COAXIAL CARBON NANOTUBES: DOUBLE-WALLED CARBON NANOTUBES

Morinobu Endo, Hiroyuki Muramatsu, Takuya Hayashi, Yoong Ahm Kim

Faculty of Engineering and Institute of Carbon Science and Technology, Shinshu University, 4-17-1 Wakasato, Nagano-shi 380-8553, Japan

Introduction

Double walled carbon nanotubes (DWCNTs) have attracted lots of attention because their intrinsic coaxial structures make them mechanically, thermally and structurally more stable than single walled carbon nanotubes (SWCNTs). Geometrically, the buffer-like function of the outer tubes in DWCNTs allow inner tubes to exhibit exciting transport and structural properties that make them promising in the fabrication of field-effect transistors, stable field emitters and lithium ion batteries. In addition, selective functionalization of the outer tubes makes DWCNTs useful for anchoring semiconducting quantum dots as well as for use as an effective multifunctional filler in producing tough, conductive transparent polymer films, while the inner tubes with diameter below 0.9 nm preserve their excitonic transitions. Several synthetic methods for producing DWCNTs have been reported: a) arc discharge, b) chemical vapor deposition [1], and c) thermal treatment of fullerene encapsulated SWCNTs, also known as peapods [2]. Among these methods, the thermal treatment of peapods is known to be an effective way of fabricating catalyst-free high purity DWCNTs because small-diameter inner tubes (i.e., 0.4 - 0.7 nm) could be formed via the coalescence of the encapsulated fullerenes. In this account, two different approaches of producing high-purity DWCNTs (e.g., catalytically grown and peapod-grown DWCNTs) will be described by comparing their respective optical and electronic properties.

Experimental

The catalytically grown DWCNTs were synthesized by the catalytic chemical vapor deposition method and the following two-step purification processes [1]. On the other hand, the synthesis of the peapod derived DWCNTs is based on highly-purity arc-produced SWCNTs (Hanwa Company, Korea). The SWCNTs with a diameter of about 1.2-1.3 nm are used as the hosting fullerene material. After vaporizing fullerenes in a vacuum-sealed glass ampoule containing SWCNTs at 600 °C for 24 hrs, the reactants were washed twice in order to remove the residual fullerenes attached to the sidewall of the bundled SWCNTs. Then, the black paper-like peapod contained SWCNTs were dried under vacuum at 100 °C for 24 hrs. Finally, by subjecting the sample thus prepared to a high-temperature thermal treatment (from 1500 to 2000 °C) in an argon atmosphere using a graphite furnace, high-purity peapod-derived DWCNTs were obtained.

We characterized the samples by TEM (JEOL JEM-2010FEF) and Raman spectroscopy (Kaiser Hololab2000system). In order to obtain PL maps, the nanotube samples (1 mg) were individually dispersed in heavy water (D_2O) with the help of sodium dodecylbenzenesulfonate (SDBS) (0.5 wt.%) under strong sonication (UP50H, ca. 600 W/cm^2) for 1 hr at 4 °C and subsequent ultracentrifugation (Optima Max-XP, Beckman Coulter, 320,000 g). Subsequently, their supernatant (70 %), rich with isolated nanotubes, was used in our optical studies. This step was followed by a measurement of the PL maps (NIR-PL system, Shimazu) using a liquid-nitrogen-cooled InGaAs array-type detector for the SDBS-dispersed DWCNT suspensions that were prepared in this way.

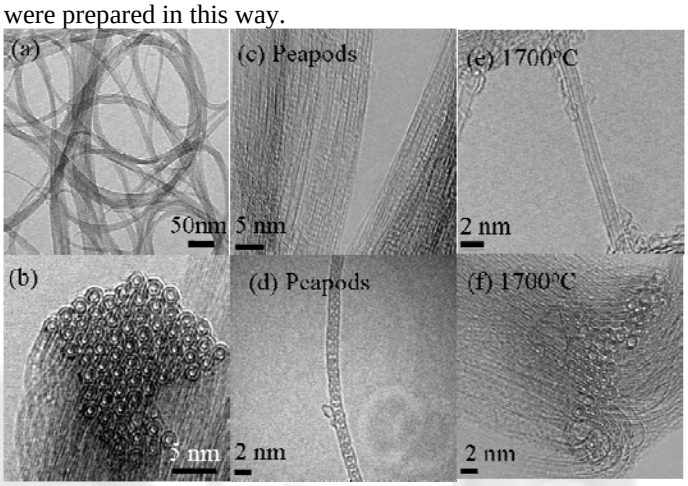

Fig. 1 TEM images of catalytically grown DWCNTs (a, b) and peapods (c, d), peapods-grown DWCNTs (e, f), respectively.

Results and Discussion

The catalytically grown DWCNT sample consists of the physically entangled long nanotube bundles (10-30nm) (Fig. 1 (a)). From the cross-sectional HRTEM image (Fig. 1 (b)), we observed that our tubes consist of relatively round, small and homogeneous-sized (below 2 nm in the outer shell) two concentric individual tubules. Furthermore, these co-axial tubes are packed in a hexagonal array. We confirmed the high yield of DWCNTs (above 95 %) in bundles, and, furthermore, with relatively homogeneous and small-sized inner tubes of mainly ca. 0.9 nm diameter and outer diameters of ca. 1.5 nm. Magnetic susceptibility studies confirmed the high DWCNT sample purity through their diamagnetic behavior. On other hand, the peapods consist of encapsulated fullerenes within SWCNTs, with a filling rate of ca. 60 - 80 % (Fig. 1 (c, d)). For peapods thermally treated at 1700 °C, coaxial structures were observed (Fig. 1 (e)), indicating that the encapsulated fullerenes coalesce and form a tubular structure inside the SWCNTs. From the cross-sectional image (Fig. 1 (f)), we observed single- and double layers as well as enlarged (coalesced) single layers exhibiting a trigonal bundle structure, suggesting that the partially formed short and imperfect tubules inside the SWCNTs are due to a deficiency of carbon

atoms to fully form a complete (defect free) sp^2 hybridized lattice.

Recently, different and distinct optical features have been observed in peapod derived-DWCNTs when compared to catalytically grown DWCNTs. For example, photoluminescence (PL) signals from the inner tubes of peapods grown DWCNTs have been found to be suppressed [3], although the inner tubes of catalytically grown DWCNTs show intense PL signals [4]. A recent optical study suggested that the PL signals from the density gradient-enriched catalytically grown DWCNT sample do not originate from the inner tube of the DWCNT but rather from impurity SWCNTs. Intrigued by contradictory reports on the PL signals from DWCNTs, we have selected peapods as starting materials in order to discard the effect of SWCNT impurity. Then, we have carried out systematic optical characterizations of peapods grown DWCNTs, which are prepared by thermally treating peapods at various temperatures in argon. Figure 2 shows the PL maps of peapods grown DWCNTs prepared at different annealing temperatures ranging from 1600 to 2000 °C. Each bright peak in the PL map corresponds to an excitation involving the second excitonic transition E^S_{22} of the semiconducting inner tubes forming the DWCNT, and emission from the corresponding first excitonic transition E^S_{11} of semiconducting inner tubes of DWNT. For DWCNTs prepared (annealed) at 1600 °C, we could not observe any PL signals, which is consistent with the results of Ref. 3. On the other hand, we were able to observe bright PL signals from the inner tubes of DWCNTs prepared (annealed) at 1700 and 1800 °C. For DWCNTs prepared at 1700 °C, an intense PL signal from the inner (6, 5) tubes can be clearly observed. Upon increasing the temperature to 1800 °C, more intense PL signals from (8, 3) and (6, 5) tubes arise, as well as the appearance of new PL signals from SWCNTs with the following chiralities: (7, 5), (7, 6) and (8, 4). This result indicates the diameter-dependent consecutive growth of semiconducting inner tubes with increasing thermal treatment temperatures. We also observed a blueshift of the E^S_{11} from the inner tubes of the DWCNTs and an enhanced PL intensity with increasing temperatures. We have reported the presence of a redshift in the excitonic transitions from the inner tubes of the catalytically grown DWCNT, as compared with those of Hipco-derived SWCNTs, and this redshift is caused by the increased dielectric screening effect originating from the shielding of the outer tubes [4]. However, since the inner tubes of the peapods grown DWCNTs have the same environment as that of the catalytically grown DWCNTs (i.e., the outer tubes were covered by SDBS molecules), the blueshift of E_{ii} is explained by the intrinsic band gap structure of both kinds of inner tubes. From these results, it appears that short semiconducting inner tubes formed from encapsulated fullerenes inside host SWCNTs at 1700 °C can be made longer and more crystalline by increasing the thermal treatment temperatures to 2000 °C. We demonstrate for the first time that the bright PL signals originate from the inner tube of peapod grown DWCNT, and not from SWCNTs.

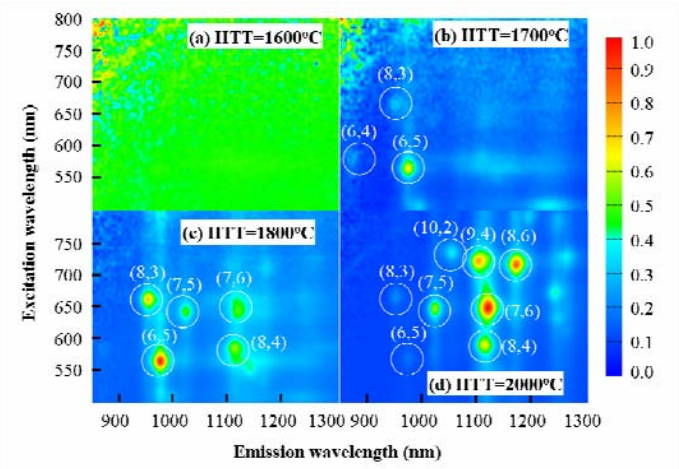

Fig. 2 Two-dimensional PL maps of the peapod-derived DWCNTs prepared at (a) 1600 °C, (b) 1700 °C, (c) 1800 °C and (d) 2000 °C. The color represents the photoluminescence intensity on a linear scale shown on the right. The open circles show the locations of all peaks, where the values of n and m indicate the chirality of the nanotube.

Conclusions

We have described two different synthetic methods of producing highly pure and small diameter DWCNTs with regard to SWCNTs. However, both DWCNT samples exhibited quite different optical properties. Interestingly, we have observed the bright PL from the inner tubes of peapod-derived DWCNTs. At a specific temperature, the metallic corrugation of the inner tube of DWCNTs is reconstructed to form a well-defined semiconducting tube, and the PL signals start to appear again. We envisage that DWCNTs will in the future replace SWCNTs in biomarker and optoelectronics applications due to their strong and stable luminescence properties.

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