Electronic Structures of Single-Walled Carbon Nanotubes Determined by NMR

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Single-walled carbon nanotubes (SWNTs) have novel electronic properties. For instance, it was predicted theoretically (1, 2) that a SWNT can be either metallic or semiconducting depending on its diameter and chirality. Recent scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS) measurements (3, 4) on individual SWNTs support this prediction. However, the chirality distribution in a bulk sample and its dependence on synthesis conditions are not known. The density-of-states (DOS) at the Fermi level, \( g(E_F) \), and its dependence on tube diameters remain to be determined experimentally. Furthermore, the influence of ambient conditions on the properties of SWNTs needs to be investigated because of the openness of the structure. Because NMR probes the local \( g(E_p) \), \(^{13}\)C NMR could provide detailed information on \( g(E_p) \), the chirality distribution, and the influence of ambient conditions on the properties of SWNTs.

Here, we report a \(^{13}\)C NMR study of SWNTs. Two types of tubes are identified in SWNT samples. One has a relatively short \(^{13}\)C spin-lattice relaxation time \( T_1 \) that follows a temperature dependence characteristic of metals; the estimated value of \( g(E_p) \) is comparable to the theoretical value. The other type of tube has a significantly longer \( T_1 \), but the associated \( g(E_p) \) appears to be finite also. The percentage of the fast- versus slow-relaxing component depends on catalysts used in the synthesis. Exposure to oxygen has a substantial effect on relaxation rates of both components.

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Fig. 1. (Left) Experimental and simulated powder XRD patterns of the three SWNT samples. All three spectra were collected using a two-dimensional imaging plate detector under the same conditions and are presented after background subtraction (7). The spectra were simulated based on a two-dimensional triangular lattice composed of uniform diameter SWNTs (5, 8) with the diameter and the lattice constant as adjustable variables. Simulations show that the average tube diameters in samples A and B are 1.40 and 1.32 nm, respectively. (Right) The Raman spectra from the same samples collected using 514-nm laser light and a micro-Raman spectrometer with a charge-coupled device detector. The average peak positions of the SWNT breathing mode are 172, 175, and 258 cm\(^{-1}\) in samples A, B, and C, respectively. Breathing mode at 258 cm\(^{-1}\) in sample C corresponds to an average tube diameter of 0.85 nm (9).

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relaxation is attributed to couplings of $^{13}\text{C}$ with conduction electron spins through the hyperfine interaction (13).

On the basis of the theoretical understanding of SWNTs (1, 2), the fast-relaxing component is attributed to tubes with indices $(m, n)$ where $m - n = 3 \times \text{integer}$, shown theoretically to be metallic. Quantitative evaluation of $g(E_F)$ in such tubes can be obtained by comparison with the NMR result in $K_2C_{60}$ (14), where $1/T_1$ of $^{13}\text{C}$ in the normal state of $K_2C_{60}$ was dominated by the dipole-dipole interaction between the electron spins of the p-p bonding and the $^{13}\text{C}$ spins. This interaction is expected to be even more dominant over other hyperfine interactions (for example, the Fermi-contact interaction) in SWNTs because of the smaller curvature of SWNTs compared to the $C_{60}$ molecule. The relaxation rate, which depends on the orientation of the $z$-axis of the $2p_z$ orbital with respect to the external magnetic field, is given by (15–17)

$$\frac{1}{T_1} = \frac{2\pi k_B}{h} A_{\text{dip}} g^2(E_F)$$

after averaging over all orientations. Here, $A_{\text{dip}} = \frac{2}{3} \gamma_e \gamma_r A^2 \frac{1}{r^3}$ is the hyperfine coupling constant, where $<r>$ indicates the average over the p-p orbital, $r$ is the position of the electron with respect to the nucleus, and $\gamma_e$ and $\gamma_r$ are the gyromagnetic ratios of the electron spin and the observing nuclear spin, respectively. Ab initio calculation of $A_{\text{dip}}$ for $K_2C_{60}$ gives $A_{\text{dip}} = 8.2 \times 10^{-7}$ eV (15). Because the wave functions at $E_F$ in both $K_2C_{60}$ and SWNTs are predominantly p-p orbitals, the $A_{\text{dip}}$ value in $K_2C_{60}$ is adopted for SWNTs. The value of $g(E_F)$ in a metallic SWNT is predicted to be inversely proportional to its diameter (19). The average diameter (1.4 nm) of the SWNTs in sample A is comparable to that of the (10,10) armchair SWNTs (1.38 nm). The calculated $g(E_F) = 0.015$ states/(eV-spin-atom) for (10,10) armchair SWNTs (19) is comparable to the experimental value. For zigzag and chiral metallic SWNTs, a small curvature-induced gap was predicted to open at $E_F$ (20). This gap is about 4 meV for SWNTs of 1.4 nm diameter (21). For this NMR study, conducted near and above 200 K, thermal energy smears out such a small gap. Thus, for all metallic SWNTs of similar diameter, the averaged DOS around $E_F$ should be similar to that of armchair SWNTs (21). Because of the small value of $g(E_F)$ in metallic SWNTs, the Knight shift is very small compared to the chemical shift effect. Naturally, the slow-relaxing component is attributed to tubes with $m - n \neq 3 \times \text{integer}$, shown theoretically to be semiconducting (1, 2). However, the linear temperature dependence of $1/T_{1\beta}$ seems to imply that the corresponding $g(E_F)$ is finite with $g(E_F) = 0.0077$ states/(eV-spin-atom) in sample A (using $A_{\text{dip}} = 8.2 \times 10^{-7}$ eV). Since $T_{1\beta}$ is quite long, other relaxation mechanisms might contribute to the relaxation. Further experimental clarification is needed.

Figure 3 also shows $M^*(t)$ of samples B and C at $T = 288$ K. The fast-relaxing impurity contribution in sample C with $T_{1\alpha} = 0.5$ s is subtracted from this curve. Fitting with double-exponential functions yields $\alpha = 0.36 \pm 0.08$, $T_{1\alpha} = 9 \pm 2$ s, and $T_{1\beta} = 52 \pm 6$ s in sample B, and $\alpha = 0.7 \pm 0.1$, $T_{1\alpha} = 8 \pm 1$ s, and $T_{1\beta} = 60 \pm 10$ s in sample C. The temperature dependence of $1/T_{1\alpha}$ and $1/T_{1\beta}$ of sample C was also measured and was found to be proportional to the temperature as well (Fig. 4). Here, $1/T_{1\alpha} = 0.00040$ K$^{-1}$ s$^{-1}$, and the corresponding $g(E_F)$ is 0.026 states/(eV-spin-atom). For the slow-relaxing component, $g(E_F) = 0.010$ states/(eV-spin-atom) in sample C. The general trend is that $T_{1\alpha}$ decreases with decreasing tube diameter, but more data and better accuracy are needed to determine the precise diameter dependence of $g(E_F)$. The values of $\alpha = 1/3$ in samples A and B are consistent with a random chirality distribution, where 1/3 of tubes are metallic with $m - n = 3 \times \text{integer}$. However, since the fast-relaxing component is more than 50% in sample C, it indicates that chirality distribution in SWNT samples is not always random and might be controllable by synthesis conditions (22).

Finally, it is worth noting that the relaxation rate changes substantially upon exposure to oxygen, as shown in the inset of Fig. 3. Relaxation rates of nearly all tubes increased dramatically. The most probable mechanism of this effect is the fluctuation of local magnetic field induced by the paramag-

Fig. 2. The static and MAS (spun at 11.7 kHz) $^{13}\text{C}$ spectra of sample C. The isotropic shift is 124 ppm based on the MAS spectrum. The fit is the powder pattern of a chemical shift tensor with $\sigma_{11} = 195$ ppm, $\sigma_{22} = 160$ ppm, and $\sigma_{33} = 17$ ppm.

Fig. 3. The $M^*(t)$ is plotted as a function of $t$ at 288 K for samples A (●), B (■), and C (▲). The fits (solid lines) were obtained using Eq. 1. For sample A, error bars larger than the size of the symbols are also shown. The inset shows room-temperature $M^*(t)$ of sample C before (+) and after (●) exposure to oxygen at 159 kPa. Similar effect was observed in samples A and B.

Fig. 4. The temperature dependence of $1/T_{1\alpha}$ for sample A (+) and C (●), and $1/T_{1\beta}$ for sample A (×) and C (▲).
netic oxygen molecules that were strongly attracted to the surfaces of SWNT bundles. However, partial contribution due to possible changes of electronic properties (i.e., they became more metallic) cannot be excluded. This issue is currently under systematic investigation. Nevertheless, interactions between SWNTs and oxygen molecules at room temperature cannot be ignored.

References and Notes

9. NMR measurements were done in a field of 9.4 T. The 

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Crossed Nanotube Junctions

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Junctions consisting of two crossed single-walled carbon nanotubes were fabricated with electrical contacts at each end of each nanotube. The individual nanotubes were identified as metallic (M) or semiconducting (S), based on their two-terminal conductances; MM, MS, and SS four-terminal devices were studied. The MM and SS junctions had high conductances, on the order of 0.1 $e^2/h$ (where $e$ is the electron charge and $h$ is Planck's constant). For an MS junction, the semiconducting nanotube was depleted at the junction by the metallic nanotube, forming a rectifying Schottky barrier. We used two- and three-terminal experiments to fully characterize this junction.

Single-walled carbon nanotubes (SWNTs) have been proposed as an ideal system for the realization of molecular electronics (1). Individual SWNTs may act as devices such as field-effect transistors (2, 3), single-electron-tunneling transistors (4, 5), or rectifiers (6–10). However, a question remains: How can individual SWNTs be joined together to form multiterminal devices and, ultimately, complex circuits? We have begun to address this question by characterizing SWNT-SWNT junctions formed by nanotubes that lie across one another on a substrate. This type of junction is easily constructed and, with the development of techniques to place nanotubes with precision on substrates (11), could conceivably be mass-produced.

Our SWNT-SWNT junctions consist of two crossed individual SWNTs or small bundles (diameter <3 nm) of SWNTs with four electrical contacts, one on each end of each SWNT or bundle (12). In addition, a gate voltage $V_g$ can be applied to the substrate to change the charge density per unit length of the SWNTs. In an atomic force microscope (AFM) image of a completed crossed nanotube device (Fig. 1), two crossed SWNTs (green) interconnect the Cr/Au contacts (yellow).

We independently measure each SWNT and determine its properties in this configuration. SWNTs may be metallic or semiconducting, depending on their chirality (13). At room temperature, metallic SWNTs have a finite conductance that is nearly independent of $V_g$. Semiconducting SWNTs are found to be p-type, conducting at negative $V_g$ and insulating at positive $V_g$ (2). Our crossed SWNT can be composed of two metallic SWNTs (MM), one metallic and one semiconducting SWNT (MS), or two semiconducting SWNTs (SS).

The two-terminal conductances measured across MM junctions are comparable to the two-terminal conductances of the individual SWNTs; the junction resistance is of the same order of magnitude as that of the tubes and their metallic contacts. This result prompted us to measure the four-terminal conductances of the crossed SWNT devices in order to accurately determine the junction conductance. Current is passed into one arm of one tube and sunk from one arm of the second tube. The other arms act as voltage probes. Figure 2A shows the four-terminal current-voltage ($I-V$) characteristic of an MM junction at 200 K (14). The slope of $I-V$ corresponds to a resistance of 200 kilohm, or a conductance $G$ of 0.13 $e^2/h$ (where $e$ is the electron charge and $h$ is Planck's constant). Similar measurements of other three-terminal junctions gave conductances of 0.086, 0.12, and 0.26 $e^2/h$.

The measured conductances of MM junctions correspond to a transmission probability for the junction $T$ = $G/(4e^2/h)$ ~ 0.02 to 0.06. Thus, an electron arriving at the junction in one SWNT has a chance of fewer than one percent of tunneling into the other SWNT. MM junctions make surprisingly good tunnel contacts, despite the extremely small junction area (on the order of 1 nm²). We have performed first-principles density functional calculations of the conductance of MM junctions (15) (see supplementary material).