Raman Spectroscopy and TEM of Long Linear Carbon Chain Formed in CNT Field Emission Cathode

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Long linear carbon chains (LCCs) encapsulated in carbon nanotubes (CNTs) were produced on a film scale by field emission discharge of CNT films. LCCs inside CNTs were characterized by Raman spectroscopy and transmission electron microscopy. After an electric discharge of a CNT film cathode, long LCCs encapsulated in single-wall CNTs as well as double-wall and triple-wall CNTs were formed in the film. The length of LCCs is longer than 30 nm (i.e., more than 230 carbon atoms). Not only a single LCC but also two or three LCCs in parallel inside a CNT were found. Raman spectra showed prominent peaks, called “LCC bands”, in a region from 1790 to 1860 cm^{-1} originating from longitudinal optical phonons of LCCs. The observation of strong LCC bands are due to resonance Raman scattering, i.e., the excitation photon energies between 1.85–2.54 eV match with energy gaps of the long LCCs inside CNTs.

Keywords Carbyne; Carbon nanotube; Linear carbon chain; Raman scattering; Electron microscopy

I. INTRODUCTION

Carbyne, an infinite carbon chain, has attracted much interest and induced significant controversy for many decades [1–5]. Linear carbon chains (LCCs) in its own forms are unstable in an ambient environment. In solution, LCCs up to C_{12}H_2 are formed [6]. When both ends of carbon chains are anchored by bulky molecules, polyynes consisting of carbon atoms up to 44 have so far been chemically synthesized [7, 8]. Recently, long LCCs stably confined inside carbon nanotubes (CNTs) were found in multiwall CNTs (MWCNTs) produced by arc-discharge [9] and in double-wall CNTs (DWCNTs) annealed at high-temperature in vacuum [10]. Carbyne can be considered to be a long polyyne with effectively infinite length, in which the sp hybridized orbitals form alternated single and triple bonds between carbon atoms in the one-dimensional (1D) chain, and thus an electronic band gap is open at the Fermi level.

The electronic energy gap of hydrogen-capped polyynes C_{2m}H_2 is expected to be in a range from 4.1 eV for $2m = 8$ to 2.2 eV for an infinitely long polyyne [11]. Reflecting the energy gap in 1D materials, strong resonance Raman scatterings are expected. Actually, a Raman scattering characteristic to LCC (called “LCC bands”) are observed at around 1850 cm^{-1} , with enhanced intensities at certain photon energies of incident laser (ca. 1.8–2.6 eV). The LCC bands originate from one-dimensional stretching vibration of triple-bonded carbon bonds [6, 12–15]. The presence of LCC inside CNT (LCC@CNT) was substantiated by Raman spectroscopy and high resolution transmission electron microscopy (TEM).

The length of stable polyyne prepared by chemical synthesis is limited to 44 carbon atoms. Methods for preparing longer 1D carbon chains are limited so far to physical methods with high temperature annealing of DWNTs and electric arc discharge for preparing multiwall

Figure 1: SEM image of a SWCNT film after FE.

CNTs. In the latter physical method, 1D carbon chains were obtained as by-products of multiwall CNTs. We discovered a novel method to produce long LCCs encapsulated inside single-wall CNTs (SWCNTs) on a film scale after field emission (FE) experiments of the CNT film cathode, as reported in the previous ALC '17 [16].

In the present report, additional findings obtained especially by Raman spectroscopy are presented. Raman spectroscopy of CNT films containing carbyne were carried out with a range of excitation photon energies from 1.58 to 3.49 eV to show the resonance effect and a distribution of LCC bands. TEM study was also carried out to reveal the appearance and morphology of carbyne in the CNT films; the long carbon chains consisting more than 230 atoms were encapsulated in the central cavity of CNT, and occasionally, two chains in parallel with each other were encapsulated in the one CNT.

II. EXPERIMENTAL

A thick film of eDIPS SWCNT (Meijo Nano Carbon) was used as an FE cathode, and an anode made of a tungsten grid

was placed in front of the SWCNT cathode with a separation of about 1.6 mm in a high vacuum of 10^{-6} Pa. Details of the FE set-up for the production of LCC@CNT have been described in our previous reports [16, 17]. When an excessive voltage was applied between the electrodes, a spark discharge occurred. The SWCNT cathodes after the severe FE experiment were investigated by Raman scattering spectroscopy using several excitation laser wavelengths (355, 488, 532, 633, 671, and 785 nm) at room temperature. TEM at an acceleration voltage 120 keV was also carried out to see the morphology of long LCCs in the CNT film.

III. RESULTS AND DISCUSSION

Figure 1 shows a SEM image of a SWCNT film after the FE experiment. In the right hand part of the film the surface is rugged and partly ripped up, showing damage arising from the electric discharge during FE. In the other part (left hand part) the surface is uniform and intact, indicating free from any damage. Raman spectra observed from the intact region marked by A and the damaged region marked by B with 532nm incident laser are shown in Figures 2(a, b), respectively. The spectrum from the intact region [Figure 2 (a)] is a typical one for SWCNTs, showing a prominent G band accompanied by radial breathing modes (RBM), D and 2D bands. On the other hand, in the spectrum from the damaged region [Figure 2 (b)], a new band, called “LCC band”, is observed at $\sim 1850\text{ cm}^{-1}$ in addition to RBM, G, D, and 2D modes. The LCC band originates from the longitudinal optical phonons (out-of-phase CC stretching vibrations of the triple and single bonds) in long polyynes [12, 18, 19]. The intensity of the LCC band in this spectrum is very strong, stronger than the G band. Furthermore, higher order harmonics are also clearly observed. These behaviors indicate the resonance Raman scattering of the LCC bands; the

Figure 2: Raman spectra from (a) an intact region (A in Figure 1) and (b) a damaged region (B in Figure 1), measured by 532 nm laser excitation at RT. In (b), a spectrum range is extended up to 6000 cm^{-1} in order to observe higher order harmonics of LCC bands.

Figure 3: TEM images of LCCs encapsulated in CNTs: (a) a single LCC inside SWCNT and (b) two LCCs inside DWCNT.

excitation photon energy is in resonance with an electronic excitation of LCCs.

TEM revealed the presence of LCC encapsulated inside SWCNT as well as double-wall and triple-wall CNT (TWCNT) in damaged regions of the CNT film. DWCNT and TWCNT were contained as minor species in the original eDIPS-SWCNT film. Figure 3 presents two examples of TEM images: a single LCC inside SWCNT, and two LCCs in parallel inside DWCNT. When the inner diameter of CNTs was larger than 1.1 nm, two and three LCCs in parallel with each other were also found. Long LCCs inside CNTs were longer than 30 nm (i.e., more than 230 carbon atoms).

Figure 4 shows Raman scattering spectra from CNT films containing LCCs measured using a series of excitation laser wavelengths (355, 488, 532, 633, 671, and 785 nm). LCC bands were observed with excitation wavelengths of 488, 532, 633, and 671 nm, while no LCC peak was observed at 355 and 785 nm excitations. The intensity and profiles of LCC bands depend on the incident photon energies; the highest intensity is observed at 532nm excitation, and splitting of the band was clearly observed at lower energy excitation (633 and 671 nm).

A diagram showing wavenumbers and intensities of LCC bands as a function of the incident photon energy is shown in Figure 5. A tendency that the LCC wavenumber becomes higher with the increase of the excitation photon energy is found; the observed LCC wavenumbers are concentrated around 1855 cm^{-1} for 2.54 eV excitation and around 1850 cm^{-1} for 2.33 eV while at lower excitation energies (1.96 and 1.85 eV) the LCC peaks scatter toward lower wavenumbers down to around 1790 cm^{-1} . The dependence of the intensity and peak positions of LCC bands on the excitation

Figure 4: Raman spectra depending on the incident laser wavelength.

photon energy also reflects the resonance nature. The strong resonant Raman scatterings at excitation photons (1.85–2.54 eV) indicate that the energy gaps of LCCs formed inside CNTs are distributed in this energy range. The wide distribu-

Figure 5: LCC peak positions and intensity versus excitation energy. Size of circles represents roughly the intensity of LCC peaks; larger circles shows higher intensity.

Figure 6: G-band spectra from (a) a CNT sample with LCC signals, and (b) a pristine CNT film.

tion of the energy gaps is presumably caused by the different length of LCCs and the effect of circumstance surrounding LCCs, i.e., a diameter of encapsulating CNTs, presence or absence of neighboring LCCs inside a LCC, and so on.

It is theoretically predicted that the vibrational frequency as well as the energy gap of LCC depends on its length [11, 19]; the longer the length, the lower the vibrational frequency and the narrower the energy gap. The confinement of LCC inside a CNT may have some influences on the vibrational frequency as well as the energy gap due to the interaction between the LCC and CNT wall. Neighboring LCCs, when two or three LCCs are encapsulated in parallel inside a CNT hollow, also affect each other. Details of these effects are not known, and the clarification of this matter is future study by using LCC@CNT samples precisely separated according to the LCC length, the CNT diameter, and a number of LCCs encapsulated.

The peak positions of the G-band were observed to shift to lower frequencies by about 5 cm^{-1} in average when LCCs are contained in CNTs; the G-peak position for the pristine CNT samples is 1589 cm^{-1} , while that for CNT samples containing LCCs is about 1584 cm^{-1} , as shown in Figure 6. It is known that the peak position of the G-band of CNTs shifts by lattice strain or by doping of charge. The strain in CNTs shifts the G-band to the lower frequencies [20], while the charge transfer shifts the G-band to the higher frequencies irrespective of charge polarities [21]. Therefore, the present red-shift of the G-band is considered to be due to the strain brought about by encapsulation of LCCs and/or damages caused by discharge. The effect of damage to CNTs is also manifested in the G/D ratio (intensity ratio of G band to D band); the ratio was typically about 38 in the intact region, while it was 16 in the damaged region.

Mechanism of LCC encapsulation into CNTs is still under speculation. Besides the present method, LCCs formation inside CNTs was reported so far either by arc-discharge between graphite electrodes for the production of multiwall CNTs [9], thermal annealing at around 1400°C [10], and X-ray irradiation of SWCNTs followed by thermal annealing at $450\text{--}500^{\circ}\text{C}$ [22]. Taking these physical conditions for preparing LCCs inside CNTs into consideration, it is specu-

lated that some carbon atoms and clusters present inside CNTs or formed by electric discharge were annealed to coalesce and polymerize in a narrow cavity to form a long LCC. Another possible scenario is permeation of carbon-containing molecules existing outside CNTs through defects or holes of CNT walls created by collision of energetic particles, followed by coagulation of these carbon species into a chain inside a CNT cavity.

IV. CONCLUSIONS

Raman scattering spectroscopy and TEM of linear carbon chains (LCCs) formed by vacuum electric discharge of carbon nanotube (CNT) sheets were carried out. Long LCCs (the maximum length being at least 30 nm) were encapsulated in single-wall CNTs as well as double-wall and triple-wall CNTs. Not only a single LCC but also two or three LCCs in parallel inside a CNT were found. Raman spectra showed prominent peaks, called LCC bands, in a region from 1790 to 1860 cm^{-1} originating from longitudinal optical phonons of LCCs. The observation of strong LCC bands due to resonance Raman scattering indicates that the energy gaps of long LCCs inside CNTs are located between 1.85 and 2.54 eV.

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