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Structure of flattened carbon nanotubes

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Abstract

A large number of flattened multi-walled carbon nanotubes have been synthesized using chemical vapor deposition. They are often capped with elongated crystalline cobalt catalyst nanoparticles. Sample rotation studies inside the transmission electron microscope show that the catalyst nanoparticles have a cylindrical rather than a rectangular shape, indicating that the flattened structure of the nanotubes is not templated by the shape of the catalyst particles. Observations reveal the existence of nanotube flattening parallel to the long axis and a spiraling of fully flattened nanotube around the long axis of the nanotube. The flattening of the nanotubes is attributed to the pressure difference between the inside and outside of the nanotubes which are sealed by the catalyst nanoparticles during their growth. The flattening and the spiraling are ascribed to axial compression and torsion, respectively.

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1. Introduction

Carbon nanotubes [1], as perfect one-dimensional systems, have attracted a great of interest in the research community. Single-walled carbon nanotubes (SWNTs) can behavior either as semiconductor or metal depending on the hexagonal arrangement of carbon atoms in their cylindrical graphitic sheets [2,3]. Carbon nanotubes are very stiff in their axial directions but flexible in radial directions [4,5]; even van der Waals force between adjacent nanotubes can deform them substantially, resulting in flattening of the nanotubes in their contact region [6]. The electrical properties of flattened nanotubes will be different from that of perfect cylindrical nanotubes. It has been predicted that a semiconductor to metal transition [7] or a metal to semiconductor transition [8] can occur in flattened SWNTs. Simulation results indicate that SWNTs can be deformed by external forces. For instance, under hydrostatic pressure, SWNTs or their bundles can undergo shape transitions from circular cross-section to collapsed cross-section [9,10]. On the other hand, under mechanical load, such as axial compression, bending, and torsion, SWNTs will undergo different shape deformation such as two-fin pattern, kink, and straight axis spiral [11,12].

Multi-walled carbon nanotubes (MWNTs) are SWNTs arranged concentrically and they can also experience the shape deformation or flattening during their growth [6]. Cylindrical MWNTs are expected to be metallic and show no gate effect [13,14]; however, structure deformation such as flattening can change their electronic properties. For example, flattened MWNTs showed field-effect transport property [14]. Fully flattened MWNTs were first observed in the samples prepared by carbon-arc discharge method [15], and these flattened MWNTs had layers of 6–9 and outer width of 20–22 nm. It was postulated that the flattening was caused by external mechanical forces [15,16]. Alternatively, large thick flattened MWNTs were synthesized using hydrothermal method at autogenic pressure [17], and the flattened MWNTs had layers of 13–40 and outer width of 43–121 nm. The fraction of the flattened MWNTs was about 8% in the synthesized material. It was proposed that the high pressure at the beginning of the reaction played an important role in the formation of the flattened MWNTs.
We present here our experimental results on the flattened MWNTs synthesized by chemical vapor deposition. In the synthesized material, almost all of the nanotubes are flattened, and most of the flattened nanotubes are capped with metal catalyst particles at one of their tips. The structure of the flattened nanotubes has been investigated by electron microscopy via *in situ* rotation of the samples inside transmission electron microscope. We observed two new types of flattenings of nanotubes in our experiment. The first type of flattening is parallel to and symmetric about the long axis of the nanotube. Unlike the reported kink which usually causes the nanotube to bend, this flattening still keeps the nanotube straight. We refer to this type of flattening as parallel flattening. The second type of flattening is a spiraling of fully flattened nanotube around the long axis of the nanotube. We refer to this type of flattening as spiral flattening. Based on the microscopic observations, the formation mechanism of the flattened nanotubes has been discussed.

2. Experimental

The synthesis was carried out in a horizontal tube furnace with a quartz tube of 46 mm inner diameter as the reaction chamber. The catalyst used for growing the nanotubes was prepared by immersing MgO powder (Nantek Inc.) in cobalt nitrate ethyl alcohol solution. The weight ratio of Co–MgO was 2.5%. For loading the Co catalyst onto the MgO powder, cobalt nitrate hexahydrate (Co(NO₃)₂·6H₂O, 98%, Aldrich) was dissolved in ethyl alcohol (Aldrich, denatured with 5% isopropyl alcohol and 5% methyl alcohol) by sonicating for 5 min, then MgO powder was immersed in the solution and sonicated for 50 min. After drying, the material was baked at 130 °C for 14 h followed by grinding in mortar to break the chunks into powder.

For carbon nanotube growth, about 50 mg of Co/MgO powder loaded on a molybdenum boat was reduced at 1000 °C for 1 h in flowing gases H₂ (40 sccm) and N₂ (100 sccm) at a pressure of 200 Torr, then the N₂ was replaced with CH₄ (10 sccm) to start the carbon nanotube growth. The growth lasted for 1 h.

The nanotubes were examined by scanning electron microscopy (SEM, JEOL JSM-6340F), and transmission electron microscopy (TEM, JEOL 2010F) attached with an energy dispersive X-ray spectrometer (EDS).

The specimen for TEM analysis was prepared by dispersing the sample in ethanol. A few drops of the suspension were dripped onto a microgrid covered with a holey carbon thin film.

3. Results and discussion

For SEM imaging, the as-grown sample was dispersed on carbon adhesive pad which was stuck on the SEM sample stage. It was found that the nanotubes grew on the surface of MgO clusters as shown in Fig. 1. Contrary to the often reported rod-like cylindrical nanotubes, the nanotubes synthesized in the current experiments are flattened and twisted as presented in Fig. 1a. An extensive SEM examination indicates that nearly all the nanotubes are flattened, in other words, the fraction of flattened carbon nanotubes is about 100%. One can see from the strong contrast (in Fig. 1b) that some carbon nanotubes are capped with rod-like Co catalyst particles, as indicated by the white arrow heads. It should be pointed out that a similar synthesis procedure also resulted in double-walled carbon nanotubes; however, the rod-like catalyst particles attached to the ends of double-walled carbon nanotubes were not observed [18]. In the current experiment, double-walled carbon nanotubes have not been detected, and all the flattened nanotubes are multi-walled. Since the CVD experiment involves multiple steps, any minor discrepancy may cause different growth of carbon nanotubes — flattened nanotubes or double-walled cylindrical nanotubes. The critical parameter that dictates the formation of the flattened or double-walled nanotubes has not been identified. However, it is speculated that the rod-like catalyst particles keep the carbon nanotubes closed during their growth and the inside channels of these sealed nanotubes are at low pressure. The low pressure inside the nanotubes causes the nanotube to flatten.

Fig. 2a and b shows typical TEM images of the flattened carbon nanotubes. The observed maximum width of the flattened nanotubes is about 35 nm. Catalyst particles attached to the ends of the nanotubes are often

![Fig. 1. SEM images of flattened carbon nanotubes. (a) Flattened carbon nanotubes are laying on the surface of clusters of MgO nanoparticles and they are often twisted. (b) Some elongated Co catalyst particles are attached to the tips of the flattened carbon nanotubes, as indicated by the arrow heads.](image-url)
observed in TEM examination, as indicated by the white arrow heads in Fig. 2b. To see how the nanoparticles are attached to the nanotubes, the synthesized sample was treated with hydrochloric acid (HCl, 38%, Aldrich) at room temperature and then washed with distilled water. TEM and EDS examinations indicate that the MgO particles and the exposed Co catalyst particles have been removed by the acid treatment. However, it is found that the particles capping the tips of the nanotubes remain intact after the acid treatment. This result indicates that these catalyst particles are sealed inside the nanotubes and well protected by the graphene layers.

The composition and structure of the catalyst particles at the tips of the nanotubes have been investigated by high-resolution TEM examination and Fast Fourier Transformation (FFT), as shown in Fig. 3a and the inset. Fig. 3a shows that a Co catalyst particle encapsulated in the tip of a nanotube with 12 graphite layers. The Co catalyst is a single crystal; FFT of the boxed area of the TEM image of the Co particle indicates that the particle has a cubic structure with its (111) direction parallel to the axis of the carbon nanotube (inset in Fig. 3a). The chemical composition of the catalyst particles at the tips of the nanotubes has been further studied by EDS. Fig. 3b shows the EDS spectrum of the nanoparticle, and it shows clearly that the particle consists of only Co (note: carbon peak is from the carbon nanotube and copper peak is from the TEM copper grid). This result also suggests that pure Co is the catalyst of the flattened carbon nanotubes.

It seems from Fig. 3a that the catalyst particles are rectangular in shape, which gives one an impression that the shape of the flattened carbon nanotubes could be templated by the shape of the rectangular particles. Therefore, it is necessary to investigate the geometry of the catalyst.
particles and to clarify the relationship between the shape of the catalyst particles and the shape of the carbon nanotubes. In order to verify the shape of the catalyst particles, the samples are rotated inside the TEM. Fig. 4 shows the images of a catalyst particle encapsulated at the end of a nanotube before (Fig. 4a) and after (Fig. 4b) rotation of about 35°. It is found that the top end of the catalyst particle changes its shape slightly, but the bottom (inside) end of the particle does not change its diameter. This result indicates that the catalyst particle is not rectangular but nearly conical and the cross-section of the bottom (inside) end is circular. Although we cannot rotate the sample for a large angle to show directly the entire contour of the catalyst particle at different azimuth angle due to the limit of the TEM sample stage, we have performed similar rotation study on other catalyst particles attached to flattened carbon nanotubes, and found that the catalyst particles are either cylindrical or slightly conical. The finding demonstrates that the flattening of the carbon nanotubes is not templated by the shape of the catalyst particles.

Fig. 5 shows the shape change of a flattened nanotube when it is rotated in TEM for 35°. The outer diameter of

Fig. 4. TEM images of a Co particle attached to the end of a carbon nanotube before (a) and after (b) rotation of 35° in TEM chamber. The top end of the particle changes its shape slightly while the bottom (inside) end of the particle remains the same in diameter before and after rotation. This particle is conical rather than rectangular in shape, and it has a length of 210 nm and diameter of 22.5 nm in its inside end.

Fig. 5. Structure change of a flattened nanotube before (a) and after (b) rotation of 35° in TEM chamber. The inside end (denoted by letter “A”) of the catalyst particle does not change its diameter during the rotation, but the nanotube changes its shape dramatically at points “M” and “B”. The width of the nanotube at point “B” changes from 35.7 nm before rotation to 31.4 nm after rotation.
this nanotube at point “A” is 25.0 nm before rotation (Fig. 5a) and does not change after the rotation (Fig. 5b), indicating that the nanotube has a circular cross-section at point “A”. Therefore, the carbon nanotube surrounding the catalyst at point “A” is in cylindrical shape. By using the measured data, we can show that this nanotube is completely flattened at point “B”. In Fig. 5a, the outer diameter and wall thickness of the nanotube at point “A” is 25.0 nm and 3.50 nm, respectively. At point “B” the width of the nanotube is 35.7 nm. From a simple calculation [15], a cylindrical nanotube with outer diameter of 25.0 nm and wall thickness of 3.50 nm will form a ribbon with width of 35.2 nm if it is completely flattened. This calculated data matches very well with the measured width of 35.7 nm at point “B” of the flattened nanotube in Fig. 5a. We conclude that the nanotube is completely flattened at point “B”. It can be seen in Fig. 5a that this nanotube is also flattened at point “M” in a direction different from that at point “B”, which has been evidenced by rotating the specimen for 35°, as shown in Fig. 5b. The two local flattenings at points “B” and “M” are all parallel to the long axis of the nanotube. It is speculated that the two adjacent flattenings at points “M” and “B” in Fig. 5 are a two-fin pattern [11,12], which are actually two parallel flattenings at different directions.

It is noteworthy that the observed parallel flattening is different from the reported kink [4,19], which usually causes the nanotube to bend and change the direction of long axis. Here, the nanotube with the parallel flattening is not bended but still straight. Fig. 6 shows the detailed structure of the parallel flattening on another carbon nanotube. The flattening direction at point “B”

Fig. 6. (a) A nanotube with a parallel flattening. Note that the axis of the flattened tube is still straight and the flattening is symmetric about its axis. (b) A schematic drawing of the nanotube with parallel flattening. (c) and (d) High magnification TEM images of the same nanotube showing the detailed structure in the three regions “A”, “B”, and “C”.
is perpendicular to the normal of the page and the axis of the nanotube, see Fig. 6a. The edge of the flattened part at point “B” of this nanotube is facing the TEM electron beam, so that the hollow channel does not exist in the “B” region. Although the nanotube is flattened at point “B”, its axis is still straight and the flattening is almost symmetric about the axis of the nanotube. Fig. 6b is a schematic drawing of the nanotube shown in Fig. 6a. Figs. 6c and d are high magnification TEM images of the same nanotube, showing the detailed structure of this flattened nanotube in the regions “A”, “B”, and “C”. One can see that in regions “A” and “C” the two groups of fringes of the side walls of the nanotube are separated by the hollow core, while in region “B” the two groups of fringes are collapsed to form one group of fringes. It is clear that in region “B” the original two groups of fringes do not cross each other, indicating that the nanotube is not twisting [15] but a simple flattening in region “B”, as illustrated in Fig. 6b. It should be pointed out that the total number of the fringes in the region “B” is not exactly the sum of the two groups of fringes in either region “A” or region “C”; this is attributed to the break and loss of some graphene layers due to the flattening of the nanotube.

Fig. 7. (a) A long flattened nanotube with several visible nodes along its length. (b) A model of the spiraling of the fully flattened tube. (c) An enlarged image of the boxed area of the flattened nanotube in (a). (d) Image of the same area as in (c) after 32° rotation. (e) A high magnification TEM image of the node “C” in (a) after 17.5° rotation. (f) A line drawing to clarify the image in (e).
Besides the parallel flattenings, we have also observed the spiraling of fully flattened nanotube around the long axis of the nanotube. Fig. 7a presents a long flattened nanotube with a maximum width of 26.9 nm and 10 graphite layers, which corresponds to an inflated cylindrical nanotube of diameter 19.6 nm. Along its 1.35 μm length, there are five nodes (indicated by letters “A”, “B”, “C”, “D”, and “E”), which are formed due to the twist of the flattened nanotube. TEM examination shows that although this flattened nanotube has been twisted many times, the nanotube is still straight from “A” to “D” relative to its long axis, indicating that the twist does not cause the flattened nanotube to bend as it usually does [15]. Fig. 7c is a close-up of the boxed area in Fig. 7a, and it further shows the symmetric feature of the flattened nanotube about its axis. Fig. 7d is the same area as shown in the Fig. 7c but after 32° rotation, and it shows that the node “B” disappears and the node “C” remains almost the same. The part below the node “C” of the flattened nanotube becomes a narrow line, indicating that this flattened part is now positioned with its edge facing the TEM electron beam. Fig. 7e presents a high magnification TEM image of the node “C” in Fig. 7a after 17.5° rotation. Fig. 7f is a line drawing to clarify the TEM image in Fig. 7e. Fig. 7e shows the cross-over fringes of the graphite layers at node “C” of this flattened nanotube, which confirms that the node is not a parallel flattening as shown in Fig. 6. In fact, the nanotube shown in Fig. 7a is a fully flattened along and twisted around its long axis. In other words, it is a spiral of a fully flattened ribbon-like nanotube, and it spirals around the long axis of the nanotube, as predicted by the molecular dynamics simulations [11,12]. We refer to this type of flattening as spiral flattening. Fig. 7b is a model of the nanotube with spiral flattenings as shown in Fig. 7a. It is predicted that carbon nanotubes under torsion will flatten to a ribbon-like shape, then, it buckles to form a spiral [11,12]. In our experiment, the torsion could be from the turbulence of the flowing gas or from the force exerted on the attached catalyst by other nanoparticles during the growth of the nanotubes.

Several formation mechanisms for flattened carbon nanotubes have been proposed. One explanation is that flattening happens when a conventional cylindrical nanotube is kinked or twisted by external mechanical forces. The kink will cause the inner tube wall collapse locally, and then a zipper effect flattens the nanotube down its entire length [15]. For flattened nanotubes synthesized by using hydrothermal method at high pressure, it is proposed that the temporary high pressure at the beginning of reaction plays an important role in the deformation of the nanotubes [17]. Molecular dynamics simulation demonstrates that under axial compression or torsion nanotubes will flatten to form two-fin pattern or spirals [11,12]. In our experiment, all nanotubes checked by TEM are partially or entirely flattened. Flattening is a common feature for the nanotubes in our experiment rather than separate cases [15,17]. Since the nanotubes are capped with catalyst particles during their growth, their inside channel may be at very low pressure whereas the pressure outside the nanotube is at the synthesis pressure of 200 Torr, the pressure difference between the inside and outside of the nanotubes will render a huge net force on the wall of carbon nanotubes. At the beginning of the growth, the nanotubes are short and can sustain the force. However, with the growth of the nanotubes, their surface area increases dramatically, which results in a rapid increase in the compression force exerted on their surfaces. When the force exceeds the sustainable limit, the nanotubes flatten. The force exerted to the two ends of a nanotube by the pressure difference may serve as the axial compression force, which will promote the formation of the parallel flattening in order to keep the strain energy of the nanotube at minimum. The axial compression force may also be provided by other nanoparticles in the form of reaction force if the growing nanotubes are pushing those nanoparticles. On the other hand, if torsion is exerted on the growing and catalyst-nanoparticle-sealed nanotube the nanotube will flatten and twist to form spiral flattenings. Such torsion could be resulted from the gas turbulence in the reaction chamber or from the interaction between the growing nanotube and its surrounding objects, such as MgO particles, catalyst particles, and nanotubes.

4. Conclusion

A large fraction of flattened multi-walled carbon nanotubes have been synthesized by chemical vapor deposition method. The flattened nanotubes are capped with single crystal cobalt nanoparticles, which are oriented with their (111) direction parallel to the growth direction of the nanotubes. Specimen rotation studies inside TEM reveal that the nanoparticles have cylindrical or conical shape and the flattening of the nanotubes is not templated by the shape of the nanoparticles. Nanotubes with parallel flattening and spiral flattening have been observed in our experiments. Since the nanotubes are sealed by the nanoparticles, they are under compression resulted from the pressure difference between the inside and the outside of the nanotubes during the growth. When the compression exceeds the sustainable limit of the nanotubes, they flatten. It is speculated that the parallel flattening and spiral flattening of the nanotubes are formed due to the axial compression and torsion exerted on the nanotubes, respectively.

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