-derived material [5]. The thermoelectric power data $S(T)$ for arc- and laser-derived material were in reasonably good agreement

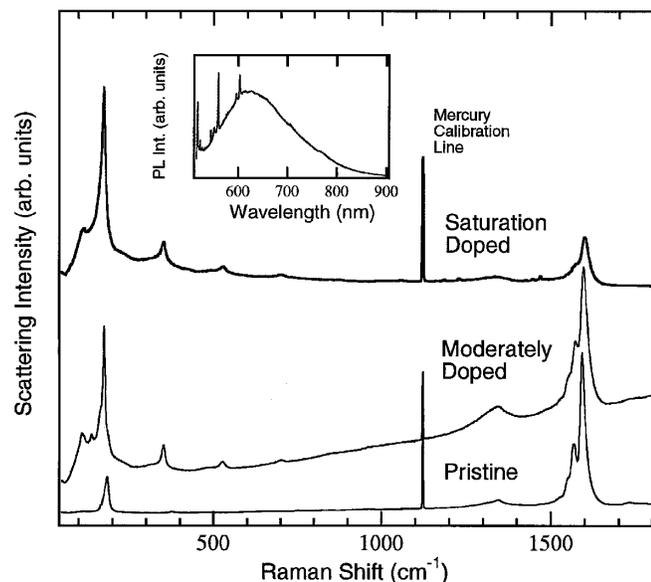


FIG. 3. Raman scattering spectra of pristine, moderately doped, and saturation-doped SWNT samples ($T = 300$ K, 514.5 nm excitation). The inset shows the photoluminescence spectrum ($T = 300$ K, 514.5 nm excitation) due to the intercalated polyiodide chains in the moderately doped sample. Sharp Raman lines are superimposed on the broader PL spectrum.

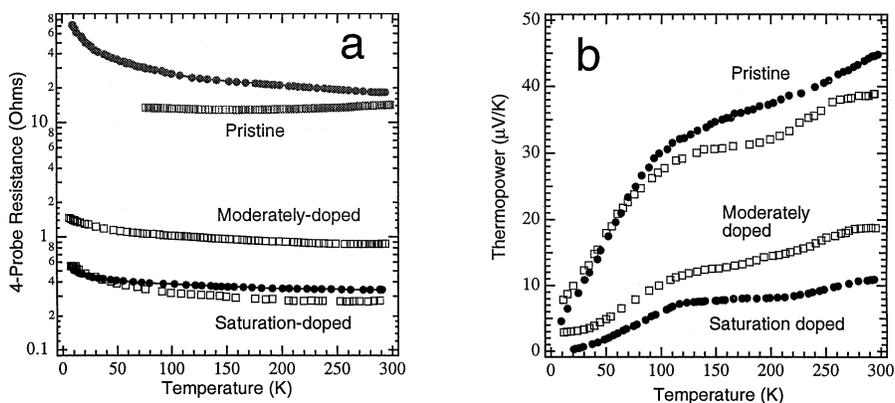


FIG. 4. Temperature dependence of four-probe electrical resistance (a) and thermopower (b) in pristine and iodine-doped SWNT samples. Data obtained on arc-derived (closed symbols) and laser-derived (open symbols) SWNTs are presented.

with recently published data [21]. The effect of iodine doping on both SWNT materials (arc and laser) was found to produce essentially identical results. As can be seen in Fig. 4(a), increasing iodine concentration in the ropes reduces the mat resistance over the entire temperature range; a factor of ~ 40 reduction was observed at $T = 300$ K upon saturation doping. For pristine SWNT mats, $S(T)$ is strongly positive and a factor of ~ 20 larger than that observed for semimetallic graphite ($\sim 2 \mu\text{V}/\text{K}$). This may be due to semiconducting tubes present in the material, as considered in a model proposed recently [21]. Upon increased iodine doping, the overall thermopower remains positive, but it is significantly reduced over the entire temperature range. The lower values are more consistent with that of a metallic system, and suggest that the semiconducting tubes have been degenerately doped in the process. Taken collectively, the $R(T)$ and $S(T)$ data indicate that the effect of iodine doping is to introduce a significant increase in the concentration of mobile holes in nanotube π -electron bands. Further details and discussion of the transport data will be published separately [22].

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