Controllable preparation of triple-walled carbon nanotubes and their growth mechanism†

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Triple-walled carbon nanotubes (TWNTs) with three concentric cylindrical graphene layers have been selectively synthesized for the first time from decomposition of ferrocene encapsulated inside double-walled carbon nanotubes, and were identified by high-resolution transmission electron microscopy (HRTEM) and Raman spectroscopy; HRTEM observations reveal that the formation of inner tubes of TWNTs follows a base-growth mechanism.

Due to their unique structures and intriguing physical properties,[1] carbon nanotubes (CNTs) are attracting increasing interest and attention in the fields of both fundamental and applied science. Selective production of specific types of CNTs with distinct structures and properties is one of the principal and challenging goals; it would be ideal and desirable to make CNTs with precisely controlled numbers of layers from one to two to three and so on. Single-walled carbon nanotubes (SWNTs) with unique electronic properties have been studied in great detail in the past decade, and have been regarded as a promising material in nanoelectronic devices.[2] Double-walled carbon nanotubes (DWNTs), the ideal and the thinnest multi-walled carbon nanotubes (MWNTs), possess the advantageous properties of both SWNTs and MWNTs (*i.e.* their lower threshold voltage for electron emission and good durability), which makes them potential field-electron emitters[3] or nanoscale bearings.[4] Accordingly, it would be interesting to prepare another specific type of CNTs with three concentric cylindrical graphene layers, (tentatively called triple-walled carbon nanotubes, TWNTs), which might possess many new properties and potential applications differing from other types of CNTs. Here we report for the first time a layer controlled synthesis of TWNTs.

Microporous aluminophosphate $AlPO_4$-5 crystals (AFI) with a size-confining tubular interior have heen used as a template to produce small CNTs by the pyrolysis of tripropylamine encapsulated in AFI.[5] Anodic alumina membranes (AAM) have also been tested as a template to prepare amorphous CNTs.[6] These reports inspire us to explore the possibility of making TWNTs by replacing AFI with DWNTs. Our approach involved two stages, of which the details are described below. The starting materials, DWNTs, were synthesized by a DC arc-discharge method using chloride as a promoter and purified before use.[7a] Ferrocene was filled into the nanopores of purified DWNTs by sublimation or a vapor diffusion method, which is similar to the method of filling SWNTs with ferrocene reported previously.[7b] For a typical run, purified DWNTs and sufficient ferrocene were loaded in the two sub-tubes of a reaction vessel which was evacuated to 3×10^{-4} Pa. During the evacuation step, the sub-tube loaded with DWNTs was heated and degassed at 450 °C for 5 h, while another sub-tube loaded with ferrocene was cooled by liquid nitrogen to avoid sublimation of ferrocene. Subsequently the whole vessel was sealed and annealed at 320 °C for 48 h. After removing ferrocene adsorbed on the outer tube surface of DWNTs by washing several times with diethyl ether, the DWNTs sample was heated at 900 °C for 1 h under Ar atmosphere. The DWNTs samples were dispersed in ethanol and sonicated for 10 min, and then a few drops of the mixture were placed on carbon-coated copper grids for HRTEM examination (Hitachi-9000NAR).

The HRTEM examinations reveal that a significant amount of nanotubes with three concentric cylindrical graphene layers is obtained. Raman spectra measured at room temperature also confirm the formation of the tertiary graphene layer inside DWNTs. Both the HRTEM and Raman studies reveal that the growth of new single-walled nanotubes is directly from the thermal decomposition of the ferrocene confined within the central cavity of DWNTs.

Fig. 1 shows typical HRTEM images of the TWNT bundles and an individual TWNT (see the inset), revealing clearly that each nanotube consists of three concentric graphene sheets, *i.e.* triple-walled carbon nanotubes are obtained. On average, the TWNTs have outer diameters ranging from 3 nm to 5 nm. For the individual TWNT shown in the inset of Fig. 1, its outer diameter is 3 nm with an interlayer spacing of 0.4 nm. The HRTEM examinations reveal the purity or the ratio of TWNTs to all nanotubes is over 50%, which is strongly dependent on the filling rate of ferrocene and the inner diameters of DWNTs. In general, for DWNTs with outer diameters larger than 3 nm, high quality TWNTs are favored and formed more easily inside the tubes. When the inner diameters of DWNTs are smaller than 3 nm, few TWNTs are obtained.

Raman spectroscopy is another powerful tool to identify nanotubes. Fig. 2 shows typical Raman spectra of the parent empty-DWNTs and TWNTs, respectively, which were recorded at room temperature with 633 nm excitation (Renishaw system 1000). Fig. 2(a) shows the radial breathing modes (RBM) of both DWNTs (bottom) and TWNTs (top) in a low frequency region. Several new RBM peaks are clearly seen in the case of TWNTs (top curve in Fig. 2(a)), though the signals at frequencies below

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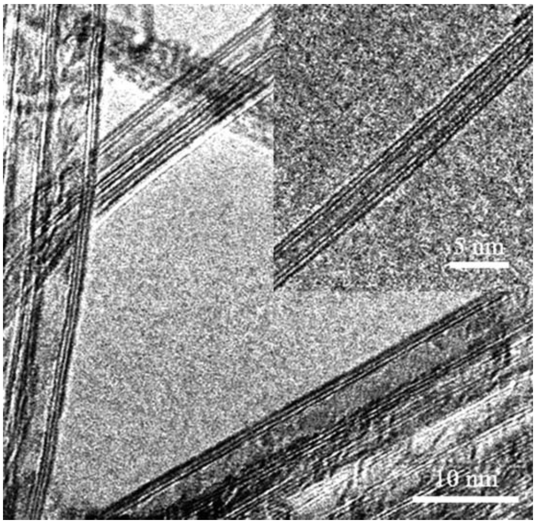

Fig. 1 A typical HRTEM image of TWNTs bundles. Top-right inset, an individual TWNT with clearly resolved graphitic layers.

Table 1 Raman peak position and the corresponding diameters for the tertiary nanotubes of TWNTs

Raman shift ω_r (cm^{-1})	Inner diameter of TWNTs (nm)
146	1.6
156	1.5
192	1.2
208	1.1
220	1.0
254	0.9

100 cm^{-1} are difficult to detect by the current resonant Raman spectrometer employed due to the weaker Raman cross-sections exhibited by larger nanotubes. The new peaks in Fig. 2(a) are evidence that novel carbon nanotubes with smaller diameters have been formed after the heat treatment of ferrocene inside DWNTs. From these new Raman peaks, the corresponding tube diameters can be calculated with the equation $\omega_r = 6.5 + 223.75/d$,[8] and these are listed in Table 1. In the present study, the smallest tertiary tube detected by Raman spectroscopy has a diameter of 0.9 nm, implying that the template DWNTs should have an inner diameter of about 1.6 nm. In other words, DWNTs with inner diameters larger than 1.6 nm would favor the growth of the tertiary carbon nanotubes. As can be seen from Table 1, the largest inner tube of TWNTs is 1.6 nm, but in reality this is unlikely to be the largest tertiary tube formed in the experiments. Some Raman peaks lower than 146 cm^{-1}, corresponding to tubes with a diameter of 1.6 nm, are hard to detect because of their weak cross-sections and/or because of being overlapped by the peaks from the template DWNTs and from the larger nanotubes. In comparison with the Raman spectrum from DWNTs (bottom curve in Fig. 2b), the G-band from TWNTs centering at 1581 cm^{-1} (top curve in Fig. 2b) is upshifted 5 cm^{-1}, while the D-band position remains the same though the strength or density of the D-band for TWNTs becomes much stronger. The I_G/I_D ratio of the TWNTs sample is lower than that of the DWNTs, implying that the new nanotubes formed in the decomposition process of ferrocene have a higher defect density than the original template DWNTs prepared by the arc discharge method. The Raman results are in very good agreement with HRTEM observations, all providing evidence of the formation of new nanotubes inside DWNTs.

Structure details of TWNTs may render some information on their growth mechanism. It has been found that both capped and open-ended nanotubes are formed inside the inner central cavities of DWNTs, as shown in Fig. 3(a) and (b), respectively. Fig. 3(a) shows that a single-walled carbon nanotube with a closed-tip made of a hemispherical graphene carbon cap (indicated by the white arrow) is inside a DWNT, which is formed during the pyrolysis of ferrocene in the tubular interior of DWNTs with an outer diameter of 2.5 nm. It is also interesting to note that there are no catalyst particles at the tube tips. Compared to the parent empty-DWNTs, the wall of a newly formed tertiary tube is not straight and has a diameter of about 0.9 nm, indicating a high defect density induced by the growth condition of chemical vapor deposition (CVD). These results are in agreement with the Raman measurements. Fig. 3(b) shows an inner tube with an open-end, as indicated by the upper arrow. It is noticeable that something black is packed right

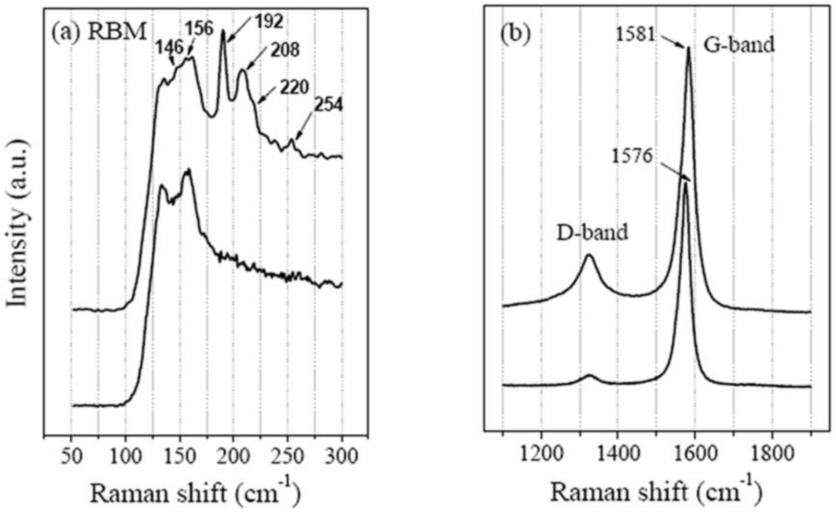

Fig. 2 Raman spectra (633 nm excitation) from empty DWNTs (below) and TWNTs (top) showing radial breathing modes (RBM) (a), D-band and G-band (b).

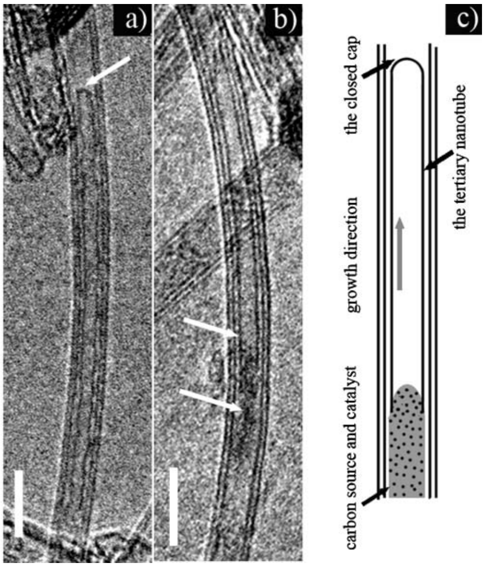

Fig. 3 HRTEM images of an individual TWNT, showing how the tertiary carbon layer is formed, (a) and (b); (c) schematic illustration of growth mechanism of the TWNTs. Scale bars, 5 nm.

at the root of the tube (indicated by lower arrow). The energy dispersive X-ray (EDX) analysis (ESI†) reveals that the black substances are small iron particles formed during the decomposition of encapsulated ferrocene molecules when they are heated to 900 °C inside the central cavity of DWNTs. All of the information mentioned above leads one to believe that the formation of inner carbon nanotubes in the present work follows the base-growth mechanism, which is schematically illustrated in Fig. 3(c).

In the present study, the growth of carbon nanotubes conforms to a vapor–liquid–solid (VLS) mechanism.[9,10] Firstly, ferrocene undergoes decomposition to release a series of hydrocarbons and Fe species at temperatures over 500 °C.[11] Theoretical calculations and molecular dynamics simulations[12] revealed that the hydrogen atoms will leave the ferrocene first due to the weaker C–H bond (492 kJ mol^{-1}), and then the cyclopentadienyl ring with higher C–C bond energy (602 kJ mol^{-1}) will start to break up, followed by the breakage of the C–Fe bonds (1480 kJ mol^{-1}) in combination with the remaining C–C bonds. Hence the fragments obtained from decomposition of ferrocene are sequentially C–H, C, C_2 and C_3, and finally Fe. The time required for a complete fragmentation of ferrocene (approximately 300 fs[12]) is far shorter than the long period of heat treatment (1 hour) in our study. Therefore during the pyrolysis process, the Fe species serve as catalyst and those hydrocarbons work as carbon sources. On increasing the temperature to 900 °C, those hydrocarbon species and C clusters dissolve into the iron nanoparticles, diffuse through them and precipitate, thus reacting with each other and promoting the growth of carbon tubular structures under the confinement effect of the DWNTs template. The diameter of the newly-formed tube is strictly controlled by the diameter of the template, *i.e.* by the inner tube diameter of DWNTs, and is usually smaller by 0.7–0.8 nm. Moreover, the formation of new nanotubes is strongly dependent on the amount of ferrocene encapsulated inside DWNTs and on the pyrolysis conditions. DWNTs with large diameters may contain a large amount of ferrocene, accordingly favoring the growth of nanotubes with increased lengths and good structures, while the small template is apt to produce nanotubes with a finite length and imperfect structures.

In conclusion, the controllable synthesis of TWNTs is successfully conducted using DWNTs as a template under which new carbon nanotubes are grown from decomposition of the ferrocene encapsulated in the central cavity of DWNTs. This not only provides experimental validation for the theory on the growth mechanism of nanotubes but also opens a way to investigate their properties and potential applications. Like the discoveries of SWNTs and DWNTs, one can expect more from TWNTs.

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