Carbon Nanowire Made of a Long Linear Carbon Chain Inserted Inside a Multiwalled Carbon Nanotube

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A new type of one-dimensional (1D) carbon structure, carbon nanowires (CNWs), was discovered in the cathode deposits prepared by hydrogen arc discharge evaporation of carbon rods. Observation of high-resolution transmission electron microscopy (HRTEM) indicates that a CNW consists of a multiwalled carbon nanotube (MWNT) with a long 1D linear carbon chain (C chain) inserted into its innermost tube of 0.7 nm in diameter. The characteristic Raman peaks of CNWs appeared at around 1850 cm\(^{-1}\). Raman scattering and HRTEM studies show the formation of a long linear C chain involving more than 100 carbon atoms inside a MWNT. This novel 1D carbon allotrope has potential applications in nanoelectronics, nanomechanics, and nanomaterials.

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A typical HRTEM micrograph displaying both H\(_2\)-arc MWNT (left-hand part) and CNW (right-hand part) is shown in Fig. 2(a). The MWNT has 26 lattice images of the graphite structure, indicating that the MWNT possesses a seamless tubular structure [4] of 13 rolled-up layers. The CNWs were grown in cathode deposits obtained by the dc arc discharge evaporation of pure carbon electrodes in hydrogen gas (8.0 \times 10\(^3\) Pa). The preparation method [13] is similar to those used by Bacon for growing graphite whiskers [14] and by Ebbesen and Ajayan for synthesizing MWNTs [15], except that hydrogen gas is used instead of inert gas. We have used hydrogen arc discharge to prepare the smallest carbon nanotubes (0.4 nm in diameter) confined inside MWNTs [16], because hydrogen arc can cause both very high temperature and reactive arc plasma.

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graphitic sheets. The MWNT has a uniform outermost diameter of 9.5 nm, but its innermost diameter (marked by double lines) decreases gradually from 1.0 nm (left-hand end of the MWNT) to 0.7 nm (right-hand end). The faint grainy image seen in its innermost tube implies the existence of some carbon species trapped inside the innermost tube. At the center of CNW [see the right-hand part of Fig. 2(a)], a new straight line with the length of 13.5 nm (marked by an arrow) appears between the two lines of the innermost tube (diameter, \(d = 0.7\) nm). As a result, the number of parallel lines increases from even (26) to odd (27). This new straight line originates from the 1D linear C chain, not isolated carbon species, and the large contrast possibly results from the high density of \(\pi\) electrons (two per carbon atom) in the C chain.

In Fig. 2(b), we show another HRTEM micrograph of two horizontally aligned CNWs. Each CNW consists of the central line of the C chain and the symmetrical five layers of MWNT, as indicated by a pair of lines marked by arrows. The inserted C chains have a length of 20 nm, which include more than 100 atoms even if the maximum C-C bond length of 0.1389 nm is assumed (see the first-principles calculations below). The left ends of each CNW are capped with hemispheres, and each innermost tube \((d = 0.7\) nm) is capped with a hemisphere of \(C_{60}\). The observation of hemispherical caps excludes the possibility that the present HRTEM images originate from spiral graphite sheets. On the basis of our x-ray diffraction measurements, the \(H_2\)-arc MWNTs with the outermost diameter less than 10 nm have a Russian doll structure [17]. Considering that the observed CNWs are all thinner than 10 nm in diameter, we can also draw the conclusion that the MWNTs including C chains inside possess a perfect tubular structure.

Owing to HRTEM observation of CNWs, the following points are revealed. Although \(H_2\)-arc MWNTs can reach the length of 10 \(\mu\)m, only some parts of the innermost tube of MWNT get inserted with C chains, whose length is usually longer than 10 nm. Moreover, once C chains are formed in the MWNTs, their innermost diameter is found to be 0.7 nm, resulting in the expected van der Waals spacing between C chains and the innermost tube, 0.34 nm, as shown in Fig. 2(a). Our calculation of cohesive energy of various carbon allotropes indicates that the CNWs are energetically more stable than the fullerene \(C_{60}\) but are less stable than carbon nanotubes. As for the nanostructure of CNW (see Fig. 1), it is very similar to that of a gold nanowire possessing helical multishells [18]. However, the linear C chains can possess either cumulenic (\(\cdots =\text{C} =\text{C} =\text{C} =\text{C}\)) or polyynic (\(\cdots =\text{C} =\text{C} =\text{C}\)) structure. Because of the ideal 1D atomic structure of a linear C chain, the 1D electronic density of states exhibits sharp singularities below and above the Fermi level, \(E_F\). Therefore, we can use Raman scattering to probe both the phonon spectrum and the electronic structure of a C chain through the resonant Raman effect and to confirm the formation of C chains inside MWNTs.

On the basis of theoretical calculations and experimental measurements of Raman spectra, there is a Raman mode at around 2000 cm\(^{-1}\), corresponding to the stretching mode of a 1D linear C chain [8,11]. We observed some peaks at lower frequency around 1850 cm\(^{-1}\) in the Raman spectra as seen in Fig. 3(a), which was taken from the cathode deposits containing both MWNTs and CNWs. Resonant Raman study, using the laser excitation energy \(E_{\text{laser}} = 1.75, 2.41, 2.54, \) and 2.71 eV, indicates that these peaks cannot be attributed to the second-order harmonics or combination modes in \(sp^2\) carbon allotropes [19]. We can assign these peaks to the 1D long linear C chains consisting of more than 40 atoms inside MWNTs observed by HRTEM because of the following reasons. First, the maximum intensities were observed at the laser excitation energy of \(~2.5\) eV. This value is in good agreement with the highest occupied molecular orbital—lowest unoccupied molecular orbital transition energy [11] for the long linear C chains including more than 40 carbon atoms. Second, since the Raman
frequency decreases with an increasing number of carbon atoms composing a C chain, the peak frequencies were found to be about 200 cm⁻¹ lower than that of carbyne possessing the average conjugation length of about 8–12 carbon atoms [11]. Finally, we have not observed the reactivity and aging effect of these C chains, showing that these long C chains were entirely protected by outside MWNTs.

In fact, Fig. 3(a) shows typical polarized Raman spectra (Ar⁺ laser: 2.41 eV) taken from a straight bundle consisting of MWNTs and CNWs. The bundle oriented along the Z direction and the light propagated along the Y direction. Because no signals were detected in (XX) and (XZ) polarization geometry, where the letters indicate the polarization directions of the (incident, scattered) light, we display only the Raman spectra of (ZZ) and (ZX) polarization geometry in Fig. 3(a). For the G-band modes of MWNTs, three peaks (1582, 1591, and 1610 cm⁻¹) can be observed in the (ZZ) geometry and only one peak (1583 cm⁻¹) in the (ZX) geometry. This indicates that the G band of MWNTs contains several modes with different symmetries. On the other hand, for C chains (marked by dotted rectangle), two peaks at 1825 and 1852 cm⁻¹ can be seen in both the (ZZ) and (ZX) geometries, although the peak intensities in the latter are much lower than that in the former. The decrease of peak intensities in the (ZX) geometry and disappearance of peaks in the (XX) and the (XZ) geometries can be explained by the depolarization effects due to 1D linear atomic structure of C chains, which have been observed for semiconducting/metallic nanowires and SWNTs.

Figure 3(b) shows the Lorentz fit to the C chain peaks in the (ZZ) geometry in Fig. 3(a) using three Lorentzians with frequencies of 1823(11), 1850(10), and 1860(11) cm⁻¹, where the full width at half maximum (FWHM) is given in parentheses. The fit to the C chain peaks in the (ZX) geometry using three Lorentzians with frequencies (FWHMs) of 1823(12), 1851(9), and 1859(10) cm⁻¹ is shown in Fig. 3(c). The value of the FWHMs (∼10 cm⁻¹) is much smaller than that of carbyne [11] and is in good agreement with the typical value for the width of phonons in crystals. This shows that the C chains inside MWNTs have perfect linear chain structure. It is difficult to distinguish between cumulenic and polyynic structures based on Raman spectra [8]. Therefore, these three peaks may come from the C chains with different structures (cumulenic or polyynic) or from cumulenic structure with different C-C bond lengths.

In order to study the atomic and electronic structures of CNWs, the first-principles calculations based on the density functional theory [20] have been performed using the pseudopotential plane-wave method [21]. For modeling the CNWs, we have used an armchair SWNT (5,5) (d = 0.6774 nm) or a zigzag SWNT (9,0) (d = 0.7046 nm) with a linear C chain inside its hollow core. For convenience, we refer to these two CNW models as CNW (5,5) and CNW (9,0), respectively. The optimized isolated C chain is a straight linear C chain having an identical C-C bond length, \( L = 0.1266 \text{ nm} \) (cumulenic-type bonds). Compared with the isolated C chain, the C-C bond length in the C chains confined in the SWNTs is tuned by the projected C-C distance of SWNTs on the nanotube axis. For example, in the case of CNW (5,5), the C-C bond length is shortened to \( L = 0.1229 \text{ nm} \), whereas it is stretched to \( L = 0.1389 \text{ nm} \) in the case of CNW (9,0). On the other hand, the insertion of the C chain does not lead to a significant modification of the atomic structure of SWNTs themselves. However, an inspection of the electronic structure shows that the inserted C chain obviously increases the 1D densities of states at Fermi level, \( E_F \). This infers that the insertion of C chains may improve the conductivity of metallic SWNTs and even
transit a semiconducting SWNT to a metallic SWNT. The details will be published elsewhere.

It has been reported that long C chains including more than 20 atoms become energetically unstable [9,22,23]. In the present study, however, the nanoscale confinement due to the carbon nanotubes may stabilize the extraordinarily long linear C chain structure. The growth mechanism for CNWs should be similar to that for the smallest carbon nanotubes [16] inside MWNTs because both of them can be observed in the same HRTEM samples. Both hydrogen atoms and very high temperature produced by arc plasma play an important role in their formation. Considering the unique nanostructure of CNWs, it can be expected that the CNWs should have a higher Young’s modulus, strength, and toughness than commercial carbon fibers, graphite whiskers, and MWNTs. It remains a challenge to insert C chains into SWNTs to form the smallest possible CNWs, C-chain@SWNTs, which may lead to the achievement of the smallest metal-metal junction, metal-semiconducting junction, and diodes in nanoelectronics.

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